PROGRESSIVE METAMORPHISM OF FLINTON GROUP PELITIC SCHISTS
GRENVILLE PROVINCE, SOUTHEASTERN ONTARIO

by

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A thesis submitted to the Faculty of Graduate Studies and Research
in partial fulfilment of the requirements for the degree of
Doctor of Philosophy

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The undersigned hereby recommend to
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submitted by

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Abstract

The following five reaction isograds were mapped through the study area:

The assemblage garnet-chlorite with or without chloritoid is characteristic of the lowest-grade pelites in the area. This assemblage is found near Madoc and Bishop Corners in two geographically discrete areas of greenschist facies metamorphism that are not connected. Garnet-chlorite pelites typically contain trace amounts of chloritoid, either as inclusions in garnet or as xenoblastic relicts armoured in matrix quartz grains. This evidence indicates that chloritoid is unstable in the presence of garnet and chlorite, possibly due to the following continuous reaction in the KFLASH system:

Most of the porphyroblast growth associated with the reactions above took place after the development of the primary S1 schistosity, but prior to the later D2 and D3 deformational events. (S1 formed during the main deformational phase that produced the synclinal structures hosting the Flinton Group sediments). The isograds were initially relatively flat lying, and were refolded by later deformational events about northeast and northwest trending folds. The resulting dome and basin interference pattern formed two low-grade nodes in the study area, a greenschist facies node centred on Bishop Corners and a lower amphibolite facies node in the northern portion of the Clare River synclinorium near Kaladar.

Pelites on the margin of the Mooroton shear zone contain kyanite and staurolite that has been fractured and deformed, showing that the isograds have also been displaced by late-stage (post-peak metamorphic) movement along the shear.

A set of thermodynamic data for chloritoid (fctd, $\text{FeAl}_2\text{SiO}_5(\text{OH})_2$), magnesiochloritoid (mctd, $\text{MgAl}_2\text{SiO}_5(\text{OH})_2$), chamosite (iron chlorite – fchl, $\text{Fe}_5\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_8$) and magnesiostaurolite (mst, $\text{Mg}_4\text{Al}_{18}\text{Si}_{17.5}\text{O}_{44}(\text{OH})_4$) was derived using published experimental data and Fe-Mg partitioning data from natural assemblages (see summary table below), this data is consistent with the Berman (1988) database.

	$\Delta H^\circ_{f,298.15}$ (J/mol)	$\Delta S^\circ_{298.15}$ (J/K·mol)	$\Delta V^\circ_{298.15}$ (J/bar)	k_0	k_1	k_2	k_3	$v_1 \times 10^{-5}$	$v_2 \times 10^{-5}$	$v_3 \times 10^{-5}$	$v_4 \times 10^{-8}$
fctd	-3211482.5	160.9879	6.98	426.537	-3182.8	-7219860	1099977000	2.7869	0	-0.0863	0
mctd	-3556491.6	133.2477	6.875	407.697	-2759.53	-8624440	1207092000	2.9739	0	-0.06486	0
fchl	-7120000	580.7	21.34	1229.233	-10256.46	-12276980	2121507000	2.6124	0	-0.1798	0
mst	-25156000	876.2	44.26	2502.312	-14572.16	-66804220	9120506500	1.8000	0.0009	-0.0800	0.0004

The thermodynamic data was used in conjunction with the TWQ program (Berman, 1991) to estimate peak metamorphic temperature and pressure conditions for samples located throughout the study area. Calculated metamorphic temperatures range from 540°C in low-grade areas (Madoc and Bishop-Corners) to 650°C in the highest-grade portions of the study area. Metamorphic pressure data showed little variation across the map area, ranging from 5000 to 5500 bars.

Garnet-chlorite was found to be stable at lower metamorphic grade than chloritoid-biotite throughout the study area. This zonation is consistent with only one of two possible invariant point configurations for the cordierite-aluminosilicate-absent invariant point (the primary chloritoid-bearing invariant point in the KFMASH system). In addition, the sequence of isograds surrounding the Bishop Corners low-grade node was found to be identical to the sequence of reactions encountered on the low-pressure side of the invariant point. This observation was used, in conjunction with TWQ thermobarometry results, to estimate the location of the cordierite-aluminosilicate-absent invariant point, which appears to be located in the kyanite stability field at a pressure of 6000±1000 bars and a temperature of 550±10°C.

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Chapter 1 - Introduction

Hounsflow & Moore first described the metamorphism of Flinton Group aluminous schists (pelites) in 1967. At that time, mineral chemistry was determined by careful separation and wet-chemical analysis of the various phases in a rock. This technique obscured internal zonation in minerals such as garnet, and the analytical chemistry results were subject to error caused by refractory minerals (such as garnet and staurolite which are difficult to dissolve in solution), and small inclusions in porphyroblasts (such as quartz and magnetite in chloritoid and staurolite). This study evolved out of a desire to examine the metamorphism of the Flinton Group pelitic schists using some of the more "modern" tools available to metamorphic petrologists, including microbeam analysis of mineral chemistry and geothermobarometry using internally consistent thermodynamic data.

1.1 Purpose

This study proposes the following:

- 1) Map and describe mineral isograds developed during the prograde metamorphism of Flinton Group pelitic schists, from the Madoc area, northeastward through Bishop Corners to Ompah and Plevna.
- 2) Describe the chemistry of minerals occurring in these rocks and relate this to the observed metamorphic assemblages described above.
- 3) Derive a set of thermochemical data for chloritoid, magnesiochloritoid, chamosite and magnesio-staurolite consistent with the Berman (1988) database.
- 4) Use the thermodynamic data from 3 to evaluate conditions of metamorphism in the study area.
- 5) Relate results from 4 to regional geology and provide an overview of the metamorphism of Mazinaw terrane.

1.2 Location and Geological Setting

The study area is located in the interior of the Central Metasedimentary Belt (CMB) within the Grenville Structural Province of the Canadian Shield (Wynne-Edwards, 1972; see Figure 1.1). Easton (1992) subdivided the CMB into five lithotectonic terranes based on geophysical, lithological and chronological data. From the northwestern boundary of the CMB, these terranes are the Bancroft, Elzevir, Mazinaw, Sharbot Lake and Frontenac. The Elzevir terrane has been further subdivided in three domains – the Harvey-Cardiff Arch, the Belmont domain and the Grimsthorpe domain. The study area is mostly confined within the boundaries of the Mazinaw terrane however; a small portion near the town of Madoc is located in the Grimsthorpe domain of the Elzevir terrane.

The Mazinaw terrane is structurally bounded, as are most of the terranes shown on Figure 1.1, by shear zones, with the Robertson Lake shear zone to the east (Easton, 1988; Busch et al., 1996) and the Mooroton shear zone to the west (Connelly, 1985; Ford & Skippen, 1994; Cureton et al., 1997).

The oldest rocks in the Mazinaw terrane are a metamorphosed sequence of mafic and intermediate volcanic rocks (amphibolites), which are overlain by quartzofeldspathic schists, gneisses (clastic metasediments), and carbonates (marbles). These supracrustal rocks were subsequently intruded at ca. 1250-1240 Ma by a suite of tonalite/granodiorite and granite plutons (Corfu & Easton, 1995). The older plutonic and supracrustal rocks are unconformably overlain by a younger sequence of metasedimentary rocks, termed the Flinton Group by Moore & Thompson (1980). Detrital zircon geochronology by Sager-Kinsman & Parrish (1993) shows that deposition of the Flinton Group occurred sometime after ≈ 1150 Ma. The entire sequence, including the pelitic schists that are the subject of this dissertation, was metamorphosed and deformed in the Ottawa orogeny (Moore & Thompson, 1980) sometime between 1100 and 980 Ma (Corfu & Easton, 1995; dated metamorphic monazite at 1020 ± 3 Ma).

Figure 1.1: Terrane subdivisions of the Central Metasedimentary Belt (modified from Easton, 1992). Study focused on Flinton Group pelitic schists occurring in the area outlined in red.

1.3 Regional Geology

1.3.1 Flinton Group Stratigraphy

Flinton Group stratigraphy is summarized in Table 1.1 from Moore and Thompson (1980). The stratigraphy of the Bishop Corners and Myer Cave Formations has been slightly modified to be consistent with new field observations (Easton & Ford, 1991; this study). Pelite samples, collected over several summers, were mostly obtained from the Bishop Corners, Myer Cave or Madoc Formations.

TABLE 1.1			
<i>Flinton Group Stratigraphy by Geographic Location-from Moore & Thompson (1980)†</i>			
	SW - Madoc Area	Central - Flinton Area	NE - Fernleigh/Ardoc Area
FLINTON GROUP		(14) Pegmatite Intrusive contact	
			(11) Fernleigh Formation -biotite-carbonate schist
	(13) Stewart Formation -dolomite marble -micaceous graphite- calcite marble	(9) Lessard Formation -biotite-carbonate schist -calcareous quartzo- feldspathic psammite -calc-silicate paragneiss -plutonic pebble conglomerate	(10) Myer Cave Formation -megabreccia / carbonate conglomerate -graphitic pelite -massive graphitic schist -calcite marble -laminated graphitic schist -dolomite marble
	(12) Madoc Formation -pelitic schist	(8) Bishop Corners Formation -pelitic schist -quartz pebble conglomerate -quartzite conglomerate -quartzite quartzo-feldspathic psammite -white quartzite conglomerate	
		Minor unconformity	
	(6) Skootamatta Formation -volcanic pebble conglomerate -carbonate pebble conglomerate -calcareous phyllite, psammite	(7) Ore Chimney Formation -garnet-biotite schist	
		Major unconformity	
		(5) plutonic rocks	
		(1-4) Grenville Supergroup – marble, meta-wacke, meta-volcanic	

† includes minor modification to stratigraphy of Bishop Corners and Myer Cave Formations indicated by this study and Easton & Ford (1991).

1.3.2 Metamorphism

An overall increase in metamorphic grade from west to east has been documented within the Mazinaw terrane in several different rock-types including: marbles (Hutcheon & Moore, 1973), calcareous schists (Thompson, 1973), metavolcanics (Sethuraman & Moore, 1973), and pelites (Hounslow & Moore, 1967; Thompson, 1972; Carmichael et al., 1978). Previously defined metamorphic isograds are shown on Figure 1.2. This figure also shows the outline of the Hastings Metamorphic Low, a region of upper greenschist facies metamorphism that contains some of the lowest grade metamorphic rocks in the Grenville province (Carmichael et al., 1978). A detailed examination of the pelites in the study area shows that it is possible to define several additional isograds that are not shown on Figure 1.2. These will be discussed in Chapter 2.

1.3.3 Structural Geology

The structural geology of the study area has been determined in several previous studies including those by Thompson (1972), Rivers (1976), Chappell (1978) and Moore & Thompson (1980). These authors concluded that three major phases of deformation were required to explain the geometry of the rocks in the study area. The first phase of deformation (D_1) formed the major isoclinal folds that host the Flinton Group metasediments. The primary schistosity (S_1) in all Flinton Group rocks, including the pelites, is usually the axial planar cleavage to these D_1 folds. The second phase of deformation (D_2) resulted in the refolding of D_1 isoclines around steeply dipping axial surfaces that strike northeast – southwest (sub-parallel to the axial planar surface of the D_1 folds). Structures attributed to D_2 include the formation of a second cleavage, and asymmetrical folds that deform S_1 . The third phase of deformation (D_3) warps D_2 and D_1 structures about open folds with northwest-trending axial surfaces. Finally, a fourth minor deformational event (D_4) imposed a shallowly dipping crenulation cleavage on all the previous structures.

Figure 1.2: Isograds surrounding the Hastings Metamorphic Low. Local towns shown on diagram include Madoc (M), Kaladar (K) and Bancroft (B).

Thompson (1972) found sporadic examples of garnet, chloritoid and staurolite that contained an internal fabric at a high angle (60° to 90°) to the external S_1 foliation. Thompson (1972) proposed that the relict fabric might represent either an early deformation event pre-dating D_1 (for which no other evidence is preserved) or an early stage in the development of the S_1 foliation. This internal fabric was observed in approximately 10 samples during the course of this study. It is almost always at a high angle to S_1 , and shows no tendency to rotate into this foliation. These observations indicate that the internal fabric is not related to S_1 , but is rather an early deformation event pre-dating D_1 , termed D^* . Samples that exhibit this texture will be discussed in detail in the following chapter.

Chapter 2 - Metamorphism of Flinton Group Pelitic Schists, Petrography and Mineral Chemistry

2.1 Introduction

Figure 2.1 shows the distribution of metamorphic zones throughout the Mazinaw terrane, based on the mineral assemblage found in Flinton Group pelites. The isograds separating the various metamorphic zones are "reaction isograds" that have been mapped using the approach advocated by Thompson (1957) and Carmichael (1970). These isograds are mapped in the field by identifying univariant mineral assemblages in the ideal pelitic system $K_2O-Al_2O_3-MgO-FeO-SiO_2-H_2O$ (KFMASH). A univariant assemblage therefore requires the presence of six mineral phases, assuming the ubiquitous presence of water, or four ferromagnesian silicate minerals assuming the presence of muscovite and quartz (the kyanite-sillimanite isograd is the exception to this rule, since these two minerals form a univariant assemblage in the model system Al_2SiO_5). These four-phase assemblages represent a discontinuity in the tie-line arrangement of the AFM projection (Thompson, 1957). Isograds identified in this manner in the study area include:

The metamorphic zones described below are identified using either reactant or product assemblages of these various isograds (for example, the garnet-chlorite zone describes the low-grade area below equilibrium 2.1).

Identification of the isograds shown in figure 2.1 is based on the results of detailed, outcrop-scale field mapping, petrographic analysis by optical microscope and mineral chemistry studies using microprobe techniques. The petrographic analysis was based on the examination of approximately 700 thin sections. Note that the isograds on figure 2.1 have been drawn so that they appear to have

Figure 2.1: Pelitic isograds in the southern Mazinaw and eastern Elzevir terranes. Isograds are dashed where their location is inferred. Ornaments are on the high-grade side. Mineral assemblages used to locate the isograds are mainly from Flinton Group pelites (sample locations are indicated by yellow dots, see Appendix 4 for detailed location maps). Blue squares in the Queensborough syncline north of Madoc show the location of mineral assemblages obtained from Sampson (1972). Green square near Northbrook shows location of mineral assemblage obtained from Thompson (1972). The boundaries of the Mazinaw terrane are defined by the Mooroton shear zone (MMSZ) and the Robertson Lake shear zone (RLSZ).

been displaced by late-stage movement along the Mooroton Shear Zone. Details of this interpretation are outlined as part of the discussion in Chapters 4 and 5.

The lowest metamorphic grade pelites in the study area are characterized by garnet-chlorite-bearing mineral assemblages. These garnet-chlorite schists occur in two geographically distinct areas: the Madoc syncline north of the town-site, and the southern tip of the Fernleigh syncline, north of Northbrook near a highway intersection identified as Bishop Corners. The petrology of these two areas will be discussed separately below because of this large geographical separation.

2.2 Madoc Garnet-Chlorite Zone

Pelites in the southern portion of the Madoc syncline contain the lowest grade assemblages in the study area, indicative of upper greenschist facies metamorphism. Samples usually contain garnet and/or chloritoid with chlorite, muscovite and quartz (see photos 2.1 and 2.2). Kyanite and/or staurolite-bearing schists occur sporadically. The following list summarizes the mineral assemblages encountered in this zone, listed in approximate order of decreasing abundance (all assemblages contain muscovite and quartz)

- garnet + chlorite + biotite
- garnet + chlorite + chloritoid
- garnet + chlorite
- garnet + chlorite + staurolite
- chloritoid + chlorite
- staurolite + chlorite
- kyanite + chlorite
- staurolite + kyanite + chlorite
- chloritoid + staurolite + kyanite + chlorite

Figure 2.2 shows the observed mineral assemblages on an AFM projection using ideal, KFMASH end-member, mineral compositions.

Photo 2.1: Photomicrograph of chloritoid with hourglass inclusions in chloritoid-chlorite schist, Madoc area (sample Madoc-7e2-III).

Photo 2.2: Photomicrograph of garnet-biotite-chlorite schist (sample Madoc-7b2-II). Garnet growth post-dates development of the biotite porphyroblasts, as shown by the relatively inclusion-free square pseudomorphs in garnet, which are after biotite porphyroblasts. The garnet in the centre of the photograph is overgrowing the neighbouring biotite at the point indicated by the arrow.

Figure 2.2: Observed muscovite-bearing pelitic assemblages in the chlorite-garnet zone near Madoc (indicated by red dots). Mineral compositions shown on diagram correspond to ideal KFMASH end-members. Three-phase fields are shown shaded in yellow.

2.3 The Staurolite-Chlorite “Isograd”

The assemblage chloritoid-kyanite-staurolite-chlorite occurs sporadically at locality Madoc-4 as layers (beds?) in muscovite-quartz-bearing pelites. Chloritoid in these samples, shown below in photos 2.3 and 2.4, appears somewhat ragged, with textures indicating that it is being replaced by the three remaining minerals. These textures are consistent with the occurrence of a reaction in the six-phase assemblage, which is univariant in the KFMASH system (assuming the presence of a hydrous fluid phase). This reaction can be expressed by the following equilibrium:

Figure 2.3 shows how this reaction changes the topology of the AFM projection, using ideal mineral compositions in the KFMASH system. Equilibrium 2.6 was balanced using mineral compositions obtained by electron microprobe analysis from sample Madoc-4a-I. Stoichiometric coefficients for the resulting equilibrium (2.7 below) were normalized to ten moles of water.

Equil 2.7

Unfortunately, this isograd cannot be mapped in the field area, since the chloritoid-kyanite-staurolite-chlorite assemblage is preserved only at this single locality. However, there are indications that the Madoc area is already on the high-grade side of the isograd, since the product-assemblage (staurolite-chlorite-kyanite) can be observed in different layers in the same outcrop, implying that the reaction is already in progress.

Figure 2.3: Chloritoid + kyanite = staurolite + chlorite reaction (Equil 2.6), depicted on an AFM projection. Mineral compositions shown on diagram correspond to ideal KFMASH end-members. Three-phase fields are shown shaded in yellow; the univariant four-phase field is shown in pink.

Photo 2.3: Photomicrograph of pelite from locality Madoc-4a-II, showing chloritoid porphyroblasts (with hourglass inclusions) co-existing with staurolite, kyanite and chlorite, in a quartz + muscovite matrix.

Photo 2.4: Replacement of chloritoid porphyroblasts by chlorite, staurolite and kyanite (sample Madoc-4a-II). White arrows identify relict chloritoid crystals.

Photo 2.5: Photomicrograph of Grt-Chl schist (sample 92-6f1-l). Relict chloritoid crystals are scattered throughout the matrix (one example is indicated by the blue arrow on the left, where a xenoblastic chloritoid crystal is armoured in quartz).

Photo 2.6: Photomicrograph of chloritoid-chlorite assemblage in sample 93-26e-l. Chloritoid porphyroblasts cross-cut the matrix consisting of chlorite, quartz and muscovite. Chloritoid crystals exhibit twinning and hourglass inclusion structures. Orange arrows identify scattered margarite laths (Ca-mica).

Mineral compositions for iron-rich chloritoid and garnet-bearing assemblages were measured by electron microprobe (mineral chemistry results are summarized in Appendix 5). These compositions are shown on an AFM projection in figure 2.5. The single staurolite-bearing sample shown on the diagram (93-13b-I) is discussed in further detail below.

Figure 2.5: AFM projection of Fe-rich chloritoid and garnet-bearing assemblages from the Bishop Corners garnet-chlorite zone. Mineral chemistry used in diagram was obtained by microprobe; see results summarized in Appendix 5. Sample 93-13b-I contains manganese-rich garnets that do not lie in the AFM plane.

2.4.1 Early Foliation in Porphyroblasts and Timing of Mineral Growth

Flinton Group pelites throughout the study area exhibit structures that can be attributed to four phases of deformation, identified as D1 through D4 (Thompson, 1972; Rivers, 1976; Chappell, 1978; and Moore & Thompson, 1980). The first deformational phase (D1) was responsible for the formation of the main synclinal structures that contain the Flinton Group rocks. The dominant foliation in Flinton Group rocks throughout the study area is a schistosity (S1) that lies parallel to the axis trace of these major D1 folds. S1 is typically defined by the alignment of micaceous minerals, including chlorite, biotite and muscovite, and Fe-Ti oxides.

Most of the major porphyroblast growth appears to have taken place after the development of the main S1 schistosity (see Figure 2.6 below for a summary of the timing of porphyroblast growth relative to the major deformational events). In most of the pelites examined, garnet porphyroblasts typically lack pressure shadows and contain quartz inclusion trails that are continuous with the external S1 foliation, indicating post-D1 growth. In approximately ten percent of the samples examined, S1 is partially deformed around, and included by, garnet porphyroblasts, indicating syn-D1 growth.

Figure 2.6 includes an earlier deformational event than D1 identified as D*. Thompson (1972) identified porphyroblasts of garnet, chloritoid and staurolite that occasionally contained an internal fabric that was at a high angle (60° to 90°) to the external S1 foliation. He proposed that this relict fabric may have developed either during a period of deformation prior to the main D1 deformation, or during an early stage of development of S1. Photos 2.7 and 2.8 show examples of this early relict foliation (identified as S* in this study, attributed to the D* deformational event). The S* foliation was observed in a relatively limited number of samples, widely scattered throughout the low and medium-grade portions of the study area. The foliation is defined by the alignment of quartz and Fe-Ti oxide inclusions in chloritoid, garnet and staurolite. The S* foliation is best preserved in chloritoid, consistent with an earlier, lower temperature development.

Photo 2.9 shows a garnet crystal that contains a well-defined idioblastic core. This texture implies that there may have been two discrete periods of garnet growth, the first after the D* deformation (at which time the core developed) and the second during or after D1. Having two stages

of garnet growth supports the hypothesis that D* is a unique deformational event, discrete in time from D1. However, the S* foliation was observed in only a limited number of samples, implying that there is insufficient evidence at this time to indicate that S* was a unique deformational event.

Late-stage (crosscutting) mica foliations, attributed to later D2 and D3 deformational events, can be observed in approximately twenty percent of the samples. It is estimated that approximately sixty to seventy percent of the porphyroblast development took place prior to the D2 and D3 events. Evidence for this includes: 1) the rotation of syn- to post D1 porphyroblasts by later deformation and 2) warping of the D2 foliation, where developed, around pre-existing porphyroblasts. However, porphyroblast growth did not stop completely after the D1 event, since some garnet porphyroblasts have developed a relatively thin outer rim that contains inclusion trails that are continuous with, but have been rotated relative to the post-D1 core. This implies that at least some porphyroblast growth took place during D2.

Most prograde metamorphic minerals, with the exception of margarite, appear to have stopped growing prior to the D3 deformation. Margarite is the only mineral, other than muscovite, to show clear evidence of growth during all three major deformational events.

The final phase of deformation (D4) is not included in figure 2.6 because it appears to be a relatively low temperature post-metamorphic event. Evidence for this includes mica and chlorite that exhibit undulatory extinction in the hinge-zones of D4 crenulation folds, indicating that the sheet-silicates did not recrystallize during the deformation.

Figure 2.6: Timing of porphyroblast growth relative to the main deformational events in the study area. Increasing porphyroblast development is indicated by increasing thickness of the corresponding lozenge. D* is the oldest deformational event in the area, proceeding the main D1 deformation. However, evidence of the D* event is only preserved as inclusion trails in porphyroblasts.

Photo 2.7: Photomicrograph of Garnet with internal foliation defined by quartz inclusions (sample 93-16b-I). The internal foliation (S^* -white lines) crosscuts inferred bedding (S_0 -green line) and is discordant with the primary schistosity in the rock (S_1). The internal foliation wraps around one of several chloritoid inclusions in the garnet (blue arrows), indicating that chloritoid grew either during or before development of the S^* foliation (chloritoid is syn- to pre- D^*). Quartz-rich pressure shadows developed on either side of the garnet porphyroblast during the main D_1 deformation (red lines), indicating that garnet growth either accompanied or preceded this event (garnet is syn- to pre- D_1). The pressure shadows are now asymmetric due to garnet rotation during a later deformational event (either D_2 or D_3).

Photo 2.8: Photomicrograph of relict S* inclusion trails (indicated by white arrows) in chloritoid porphyroblasts from sample 93-24b-I. The porphyroblasts have been rotated by later deformation, so the inclusion trails are no longer aligned. The yellow lines indicate the trace of the primary S1 foliation, which has been warped around the pre-existing chloritoid porphyroblasts. A quartz-rich pressure shadow has developed around the upper right chloritoid porphyroblast (shown by red outline), confirming pre-D1 growth of chloritoid. The primary S1 schistosity has been folded by a later deformational event. Orange arrows show where biotite is nucleating on chloritoid.

Photo 2.9: Photomicrograph showing one of several garnet porphyroblasts in sample 93-13e-I that contain an inner ring, possibly indicating the presence of a ghost crystal within the porphyroblast that grew during an earlier phase of garnet growth. Inclusion trails in the outer portion are continuous with the external S1 foliation, indicating post-D1 growth. Inclusion trails in the ghost core are slightly discordant with S1, and are attributed to the earlier phase of deformation D* (indicating syn- to post D* growth for the core).

2.4.2 Chloritoid Textural Disequilibrium

Samples of garnet-chlorite-chloritoid schist from several localities exhibit textures that indicate chloritoid is reacting with the surrounding assemblage. Photos 2.10 and 2.11 show an example of a Grt-Ctd-Chl-schist (sample 91-27e-I) that contains ragged/corroded chloritoid grains. The chloritoid-consuming reaction appears to be proceeding faster in the inclusion-rich core of the chloritoid crystals, (the area that had formerly contained the hourglass structure - see chloritoid grains along right-hand side of photo 2.11); leaving only the relatively inclusion-poor rims stranded in the matrix. Formation of this texture indicates that a reaction is occurring among the three-phases, which is a divariant assemblage in KFMASH system. Divariant reactions, or continuous reactions, take place over a broad pressure-temperature range. The following equilibrium in the KFASH system describes the continuous reaction responsible for the gradual elimination of chloritoid in garnet-chlorite-bearing assemblages:

The reaction of chloritoid in garnet-chlorite schists was confirmed by two additional observations: 1) chloritoid-free garnet-chlorite schists typically contain garnets that have inclusions of chloritoid (Photo 2.12), and 2) trace amounts of chloritoid were observed in garnet-chlorite schists as relict grains in the matrix armoured by quartz (Photos 2.13 and 2.14). Both observations indicate that the garnet-chlorite schists had been chloritoid-bearing in the past, but that chloritoid had been subsequently eliminated from the assemblage, presumably by an equilibrium similar to 2.8.

Photo 2.10: Photomicrograph of Grt-Ctd-Chl schist (sample 91-27e-l), with corroded chloritoid grains. Some of the corroded grains have been rotated and dislocated, indicating the reaction took place prior to, or during D2 deformation. Garnet contains an inclusion-rich core, which appears to be syn- to post-D*. The surrounding rim contains inclusion trails that are continuous with the external D1 foliation, indicating syn- to post-D1 growth. This texture suggests that there may have been two stages of garnet growth.

Photo 2.11: Photomicrograph of corroded chloritoid grains in sample 91-27e-l. Reaction appears to be proceeding more rapidly in the inclusion-rich cores (formerly the hour-glass structure). White arrows show location of relict Ctd cores. Red arrows point to isolated Ctd rims (cores have been reacted out). The relict cores are typically hosted in quartz and/or chlorite, which serve to isolate them from the bulk assemblage.

Photo 2.12: Photomicrograph of Grt-Chl schist (sample 90-10d-I). The matrix is chloritoid-free; however, the garnet crystals contain inclusions of chloritoid (indicated by white arrows). Inset photo shows location of garnet crystal.

Photo 2.13: Photomicrograph of relict chloritoid grains (indicated by blue arrows), in a sample of garnet-chlorite-chloritoid schist (93-24a-II). Chloritoid grains occur both as inclusions in garnet and as relict grains in the matrix. Yellow arrows identify margarite crystals, which grow both parallel to the foliation (pre- to syn-D1), and crosscut it (post-D1, upper left).

Photo 2.14: Detailed view of chlorite-muscovite matrix from previous photo showing relict chloritoid crystals (sample 93-24a-II). The relict chloritoid grains are generally small (100 to 200 μm in size) with xenoblastic/irregular boundaries.

2.4.3 Low-grade Muscovite Pseudomorphs

The continuous reaction of chloritoid with chlorite, expressed above in equilibrium 2.8, does not appear to be the only reaction responsible for the elimination of chloritoid from pelitic schists in the study area. Relatively coarse-grained muscovite also appears to have replaced earlier chloritoid porphyroblasts, forming muscovite pseudomorphs that can be observed at many localities throughout the garnet-chlorite zone (see photos 2.15 to 2.17). The preservation of relict chloritoid in the muscovite pseudomorphs at several localities, confirms that chloritoid was the pre-cursor mineral (see photo 2.15).

Deflection of the main S1 schistosity around the muscovite pseudomorphs indicates that the ridged precursor mineral (chloritoid) was still present during the main D1 deformation. This conclusion is supported by the development of quartz pressure shadows along the margins of some of the pseudomorphs. Both of these textural observations are consistent with mineral growth timing discussed in section 2.4.1 above, where chloritoid (the precursor mineral) was generally found to have grown either before or during the D1 deformation.

Photo 2.15: Photomicrograph of muscovite pseudomorphs with relict chloritoid in sample 93-13b-I. The formation of pressure shadows on either side of the pseudomorph indicates chloritoid growth preceded the main deformation event (D1). Rotation of the chloritoid porphyroblasts during later deformation is indicated by asymmetry of the pressure shadows.

The apparent rigid behaviour of the pseudomorphs during the D1 deformation implies that muscovite replacement of chloritoid must have taken place after the D1 event. Furthermore, the lack of any preferred orientation by muscovite in the pseudomorphs is evidence that the replacement took place at relatively low temperatures during cooling after the major deformational events had occurred.

It is proposed that the muscovite pseudomorph formation is a relatively low-temperature, late-stage metasomatic effect, involving the transfer of potassium ions to, and the removal of iron ions from, the pseudomorph growth site (although iron may not migrate that far from the site, since magnetite is commonly scattered throughout the pseudomorph). Pseudomorph development is therefore not related to any high-temperature metamorphic equilibrium described in this chapter, including the reaction responsible for the development of the chloritoid disequilibrium textures described in the previous section.

Photo 2.16: Photomicrograph of muscovite pseudomorphs after chloritoid in sample 93-13b-I. Blue arrows point to relict chloritoid grains in the pseudomorphs. The yellow arrow points to a chloritoid inclusion in garnet. The development of pressure shadows around the pseudomorphs indicates that chloritoid was present during the main D1 deformational event (pre- to syn-D1) and that pseudomorph formation post-dates the D1 event.

Photo 2.17: Photomicrograph of muscovite pseudomorphs after chloritoid in sample 92-4a-I. Blue arrows point to relict chloritoid grains in the pseudomorphs. The muscovite pseudomorphs are overgrown by later-formed margarite laths (yellow arrows) and staurolite grains (although staurolite may have overgrown the chloritoid precursor).

2.4.4 Low Grade Staurolite

Staurolite does not become widespread in Bishop Corners pelites until it begins to form as a product of chloritoid breakdown at the chloritoid-out isograd (Equil 2.2). However, staurolite does occur at two localities in the garnet-chlorite zone in association with the following minerals:

93-13	staurolite + garnet + chlorite + chloritoid
92-7	staurolite + kyanite + chlorite

The AFM projection for the garnet-chlorite zone (figure 2.4) includes a stability field for the assemblage staurolite-kyanite-chlorite (from locality 92-7), at relatively magnesium-rich bulk compositions. However, the four-phase assemblage present at locality 93-13 is univariant in the KFMASH and can only be stable if a chloritoid-eliminating reaction, such as equilibrium 2.9 below, is taking place.

It seems unlikely however, that equilibrium 2.9 is stable at the pressure and temperature conditions experienced by Bishop Corners pelitic schists, since the product assemblage was only observed at locality 93-13 and the reactant assemblage (chloritoid-quartz) is widely distributed throughout the area. It is more likely that the presence of an additional chemical component is responsible for stabilizing one or more of the phases in the assemblage.

Figure 2.7 below, obtained by completing a microprobe traverse across a garnet crystal, shows that the manganese content (spessartine end-member) of the garnet in sample 93-13b-I is relatively high, ranging from 42% spessartine in the core (18.5 wt.% Mn) to 28% at the rim (13 wt.% Mn). This relatively high level of manganese is most likely responsible for stabilizing garnet in the assemblage, which would then plot in the divariant staurolite-chloritoid-chlorite field of figure 2.4.

Photo 2.18: Photomicrograph of staurolite porphyroblast with muscovite pseudomorphs after chloritoid (sample 93-13b-I). Note pressure shadow formed around magnetite .

Photo 2.19: Photomicrograph of staurolite and kyanite porphyroblasts in sample 92-7a-I. .

Figure 2.7: Microprobe traverse across garnet in sample 93-13b-l. Garnet is coexisting with chlorite-muscovite and quartz with trace staurolite and relict chloritoid in Chl+Ms pseudomorphs. The garnet core in the upper central portion of diagram contains less than 0.5 mole percent almandine. The left-hand scale should be applied to this portion of the almandine profile.

2.4.4.1 Staurolite chemistry

Most of the iron in the staurolite crystal structure occurs in the tetrahedrally coordinated T2 site (Hawthorne et al., 1993). This crystal structure favours the substitution of zinc, which is also tetrahedrally coordinated. Zinc substitution can therefore expand the stability field of staurolite in the same manner that manganese partitioning expands the stability of garnet.

Staurolite mineral chemistry is summarized below in figure 2.8. (Staurolite chemistry was determined by electron microprobe as part of the geothermobarometry study described in chapter four, results are listed in Appendix Table A5.8). Staurolite zinc content was found to be highly variable, ranging from 0.12 wt.% (sample 93-45a-l) to 6.6 wt.% ZnO (sample 93-26g-l). Figure 2.8 shows there is essentially no relationship between zinc content (expressed as Zn atoms per staurolite formula unit) and iron:magnesium ratio in staurolite. This is unusual, since zinc is assumed to substitute for iron in the crystal structure and the two variables should be negatively correlated. Data

points on the diagram have also been coloured according to the metamorphic zone in which the staurolite was found. Results indicate that zinc-rich staurolite occurs more frequently in low metamorphic grade areas. However, there are exceptions to this trend, with zinc-poor staurolite also occurring in the garnet-chlorite and chloritoid-biotite zones.

Guidotti (1970) documented a negative correlation between staurolite zinc content and modal abundance in pelitic schists from New England (samples had either a large amount of low-Zn staurolite or a small amount of high-Zn staurolite). This is a more appropriate explanation for the occurrence of high-zinc staurolite in the study area, since zinc-rich staurolite occurs only in samples on Fig 2.8 that contain less than 1% modal staurolite. This effect is related to the preferential concentration of zinc in staurolite, whereby all available zinc in a rock is scavenged into those few staurolite crystals that nucleate first. Hollister (1966) documented similar behaviour in garnet, whereby manganese in a rock is incorporated into the garnet crystals that nucleate first, producing garnets that exhibit characteristic bell shaped zoning profiles with high manganese cores. The correlation between low metamorphic grade and the incidence of high-zinc staurolite shown in figure 2.8 is therefore incidental, since staurolite is not very abundant in iron-rich pelites at these low temperatures. It is certain that preferential zinc partitioning will expand the relative stability field of staurolite; however, this effect appears to have a minimal effect on the observed mineral assemblages in the study area.

Figure 2.8: Summary of staurolite chemistry throughout the study area (data was obtained by microprobe analysis, all Fe is assumed to be Fe^{2+}). Points have been coloured according to metamorphic grade. Zinc-rich staurolite occurs more frequently at lower metamorphic grade, however samples from these areas typically have a low modal abundance of staurolite.

2.4.5 Low Grade Kyanite

Kyanite schists are found sporadically throughout the garnet-chlorite zone (localities 93-13, 90-10, 93-23, 92-7). The kyanite-bearing rocks stratigraphically overlie the more Fe-rich garnet-bearing schists (closer to the overlying Myer Cave Formation). Kyanite is associated with chlorite, plagioclase and two types of muscovite pseudomorphs (either spherical after plagioclase, or rectangular/blocky after chloritoid).

Photo 2.20: Photomicrograph of syn-D1 kyanite porphyroblasts with muscovite pseudomorphs after plagioclase in sample 93-13c-l. Kyanite porphyroblasts have been stretched and fractured by later deformation (possibly D2).

Photo 2.21: Photomicrograph of kyanite bundles with blocky muscovite pseudomorphs after chloritoid (sample 93-23b-l).

2.4.6 Occurrence of Paragonite

Inclusions of the sodium mica paragonite, ideally $\text{NaAl}_2(\text{AlSi}_3)\text{O}_{10}(\text{OH})_2$, were discovered in garnet from a sample of garnet-chlorite schist (93-16b-I) during routine microprobe examination. This discovery is thought to be the first documented occurrence of paragonite in the Grenville Province. Photo 2.22 below shows the paragonite inclusions, which occur as 100 to 200 μm laths intergrown with muscovite. The garnet-chlorite schist also contains chloritoid, which occurs as inclusions in garnet (see photo 2.22) and as relict xenoblastic grains in the matrix. While volumetrically insignificant, the paragonite inclusions indicate that sodic-mica played some unknown role in the development of the garnet-chlorite schist.

Photo 2.22: Back-scattered electron image of paragonite in garnet-chlorite schist (sample 93-16b-I). High magnification photo on right shows paragonite laths (dark grey) intergrown with muscovite (medium grey). Low magnification photo on left shows location of paragonite inclusions in garnet core. Sample also contains chloritoid, which occurs as inclusions in garnet and as relict armoured grains in the matrix.

The results of seven paragonite analyses are listed in Table 2.1 below. The inclusions are approximately 88% paragonite end-member with 8% muscovite and 4% margarite substitution. Iron appears to be the only other major impurity in the paragonite laths

Table 2.1: Paragonite Analyses from Sample 93-16b-I									
	Pg 2.2	Pg 2.4	Pg 2.5	Pg 2.6	Pg 2.7	Pg 2.8	Pg 2.9	Avg.	St. Dev.
	(2,1)	(2 σ)	(5,2)	(2 σ)	(4,1)	(2 σ)	(2,1)	n=7	(2 σ)
SiO ₂	45.36	45.84	45.93	45.48	45.14	45.46	45.23	45.49	0.59
Al ₂ O ₃	41.61	41.42	41.09	41.33	40.92	41.59	41.42	41.34	0.51
Cr ₂ O ₃	0.00	0.10	0.00	0.09	0.08	0.06	0.04	0.05	0.08
TiO ₂	0.07	0.20	0.14	0.24	0.22	0.18	0.16	0.17	0.11
FeO	1.16	1.30	1.25	1.29	1.14	1.16	1.21	1.21	0.13
MnO	0.31	0.34	0.34	0.28	0.28	0.21	0.38	0.31	0.12
MgO	0.09	0.11	0.09	0.13	0.09	0.16	0.08	0.11	0.06
CaO	0.55	0.55	0.51	0.59	0.54	0.61	0.53	0.56	0.06
Na ₂ O	6.73	6.07	5.85	6.67	6.67	6.60	6.02	6.37	0.75
K ₂ O	1.01	0.76	0.76	0.99	0.86	0.91	0.91	0.88	0.20
BaO	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02
TOTAL	96.91	96.69	95.95	97.07	95.93	96.94	95.96	96.49	1.05
<i>Cation proportions on the basis of 11 oxygens</i>									
Si	2.876	2.901	2.922	2.880	2.888	2.877	2.886	2.890	0.033
Al	1.124	1.099	1.078	1.120	1.112	1.123	1.114	1.110	0.033
Sum	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	0.000
Al	1.984	1.990	2.004	1.964	1.973	1.979	2.001	1.985	0.029
Cr	0.000	0.005	0.000	0.004	0.004	0.003	0.002	0.003	0.004
Ti	0.004	0.009	0.007	0.011	0.010	0.009	0.008	0.008	0.005
Fe	0.062	0.069	0.066	0.068	0.061	0.061	0.064	0.064	0.007
Mn	0.016	0.018	0.018	0.015	0.015	0.011	0.021	0.016	0.006
Mg	0.008	0.010	0.008	0.012	0.009	0.015	0.007	0.010	0.006
Sum	2.074	2.102	2.104	2.075	2.072	2.079	2.103	2.087	0.030
Ca	0.037	0.037	0.035	0.040	0.037	0.041	0.037	0.038	0.004
Na	0.827	0.745	0.721	0.818	0.827	0.810	0.744	0.785	0.092
K	0.081	0.061	0.061	0.080	0.070	0.074	0.074	0.072	0.016
Ba	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001
Sum	0.946	0.843	0.817	0.938	0.934	0.925	0.854	0.894	0.107
K/(K+Na+Ca)	0.086	0.073	0.075	0.085	0.075	0.080	0.086	0.080	0.012
Na/(K+Na+Ca)	0.874	0.883	0.882	0.872	0.885	0.876	0.871	0.878	0.011
Ca/(K+Na+Ca)	0.040	0.044	0.043	0.043	0.040	0.045	0.043	0.042	0.004

2.4.7 Occurrence of Margarite

The calcium mica margarite (ideally $\text{CaAl}_2(\text{Al}_2\text{Si}_2)\text{O}_{10}(\text{OH})_2$) occurs in Flinton Group pelites from the garnet-chlorite zone near Bishop Corners up-grade to the upper staurolite-garnet-biotite zone near Marble Lake (discussed in further detail in section 2.8.2). Photos 2.26 through 2.29 show how

margarite can be distinguished optically from muscovite by its acicular to sheaf-like habit, higher relief (refractive index), and lower birefringence (typically first order orange to second order blue). Textural evidence indicates that margarite growth appears to have taken place during all major deformational events, with examples of both primary foliation defining syn-D1 margarite and late-stage post-deformational (post-D3, cross-cuts all foliation) margarite commonly occurring in the same sample.

Coexisting white mica (muscovite, margarite and paragonite) mineral chemistry obtained by microprobe is summarized below in figure 2.9 (full results listed in Appendix 5). Both margarite and muscovite display a minor amount of sodium solubility (ranging between 10 and 20 mol% paragonite).

Margarite and muscovite show very limited solubility towards each other (evidence for a miscibility gap between the two). Micras occurring with paragonite inclusions in sample 93-16b-I are the most sodium-rich.

Figure 2.9: Co-existing white mica chemistry expressed as mole fraction margarite, muscovite and paragonite (tie lines join coexisting mica crystals).

Photo 2.23: Photomicrograph of Ca-mica margarite with co-existing biotite, chlorite, muscovite, quartz and oxides in sample 92-8e-1. Margarite occurs as colourless, bladed crystals with higher relief than quartz and muscovite.

Photo 2.24: Same as previous photo, with crossed nicols. Margarite shows characteristic first order yellow and red interference colours.

Photo 2.25: Photomicrograph of sample 93-6a-I, showing Ca-mica margarite defining the S1 foliation in a garnet-biotite-staurolite pelite from the staurolite-chlorite zone. The S1 foliation has been wrapped around syn-D1 staurolite porphyroblasts by later D2 deformation (the S2 foliation is sub-parallel to S1).

Photo 2.26: Same as previous photo, with crossed nicols. Margarite shows characteristic first order yellow and red interference colours.

2.4.8 Ankerite Inclusions

Garnets from sample 91-27 (garnet-chlorite schist) contain inclusions of the iron-carbonate ankerite. Similar carbonate inclusions were not documented in any other sample. Microprobe results (Table 2.2) show that the inclusions contain 13 to 14 wt.% FeO, 2 to 5 wt.% MnO, and 9 to 13 wt.% MgO. It seems unlikely that the ankerite would have occurred only as inclusions in garnet, implying that the matrix of the garnet-chlorite schist was once carbonate bearing. These carbonate minerals may have provided a source of iron, manganese, magnesium and calcium for silicate minerals that grew later in response to increasing temperature during prograde metamorphism.

Table 2.2: Ankerite Analyses from Sample 91-27a-I

	Ank. Incl. 1a		Ank. Incl. 1b		Ank. Incl. 1c		Ank. Incl. 1d		Ank. Incl. 1f	
	Grt. core		mid. Grt.		mid. Grt.		mid. Grt.		Grt. core	
	Avg.	St. Dev.	Avg.	St. Dev.	Avg.	St. Dev.	Avg.	St. Dev.	Avg.	St. Dev.
	n=3	(2σ)	n=3	(2σ)	n=32	(2σ)	n=2	(2σ)	n=2	(2σ)
FeO	13.37	0.40	13.29	0.27	11.74	0.07	14.36	0.34	12.91	0.23
MnO	3.10	0.03	2.62	0.31	2.37	0.51	4.85	0.28	2.98	0.07
MgO	10.80	0.49	11.49	0.43	12.75	0.54	8.80	0.01	11.50	0.45
CaO	27.17	0.25	27.08	0.37	26.60	0.56	26.35	0.10	26.71	0.38
Na ₂ O	0.05	0.11	0.12	0.22	0.04	0.12	0.04	0.11	0.08	0.17
BaO	0.02	0.03	0.04	0.15	0.03	0.08	0.00	0.00	0.03	0.03
CO ₂ (Calc*)	43.32	0.36	43.75	0.41	43.52	0.57	42.15	0.10	43.40	0.54
TOTAL	97.84	0.75	98.39	0.76	97.04	1.03	96.54	0.15	97.61	0.97
<i>Cation proportions on the basis of 1 Cation, 2 Oxygens</i>										
Fe ²⁺	0.379	0.012	0.373	0.012	0.331	0.006	0.418	0.010	0.365	0.003
Mn	0.089	0.002	0.074	0.009	0.067	0.014	0.143	0.008	0.085	0.003
Mg	0.545	0.022	0.575	0.016	0.640	0.020	0.456	0.001	0.580	0.017
Sum	1.013	0.010	1.022	0.002	1.038	0.028	1.017	0.000	1.030	0.017
Ca	0.985	0.011	0.974	0.005	0.960	0.031	0.982	0.004	0.967	0.023
Na	0.004	0.007	0.008	0.014	0.003	0.008	0.003	0.008	0.005	0.011
Ba	0.000	0.000	0.001	0.002	0.000	0.001	0.000	0.000	0.000	0.000
Sum	0.989	0.010	0.982	0.008	0.963	0.024	0.984	0.003	0.973	0.012
C (ideal, assumed)	2	0	2	0	2	0	2	0	2	2
Fe/(Fe+Mg)	0.410	0.017	0.394	0.014	0.341	0.011	0.478	0.006	0.386	0.005
Ankerite (Fe)	0.374	0.014	0.365	0.011	0.318	0.014	0.411	0.009	0.354	0.003
Kutnahorite (Mn)	0.088	0.002	0.073	0.009	0.065	0.012	0.141	0.008	0.083	0.004
Dolomite (Mg)	0.538	0.016	0.562	0.016	0.617	0.003	0.449	0.001	0.563	0.007

* CO₂ content calculated from ideal stoichiometry, assuming 2 carbon atoms per 6 oxygens

2.5 The Chloritoid-Biotite Isograd and Petrology of Pelites in the Ctd-Bt Zone

The chloritoid-biotite isograd is located in the field by identifying the first occurrence of biotite in garnet-chlorite-chloritoid pelites. This typically occurs when biotite nucleates as small (50 μ m) laths on the surface of chloritoid crystals (see Photos 2.27 to 2.29 below). The resulting six-phase assemblage (garnet-chlorite-chloritoid-biotite-muscovite-quartz) is univariant in the KFMASH system (assuming the presence of a hydrous fluid phase), resulting in the following equilibrium:

Equilibrium 2.1 was balanced in the KFMASH system using mineral compositions obtained from sample 92-6f1-II, a Grt-Chl-Ctd-Bt schist located on the isograd. Stoichiometric coefficients for the resulting equilibrium (2.10 below) were normalized to one mole of water. Equil 2.10

Figure 2.10 shows how this reaction changes the topology of the AFM projection, using ideal mineral compositions in the KFMASH system. This isograd marks the first appearance of chloritoid-biotite as a stable assemblage, and the geographical area above the isograd is therefore referred to as the chloritoid-biotite zone. Pelites in this zone typically contain porphyroblasts of chloritoid and garnet in a matrix of biotite, muscovite and quartz (see photos 2.30 and 2.31). The following list summarizes the mineral assemblages encountered in this zone (in approximate order of decreasing abundance):

- garnet + chlorite
- garnet + chlorite + biotite
- garnet + chlorite + chloritoid
- garnet + chlorite + chloritoid + biotite
- garnet + chloritoid + biotite
- garnet + chlorite + chloritoid + staurolite
- garnet + chlorite + biotite + staurolite
- chloritoid + chlorite + staurolite
- kyanite + chlorite

Figure 2.10: Reaction at the chloritoid-biotite isograd, depicted on the AFM projection. Mineral compositions shown on diagram correspond to ideal KFMASH end-members. Three-phase fields are shown shaded in yellow; the univariant four-phase field is shown in pink.

Photo 2.27: Photomicrograph showing how biotite first appears in sample 93-24b-I (a Grt-Chl-Ctd-Bt schist) as small 50µm laths nucleating on the surface of chloritoid crystals.

Photo 2.28: Photomicrograph of garnet-chlorite-chloritoid-biotite pelite (sample 93-24c-l) showing sparse xenoblastic biotite crystals (indicated by red arrows) nucleating next to corroded chloritoid porphyroblasts.

Photo 2.29: Photomicrograph of sample 92-8d-l, showing biotite nucleating on the chloritoid basal {001} cleavage (indicated by yellow arrows). Sample is a margarite-bearing Chl-Grt-Ctd-Bt schist, located approximately 200 metres up-strike (and up-grade) from the previous sample (93-24b-l).

Photo 2.30: Photomicrograph of garnet-chloritoid-biotite assemblage in sample 92-41b-I.

Photo 2.31: Photomicrograph of chloritoid-biotite-garnet assemblage with muscovite, quartz and oxides in sample 93-20f-II. Sample is located approximately 200 metres west (down-grade) of the first appearance of staurolite in chloritoid-bearing rocks.

2.5.1 Effect of Manganese on the location of the Chloritoid-Biotite Isograd

Samples containing the four-phase assemblage garnet-chlorite-chloritoid-biotite (indicative of equilibrium 2.1) persist up-grade beyond the first occurrence of chloritoid-biotite for approximately 500 metres. Within this area, it is also possible to find samples containing *either* just the product assemblage of equilibrium 2.1 (chloritoid-biotite) or the reactant assemblage (garnet-chlorite). The chloritoid-biotite isograd reaction thus appears to take place within a discrete zone, rather than along a line. This “isograd spreading” is commonly due to the presence of an additional chemical component in natural system, which causes the univariant assemblage in the model system (in this case KFMASH) to become divariant.

To test this hypothesis, ferromagnesian silicate chemistry was determined for three samples collected from locality 92-6, an outcrop lying on or just above the chloritoid-biotite isograd. The three samples contain different mineral assemblages listed below (shown in photos 2.32 to 2.35).

92-6a	Grt+Chl+Ms+Qtz	trivariant reactant assemblage
92-6f1	Grt+Chl+Ctd+Bt+Ms+Qtz	univariant assemblage
92-6c	Grt+Ctd+Bt+Ms+Qtz	divariant product assemblage

Mineral chemistry was determined using the scanning electron microscope (results are summarized in Appendix 5). As part of this study, a microbeam traverse was completed across one of the larger garnet crystals in each sample. Garnet zoning profiles obtained in this manner are summarized below in figure 2.11. Garnet from each sample has a characteristic bell shaped spessartine profile, with a manganese-enriched core. Note however that garnet from sample 92-6a (garnet-chlorite) has a much higher manganese content than garnet coexisting with the four-phase assemblage (sample 92-6f1), which in turn has a higher manganese content than garnet from the chloritoid-biotite-bearing sample (92-6c). This pattern suggests that manganese is having some effect on the observed mineral assemblage.

Figure 2.12 shows ferromagnesian silicate compositions plotted on an isometric AFM projection with Mn-oxide on the vertical axis (adapted from Droop & Harte, 1995; and Karabinos, 1985). Garnet rim compositions for all three samples lie above the AFM plane, indicating that manganese is having a stabilizing effect on garnet (the addition of Mn to the KFMASH model system is stabilizing an additional phase – garnet, with no change in the variance of the system).

Photo 2.32: Photomicrograph of garnet-chlorite pelite (sample 92-6a-I).

Photo 2.34: Photomicrograph of garnet-chlorite-chloritoid-biotite pelite (sample 92-6b-I). White arrows point to biotite nucleating on post D1 chloritoid.

Photo 2.33: Photomicrograph of garnet-chlorite-chloritoid-biotite pelite (sample 92-6f2-I). Syn- to post-D1 chloritoid has overgrown chlorite-rich matrix. Garnet and late-stage biotite overgrow the chloritoid porphyroblasts.

Photo 2.35: Photomicrograph showing abundant biotite in equilibrium with chloritoid and garnet (sample 92-6c-II).

Figure 2.11: Microprobe garnet traverses from locality 92-6. Garnet in the garnet-chlorite assemblage from sample 92-6a-I contains the highest manganese (spessartine-Sps) content, while garnet from the chloritoid-biotite assemblage (sample 92-6c-III) has the lowest.

Figure 2.12: Ferromagnesian silicate mineral chemistry from locality 92-6 shown on an isometric AFM projection with Mn-oxide added as the third vertical axis. All three samples contain manganese-bearing garnets, with compositions lying above the AFM plane.

Minerals lying within the AFM plane on the floor of figure 2.12 do not have crossing tie lines, and display phase assemblages that are consistent with the outcrop being on the reactant side of the chloritoid-biotite isograd (true KFMASH assemblages would be chloritoid-biotite, chloritoid-biotite-chlorite and chlorite for samples 92-6c, 92-6f and 92-6a respectively). These results indicate that manganese partitioning into garnet is responsible for the persistence of the garnet-chlorite assemblage into the chloritoid-biotite zone.

The results shown on figure 2.12 indicate that the occurrence of garnet, and therefore the stability of garnet-chlorite, is solely a function of manganese. This observation, if true, implies that

garnet-chlorite-bearing assemblages are not stable in the KFMASH system, and that the garnet + chlorite + muscovite = chloritoid + biotite isograd (equilibrium 2.1) is not a stable reaction (chloritoid-biotite would therefore be the stable mineral assemblage in low-grade iron-rich pelites, with garnet appearing only as a function of increasing manganese bulk composition).

To test this hypothesis with a larger data set, all available ferromagnesian mineral compositions for garnet-chlorite and chloritoid-biotite-bearing assemblages were plotted on a similar block diagram. Figure 2.13 below shows 1) that both garnet-chlorite (sample Madoc-7b2) and chloritoid-biotite (sample 93-20f) are stable in low-manganese bulk compositions and 2) that chloritoid-biotite occurs in equilibrium with manganese-rich garnet (chloritoid-biotite assemblages are not restricted to manganese-poor bulk compositions). Thus, it appears that garnet-chlorite forms a stable assemblage in the KFMASH system, and that preferential manganese partitioning increases the stability field of garnet into the chloritoid-biotite zone on the high temperature side of equilibrium 2.1.

Figure 2.13: MnAFM isometric projection showing ferromagnesian silicate mineral chemistry for all available garnet-chlorite and chloritoid-biotite-bearing assemblages in the study area. Garnet-chlorite-bearing assemblages are joined by red lines, chloritoid-biotite assemblages by blue, and four-phase assemblages by green. Two samples, Madoc-7b2 and 93-20f contain Mn-poor garnets that lie within the AFM plane.

2.5.2 Occurrence of Staurolite-Biotite in Garnet-free assemblages

Staurolite and biotite appear with chloritoid, chlorite, muscovite and quartz (see photo 2.36 below), approximately 50 to 100 metres up-grade of the chloritoid-biotite isograd (garnet-bearing samples from this same locality contain the assemblage garnet-chlorite-chloritoid-biotite). The formation of staurolite and biotite with coexisting chloritoid-chlorite-muscovite-quartz can be expressed by the following univariant equilibrium in the KFMASH system (assuming the presence of a hydrous fluid phase):

Figure 2.14 shows how this reaction changes the topology of the AFM projection, using ideal mineral compositions in the KFMASH system. Equilibrium 2.11 marks the first appearance of coexisting staurolite-biotite in muscovite-quartz-bearing schists, so this reaction is identified as the staurolite-biotite isograd. The trace of this isograd cannot be mapped through the field area however, since the four-phase reactant assemblage: chloritoid-chlorite-staurolite-biotite was observed only at a single locality (93-26). Hypothetical phase assemblages in the staurolite-biotite zone above the isograd are shown on figure 2.15 below.

Photo 2.36: Photomicrograph showing biotite (red arrow) and staurolite (yellow arrow) nucleating in chloritoid-chlorite schist (sample 93-26i-I), up-grade of the chloritoid-biotite isograd. Margarite laths are scattered throughout the matrix (orange arrow).

Figure 2.14: Chloritoid + chlorite = staurolite + biotite reaction (Equil 2.11), depicted on an AFM projection. Mineral compositions shown on diagram correspond to ideal KFMASH end-members. Three-phase fields are shown shaded in yellow; the univariant four-phase field is shown in pink.

Figure 2.15: Topology of the AFM projection above the staurolite-biotite isograd (Equil 2.11). Mineral compositions shown on diagram correspond to ideal KFMASH end-members. Three-phase fields are shown shaded in yellow.

2.6 The Garnet-Staurolite-Biotite Isograd (Chloritoid-out Isograd)

Staurolite first appears with chloritoid, biotite and garnet approximately 600 to 1000 metres up-grade from the chloritoid-biotite isograd. At this point, small (100-500 μ m) staurolite crystals develop, either overgrowing pre-existing chloritoid (see photo 2.37, and 2.39-2.40), or nucleating at the point where adjacent chloritoid crystals are impinging on one another (see photo 2.38).

The reaction by which staurolite first appears with garnet and biotite can be modeled in the KFMASH system as:

Equilibrium 2.2 was balanced in the KFMASH system using mineral compositions obtained from sample 92-10a-II, a Ctd-Grt-St-Bt schist located on the isograd. Stoichiometric coefficients for the resulting equilibrium (2.9 below) were normalized to ten moles of water. Equil 2.12

Figure 2.16 shows how this reaction changes the topology of the AFM projection, using ideal mineral compositions in the KFMASH system. This reaction isograd marks the first appearance of staurolite together with biotite and garnet as a stable assemblage in Fe-rich pelites, and the geographical area above the isograd is therefore referred to as the garnet-staurolite-biotite zone.

Photo 2.37: Photomicrograph showing two small staurolite crystals (indicated by yellow arrows) overgrowing chloritoid in sample 92-8d-II (a Chl-Grt-Ctd-Bt schist with margarite).

Photo 2.38: Photomicrograph showing staurolite (indicated by yellow arrows) nucleating along chloritoid grain boundaries in sample 92-10a-I. This outcrop contains the first occurrence of the assemblage Grt+Ctd+Bt+St, which is characteristic of the Chloritoid-out isograd.

Figure 2.16: Reaction at the garnet-staurolite-biotite isograd, depicted on an AFM projection. Three-phase fields are shown shaded in yellow; the univariant four-phase field is shown in pink. The dot in the centre of the four-phase field represents the last chloritoid composition in equilibrium with staurolite, garnet and biotite. Mineral compositions shown on diagram correspond to ideal KFMASH end-members.

2.7 Petrology of Pelites from the Garnet-Staurolite-Biotite Zone

Iron-rich muscovite-bearing pelitic schists contain coexisting garnet, staurolite, and biotite in this zone, which is approximately equivalent to the staurolite-biotite zone of Carmichael (1970). The garnet-staurolite-biotite zone can be sub-divided into an upper (chloritoid-free) and lower (chloritoid-bearing) portion, based on the presence of chloritoid, which persists up-grade beyond the chloritoid-out isograd for approximately 3 kilometres. Chloritoid occurs only as inclusions in garnet northeast of locality 93-30, which marks the start of the upper garnet-staurolite-biotite zone.

2.7.1 *The Lower Garnet-Staurolite-Biotite Zone*

Pelites in this zone commonly contain the univariant assemblage chloritoid-garnet-staurolite-biotite. Samples display textures consistent with equilibrium 2.2 above, with garnet and staurolite porphyroblasts overgrowing and replacing pre-existing idioblastic to sub-idioblastic chloritoid porphyroblasts that range in size from 500 μm to 8cm (see photos 2.39 and 2.40). Additional mineral assemblages encountered in this zone are listed below in approximate order of decreasing abundance:

chloritoid + garnet + biotite + staurolite
 staurolite + garnet + biotite
 chloritoid + garnet + biotite
 chloritoid + biotite + staurolite (no muscovite)

Mineral compositions for iron-rich chloritoid-bearing assemblages were measured by electron microprobe (mineral chemistry results are summarized in Appendix 5). These compositions are shown on an AFM projection in figure 2.17 below. Note that the measured chloritoid compositions always fall within the three-phase garnet-staurolite-biotite triangle, as predicted by equilibrium 2.2. Figure 2.17 also shows how the three-phase garnet-staurolite-biotite triangle migrates in the direction of more magnesium-rich bulk compositions with increasing metamorphic grade, presumably due to continuous reactions that are taking place in response to increasing temperature.

Figure 2.17: AFM projection of Fe-rich chloritoid-bearing assemblages from the lower garnet-staurolite-biotite zone. Sample 93-20f-I is a pelite from the chloritoid-biotite zone, located approximately 200 metres down-grade of the chloritoid-out isograd. Samples are presented in order of increasing metamorphic grade. Mineral chemistry used in diagram was obtained by microprobe; see results summarized in Appendix 5.

Photo 2.39: Photomicrograph showing replacement of chloritoid by staurolite in garnet-chloritoid-staurolite-biotite pelite (sample 93-28b-l).

Photo 2.40: Photomicrograph of chloritoid-garnet-staurolite-biotite assemblage with muscovite, quartz and oxides in sample 92-27a-l. Staurolite (indicated by yellow arrows) is replacing chloritoid. Porphyroblastic matrix chloritoid disappears approximately 300 metres northeast (up-grade) of this locality (at outcrop 92-30).

2.7.2 *Chloritoid in the Myers Cave Formation*

The Myers Cave Formation directly overlies the Bishop Corners pelites in the Flinton syncline.

This formation is composed of interbedded carbonates and various silici-clastic rocks including graphitic and sulphidic schists and pelites that are characterized by the occurrence of coarse-grained staurolite porphyroblasts. Several outcrops in the lower garnet-staurolite-biotite zone near locality 90-20 contain coarse-grained chloritoid (see photo 2.41 below), which appears to be the precursor mineral of the coarse-grained staurolite porphyroblasts (see photo 2.42). This is a first reported occurrence of chloritoid in the Myers Cave Formation.

Photo 2.41: Chloritoid poikiloblast in Myers Cave Formation pelitic schist (sample number 90-20b-III). Chloritoid occurs with garnet, biotite, muscovite, quartz, and a very small amount of staurolite.

Photo 2.42: Photomicrograph of garnet-staurolite-biotite schist from the Myers Cave Formation south of Marble Lake (sample 91-20c-II). Sample contains large staurolite poikiloblasts, which have relict chloritoid inclusions (blue arrows), indicating that the staurolite grew from pre-existing chloritoid.

2.7.3 *The Upper Garnet-Staurolite-Biotite Zone*

The disappearance of chloritoid in the Fernleigh syncline marks the transition between the lower and upper portions of the garnet-staurolite-biotite zone. Myers Cave Formation pelites from the upper zone are characterized by relatively monotonous staurolite-garnet-biotite-assemblages. Bishop Corners pelites along the syncline margin typically display a wider range of staurolite-bearing assemblages than was observed in stratigraphically equivalent pelites from the lower portion of the zone (where chloritoid-garnet-staurolite-biotite assemblages are common). Staurolite-chlorite-bearing assemblages are common, indicating that the bulk composition of pelites from this zone is more magnesian. Garnet was observed in nearly every pelite examined, including the staurolite-chlorite schists (see photos 2.43 and 2.44). Garnet-chlorite stability is not attributed to a decrease in metamorphic grade however, because the widespread occurrence of garnet throughout the zone implies it is being stabilized by at least one additional chemical component outside of the KFMASH system. This is confirmed by figure 2.18, a MnAFM isometric projection, which shows that garnets from the upper garnet-staurolite-biotite zone are highly enriched in manganese relative to garnets from either the lower garnet-staurolite-biotite or kyanite-biotite zones. The high manganese content of

the garnet causes increased garnet stability, which in turn increases the frequency of six-phase univariant mineral assemblages throughout the zone. The four samples shown in figure 2.18 would have the following KFMASH compatible mineral assemblages:

91-21c2	staurolite-chlorite
92-9i2	chlorite-biotite
93-10b	staurolite-chlorite-biotite
92-26b	staurolite-chlorite-kyanite

The list below summarizes the mineral assemblages observed in this zone (in approximate order of decreasing abundance). All assemblages include muscovite and quartz. Six-phase (univariant) assemblages are shown in bold type:

garnet + staurolite + biotite $\pm$ margarite
 garnet + chlorite + staurolite $\pm$ plagioclase
 garnet + chlorite + biotite + plagioclase
garnet + chlorite + staurolite + biotite $\pm$ plagioclase
garnet + chlorite + staurolite + kyanite + plagioclase
staurolite + biotite + garnet + kyanite + plagioclase

Figure 2.18: MnAFM isometric projection of mineral compositions from the upper garnet-staurolite-biotite zone. Garnets from this zone are manganese-rich; Results for two chloritoid-garnet-staurolite-biotite pelites from the lower garnet-staurolite-biotite zone and one garnet-staurolite-biotite pelite from the kyanite-biotite zone are included for comparison. Mineral chemistry used in diagram was obtained by microprobe; see results summarized in Appendix 5.

Photo 2.43: Photomicrograph of sample 91-21d-I, showing the assemblage garnet + chlorite + staurolite extending beyond the limit of chloritoid stability into the upper garnet-staurolite-biotite zone. Chlorite occurs mostly as part of the matrix assemblage. Chloritoid is present in the sample, but only as inclusions in garnet.

Photo 2.44: Photomicrograph of St-Chl-Grt schist (sample 92-36L-I), showing the persistence of the garnet-chlorite assemblage beyond the stability field of chloritoid.

2.7.4 High-Grade Muscovite Pseudomorphs

Micaceous pseudomorphs composed of coarse-grained muscovite with oxide inclusions occur throughout the garnet-staurolite-biotite zone. The pseudomorphs occur in both the Myers Cave and Bishop Corners Formations, but appear to be more common in the former unit. The occurrence of relict chloritoid grains in coarse-grained mica indicates that the pseudomorphs formed by replacement of earlier chloritoid porphyroblasts (see photo 2.45 below). The pseudomorphs are therefore the high-grade equivalent of the mica pseudomorphs described in section 2.2.2. The random alignment of constituent muscovite laths in the high-grade pseudomorphs indicates that pseudomorph development took place after the main D1 deformational event (same relative timing as the low-grade examples).

Photo 2.45: Photomicrograph showing relict chloritoid inclusions (indicated by blue arrows) in several muscovite pseudomorphs and a garnet porphyroblast. Photo is from sample 90-11c-II, a garnet-biotite-staurolite-margarite pelite. Inset photograph shows detail of relict chloritoid in coarse-grained muscovite from the central pseudomorph.

2.8 The Kyanite-Biotite Isograd at Marble Lake

In the Fernleigh syncline, coexisting kyanite and biotite begins to develop in staurolite-chlorite-bearing pebble schists approximately two kilometres up-grade from the last outcrop of chloritoid-bearing pelite (see photo 2.46). The seven-phase KFMASH univariant assemblage (kyanite-biotite-staurolite-chlorite-muscovite-quartz) is initially found only in the thin layers of conglomerate and pebble schist at the base of the Flinton Group. Staurolite-chlorite assemblages remain stable in the upper pelitic beds of the formation, indicating that fluid infiltration from underlying amphibolites and carbonates is affecting the relative stability of two assemblages. This fluid-phase dependence occurs because the reaction responsible for the formation of the kyanite-biotite assemblage (Equil 2.3 below) is a dehydration reaction that occurs at lower temperatures in the presence of a mixed H₂O-CO₂ fluid, where water activities are less than unity (<1):

Figure 2.19 shows how this reaction changes the topology of the AFM projection, using ideal mineral compositions in the KFMASH system. Equilibrium 2.3 marks the first appearance of kyanite-biotite as a stable assemblage in muscovite-quartz-bearing rocks, and the geographical area above the isograd is therefore referred to as the kyanite-biotite zone.

Figure 2.20 below shows observed mineral assemblages from the Marble Lake kyanite-biotite zone on an AFM projection using mineral compositions from the ideal KFMASH system. These are listed below, in approximate order of decreasing abundance (All assemblages include muscovite and quartz). Six-phase (univariant) assemblages are shown in bold type:

1. staurolite ± kyanite + plagioclase
2. garnet + staurolite + biotite ± plagioclase ± margarite
3. kyanite + biotite + staurolite + plagioclase (see figure 2.47)
4. staurolite + biotite + plagioclase
5. **staurolite + chlorite + kyanite + biotite + plagioclase**
6. garnet + staurolite ± kyanite
7. garnet + biotite + margarite
8. staurolite + chlorite + kyanite + plagioclase
9. staurolite + chlorite + biotite
10. garnet + staurolite + kyanite
11. **garnet + staurolite + biotite + kyanite**

Figure 2.19: Reaction at the kyanite-biotite isograd, depicted on an AFM projection. Three-phase fields are shown shaded in yellow; the univariant four-phase field is shown in pink. Mineral compositions shown on diagram correspond to ideal KFMASH end-members.

Figure 2.20: Observed muscovite-bearing pelitic assemblages in the kyanite-biotite zone near Marble Lake. Mineral compositions shown on diagram correspond to ideal KFMASH end-members. Three-phase fields are shaded yellow.

Photo 2.46: Photomicrograph showing the first occurrence of kyanite and biotite, with coexisting staurolite and chlorite (green arrows), in a pebble-schist at the base of the Flinton Group in the Fernleigh syncline (locality 92-36).

Photo 2.47: Photomicrograph of coexisting biotite and kyanite in pelite from Marble Lake (sample 92-16e-l). Scattered staurolite grains are indicated by yellow arrows.

Coexisting kyanite and biotite become widely distributed throughout pelitic units immediately south and east of Marble Lake, approximately 2 kilometres up-grade of the first appearance of this assemblage in the lower conglomeratic beds of the Flinton Group (see photo 2.47). However, lower-grade chlorite-staurolite assemblages persist in scattered locations throughout this area as well. The scattered, irregular distribution of kyanite-biotite throughout this area is likely a reflection of the fluid-phase dependence of equilibrium 2.3, with the product assemblage (kyanite-biotite) being stabilized by the infiltration of CO₂-rich fluids from adjacent marble units (carbon dioxide infiltration lowers the activity of water in the pelites and depresses the equilibrium temperature of the reaction 2.3). The irregular distribution of the kyanite-biotite assemblage could therefore be explained by non-uniform infiltration of the CO₂-rich fluids through the pelites.

Two observations support the hypothesis that the kyanite-biotite assemblage is being stabilized by infiltrating CO₂-rich fluids.

- 1) Staurolite-chlorite remains stable in pelitic schists that overlie conglomeratic units containing kyanite-biotite, implying that the reactant assemblage is being stabilized by fluid infiltration from underlying units.
- 2) Pelites directly overlying carbonate metasediments at Marble Lake (locality 90-1) contain an anomalously high-grade assemblage: garnet-staurolite-biotite-kyanite (assemblage 12 above, also noted Davidson et al., 1990), that is indicative of staurolite breakdown in the kyanite stability field (equilibrium 2.5). Electron microprobe data was used in conjunction with the program TWQ (Berman, 1991) to calculate and plot all possible reaction curves for a staurolite-garnet-biotite-muscovite-quartz schist obtained from this same locality (see Chapter 4 for additional details). Dehydration curves for this sample generally lie at high temperature and pressure values assuming unit water activities, however, these curves become coincident with fluid-absent equilibria, such as the garnet-biotite thermometer, if the activity of water is reduced to approximately 0.5 (see figure 4.7 for additional discussion). It is proposed that the activity of water was reduced to this level (0.5) by infiltrating CO₂-rich fluids from the adjacent marbles and that these low water activities shifted the equilibrium temperature of both the kyanite-biotite isograd (equilibrium 2.3) and the staurolite-out isograd (equilibrium 2.5) to lower

temperature values, stabilizing the kyanite-biotite and garnet-staurolite-biotite-kyanite assemblages observed at locality 90-1.

Thus, stability of kyanite-biotite in the Marble Lake area is more likely due to reduced water activity, than increasing metamorphic temperature.

2.8.1 High-grade Chloritoid Inclusions

Garnets from a staurolite-garnet-biotite schist at locality 90-4 contain inclusions of chloritoid, making this locality the highest grade occurrence of chloritoid (see photo 2.48 below). Armoured inclusions of chloritoid can be found in garnet and more rarely in quartz and muscovite, throughout the upper garnet-staurolite-biotite zone.

Photo 2.48: Photomicrograph of garnet-staurolite-biotite schist from locality 90-4 (sample 90-4h-l). Garnets contain inclusions of chloritoid (blue arrow) and staurolite (yellow arrow). This locality has the highest-grade occurrence of chloritoid as garnet inclusions.

2.8.2 The disappearance of Margarite

The calcium mica margarite ($\text{CaAl}_2(\text{Al}_2\text{Si}_2)\text{O}_{10}(\text{OH})_2$) occurs with garnet-plagioclase-biotite-muscovite and quartz on the southern shore of Marble Lake near highway 506 (see photos 2.49 and 2.50 below). This locality (90-2) is the highest-grade occurrence of margarite.

Two equilibria can be written for the mineral assemblage above. The first, in the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ system, describes the elimination of margarite in favour of plagioclase:

The second, in the $\text{CaO-K}_2\text{O-Al}_2\text{O}_3\text{-MgO-FeO-SiO}_2\text{-H}_2\text{O}$ system describes the reaction of biotite and margarite to form the commonly observed assemblage muscovite, plagioclase and garnet.

Regardless of the exact equilibrium, both equations show that margarite will be eliminated with increasing temperature in favour of plagioclase-bearing assemblages.

Photo 2.49: Photomicrograph showing three generations of margarite (Ca-mica) co-existing with pre-D1 plagioclase, syn-D1 garnet, biotite, quartz and muscovite in sample 90-2a-II. Coloured arrows identify three generations of margarite growth: syn-D1 margarite - blue, syn-D2 - green and post-D2 - red. Margarite occurs as colourless, bladed crystals with higher relief than quartz and muscovite.

Photo 2.50: Same as previous photo, with crossed nicols. Margarite shows characteristic first order yellow interference colours. Plagioclase poikiloblasts in lower portion of photo do not exhibit 1st order interference colours because they have been partially altered to fine-grained clay minerals.

2.8.3 The Mississagagon Lake Garnet-Staurolite-Biotite Zone

Kyanite-biotite, present in pelites near Marble Lake, is replaced by staurolite-chlorite and garnet-chlorite-bearing assemblages at locality 92-31, south of Mississagagon Lake. The apparent reversal of the kyanite-biotite isograd (see photo 2.51) occurs approximately four kilometres beyond the first occurrence of kyanite-biotite, forming a relatively high-grade dome along the south shore of Marble Lake (see Figure 2.1). Lower-grade, chlorite-bearing pelites from the Mississagagon Lake garnet-staurolite-biotite zone are found northeast of this dome within the Fernleigh syncline for approximately five kilometres. Pelites in this area have the same texture and mineralogy as those found in the upper garnet-staurolite-biotite zone south of Marble Lake (section 2.7.3 above), and the two zones are believed to be of approximately equivalent metamorphic grade. Syn-D1 matrix chlorite defining the primary S1 foliation can be found in both areas (see photo 2.52 below, and 2.43 above), implying that chlorite formation is not related to retrograde metamorphism.

Photo 2.51: Replacement of kyanite-biotite (indicated with red arrows) by staurolite-chlorite in pelite south of Mississagagon Lake (sample 92-31a-l).

Photo 2.52: Photomicrograph of garnet-chlorite-staurolite assemblage south of Mississagagon Lake (sample 92-36L-I). Matrix chlorite laths lie parallel to the main foliation (S1), which wraps around the pre-D1 garnets.

Photo 2.53: Photomicrograph of Chl-Grt-St-Ky schist (sample 91-24a-II), showing coexisting garnet and chlorite in the garnet-staurolite-biotite zone south of Mississagagon Lake. Biotite was not observed in any sample collected from this locality.

Garnet-chlorite-bearing assemblages are frequently encountered in the Mississagagon Lake area (see photos 2.52 and 2.53 above), as was the case in the upper garnet-staurolite-biotite zone south of Marble Lake. Comparing figure 2.21 below with figure 2.18 shows that garnet-bearing assemblages in the Mississagagon Lake area are compositionally similar to those observed in the upper garnet-staurolite-biotite zone, with garnet-chlorite-bearing assemblages containing relatively manganese-rich garnets. Thus, the occurrence of garnet-chlorite in pelites south of Mississagagon Lake is attributed to preferential manganese partitioning in garnet (as is the case in the upper garnet-staurolite-biotite zone).

Figure 2.21 shows that relatively manganese-poor garnet (lying in the AFM plane) occurs only in the assemblage garnet-staurolite-biotite. Garnet is stabilized in all other assemblages due to the presence of manganese, an additional component outside of the ideal pelitic KFMASH system. Figure 2.22 shows observed mineral assemblages from the Mississagagon Lake garnet-staurolite-biotite zone in an AFM projection, excluding garnet observed in all assemblages other than garnet-staurolite-biotite (assumes all other assemblages have high spessartine garnet). A complete list of observed mineral assemblages is included below, in approximate order of decreasing abundance (all assemblages include muscovite and quartz, assumed manganese-rich garnet is indicated by italics):

1. *garnet* + chlorite + staurolite ± plagioclase
2. garnet + staurolite + biotite ± plagioclase
3. staurolite + chlorite + kyanite + plagioclase
4. kyanite + chlorite ± plagioclase
5. *garnet* + chlorite + plagioclase
6. staurolite + biotite ± plagioclase
7. garnet + biotite + plagioclase
8. ***garnet* + chlorite + staurolite + kyanite**
9. staurolite + kyanite + plagioclase

Figure 2.21: MnAFM isometric projection of mineral compositions from the Mississagagon Lake garnet-staurolite-biotite zone. Tie lines have been coloured according to the mineral assemblage lying in the AFM plane. Note that garnets in equilibrium with chlorite in this zone are manganese-rich, lying above the AFM plane; confirming that garnet is stabilized in chlorite-bearing rocks from this zone due to the presence of an additional chemical component outside of the AFM system. Results for three samples from the surrounding kyanite-biotite zone have been included for comparison. Mineral chemistry used in diagram was obtained by microprobe; see results summarized in Appendix 5.

Figure 2.22: Observed muscovite-bearing pelitic assemblages in the Mississagagon Lake garnet-staurolite-biotite zone. Garnet observed in all assemblages other than garnet-biotite and garnet-staurolite-biotite has been excluded from the diagram because it is assumed to be manganiferous. Mineral compositions shown on diagram correspond to ideal KFMASH end-members. Three-phase fields are shown shaded in yellow.

2.8.3.1 Chlorite Mineral Chemistry

Chlorite compositions obtained from pelitic schists are summarized below in Figure 2.23 according to the classification scheme of Hey (1954). All measured chlorite compositions fall in the ripidolite field. Chlorites from the garnet-chlorite and chloritoid-biotite zones have overlapping compositions, which are generally more iron-rich than chlorites from higher-grade areas (the sole exception being chlorite from Madoc-4a, a garnet-free magnesium-rich pelite containing the assemblage Ctd-Ky-St-Chl). Chlorites from the upper garnet-staurolite-biotite zone have a similar composition to those found in the Mississagagon Lake garnet-staurolite-biotite zone, an observation that is consistent with the hypothesis that the two zones are of equivalent metamorphic grade. Chlorite-bearing pelites were only found in the lower portions of the kyanite-biotite zone, where chlorite appears to persist above the $\text{St} + \text{Chl} = \text{Ky} + \text{Bt}$ isograd (Equil 2.3). Chlorite in the kyanite-biotite zone is therefore compositionally similar to lower-grade chlorite from the garnet-staurolite-biotite zone.

Figure 2.23: Classification diagram of Hey (1954) showing chlorite mineral chemistry for pelites in the study area. Microprobe results used to prepare the diagram are summarized in Appendix 5.

2.9 The Kyanite-Biotite Isograd and Petrology of Pelites in the Ky-Bt Zone

Kyanite-biotite-bearing pelites reappear in the Fernleigh syncline towards the eastern end of Mississagagon Lake (at locality 91-1, see photo 2.54 below), marking the second occurrence of the kyanite-biotite isograd. Kyanite-biotite forms at the expense of staurolite-chlorite-bearing assemblages according to the following equilibrium:

Equilibrium 2.3 was balanced using real mineral compositions obtained by electron microprobe analysis from sample 91-1. Stoichiometric coefficients for the resulting equilibrium (2.15 below) were normalized to ten moles of water.

Equil 2.15

Staurolite-chlorite persists with kyanite-biotite up-grade for approximately three kilometres. The kyanite-biotite isograd strikes southwest from locality 91-1 towards the Flinton synclinorium, where four-phase staurolite-chlorite-kyanite-biotite assemblages were observed in pebble schists and pelites at the Ore Chimney Mine (locality 92-1, see photo 2.55).

The topology of the AFM projection for the kyanite-biotite zone is illustrated below on figure 2.24 (with observed assemblages). Pelites from this zone typically contain garnet-staurolite-biotite, kyanite-biotite, or staurolite-biotite (see photo 2.56). The list below identifies all mineral assemblages encountered in this zone, in approximate order of decreasing abundance (all assemblages include muscovite and quartz, assumed manganese-rich garnet is indicated by italics):

1. ***garnet* + chlorite + staurolite + biotite** ± plagioclase (near Ky-Bt isograd only)
2. garnet + staurolite + biotite ± plagioclase
3. staurolite + biotite ± plagioclase
4. kyanite + biotite ± plagioclase
5. **kyanite + biotite + staurolite + *garnet*** ± plagioclase
6. kyanite + biotite + staurolite ± plagioclase
7. garnet + biotite + plagioclase
8. **kyanite + biotite + staurolite + chlorite** ± plagioclase
9. ***garnet* + chlorite + staurolite + biotite + kyanite** ± plagioclase ± epidote

Photo 2.54: Photomicrograph showing coexisting biotite and kyanite in sample 91-1e-l. The reappearance of this assemblage marks the location of the kyanite-biotite isograd along the eastern side of Mississagagon Lake. Yellow arrows point to the location of scattered staurolite crystals that are intergrown with kyanite.

Photo 2.55: Photomicrograph of coexisting kyanite and biotite, with staurolite and chlorite (green arrows), from a pebble-schist at the base of the Flinton Group (Ore Chimney Mine site, sample 92-1b-l).

Figure 2.24: Observed muscovite-bearing pelitic assemblages in the kyanite-biotite zone. Mineral compositions shown on diagram correspond to ideal KFMASH end-members. Three-phase fields are shown shaded in yellow.

Photo 2.56: Photomicrograph of kyanite-biotite-staurolite schist (sample 91-6b-l), showing a typical phase assemblage above the kyanite-biotite isograd.

Figure 2.25 shows mineral compositions from kyanite-biotite zone pelitic schists plotted on a Thompson AFM projection. (Mineral chemistry was measured by electron microprobe; results are summarized in Appendix 5). Minerals from kyanite-biotite-bearing assemblages (91-1, 91-5, 93-10 and 93-44) are more magnesium-rich than minerals belonging to the assemblage garnet-staurolite-biotite (consistent with the predicted AFM topology illustrated in figure 2.24). Figure 2.25 also shows how three-phase triangles joining garnet-staurolite-biotite and kyanite-biotite-staurolite migrate to more iron-rich bulk compositions with increasing metamorphic grade, presumably due to the following continuous reactions that are taking place in response to increasing temperature:

Figure 2.25: AFM projection showing mineral compositions from pelites in the kyanite-biotite zone (listed in approximate order of increasing metamorphic grade). Samples containing the assemblage garnet-staurolite-biotite (91-14d, 93-45a and 94-1a) have a more iron-rich bulk composition than kyanite-biotite-bearing samples (91-1e, 91-5b, 93-10b and 93-44b). Garnet in equilibrium with kyanite-biotite is manganiferous. Staurolite from sample 93-10b appears more aluminous than other staurolite because it contains a relatively large amount of zinc (3.8 wt.% ZnO versus 0.1-0.7 wt.% ZnO in the remaining samples), which substitutes for iron in the staurolite crystal structure, reducing the Fe/Al ratio. (Zn was not included in the calculation of this projection). Mineral chemistry used in diagram was obtained by microprobe (see Appendix 5).

2.10 The Kyanite to Sillimanite Isograd

Locality 93-45, approximately one and a half kilometres east of the village of Fernleigh marks the first appearance of sillimanite in kyanite-bearing pelites. Bundles of extremely fine sillimanite needles can be observed in kyanite-biotite and kyanite-staurolite-biotite pelites (see photos 2.57 and 2.58). The sillimanite appears to be nucleating in quartz-rich domains, rather than growing directly on kyanite poikiloblasts.

Photo 2.57: Photomicrographs of coexisting sillimanite (photos A and B in plane-polarized and cross-polarized light) and kyanite (photos C-PPL and D-XPL) in sample 93-45b2-II. The sillimanite fibres occur in bundles that nucleate in quartz, rather than directly on the surface of the nearby kyanite poikiloblast.

Photo 2.58: Photomicrograph of coexisting kyanite and sillimanite in cross-polarized light. The sillimanite fibres occur in bundles that nucleate in quartz, rather than directly on the surface of the nearby kyanite poikiloblast (sample 93-45b2-1).

2.11 The Sillimanite-Garnet-Biotite Isograd (Staurolite-out Isograd)

In the Fernleigh syncline, sillimanite first appears with staurolite, garnet and biotite in muscovite-quartz-bearing pelites near the village of Ardoc, approximately 3.5 kilometres up-grade of the kyanite to sillimanite isograd. At this locality, sillimanite generally occurs in thin lenses, separated from surrounding staurolite by monomineralic layers of biotite (see photo 2.59 below). The six-phase assemblage present at this locality, together with a hydrous fluid phase, comprises a univariant assemblage in the KFMASH system that can be expressed by the following equilibrium:

Figure 2.26 shows how this reaction changes the topology of the AFM projection, using ideal mineral compositions in the KFMASH system. Equilibrium 2.5 was balanced using real mineral compositions obtained by electron microprobe analysis from sample Ardoc-1. Stoichiometric coefficients for the resulting equilibrium (2.18 below) were normalized to ten moles of water.

This reaction marks the disappearance of staurolite in muscovite-bearing rocks, and the first appearance of coexisting biotite and aluminosilicate with garnet. For this reason, the geographical area above the isograd is referred to as the sillimanite-garnet-biotite zone.

This staurolite-out isograd formed by equilibrium 2.5 strikes southwest from the village of Ardoc towards Kaladar (see figure 2.1), where six-phase staurolite-garnet-biotite-sillimanite-quartz-muscovite schists are interbedded with conglomerates in the Kaladar metasediments (see photo 2.60). The same mineral assemblage can also be observed in pelites south of Kaladar in the Clare River synclinorium (discussed separately in section 2.13 below).

Figure 2.26: Reaction at the staurolite-out isograd, depicted on an AFM projection. The univariant four-phase field is shown in pink. The dot in the centre of this field represents the last staurolite composition in equilibrium with garnet, biotite and sillimanite. Mineral compositions shown on diagram correspond to ideal KFMASH end-members.

Photo 2.59: Photomicrograph showing the first occurrence of sillimanite in garnet-staurolite-biotite pelite (sample Ardoc-201-V), marking the location of the staurolite-out isograd. Sillimanite is separated from adjacent staurolite-muscovite-biotite-rich layers by a zone of biotite. Yellow arrows in the upper portion of the photograph indicate the location of relict staurolite crystals. Several relict kyanite crystals are also preserved in the area surrounding the garnet.

Photo 2.1: Photomicrograph of garnet-staurolite-biotite-sillimanite pelite (sample 93-40d-I) from the Kaladar metasediments. Mineral assemblage is indicative of the staurolite-out isograd.

2.1 Petrology of Pelites from the Sillimanite-Garnet-Biotite Zone

Pelites from this zone typically contain either the divariant assemblage sillimanite-garnet-biotite (see photo 2.61) or the trivariant assemblage sillimanite-biotite. Staurolite persists in muscovite-bearing schists as corroded xenoblastic grains up-grade of the staurolite-out isograd for seven kilometres (see photo 2.62). Idioblastic staurolite remains stable in muscovite-free schists with co-existing with biotite and garnet throughout most of the sillimanite-garnet-biotite zone.

Metastable kyanite porphyroblasts can be found in staurolite-free rocks with **no** sillimanite up-grade of the staurolite-out isograd for approximately 2.5 kilometres (see photo 2.63, staurolite-muscovite-bearing schists all contain sillimanite). Co-existing kyanite and sillimanite occur up-grade of the staurolite-out isograd for about 4 kilometres.

Figure 2.27 below shows observed mineral assemblages from the sillimanite-garnet-biotite zone on an AFM projection using mineral compositions from the ideal KFMASH system. These assemblages are listed below, in approximate order of decreasing abundance (unless noted, all assemblages include muscovite and quartz). Six-phase (univariant) assemblages are shown in bold type:

sillimanite + biotite + plagioclase $\pm$ kyanite
 garnet + sillimanite + biotite + plagioclase
 garnet + biotite + plagioclase
staurolite + garnet + sillimanite + biotite + plagioclase
 staurolite + garnet + biotite + quartz (No muscovite)

Figure 2.27: Observed muscovite-bearing pelitic assemblages in the sillimanite-garnet-biotite zone, up-grade of the staurolite-out isograd. Mineral compositions shown on diagram correspond to ideal KFMASH end-members. Three-phase fields are shaded yellow.

Figure 2.28 shows mineral compositions for iron-rich staurolite-bearing schists plotted on a Thompson AFM projection. (Mineral chemistry was measured by electron microprobe; results are summarized in Appendix 5). Note that measured staurolite compositions always fall within the three-phase sillimanite-garnet-biotite triangle, as predicted by equilibrium 2.5. Figure 2.28 also shows how the three-phase triangle joining sillimanite-garnet-biotite migrates to more iron-rich bulk compositions with increasing metamorphic grade, presumably due to the following continuous reaction that is taking place in response to increasing temperature:

Equil 2.19

Figure 2.28: AFM projection showing mineral compositions from Fe-rich staurolite-bearing assemblages in the sillimanite-garnet-biotite zone. Samples are listed in approximate order of increasing metamorphic grade. Mineral chemistry used in diagram was obtained by microprobe (see Appendix 5).

Photo 2.61: Photomicrograph of garnet-biotite-sillimanite pelite, located approximately 1.5km east of the village of Ompah (sample 93-46b-I). No staurolite is present in the rock. Some of the sillimanite appears to be overgrowing coarse-grained muscovite flakes.

Photo 2.62: Photomicrograph of garnet-staurolite-biotite-sillimanite pelite (sample 92-34a-I) approximately 2.5km up-grade of the staurolite-out isograd. Staurolite (indicated by yellow arrows) is xenoblastic and relatively fine-grained. Some of the staurolite grains appear to be armoured in quartz.

Photo 2.63: Metastable persistence of kyanite into the sillimanite stability field (sample 92-34c-I), a kyanite-biotite pelite from the same locality as the previous photomicrograph.

2.13 Clare River Synclinorium Low-grade Node

Staurolite and kyanite-bearing assemblages occur in the central portion of the Clare River synclinorium, immediately southwest of the village of Kaladar (see photos 2.64 and 2.65, and figure 2.1). The eastward direction of increasing metamorphic grade, characteristic of this part of the Mazinaw terrane, appears to be reversed in this area, with lower-grade staurolite and kyanite-bearing schists occurring to the northeast of sillimanite-garnet-biotite pelites in the core of the Clare River synclinorium. The occurrence of these relatively low-grade minerals inside a high-grade area cannot be easily attributed to changes in fluid-phase composition (as was done in section 2.8 above explaining the development of the high-grade kyanite-biotite dome near Marble Lake), because only the stability of relatively high-grade assemblages can be enhanced by decreasing water activity in the fluid-phase and not vice versa. (Since reactions responsible for the formation of high-grade assemblages in pelites are generally dehydration reactions, water and the high-grade mineral assemblage both occur as reactants on the same side of the equilibrium, thus decreasing water

Photo 2.64: Photomicrograph of staurolite-garnet-biotite schist from the central portion of the Clare River synclinorium (sample CR-8b-l).

Photo 2.65: Photomicrograph of garnet-staurolite-biotite-sillimanite pelite (sample CR-4a-l) from the Clare River synclinorium. Sample contains relict fine-grained, xenoblastic staurolite, indicating the outcrop is located on the high-grade side of the staurolite-out isograd (Equil 2.5).

activity expands the relative stability of the high-grade assemblage). Fluid-composition could therefore play a role in the formation of the Clare River low-grade node only if the surrounding sillimanite-garnet-biotite assemblage had been stabilized by decreased water activity (an unlikely scenario). It seems more reasonable to assume that the occurrence of staurolite and kyanite in the Clare River synclinorium is related to the folding of the kyanite-sillimanite and staurolite-out isograds (equilibria 2.4 and 2.5 respectively), forming a relatively low-grade basin surrounded by sillimanite-garnet-biotite-bearing schists. This is discussed in detail in chapter 5.

Figure 2.29 shows mineral compositions for iron-rich staurolite-bearing schists from the Clare River low-grade node plotted on a Thompson AFM projection. (Mineral chemistry was measured by electron microprobe; results are summarized in Appendix 5). Projected mineral compositions are similar to those from the upper portion of the kyanite-biotite zone (samples 93-45a-I and 94-1a-I, figure 2.25) and the staurolite-out isograd at Ardor (sample Ardor 201-V, figure 2.28), suggesting that the schists from the Clare River low-grade node may be at a similar metamorphic grade.

Figure 2.29: AFM projection showing mineral compositions from pelitic schists in the Clare Rive low-grade node. Samples are listed in approximate order of increasing metamorphic grade. Garnet-biotite tie lines for samples CR-3a and CR-8b appear to be crossed, however sample CR-3a contains relatively manganese-rich garnets (approximately 20% spessartine versus 8% spessartine in sample CR-8b), therefore the garnet-biotite tie line for sample CR-3a does not lie in the AFM plane. Note that measured staurolite composition for sample CR-4a-I falls within the three-phase sillimanite-garnet-biotite triangle, as predicted by equilibrium 2.5. Mineral chemistry used in diagram was obtained by microprobe (see Appendix 5).

2.14 Summary of Mineral Chemistry Changes in Fernleigh Syncline Pelites: Evidence for Continuous and Discontinuous Reactions in the KFMASH System

Figure 2.30 below summarizes changes in iron and magnesium mineral chemistry for selected pelites from the Fernleigh syncline with assemblages more iron-rich than staurolite-chlorite (those assemblages containing garnet-chlorite, chloritoid-chlorite, chloritoid-biotite and/or staurolite-biotite). Samples have been arranged in approximate order of increasing metamorphic grade, represented by increasing distance along the strike of the Fernleigh syncline from the western fold closure near Bishop Corners (lowest grade area). The five isograds mapped throughout the study area (equilibria 2.1 to 2.5) are shown as horizontal lines drawn through the lowest-grade locality where the product assemblage of the reaction was first observed. These isograd reactions are also known as discontinuous reactions, because each results in a marked rearrangement of tie lines on the Thompson AFM projection (a discontinuity in the arrangement, Thompson, 1957). In the ideal pelitic system (KFMASH), these reactions are univariant, involving four ferromagnesian silicates, muscovite, quartz and a hydrous fluid phase.

Progressive changes in ferromagnesian silicate composition with increasing metamorphic grade (expressed as molar magnesium to iron ratio, $X_{Mg} = Mg/(Fe+Mg)$) are presumably due to continuous reactions, which are divariant reactions that take place over a wide temperature range. Continuous reactions appear on the Thompson AFM projection as shifting divariant fields, which move to higher or lower magnesium:iron (X_{Mg}) values as a function of changing temperature, without rearranging the tie lines on the projection. The X_{Mg} trend for various minerals is shown on figure 2.30 as colour-keyed diagonal lines (approximate best fit drawn by eye). These trends are related to specific continuous reactions listed for the various metamorphic zones below.

Figure 2.30: Variation in ferromagnesian silicate mineral chemistry (expressed as Mg:Fe ratio) as a function of distance along the axis of the Fernleigh syncline (approximately equivalent to increasing metamorphic grade). Solid horizontal lines show location of discontinuous reaction isograds (Equilibria 2.1 to 2.5). Microprobe results are summarized in Appendix 5.

The Mg:Fe ratio of garnet, chloritoid and chlorite increases in the garnet-chlorite zone due to the following continuous reaction:

This reaction causes the three-phase garnet-chloritoid-chlorite triangle to migrate towards more magnesian bulk compositions, which increases the stability field of garnet-chlorite on the AFM projection. Textural evidence presented in section 2.4.2 above indicates that this reaction is responsible for the elimination of chloritoid in garnet-chloritoid-chlorite schists.

Two continuous reactions appear to be affecting ferromagnesian silicate chemistry in the chloritoid-biotite zone (which includes the poorly defined staurolite-biotite zone). The first reaction takes place in chlorite-bearing assemblages, which become increasingly magnesium rich throughout the chloritoid-biotite zone as a result of the following continuous reaction:

Equilibrium 2.20 causes the three-phase chlorite-chloritoid-biotite triangle to migrate towards more magnesian bulk compositions, increasing the stability field of chloritoid-biotite on the AFM projection.

The second reaction,

Equil 2.21

observed in relatively iron-rich pelites, causes the three-phase garnet-chloritoid-biotite triangle to migrate towards more magnesian bulk compositions. Equilibrium 2.21 is consistent with petrographic observations outlined in section 2.5 above, where garnet crystals appear to be overgrowing chloritoid and biotite (see photos 2.30 and 2.31). This reaction thus appears to be partially responsible for the elimination of chloritoid in pelitic schists.

Two and possibly three continuous equilibria appear to be affecting ferromagnesian silicate chemistry in the garnet-staurolite-biotite zone. The first can be observed in chloritoid-bearing schists from the lower part of the zone:

Equilibrium 2.22 causes the three-phase chloritoid-garnet-staurolite triangle to migrate towards more magnesian bulk compositions, increasing the stability field of garnet-staurolite on the AFM projection. This reaction appears to be partially responsible for the elimination of chloritoid in chloritoid-garnet-staurolite-biotite schists.

The second continuous reaction can be observed in chlorite-bearing schists from the upper part of the garnet-staurolite-biotite zone:

Equil 2.23

This reaction causes the three-phase chlorite-staurolite-biotite triangle to migrate towards more magnesian bulk compositions, increasing the stability field of staurolite-biotite on the AFM projection. Equilibrium 2.23 may be partially responsible for the elimination of chlorite from upper garnet-staurolite-biotite zone pelitic schists.

A third continuous reaction may also be affecting the mineral chemistry of garnet-staurolite-biotite schists from the upper garnet-staurolite-biotite zone:

This reaction causes the three-phase garnet-staurolite-biotite triangle to migrate towards more magnesian bulk compositions, increasing the stability field of garnet-biotite on the AFM projection.

The Mg:Fe ratio of garnet, staurolite and biotite decreases in the kyanite-biotite zone due to the following continuous reaction,

Equil 2.25

which causes the three-phase staurolite-kyanite-biotite triangle to migrate towards more iron-rich bulk compositions, increasing the stability field of kyanite-biotite on the AFM projection. (This reaction is

responsible for the elimination of staurolite from pelitic schists at grades lower than the staurolite-out isograd).

Above the staurolite-out isograd (sillimanite-garnet-biotite zone) the Mg:Fe ratio of co-existing garnet and biotite decreases due to the following continuous reaction:

This reaction causes the three-phase sillimanite-garnet-biotite triangle to migrate towards more iron-rich bulk compositions, increasing the stability field of biotite-sillimanite on the AFM projection.

Chapter 3 - Thermochemical Data For Chloritoid, Magnesiochloritoid, Chamosite and Magnesiostaurolite

3.1 Introduction

The purpose of this chapter is to derive and evaluate a set of thermochemical data for chloritoid, magnesiochloritoid, chamosite (iron chlorite), and magnesiostaurolite that is internally consistent with the Berman (1988) database. Available experimental data and data from natural assemblages will be used in the derivation.

The methods used to extract various thermodynamic properties will be explained in detail using chloritoid as an example, since experimental results for this phase are more plentiful than for the remaining three phases. Two methods of data extraction will be utilised to determine the enthalpy and entropy of chloritoid. The first method, herein identified as the method of simultaneous solution, uses the location of two chloritoid-bearing invariant points in pressure-temperature space to solve two independent free energy equations for H_{Cld} and S_{Cld} . The second method, the method of linear regression, uses linear regression on individual experimental data sets to obtain chloritoid enthalpy and entropy.

3.2 Chloritoid Enthalpy and Entropy by the Method of Simultaneous Solution

3.2.1 Introduction

The data extraction method outlined below uses the P-T location of two invariant points to solve two linearly independent Gibbs free energy equations for the enthalpy and entropy of chloritoid. The methodology and logic underlying the procedure may be summarised as follows:

- 1) Each invariant point has a chloritoid absent reaction passing through it. This reaction may be located in P-T space using existing thermochemical data in the Berman (1988) data set.

2) Addition of chloritoid to the chloritoid-absent phase assemblage cited in step 1 above, results in the formation of an invariant point. To be internally consistent with the Berman (1988) data set, this invariant point must lie on the chloritoid-absent reaction. Experimentally derived stability brackets for chloritoid-bearing reactions, which pass through the invariant point in question, provide a constraint on the P-T location of this invariant point. Thus, the approximate P-T location of various chloritoid-bearing invariant points can be determined by the trace of the chloritoid-absent reaction and the available experimental brackets established by chloritoid stability studies.

3) Each invariant point also has a vapour-conserving, or solid-phase reaction passing through it. These reactions were utilised in the simultaneous solution method to minimise the effect of various water fugacity models (for example Haar et al., 1984; or Holland and Powell, 1990) on the data extraction results.

4) For each vapour-conserving reaction passing through the invariant point, it is possible to write one equation expressing the Gibbs free energy change (ΔG) for that reaction. Since all member reactions, including the chloritoid-absent reaction and the vapour-conserving reaction, are in equilibrium at the invariant point, the derived free energy equations are equal to one another (with $\Delta G=0$). Since the P-T location of each invariant point has been determined in step 2 above, and the thermochemical properties of all other phases involved in invariant point and its member reactions except chloritoid can be obtained from Berman (1988), the only unknown quantities in the free energy equation are the thermochemical properties of chloritoid. In a multi-system, with more than one chloritoid-bearing invariant point, it is possible to derive a set of these free energy equations (one for each vapour-conserving reaction at every invariant point in the multi-system). This set of equations may be solved simultaneously for the unknown thermochemical properties of chloritoid.

The number of unknown chloritoid thermochemical properties that may be obtained in this manner is equal to the number of linearly independent free energy equations that can be derived. It can be shown that one independent equation, or thermochemical property, can be obtained for each known invariant point location.

3.2.2 Chloritoid Experimental Data and Location of Invariant Points

Chloritoid experimental data are available from three sources summarised in Table 3.1 below. The four available experiments belong to two invariant point assemblages in the FeO-Al₂O₃-SiO₂-H₂O (FASH) system. Ganguly (1969) and Vidal et al. (1994) describe two reactions around the Corundum+Water+Almandine+Chloritoid+Kyanite+Diaspore (CoWACKD) invariant point while the Rao & Johannes (1979) data belong to the Quartz+Water+Almandine+Chloritoid+Kyanite+Staurolite (QWACKS) invariant point. The experimental data will first be used to locate these two invariant points in pressure-temperature space consistent with the Berman (1988) database.

Reference	Equilibrium Studied	Absent Phase	Buffer	Temperature Range (°C)	Pressure Range (bars)
Ganguly (1969)	3ctd=alm+2cor+3H ₂ O	(dsp)	NNO	480-670	8500-22000
Rao and Johannes (1979)	23ctd+8αQtz=4st+5alm+21H ₂ O	(ky)	QFM	560-600	6000-14000
	8ctd+10ky=2st+3αQtz+4H ₂ O	(alm)	QFM	530-590	6000-14000
Vidal et al. (1994)	3ctd=alm+4dsp+H ₂ O	(cor)	NNO	594-689	29600-45000

Fig 3.1 and 3.2 show the experimental brackets for the reactions listed in Table 3.1. Also shown are the two chloritoid absent reactions for each invariant point:

These reactions were located in P-T space using the program TWQ, which uses the Berman (1988) thermodynamic database and the Haar et al. (1984) equation of state for water, to locate reactions in P-T space. The addition of chloritoid to the equilibrium 3.1 assemblage results in the formation of the invariant point QWACKS. Likewise, the addition of chloritoid (with

almandine+kyanite) to equilibrium 3.2 stabilizes CoWACKD. As mentioned previously, if the derived thermochemical properties of chloritoid are to be internally consistent with the Berman (1988) database, the two resulting invariant points must be located on these reactions.

An additional constraint on the P-T location of the two invariant points is provided by the experimental brackets, which constrain the minimum and maximum possible slope for two member reactions at each invariant point. These minimum and maximum slope lines are indicated on Fig 3.1 and 3.2. Note that these slope lines assume that $\Delta V_{\text{solids}} = \Delta V_{\text{fluid}} = 0$, since they do not deviate with increasing pressure.

Figure 3.1: Location of invariant point QWACKS. Shaded area outlines P-T region constrained by experimental data (filled symbols indicate that the reactant assemblage is stable). The invariant point is further constrained to lie on the staurolite+quartz dehydration curve plotted using Berman (1988). The hexagon indicates the assumed invariant point location based on these constraints, with crosses indicating the maximum and minimum possible variation.

Figure 3.2: Location of invariant point CoWACKD. Shaded area outlines P-T region constrained by experimental data (filled symbols indicate that the reactant assemblage is stable). The invariant point is further constrained to lie on the diaspore dehydration curve plotted using Berman (1988). The hexagon indicates the assumed invariant point location based on these constraints, with crosses indicating the maximum and minimum possible variation.

The four possible slope lines present on both Fig 3.1 and 3.2, thus define an area in which the invariant point must be located. This area, combined with the fact that the invariant points must lie on reactions 3.1 and 3.2 above, serves to locate a minimum and maximum possible pressure-temperature point for each of the two invariants. These results are summarized on Figs 3.1 and 3.2 and in Table 3.2 below:

Invariant Point	Minimum Pressure Location	Maximum Pressure Location	Average Pressure Location
QWACKS	T=596°C P=14745 bars	T=584°C P=15485 bars	T=590°C P=15115 bars
CoWACKD	T=679°C P=31144 bars	T=696°C P=33315 bars	T=688°C P=32230 bars

3.2.3 Thermodynamic Background for the Simultaneous Solution Method

The purpose of this section is to introduce the thermodynamic equations utilized by the simultaneous solution method. The location of any equilibrium may be calculated by solving the following expression of the Gibbs Free Energy equation, for P and T:

$$\begin{aligned}
 \Delta G^{P,T} = 0 = & \Delta H^{P_r,T_r} - T\Delta S^{P_r,T_r} + \Delta V^{P_r,T_r}(P - P_r) + RT\ln K \\
 & + \Delta K_0 [T - T_r + T \ln \frac{T_r}{T}] + \Delta K_1 [4\sqrt{T} - 2\sqrt{T_r} - 2\frac{T}{\sqrt{T_r}}] \\
 & + \Delta K_2 [\frac{1}{T_r} - \frac{T}{2T_r^2} - \frac{1}{2T}] + \Delta K_3 [\frac{1}{2T_r^2} - \frac{T}{3T_r^3} - \frac{1}{6T^2}] \\
 & + \Delta K_4 [\ln(T) - \ln(T_r) - (\frac{T}{T_r} - 1)] + \Delta K_5 [TxT_r - \frac{T_r^2}{2} - \frac{T^2}{2}] \\
 & + (P - P_r) [-\Delta v_3 + \Delta v_4 + \Delta v_1(T - T_r) + \Delta v_2(T - T_r)^2] \\
 & + (\frac{\Delta v_3}{2} - \Delta v_4)(P^2 - 1) + (\frac{\Delta v_4}{3})(P^3 - 1)
 \end{aligned}$$

Eq 3.1

where ΔH , ΔS and ΔV are the enthalpy, entropy and volume of reaction at reference pressure - P_r (1bar) and temperature - T_r (298K). ΔK_n are constants for the Berman and Brown (1985) heat capacity equation:

$$Cp = K_0 + K_1 T^{-1/2} + K_2 T^{-2} + K_3 T^{-3} + K_4 T^{-1} + K_5 T \quad \text{Eq 3.2}$$

The v_1 - v_4 terms in equation 3.1 are fit coefficients for the following expression from Berman (1988), which is used to account for solid phase volume change with increasing temperature and pressure:

$$\frac{V_{P,T}}{V_{P_r,T_r}} = 1 + v_1(T - T_r) + v_2(T - T_r)^2 + v_3(P - P_r) + v_4(P - P_r)^2 \quad \text{Eq 3.3}$$

Note that in equation 3.1, $\Delta v_1 = \Delta\{v_1 \times U^{Pr,Tr}/10^5\}$, $\Delta v_2 = \Delta\{v_2 \times U^{Pr,Tr}/10^5\}$, $\Delta v_3 = \Delta\{v_3 \times U^{Pr,Tr}/10^5\}$, and $\Delta v_4 = \Delta\{v_4 \times U^{Pr,Tr}/10^8\}$, where v_n is the fit coefficient from equation 3.5 and U is the molar volume of each mineral in the reaction at reference temperature (T_r) and pressure (P_r). The Holland and Powell (1990) thermodynamic database can be made compatible with this expression by making the following substitutions for the coefficients of isobaric expansion and isothermal compression provided these authors: $v_1 = \alpha$ and $v_3 = -\beta \times 0.1$.

One equation in the form of equation 3.1 will be written for each vapour-conserving reaction at each invariant point. However, even at the known P and T of the invariant point, the number of unknown variables in equation 3.1 far exceeds the two possible variables for which a solution may be found (limited by two known invariant point locations). In order to simultaneously obtain the enthalpy and entropy of chloritoid it will first be necessary to calculate or estimate the remaining thermochemical properties in the equation (molar volume, heat capacity, expansivity and compressibility). This will be done in the following sub-sections, which also include magnesio-chloritoid for the sake of completeness and brevity, since a later section on magnesio-chloritoid thermochemical properties relies on the same data.

3.2.3.1 Heat Capacity

The heat capacity of chloritoid (Ctd) or magnesiochloritoid (mCtd) has yet to be measured directly by calorimetry, however, Berman and Brown (1985) provide a set of 'oxide component' coefficients that can be used to estimate K_0 to K_3 based on the chemical formula of the mineral in question. The resulting heat capacity coefficients for chloritoid and magnesiochloritoid are listed in table 3.3 below:

TABLE 3.3				
<i>Heat Capacity Coefficients for Chloritoid and Magnesiochloritoid</i>				
Mineral	K_0	K_1	K_2	K_3
Chloritoid	426.537	-3182.8	-7219860	1099977000
Magnesiochloritoid	407.697	-2759.53	-8624440	1207092000

Substituting the Table 3.1 coefficients into equation 3.1 at fixed temperature (T) and pressure (P), such as the P-T location of invariant points QWACKS and CoWACKD, simplifies equation 3.3 to:

$$\begin{aligned}
 \Delta G^{P,T} = 0 = & \Delta H^{P_r,T_r} - T\Delta S^{P_r,T_r} + \Delta V^{P_r,T_r}(P - P_r) + RT\ln K \\
 & + K \\
 & + (P - P_r)[-\Delta v_3 + \Delta v_4 + \Delta v_1(T - T_r) + \Delta v_2(T - T_r)^2] \\
 & + \left(\frac{\Delta v_3}{2} - \Delta v_4\right)(P^2 - 1) + \left(\frac{\Delta v_4}{3}\right)(P^3 - 1)
 \end{aligned}
 \tag{Eq 3.4}$$

where K is the heat capacity for a given reaction at the temperature and pressure of interest.

3.2.3.2 Molar Volume

The molar volume of chloritoid and magnesiochloritoid has been determined by crystallographic studies. Helgeson et al. (1978) report a value of 6.98 J/bar for chloritoid based on unit cell parameters reported by Donnay and Ondik (1973). The molar volume of magnesiochloritoid (6.88 J/bar) was calculated using the room temperature unit cell volume of 914.4 Å³ reported by Comodi et al. (1992).

3.2.3.3 Magnesiochloritoid Compressibility and Thermal Expansivity

The discovery of magnesiochloritoid in Alpine high pressure pelitic rocks (Chopin, 1984) has prompted several investigators to study the crystallographic behaviour of this mineral at high temperature and pressure. Fig. 3.3 shows the increase in unit cell volume of magnesiochloritoid with increasing temperature determined by Ivaldi et al. (1988) using a natural crystal from the Alpine occurrence. The experiments were conducted at 1 bar with temperatures ranging from 25°C to 750°C. At each temperature, Ivaldi et al. (1988) obtained several volume measurements, the average of which is shown on Fig. 3.3. A second order fit was completed through these data to determine coefficients compatible with the Berman (1988) volume equation (Eq. 3.5). Since all the V_2 terms in the Berman (1988) database are positive, an additional constraint that V_2 must be greater than zero was applied to the fit equation. The equation for the best-fit line is thus:

$$\frac{V_{P,T}}{V_{P_r,T_r}} = 1 + 2.9739 \times 10^{-5} (T - T_r) + 2.5706 \times 10^{-17} (T - T_r)^2 \quad \text{Eq 3.5}$$

By comparison with equation 3.5, $v_1^{\text{mCtd}} = 2.9739$ and $v_2^{\text{mCtd}} = 0$, (Note that the v_1 and v_2 terms in the Berman (1988) database are multiplied by 10^{-5}).

Fig. 3.4 shows the results of an isothermal compressibility study by Comodi et al. (1992) using natural magnesiochloritoid crystals from the same locality as Ivaldi et al. (1988). Experiments were conducted at room temperature with pressure values ranging from 1 to 42000 bars. A second order fit equation was calculated through the data points in a similar fashion to the thermal expansivity data in

the preceding paragraph. The fit equation was calculated with the additional constraint that the v_4 term be greater than zero in accordance with Berman (1988). The best-fit equation is thus:

$$\frac{V_{P,T}}{V_{P_r,T_r}} = 1 - 0.06466 \times 10^{-5} (P - P_r) + 1.2848 \times 10^{-20} (P - P_r)^2 \quad \text{Eq 3.6}$$

By comparison with equation 3.5, $v_3^{\text{mCtd}} = -0.0647$ and $v_4^{\text{mCtd}} = 0$, (Note that the v_3 and v_4 terms in the Berman (1988) database are multiplied by 10^{-5} and 10^{-8} respectively).

The Holland and Powell (1990) database contains thermodynamic data for chloritoid and magnesiochloritoid, including expansivity and compressibility terms. This data will be compared with the derived values in a later section.

Figure 3.3: Magnesiochloritoid expansivity from Ivaldi et al. (1988) Figure 3.4: Magnesiochloritoid compressibility from Comodi et al. (1992)

3.2.3.4 Chloritoid Compressibility and Thermal Expansivity

The expansivity and compressibility for chloritoid have not been determined directly. It is possible to estimate these terms, however, by calculating the difference between chloritoid and magnesiochloritoid expansivity and compressibility terms in the Holland and Powell (1990) database ($\Delta v_n = v_n^{\text{Ctd}} - v_n^{\text{mCtd}}$), and applying that same difference to those values derived for magnesiochloritoid above. For the Holland and Powell (1990) database, $\Delta v_1 = 2.7221 - 2.9091 = -0.1870$, $\Delta v_3 = -0.1074 - (-0.0858) = -0.0216$. Applying these values to those derived for magnesiochloritoid above (v_n^{mCtd}) yields the following expansion and compression terms for chloritoid: $v_1^{\text{Ctd}} = \Delta v_1 + v_1^{\text{mCtd}} = -0.1870 + 2.9739 = 2.7869$, likewise, $v_3^{\text{Ctd}} = -0.0863$.

Expansivity and compressibility terms for chloritoid and magnesiochloritoid derived in this study are summarized in Table 3.4 below along with molar volume values. For comparison, the table also contains the Holland and Powell (1990) values for these terms:

Database	Mineral	V (J/bar)	v_1	v_3
This Study	Chloritoid	6.98	2.7869	-0.0863
	Magnesiochloritoid	6.875	2.9739	-0.0647
Holland & Powell	Chloritoid	6.98	2.7221	-0.1074
	Magnesiochloritoid	6.875	2.9091	-0.0858

3.2.4 Simultaneous Retrieval of Chloritoid Enthalpy and Entropy

Equation 3.4 can be simplified by substituting the values summarized in Table 3.4 into the equation at fixed temperature and pressure so that:

$$\Delta G^{P,T} = 0 = \Delta H^{Pr,Tr} - T\Delta S^{Pr,Tr} + \Pi + RT\ln K + K + \Omega \quad \text{Eq 3.7}$$

Where Π is the energy contributed by the solid phase molar volume change and Ω is the energy due to expansivity and compressibility.

Equation 3.9 can be used in conjunction with the P-T location of the two previously discussed invariant points in the FASH system (QWACKS and CoWACKD) to retrieve enthalpy and entropy values for chloritoid. To accomplish this, one chloritoid-present reaction must be selected from each invariant point. While any two equilibria may be chosen, vapour-conserving (solid phase) reactions are preferred because the $RT\ln K$ term in equation 3.9 equals zero (since the reactions involve only pure phases in the absence of a fluid phase). The following two equilibria were therefore selected for study:

The simultaneous retrieval of chloritoid enthalpy and entropy is achieved by assuming H_{Cld} and S_{Cld} are both unknown variables. In this case, equation 3.7 becomes:

$$\Delta G^{P,T} = 0 = \Delta \hat{H}^{Pr,Tr} + \alpha H_{Cld} - T(\Delta \hat{S}^{Pr,Tr} + \alpha S_{Cld}) + \Pi + K + \Omega \quad \text{Eq 3.8}$$

Where $\Delta \hat{H}^{Pr,Tr}$ is the change in enthalpy, and $\Delta \hat{S}^{Pr,Tr}$ is the change in entropy, for all minerals involved in the reaction except chloritoid. α is the chloritoid stoichiometric coefficient (negative if chloritoid is part of the reactant assemblage, positive if it is a product). At the fixed temperature and pressure of each invariant point, equation 3.8 becomes:

$$\Delta G^{P,T} = 0 = \Phi + \alpha H_{Cld} - T\alpha S_{Cld} \quad \text{Eq 3.9}$$

where Φ is some real number. H_{Ctd} and S_{Ctd} may thus be retrieved by simultaneous solution of this equation for equilibria 3.3 and 3.4, at the fixed temperature and pressure of their respective invariant points.

The constant terms in equations 3.8 and 3.9 were calculated with a Microsoft Excel spreadsheet titled PTDiag, which was developed to solve equation 3.1 by iteration (see Appendix 3 for further details on PTDiag). Table 3.5 on the following page provides equations in the form of 3.8 and 3.9 for both equilibrium 3.3 and 3.4. Simultaneous solution of these equations produces the following values for the enthalpy and entropy of chloritoid:

$$H_{\text{Ctd}} = -3211483 \text{ J/mol}$$

$$S_{\text{Ctd}} = 161.0 \text{ J/K}\cdot\text{mol}$$

These values will be compared with previously reported values in a later section.

TABLE 3.5
Equations for Simultaneous Retrieval of Chloritoid Enthalpy and Entropy

Invariant Point	Reaction	T (K)	P (bars)	$\Delta G=0=\Delta H+nH_{\text{Cld}}-T\Delta S'-TnS_{\text{Cld}}+II+K+\Omega$ $\Delta G=0=\Phi+nH_{\text{Cld}}+TnS_{\text{Cld}}$
QWACKS	$12\text{ctd} + 4\text{alm} + 38\text{ky} = 6\text{st} + 17\text{aqtz}$	862.85	15115	$\Delta G=0=-38,424,842-12H_{\text{Cld}}-1,936,592.6+10,354S_{\text{Cld}}+138,580.3+32,000.5-13,838.2$ $\Delta G=0=-40204691.7-12H_{\text{Cld}}+10354.2S_{\text{Cld}}$
CoWACKD	$3\text{ctd} + \text{cor} = 6\text{dsp} + \text{alm}$	960.65	32229.5	$\Delta G=0=-9,587,783.3H_{\text{Cld}}-481,320.4+5763.9S_{\text{Cld}}-42,896.1+11,563.6+2,029.5$ $\Delta G=0=-10098406.8-3H_{\text{Cld}}+5763.9S_{\text{Cld}}$

3.2.5 Estimated Error in Simultaneous Retrieval of Chloritoid Enthalpy and Entropy

Table 3.2 summarized the uncertainty in the location of the invariant points used to retrieve chloritoid enthalpy and entropy. This uncertainty is primarily due to the width of the available experimental brackets. Since the invariant point locations were used to derive chloritoid thermodynamic properties, uncertainty associated with their location should be reflected in the enthalpy and entropy values obtained in this study. Determination of this uncertainty was accomplished by simultaneously solving Equation 3.13 for chloritoid enthalpy and entropy using all possible combinations of minimum, average and maximum pressure locations for each invariant point (QWACKS and CoWACKD). These results are summarized in Table 3.6 below.

QWACKS			CoWACKD			Enthalpy	Entropy
Min P Location	Max. P Location	Avg. P Location	Min P Location	Max. P Location	Avg. P Location	(kJ/mol)	(J/K·mol)
X			X			-3239.7	129.8
X				X		-3208.7	165.7
X					X	-3224.1	147.9
	X		X			-3214.3	156.2
	X			X		-3183.3	192.1
	X				X	-3198.7	174.3
		X	X			-3227.1	142.9
		X		X		-3196.1	178.8
		X			X	-3211.5	161.0

Table 3.6 shows that the lowest enthalpy and entropy values (-3240kJ/mol and 130J/K/mol) were obtained using the minimum pressure invariant point location for both QWACKS and CoWACKD. Similarly, the highest enthalpy and entropy values (-3183kJ/mol and 192J/K/mol) were obtained using the maximum pressure invariant point locations. The uncertainty in the retrieved

chloritoid enthalpy and entropy values is determined by comparing these maximum and minimum values with the enthalpy and entropy values determined above using the average pressure locations (shaded in Table 3.6). This comparison reveals that maximum possible variation in the derived chloritoid enthalpy is 28.2 kJ/mol. Similarly, the maximum possible variation in the derived chloritoid entropy is approximately 31.1 J/K/mol.

These uncertainty values are much larger than those typically quoted in the literature (± 1 -10 kJ/mol for enthalpy, ± 1 -10 J/K·mol for entropy). This is most likely due to the fact that the retrieval method used relies on four experimental data sets, with a resulting increase in error, rather than just one. The large error values therefore reflect the cumulative error resulting from each experiment. However, it will be shown in the following sections that the retrieved chloritoid enthalpy and entropy values are similar to those obtained by the method of linear regression. The derived values are also similar to those obtained in previous studies and can accurately reproduce equilibrium curves within previously determined experimental brackets despite these large uncertainties. Furthermore, it should be noted that values obtained by first locating invariant points consistent with the Berman (1988) database are themselves consistent with this database, an extremely important consideration, if the chloritoid thermochemical data is to be used in conjunction with other data from Berman (1988) to determine conditions of metamorphism (as will be done in Chapter 4 of this study).

3.3 Retrieval of Chloritoid Enthalpy and Entropy by Linear Regression

The retrieval of chloritoid enthalpy and entropy from experimental data relies on the re-arrangement of Equation 3.1, as documented previously, into a form similar to equation 3-9 such that:

$$\Delta G^{P,T} = 0 = \Delta H^{Pr,Tr} - T\Delta S^{Pr,Tr} + \Pi + RT\ln K + K + \Omega \quad \text{Eq 3.7}$$

Where Π , K and Ω are the energies of reaction contributed by the change in molar volume, heat capacity, and solid phase expansivity and compressibility at the experimentally determined T and P of equilibrium (these terms may be computed using the previously tabulated values). Assuming the equilibrium involves only solid phases of pure composition, equation 3.7 may be simplified as follows, into a form similar to equation 3.12

$$-\Delta \hat{H}^{Pr,Tr} - nH_{Cld} + T(\Delta \hat{S}^{Pr,Tr} + nS_{Cld}) = \Pi + K + \Omega \quad \text{Eq 3.10}$$

Where $\Delta \hat{H}^{Pr,Tr}$ and $\Delta \hat{S}^{Pr,Tr}$ are the enthalpy and entropy change for all minerals involved in the reaction except chloritoid, calculated using the Berman (1988) data set. n is the chloritoid stoichiometric coefficient (negative if chloritoid is part of the reactant assemblage, positive if it is a product). This may be further rearranged such that:

$$\Delta \hat{H}^{Pr,Tr} - T\Delta \hat{S}^{Pr,Tr} + \Pi + K + \Omega = nS_{Cld}(T) - nH_{Cld} \quad \text{Eq 3.11}$$

It can be seen that for a given reaction, at fixed temperature and pressure, the left hand side (LHS) of equation 3.11 is a constant. Rearranged in this manner, equation 3.11 resembles the equation of a line with a slope equal to nS_{Cld} and an ordinate intercept equal to $-nH_{Cld}$.

Chloritoid enthalpy and entropy may be extracted from experimental data using equation 3.11. The procedure involves calculating the LHS of equation 3.11 at the P and T of each experimental point. If the equilibrium has been bracketed correctly, plotting these values against temperature (the abscissa) should yield a straight line separating the half-brackets. A "best-fit" equation of a line through these brackets can be obtained using a least squares linear regression technique. This has been done for each of the four experimentally investigated chloritoid-bearing equilibria. The results

are illustrated in Figures 3.5 to 3.8. Note that the stoichiometry of each reaction has been normalised to 1 mole of reactant chloritoid so that $n = -1$ in equation 3.11. The extracted chloritoid enthalpy and entropy values are summarised in Table 3.7 below:

Reference	Equilibrium	Enthalpy (J/mol)	Entropy (J/K·mol)
Ganguly (1969)	$3\text{ctd}=\text{alm}+2\text{cor}+3\text{H}_2\text{O}$	-3189162.91	184.5839
Rao and Johannes (1979)	$23\text{ctd}+8\alpha\text{qtz}=4\text{st}+5\text{alm}+21\text{H}_2\text{O}$	-3202999.52	170.7229
	$8\text{ctd}+10\text{ky}=2\text{st}+3\alpha\text{qtz}+4\text{H}_2\text{O}$	-3226708.08	143.4339
Vidal et al. (1994)	$3\text{ctd}=\text{alm}+4\text{dsp}+\text{H}_2\text{O}$	-3219296.70	152.8120
	Average	-3209541.80	162.8882
	Standard Deviation	16812.10	18.36741

Note that since there is no indication that any one of the four experiments should be favoured over the others, the average enthalpy and entropy values calculated in Table 3.7 will be used in subsequent calculations.

Figure 3.5: Linear regression through Ganguly (1969) experimental data for reaction $3ctd=zlm+2cor+3H_2O$ (normalised in this case to 1 mole chloritoid).

Figure 3.6: Linear regression through Rao & Johannes (1979) experimental data for reaction $23ctd+8cqtz=4st+5alm+21H_2O$ (normalised in this case to 1 mole chloritoid).

Figure 3.7: Linear regression through Rao & Johannes (1979) experimental data for reaction $8\text{ctd} + 10\text{ky} = 2\text{st} + 3\text{aqtz} + 4\text{H}_2\text{O}$ (normalised in this case to 1 mole chloritoid).

Figure 3.8: Linear regression through Vidal et al. (1994) experimental data for reaction $3\text{ctd} = \text{alm} + 4\text{dsp} + \text{H}_2\text{O}$ (normalised in this case to 1 mole chloritoid).

3.3.1 *Estimated Error in Retrieval of Chloritoid Enthalpy and Entropy by Linear Regression*

Uncertainty in the chloritoid enthalpy and entropy values obtained by the linear regression method is primarily due to the width of the experimental brackets used in the retrieval process (the method utilises a best fit line through these brackets, however many other fit lines are possible). The uncertainty in each of these experiments can be evaluated during the fitting process by calculating a ± 1 sigma uncertainty envelope around the best-fit line. However, in the absence of a preferred experimental result, average enthalpy and entropy values have been calculated using the four experimental data sets. The standard deviation of these average values should provide an estimate of the sum of errors resulting from the use of four different experimental results in the retrieval process. The results summarised in Table 3.7 suggest:

$$H_{\text{Ctd}} = -3209.5 \pm 16.812 \text{ kJ/mol}$$

$$S_{\text{Ctd}} = 162.9 \pm 18.4 \text{ J/K/mol}$$

The error values obtained above indicate these results are indistinguishable from the chloritoid enthalpy (-3211.5 kJ/mol) and entropy (161.0 J/K·mol) values obtained previously by simultaneous solution. The calculated errors for the linear regression method are approximately half the value of those associated with the simultaneous solution method, however, reduced error alone does not necessarily make these values preferable to those obtained earlier.

The two sets of results can be evaluated by comparison with previously published enthalpy and entropy values for chloritoid, and by comparing equilibrium curves derived from the different data sets with existing experimental brackets.

3.4 Evaluation of Derived Chloritoid Thermodynamic Properties

3.4.1 *Direct Numerical Comparison*

Table 3.8 summarizes the chloritoid thermochemical results obtained in this study, along with previously published values. Note that while it is useful to discuss certain similarities and differences amongst the data, direct numerical comparison is difficult because the various data sets employ different heat capacity functions, molar volumes, compressibilities and expansivities.

3.4.1.1 *Chloritoid Enthalpy*

The chloritoid enthalpy of formation obtained by the simultaneous solution method (-3211.5 kJ/mol) is almost identical to the values obtained by Holland & Powell (1990) (-3211.4±1.48 kJ/mol) and Vidal et al. (1994) (-3211.2 kJ/mol). These values are approximately 2 kJ/mol greater than the enthalpy value obtained by linear regression (-3209.5 kJ/mol), which is identical to the value obtained by El-Shazly & Liou (1991) (-3209.6 kJ/mol). All five possible enthalpy values therefore lie within the uncertainty range quoted by Holland & Powell (1990). The only enthalpy value that lies outside this range is given by Droop & Bucher-Nurminen (1984) (-3230.9 kJ/mol).

3.4.1.2 *Chloritoid Entropy*

The chloritoid entropy value estimated by Holland (1989) (162 J/K·mol) lies midway between the values obtained in this study (161 J/K·mol for simultaneous solution and 162.9 J/K·mol for linear regression). The Holland (1989) value was estimated independently of phase equilibrium experiments, relying instead on a documented relationship between molar volume and entropy. This estimated value was later adopted by Holland & Powell (1990), El-Shazly & Liou (1991) and Vidal et al. (1994). It is encouraging to see that the two entropy values obtained in this study bracket this estimate by ±1 J/K·mol. The entropy values obtained in this study are also close to the value used by Spear & Cheney (1990) (158 J/K·mol). However, two previously published values differ significantly from those listed above. Chloritoid entropy estimated by Helgeson et al. (1978) is approximately 15

J/K·mol greater than the study values, while the value used by Wang & Spear (1991) is 13 J/K·mol lower.

3.4.2 Comparison with Experimental Brackets

Figures 3.9 and 3.10 compare the location of previously determined experimental brackets with equilibrium curves plotted using the Berman (1988) database in conjunction with the derived chloritoid thermochemical properties. Equilibria were located using the program TWQ and the Haar et al. (1984) equation of state for water. Published experimental brackets have been widened, to account for experimental error, as follows: Temperature values were adjusted by ± 5 degrees. Pressure values for experiments conducted in cold-seal bombs (generally those conducted at pressures ≤ 6000 bars) were adjusted by ± 1.5 percent. Those conducted in piston-cylinder apparatus (> 6000 bars) were adjusted by ± 5 percent. The location of the originally published (unadjusted) data is illustrated in these figures by the end of short line connected to the bracket symbol, which is a circle for the stable reactant assemblage, and a square for the product assemblage.

Figure 3.9 shows the location of the Rao & Johannes (1979) experimental data surrounding the invariant point QWACKS. Each chloritoid-bearing equilibrium has five possible locations, corresponding to five sets of possible chloritoid thermodynamic values (This study - simultaneous solution method, This study - linear regression method, El-Shazly & Liou (1991), Holland & Powell (1990) and Vidal et al. (1994)). The garnet-absent equilibrium ($8\text{ctd} + 10\text{ky} = 2\text{st} + 3\text{qtz} + 4\text{H}_2\text{O}$), located using chloritoid thermodynamic properties retrieved by simultaneous solution, passes through two of three full experimental brackets from Rao & Johannes (1979) (shown in red on Fig. 3.9), missing the lowest pressure bracket by 25°C . The same curve, located using the linear regression values determined by this study, misses the two lowest pressure brackets. Both data sets locate the kyanite absent equilibrium ($23\text{ctd} + 7\text{qtz} = 2\text{st} + 5\text{alm} + 19\text{H}_2\text{O}$) within the Rao & Johannes (1979) experimental brackets (one full and two half-brackets, shown in blue on Fig. 3.9). The results for the remaining three data sets are summarized in Table 3.9 below. Figure 3.9 also includes the

Figure 3.9: Comparison of experimental results from Rao and Johannes (1979) with corresponding equilibrium curves derived using various thermodynamic data. Data for the garnet-absent equilibrium ($8\text{ctd} + 10\text{ky} = 2\text{st} + 3\text{qtz} + 4\text{H}_2\text{O}$) is shown in red, the kyanite-absent equilibrium ($23\text{ctd} + 8\text{qtz} = 4\text{st} + 5\text{alm} + 21\text{H}_2\text{O}$) in blue, and the chloritoid-absent equilibrium ($6\text{st} + 25\text{qtz} = 8\text{alm} + 4\text{ky} + 12\text{H}_2\text{O}$) in green. Circles represent reactant-stable assemblages, squares product-stable. Experimental brackets have been expanded for experimental error (see text).

Figure 3.10: Comparison of experimental results from Ganguly (1969 - blue), and Vidal et al. (1994 - red), with corresponding equilibrium curves derived using various thermodynamic data. Circles represent reactant-stable assemblages, squares product-stable. Experimental brackets have been expanded for experimental error (see text).

location of the chloritoid-absent equilibrium $6\text{st} + 25\alpha\text{qtz} = 8\text{alm} + 46\text{ky} + 12\text{H}_2\text{O}$, which passes through all three Rao & Johannes (1979) experimental brackets for both the Berman (1988) and Holland & Powell (1990) data sets. It should be noted that the location of this equilibrium is based solely on the tabulated thermodynamic data in each data set, and is included here only as a matter of interest.

Figure 3.10 shows reactions and experimental brackets around the invariant point CoWACKS. The location of the corundum-absent reaction ($3\text{ctd} = \text{alm} + 4\text{dsp} + \text{H}_2\text{O}$), plotted using either data set derived in this study, is consistent with all experimental data of Vidal et al. (1994, shown in red). The diaspore-absent reaction, $3\text{ctd} = \text{alm} + 2\text{cor} + 3\text{H}_2\text{O}$, located using chloritoid enthalpy and entropy values retrieved by simultaneous solution, passes through only two of the five Ganguly (1969) experimental brackets (shown in blue). However, the curve misses the remaining three brackets by less than 5°C. The same reaction, plotted using the linear regression values, passes through four of the five brackets, missing the remaining bracket by only one or two degrees.

Table 3.9 below summarises how well each of the five-chloritoid data sets fits the available experimental data. A point is given for each full or half bracket satisfied by the thermodynamic data. A perfect score would equal 16, the number of experimental full and half brackets published in the literature. Chloritoid properties derived by simultaneous solution (12pts) and linear regression (13pts) have similar scores when evaluated in this manner. This should not be too surprising given that the two results are statistically indistinguishable and both data sets use the same molar volume, heat capacity, expansivity and compressibility. The scores recorded in Table 3.9 should be used only to get a qualitative sense of how well a given data set fits the experimental results. Since the tabulated score provides no information about how well a particular data set fits, or by how much it misses, the experimental brackets.

The Holland & Powell (1990) data seem to consistently plot chloritoid-bearing equilibria on the high temperature of the experimental brackets, resulting in a poor tabulated score in Table 3.9. This is surprising, given that the enthalpy and entropy values obtained in this study are similar to those contained in the Holland & Powell (1990) database. The source of this discrepancy must lie in the heat capacity terms for chloritoid in the Holland & Powell (1990) database, which appear to

underestimate the heat capacity of chloritoid.

Figures 3.9 and 3.10, combined with Table 3.9, demonstrate that chloritoid enthalpy and entropy derived by either the simultaneous solution or linear regression methods, adequately fit the available experimental data sets. There is some indication that the linear regression values may be superior to those obtained by simultaneous solution. However, the results from both methods are statistically indistinguishable.

TABLE 3.9
Number of Chloritoid-bearing Experimental Brackets Satisfied by Various Thermodynamic Data sets

Equilibrium	Brackets	Ideal	This Study (Sim. Sol.)	This Study (Lin. Reg.)	El-S & L (1991)	H & P (1990)	V et al. (1994)
3ctd=alm+2cor+3H ₂ O Ganguly (1969)	Full	3	2	2	3	0	2
	½	2	0	2	2	0	2
23ctd+8oqtz=4st+5alm+21H ₂ O Rao and Johannes (1979)	Full	1	1	1	1	0	1
	½	2	2	2	2	0	1
8ctd+10ky=2st+3oqtz+4H ₂ O Rao and Johannes (1979)	Full	3	2	1	1	2	0
	½	0	0	0	0	0	0
3ctd=alm+4dsp+H ₂ O Vidal et al. (1994)	Full	3	3	3	3	0	0
	½	2	2	2	2	0	1
TOTAL		16	12	13	14	2	7

3.5 Thermochemical Properties of Magnesiochloritoid

3.5.1 Experimental Data and Location of Invariant Points

The occurrence of magnesiochloritoid in metamorphosed high-pressure terrains is well documented (Chopin, 1983; Kienast & Messiga, 1987; Schreyer 1988; Kienast & Pognante, 1988; Messiga et al., 1999). However, magnesiochloritoid phase equilibrium studies are relatively rare, and experimental data is available from only two sources - Chopin & Schreyer (1983) and Chopin & Monié (1984), summarized below:

Chopin & Schreyer (1983) completed an experimental investigation of four magnesiochloritoid-bearing reactions, summarised in Table 3.10. The resulting phase equilibrium grid is shown on Figure 3.11 (from Chopin & Schreyer, 1983). Reactions CS#1, CS#2 and CS#3 are the only magnesiochloritoid-bearing equilibria that have been experimentally located on this grid (the location of all other magnesiochloritoid reactions has been estimated or inferred). It is not known if the experiments were reversed and the experimental brackets are unavailable. Figure 3.11 is therefore the only source of information on the P-T location of these reactions.

Chopin & Monié (1984) proposed an alternative location for the mctd+tlc = chl+ky equilibrium (CS#3). This reaction is identified as CM#1 in this alternative location.

TABLE 3.10
Experimental Studies Involving Magnesiochloritoid

Paper	Number	Reaction
Chopin & Schreyer (1983)	CS#1	$5 \text{ mctd} = \text{chl} + 2 \text{ ky} + 2 \text{ cor} + \text{H}_2\text{O}$
	CS#2	$3 \text{ mctd} = \text{prp} + 2 \text{ cor} + 3 \text{ H}_2\text{O}$
	CS#3	$7 \text{ mctd} + \text{tlc} = 2 \text{ chl} + 4 \text{ ky}$
	CS#4	$3 \text{ mctd} + 4 \alpha\text{qtz} = \text{tlc} + 3 \text{ ky} + 2 \text{ H}_2\text{O}^*$
Chopin & Monié (1984)	CM#1	$7 \text{ mctd} + \text{tlc} = 2 \text{ chl} + 4 \text{ ky}$

* The assemblage mCtd + α Qtz is metastable in the presence of magnesiocarpholite, therefore this reaction does not appear on Fig. 3.11, having been replaced by the stable reaction $\text{car} + \alpha\text{qtz} = \text{tlc} + \text{ky} + \text{H}_2\text{O}$.

Figure 3.11: Stable phase relations in the system $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ plotted as a function of temperature and pressure (modified from Chopin & Schreyer, 1983). The P-T location of experimentally determined equilibria CS#1, CS#2 and CS#3 is shown. Equilibrium CS#4 does not appear on this diagram because it is metastable. Invariant points A through F are those involving the experimentally determined equilibria. Chopin and Monié (1984) proposed an alternative location for equilibrium CS#3 (called CM#1), resulting in two possible locations for invariant points D, E, and F (only the Chopin & Schreyer (1983) locations are shown). Note that invariant point F is metastable with respect to magnesiocarpholite-bearing assemblages.

The enthalpy and entropy of magnesiochloritoid can be retrieved from Figure 3.11 using the simultaneous solution method, outlined previously for chloritoid in section 3.2. This procedure is a two-step process, which involves:

1. Determining the pressure-temperature location of each magnesiochloritoid-bearing invariant point in Figure 3.11. (To ensure consistency with the Berman database, invariant points must be located at the intersection of two reactions; one plotted using existing thermodynamic data from Berman (1988), and the other obtained from figure 3.11).
2. Using the pressure-temperature values determined in step 1 to formulate a system of Gibbs free energy equations similar to equation 3-12, in which the enthalpy and entropy of magnesiochloritoid are treated as unknown variables. One equation can be written per invariant point; therefore, the P-T location of any two invariant points is sufficient to retrieve the enthalpy and entropy of magnesiochloritoid by simultaneous solution.

Only three of the four equilibria summarised in Table 3.10 have been shown on Figure 3.11. The fourth reaction, CS#4, cannot be shown because it is metastable with respect to magnesiochloritoid-bearing assemblages (see Chopin & Schreyer, 1983; their Fig 7, pg. 88 for an approximate location).

The three remaining reactions, CS#1, CS#2, & CS#3, are associated with five stable invariant points (labelled A through E). However, three of these invariant points (B, C, and E) are unsuitable for magnesiochloritoid data extraction because they have a phase assemblage that includes two phases not found in the Berman (1988) database. These database-absent phase pairs include magnesiochloritoid + magnesiochloritoid + magnesiochloritoid at invariant points B and C and magnesiochloritoid + magnesiochloritoid at invariant point E. The phase rule requires every associated univariant reaction surrounding these invariant points to involve at least one of the database-absent phases. It follows that the Berman (1988) database cannot be used to locate any of the univariant reactions associated with these invariant points (because there is one database-absent phase involved in each reaction). This in turn makes it impossible to locate these invariant points at pressure and temperature values that are consistent with the rest of the Berman (1988) database. Thus, A and D are only two stable invariant points that can be used to extract magnesiochloritoid thermodynamic data.

Figure 3.11 contains one additional invariant point that was not included in the original Chopin & Schreyer (1983) grid. This metastable invariant point, labelled F, is produced by extending reaction CS#3 past invariant point E until it intersects the metastable extension of the chl + qtz = tlc + ky + H₂O reaction. Extrapolation of reaction CS#3 beyond invariant point E should not result in an unreasonably large uncertainty in the location of invariant point F, since the slope of reaction CS#3 appears to be relatively constant. Invariant point F thus provides an additional equation that can be used to extract magnesiochloritoid thermodynamic data.

Chopin and Monié (1984) proposed an alternative location for the mctd + tlc = chl + ky equilibrium, which is identified as CM#1. Since this equilibrium terminates at invariant points D and F, relocating this reaction results in the formation of two new invariant points at alternative locations, identified as D2 and F2 (the original Chopin & Schreyer 1983 invariant points are identified as D1 and F1).

Figures 3.12 to 3.14 illustrate the formation of invariant points A, D1+D2, and F1+F2. These invariant points are created by the intersection of reactions CS#1, CS#3 and CM#1 with magnesiochloritoid-absent curves located using the program TWQ (Berman, 1991; thermodynamic data from Berman, 1988; equation of state for water from Haar et al., 1984). Table 3.11 below summarises the phase assemblage present at these invariant points together with their location in P-T space:

TABLE 3.11
*Phase Assemblage and P-T Location of Magnesiochloritoid Invariant Points
in the MASH system*

Invariant Point	Phase Assemblage	Temperature (°C)	Pressure (bars)
A	mctd, chl, ky, cor, dsp, H ₂ O	570	18185
D	mctd, prp, tlc, chl, ky, H ₂ O	690	29185
D2	mctd, prp, tlc, chl, ky, H ₂ O	690	29445
F	mctd, qtz, tlc, chl, ky, H ₂ O	550	24240
F2	mctd, qtz, tlc, chl, ky, H ₂ O	560	22980

Figure 3.12: Location of invariant point A, stable assemblage: mctd+cor+chl+dsp+ky+H₂O. The mctd-absent equilibrium 2 diaspore = corundum + H₂O was plotted using thermodynamic data from Berman (1988). Reaction CS#1 was located using Chopin & Schreyer (1983).

Figure 3.13: Location of invariant points D1 (Chopin & Schreyer, 1983) and D2 (Chopin and Monié, 1984). Stable assemblage: mctd+chl+ky+tlc+prp+H₂O. The mctd-absent equilibrium 3 chl + 4ky + 2tlc = 7prp + 14H₂O was plotted using thermodynamic data from Berman (1988). Reactions CS#3 and CM#1 were located using published data as indicated.

Figure 3.14: Location of invariant points F1 (Chopin & Schreyer, 1983) and F2 (Chopin and Monié, 1984). Both invariant points contain the stable assemblage: mctd+chl+ky+tlc+ α qtz+H₂O. The mctd-absent equilibrium $3\text{chl} + 14\alpha\text{qtz} = 5\text{tlc} + 3\text{ky} + 7\text{H}_2\text{O}$ was plotted using thermodynamic data from Berman (1988). Reactions CS#3 and CM#1 were located using Chopin & Schreyer (1983) and Chopin & Monié (1984).

3.5.2 Simultaneous Retrieval of Magnesiochloritoid Enthalpy and Entropy

The enthalpy and entropy of magnesiochloritoid was retrieved by simultaneous solution of free energy equations, as described above for chloritoid. The pressure-temperature locations of the invariant points in Table 3.11 were used to construct three Gibbs free energy equations similar to equation 3-13 for the following solid phase reactions present at invariant points A, D and F:

It was assumed that the two alternative data sets for invariant points D and F (Chopin & Schreyer 1983, Chopin and Monié 1984) were mutually exclusive, and the resulting invariant points were not cross-compared. Results obtained by simultaneous solution of free energy equations similar to equation 3.9 are summarized in Table 3.12 below. Note that both possible locations of invariant points D and F were included in the calculations.

TABLE 3.12
Magnesiochloritoid Enthalpy and Entropy Obtained by Simultaneous Solution

Invariant Points Used for Solution	Enthalpy (J/mol)	Entropy (J/K·mol)
A & D1	-3545894.8	147.0035
A & D2	-3546223.6	146.6123
A & F1	-3602616.4	79.7289
A & F2	-3681734.0	-14.1069
D1 & F1	-3554781.4	137.4754
D2 & F2	-3558131.1	134.2493

Magnesiochloritoid enthalpy and entropy values summarized in Table 3.12 are highly variable, being inconsistent with each other, with values published in the literature, and with the entropy value obtained by estimation (see section 3.5.3 below). The results appear to be strongly dependent on the combination of invariant point pairs (A&D, A&F, D&F) used in the data retrieval.

The location of the $\text{mctd} + \text{tlc} = \text{chl} + \text{ky}$ equilibrium (CS#3 vs. CM#1) appears to be of

secondary importance since similar invariant point pairs (A&D1, A&D2) produce similar enthalpy and entropy values. It is also clear that certain invariant point pairs (i.e. A and F) are mutually exclusive, since they result in unacceptably low entropy values for magnesiochloritoid. The results summarized in Table 3.12 indicate that simultaneous solution method cannot be used to retrieve magnesiochloritoid thermodynamic properties that are consistent with the Berman (1988) database from the Chopin & Schreyer (1983) experimental dataset.

The reason for this failure may lie in an inconsistency, noted by Berman (1988), between the Berman data and the Chopin & Schreyer (1983) grid. The inconsistency involves Massone et al. (1981) high-pressure (>12 kbar) experimental brackets for the $14 \text{ quartz} + 3 \text{ clinochlore} = 5 \text{ talc} + 3 \text{ kyanite} + \text{H}_2\text{O}$ equilibrium, which are used by Chopin & Schreyer (1983) to locate several invariant points on their grid. Berman (1988) suggests that the inconsistency between the two data sets could be due to strong pressure sensitivity in the aluminium content of talc above approximately 10 kbar. It is possible therefore that the aluminium content of talc used in the experiments of Massonne et al. (1981) and Chopin & Schreyer (1983) varied with increasing pressure above 10 kbar (this cannot be confirmed since talc compositions used in the experiments are not available). This compositional variation would displace talc-present equilibrium curves and invariant points producing the observed discrepancy between the Chopin & Schreyer (1983) experimental data and the Berman (1988) database.

3.5.3 Estimation of Magnesiochloritoid Entropy

Several authors including Helgeson et al. (1978) and Holland (1989) have proposed using entropy estimation techniques in the absence of available experimental data. McMullin et al. (1991) used an exchange reaction to estimate the entropy of annite, and the entropy of magnesiochloritoid can be estimated using a similar reaction:

Chloritoid entropy obtained earlier by simultaneous solution (161.0 J/K·mol) was used in conjunction with entropy values for periclase (Berman, 1988) and FeO (Helgeson et al., 1978) to obtain an estimated magnesiochloritoid entropy of 127.2 J/K·mol. A value of 4.7 J/cation determined by McMullin et al. (1991) was added to this value to account for the contribution of the electronic configuration and crystal-field stabilization (Helgeson et al., 1978, pg. 51). This results in a final magnesiochloritoid entropy estimate of

$$S_{\text{mctd}} = 131.9 \text{ J/K}\cdot\text{mol}$$

Table 3.13 below shows that this value is similar to magnesiochloritoid entropy values reported in Holland & Powell (1990) and Spear & Cheney (1989), but is lower than the estimate contained in Helgeson et al. (1978).

3.5.4 Retrieval of Magnesiochloritoid Enthalpy and Entropy from Natural Samples

An alternative method of obtaining magnesiochloritoid enthalpy and entropy values had to be considered, given the apparent inconsistency of the Chopin & Schreyer (1983) experimental data and the Berman (1988) database, and the absence of an alternative experimental data set. Holland & Powell (1990) used Fe-Mg partitioning data from natural phase assemblages to obtain enthalpy and entropy estimates for phases with insufficient experimental data. A similar technique, described below, can be used to obtain the enthalpy and entropy of magnesiochloritoid.

The Fe-Mg exchange reaction between chloritoid and garnet (shown below) was chosen for study because it is a relatively simple reaction that is vapour-conserving, (so a fugacity model is not required and will not influence the final data).

The equilibrium constant for this reaction is given by:

$$\ln K = \ln \left\{ \frac{a_{\text{fCld}}^3 \cdot a_{\text{Prp}}}{a_{\text{mCld}}^3 \cdot a_{\text{Alm}}} \right\}$$

Eq 3.12

The activity of chloritoid was calculated using an ideal mixing on sites solution model (see Appendix 2 for a detailed description of activity models used throughout the thesis). Garnet activity was calculated using a non-ideal solution model, the general expression for which is:

$$a_i = X_i^n \gamma_i^n$$

Eq 3.13

Where X_i^n is equal to the mole fraction of component i in an n-site crystalline solution (for garnet, n=3) and γ_i^n is the activity coefficient of component i. Garnet activity coefficients were calculated using Berman (1990) solution model. Substituting activity expressions into equation 3.12:

$$\ln K = \ln \left\{ \frac{X_{\text{fCld}}^3 \cdot X_{\text{Prp}}^3 \cdot \gamma_{\text{Prp}}^3}{X_{\text{mCld}}^3 \cdot X_{\text{Alm}}^3 \cdot \gamma_{\text{Alm}}^3} \right\} = 3 \ln \left\{ \frac{X_{\text{fCld}} \cdot X_{\text{Prp}} \cdot \gamma_{\text{Prp}}}{X_{\text{mCld}} \cdot X_{\text{Alm}} \cdot \gamma_{\text{Alm}}} \right\}$$

Eq 3.14

The equilibrium constant expression can be substituted into equation 3.7-3.8 so that:

$$\alpha S_{mCld}(T) - \alpha H_{mCld} = \Delta \hat{H}^{Pr,Tr} - T \Delta \hat{S}^{Pr,Tr} + \Pi + K + \Omega + 3RT \ln \left\{ \frac{X_{fCld} \cdot X_{Prp} \cdot \gamma_{Prp}}{X_{mCld} \cdot X_{Alm} \cdot \gamma_{Alm}} \right\}$$

Eq 3.15

Where T and P are the temperature and pressure of equilibrium, Π , K and Ω are energy terms due to the change in molar volume, heat capacity, and solid phase expansivity/compressibility calculated using data from Berman (1988) at T and P , $\Delta \hat{H}^{Pr,Tr}$ and $\Delta \hat{S}^{Pr,Tr}$ are the enthalpy and entropy change for all minerals involved in the reaction except magnesiochloritoid, and α is the magnesiochloritoid stoichiometric coefficient (negative if mCld is part of the reactant assemblage, positive if it is a product).

Equation 3.15 describes how the enthalpy and entropy of magnesiochloritoid can be extracted from natural assemblages provided the following conditions are met:

- 1) The thermodynamic properties of all other minerals in the reaction are known.
- 2) The equilibrium constant can be calculated (mineral chemistry is provided).
- 3) The pressure and temperature of equilibrium (T and P) for the natural assemblage can be obtained by some means.

If the three conditions above are met, then the right-hand side of equation 3.15 reduces to some real number (Φ), which is a function of T . Dividing equation 3.15 through by the stoichiometric coefficient from magnesiochloritoid (α) yields:

$$\Phi/\alpha = S_{mCld}(T) - H_{mCld}$$

Eq 3.16

Equation 3.16 describes the equation of a straight line with a slope equal to S_{mCld} and an ordinate intercept of $-H_{mCld}$. Magnesiochloritoid enthalpy and entropy can therefore be determined by fitting a straight line through a graph with left-hand side of equation 3.16 (Φ/α) on the ordinate axis and temperature on the abscissa.

Table 3.13 below summarises the natural assemblage data used to construct Figure 3.15, a Φ/α vs. T graph for chloritoid+garnet assemblages.

TABLE 3.13

Natural Assemblage Data Used to Extract Magnesiochloritoid Enthalpy and Entropy

Reference	Locality	Sample	Temperature (°C)	Pressure (bars)	lnK (Eq 3.14)
Wang & Spear (1991)	Appalachian Orogen Taconic Range New England USA	#106-3	529	4500	-0.615
		#107-1	525	4500	-1.137
		#108-1	513	4500	-1.455
		#193-1	505	4500	-1.316
		#199-1	521	4500	-1.287
		#282-2	525	4500	-1.120
		#284-2	502	4500	-1.406
Droop & Harte (1995)	Stonehaven coast NE Scotland	60031	610	4500	-1.811
		81-16	600	4500	-1.597
		5276	594	4500	-1.556
	SE Tauern Window Austria	GD572	566	7000	-1.101
		GD1289E	610	7000	-0.530
		GD308A	630	7000	-0.708
		GD308C	511	7000	-1.114
		GD725	499	7000	-1.211
		GD1296	600	7000	-0.726
		GD1297D	530	7000	-0.879
		GD1297P	615	7000	-0.693
		GD1297Q	565	7000	-1.210
		GD1297L	578	7000	-0.870
Ghent <i>et al.</i> (1987)	Tertiary high-pressure belt, Northern New Caledonia	23913	366	11000	-1.968
		23915	408	11000	-1.904
		23917	455	11000	-1.628
		306	464	11000	-1.556
		37101	492	11000	-1.330
		37102	443	11000	-1.550
		37103	550	11000	-1.190
Thompson & LeClair (1987)	Hastings metamorphic low, Southwestern Grenville Province	A1	517	4000	-0.700
		A2	512	4000	-1.630
		B1	500	5500	-1.373
		B2	497	5500	-1.368
Karabinos (1985)	Appalachian Orogen Southern Vermont USA	333	583	5000	-1.737
		118	500	5000	-1.163
		559	586	5000	-0.919
		120D	574	5000	-0.739
Yardley <i>et al.</i> (1980)	Connemara, Ireland	BY 230M	527	5000	-1.593
Bickle & Archibald (1984)	Yilgarn Block	NA 20	515	4200	-1.182
	Western Australia	NA 24	513	4200	-1.263
Vuichard & Ballèvre (1988)	Sesia zone	ASC16, ctd3	622	16000	-0.970
	Western Alps	ASC16, ctd4	622	16000	-0.882
		AGN6, ctd5	555	16000	-1.245
		AGN6, ctd6	555	16000	-0.837
Ashworth & Evirgen (1984)	Menderes Massif	M.93.4 W	530	5500	-1.642
	Southwestern Turkey	M.101.1 E	564	5500	-0.711

Figure 3.15: Plot of Φ/α versus temperature (K) for the chloritoid-garnet exchange reaction. Φ is defined as the right-hand side of equation 3.15. α is magnesiochloritoid stoichiometric coefficient (in this case, $\alpha=-3$). First order linear regression through the data yields the following best-fit line $\Phi=0.1332477T+3556.4916$. Comparison with equation 3.16 shows $S_{mCtd} = 133.2 \text{ J/K}\cdot\text{mol}$ and $H_{mCtd} = -3556492 \text{ J/mol}$.

Temperature estimates in Table 3.13 were obtained by Garnet-Biotite geothermometry (Ferry & Spear, 1978; with Hodges and Spear, 1982 calibration for non-ideal garnet mixing) and/or Garnet-Chlorite geothermometry (Dickenson & Hewitt, 1986 calibration) depending on the available mineral assemblage (average temperature values were used for Grt+Bt+Chl assemblages). Pressure estimates were obtained: directly from the source paper, or by estimation using aluminosilicate minerals in coexisting rocks (Holdaway, 1971), or by calculation using the GASP geobarometer (Ghent, 1976; Newton & Haselton, 1981; Koziol & Newton, 1988).

Figure 3.15 shows the first-order linear regression line through the data summarized in table 3.13. The equation for the best-fit line is $\Phi = 0.1332477T + 3556.4916$, which by comparison with equation 3.16 yields the following enthalpy and entropy values for magnesiochloritoid:

$$H_{\text{mCld}} = 3556491.6 \text{ J/mol}$$

$$S_{\text{mCld}} = 133.25 \text{ J/K}\cdot\text{mol}$$

3.5.5 Evaluation of Derived Magnesiochloritoid Thermodynamic Properties

Table 3.15 on the following page compares previously published magnesiochloritoid thermodynamic properties with those obtained in this study, either by estimation in section 3.5.3 or from Fe-Mg partitioning data in section 3.5.4.

It is encouraging to note that the magnesiochloritoid entropy value obtained using Fe-Mg partitioning data (133 J/mol/K) is almost identical to the value estimated in section 3.5.3 above (132 J/mol/K). Other authors including El-Shazly & Liou (1991), Holland & Powell (1990), Spear & Cheney (1989), and Holland (1989) have reported similar entropy values for magnesiochloritoid, ranging from 130 to 132 J/mol/K. Only two of the authors in Table 3.14 (Massonne, 1995; Wang & Spear, 1991) report a significantly lower entropy value for magnesiochloritoid, in the range of 120 to 124 J/mol/K.

TABLE 3.14

Summary and Comparison of Magnesiochloritoid Thermodynamic Properties

Database	Enthalpy (J/mol)	Entropy (J/K·mol)	V (J/bar)	k0	k1	k2	k3	k5	$v_1 \times 10^{-5}$	$v_2 \times 10^{-5}$	$v_3 \times 10^{-5}$	v_4
Entropy Estimation		131.9										
Natural Fe-Mg Partitioning.	-3556491.6	133.25	6.875	407.697	-2759.53	-8624440	1207092000	0.00	2.97390	0.00	-0.06466	0.00
Massonne (1995)	-3565090	124.0	6.874						2.7000	0.00	-0.1280	0.0003
El-Shazly & Liou (1991)	-3558844.2	132.00		464.4	-4341.1	-1147200	0.00	-0.01265	2.80950	0.00044	-0.08511	0.00
Wang & Spear (1991)		120.44	6.847	407.697	-2759.24	-8624440	1207092000					
Holland & Powell (1990)	-3557950	132.00	6.875	464.4	-4341.0	-1147200	0.00	-0.01265	2.9091	0.00	-0.0858	0.00
Holland (1989)		132.00										
Spear & Cheney (1989)		130.0	6.84	407.697	-2759.24	-8624440	1207092000					

The enthalpy value obtained from Fe-Mg partitioning data (-3556.5 kJ/mol) is within the uncertainty range quoted by Holland & Powell (1990) for their magnesiochloritoid enthalpy value of -3557.95 ± 1.48 kJ/mol, and is only 2.3 kJ/mol higher than the value obtained by El-Shazly & Liou (1991). Only Massonne (1995) reports an entropy value for magnesiochloritoid (-3565.1 kJ/mol) significantly lower than the value obtained in this study.

Additional support favouring the enthalpy value obtained from Fe-Mg partitioning data is provided by Spear & Cheney (1989), who list the enthalpy of reaction for the Fe-Mg exchange between chloritoid and garnet (equilibrium 3.8) as 22271 J/mol, similar to the ΔH_f value of 15696 J/mol obtained using data from this study and Berman (1988).

Similarity between enthalpy and entropy values obtained by previous authors and those obtained in this study using natural Fe-Mg partitioning data indicate that the data extraction technique is reliable. The thermodynamic properties of magnesiochloritoid listed in Table 3.14 will be used to evaluate the metamorphic conditions imposed on chloritoid-bearing pelitic schists in the following chapter.

3.6 Thermochemical Properties of Chamosite (Iron Chlorite)

3.6.1 Introduction

The purpose of this section is to derive a set of thermochemical properties for the iron chlorite end-member chamosite ($\text{Fe}_5\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_8$, also known as daphnite), that are consistent with the Berman (1988) database. Early experiments on iron chlorite (Turnock, 1960; McOnie et al., 1975; and James et al., 1976) cannot be used to extract chamosite thermodynamic properties because they were conducted on chlorites of unknown composition, most likely an intermediate between chamosite and the more oxidized end-member pseudothuringite - $\text{Fe}_4\text{Al}_2\text{Si}_2\text{O}_{10}(\text{OH})_8$. Later experiments by Bryndzia and Scott (1987) were conducted with documented chlorite compositions; however, their results (summarized in Table 3.15 below) are not consistent with the Berman (1988) database. Therefore, in the absence of available experimental data, the thermodynamic properties for the chamosite must be estimated or extracted from natural phase assemblages.

TABLE 3.15

Summary of Thermodynamic Properties for Chamosite

Reference	Data Source	Free Energy (kJ/mol)	Enthalpy (kJ/mol)	Entropy (J/K/mol)
Saccocia & Seyfried (1993)	Reinterpretation of Bryndzia & Scott (1987)		-7101.97 $\pm$ 4.17	583.20
Holland & Powell (1990)	Natural Fe-Mg partitioning		-7148.44	559.00
Bryndzia & Scott (1987)	Redox Experiments	-6697.33 $\pm$ 27	-7222.84 $\pm$ 46	594.96 $\pm$ 54.4
Walshe (1986)	ΔH_f estimated using Tardy & Garrels (1974), ΔS_f from Helgeson et al. (1978)	-6477.88 (-6490.88)†	-7080.83 (-7093.83)†	
Sverjensky (1985)	Estimation using linear free energy correlation	-6486.46 (-6499.46)†		
Helgeson et al. (1978)	Estimated entropy from oxide exchange reaction			596.22

† Note that the chamosite ΔG_f° and ΔH_f° values estimated by Sverjensky (1985) and Walshe (1986) utilise the Al reference state of Helgeson et al. (1978), which has been shown by Hemingway et al. (1982) to be in error by approximately +6.5 kJ/mol aluminium. These values have therefore been adjusted by -13 kJ/mol for proper comparison with other data sets.

3.6.2 Chamosite – Estimated Entropy, Heat Capacity, Molar Volume, Compressibility and Expansivity

The entropy of chamosite was estimated using the following exchange reaction:

Entropy values for clinochlore (435.1545 J/K/mol) and periclase (26.9514) obtained from Berman (1988), were used in conjunction with FeO entropy (60.752 J/K/mol) from Helgeson et al. (1978) to obtain an estimated chamosite entropy value of 604.1575 J/K/mol. This value was adjusted by -4.7 J/cation of exchanged iron (McMullin et al., 1991), to account for entropy contributions by the electronic configuration and crystal-field stabilization. This produces a final chamosite entropy estimate of:

$$S_{fchl} = 580.6575 \text{ J/K/mol.}$$

Chamosite heat capacity coefficients for equation 3.2 were estimated using the additive oxide component model of Berman & Brown (1985). Calculated coefficients from chamosite are as follows:

$$k_0 = 1229.233, \quad k_1 = -10256.46, \quad k_2 = -12276980, \quad k_3 = 2121507000$$

Chamosite molar volume (21.34 J/bar) was obtained from Helgeson et al. (1978) and Holland & Powell (1990). Expansivity and compressibility values were estimated in the same manner as was done for chloritoid in section 3.2.3.4, by applying the difference between clinochlore and chamosite expansivity and compressibility terms ($\Delta v_n = v_n^{fchl} - v_n^{chl}$) found in the Holland & Powell (1990) database to the values for clinochlore already contained in Berman (1988). For the Holland & Powell (1990) database $\Delta v_1 = v_1^{fchl} - v_1^{chl} = 2.7648 - 2.7975 = -0.0327$, and $\Delta v_3 = 0.0021$. Applying these values to the clinochlore expansivity and compressibility values contained in Berman (1988) yields: $v_1^{fchl} = \Delta v_1 + v_1^{chl} = -0.0327 + 2.6452 = 2.6125$, and $v_3^{cham} = \Delta v_3 + v_3^{clino} = 0.0021 + (-0.1819) = -0.1798$. Chamosite heat capacity, molar volume, expansivity and compressibility will be used in the following section with Fe-Mg partitioning data to obtain chamosite enthalpy and entropy values consistent with the Berman (1988) database.

3.6.3 Retrieval of Chamosite Enthalpy and Entropy from Natural Assemblages

The Fe-Mg exchange reaction between chlorite and garnet (equilibrium 3.10 below) was chosen as the most suitable equilibrium to use for the extraction of chamosite enthalpy and entropy. The reaction was selected because it is vapour-conservative, and because the thermodynamic properties of the remaining three phases involved are relatively well known and are already present in the Berman (1988) database.

Equil 3.10

The equilibrium constant for this reaction is given by:

$$\ln K = \ln \left\{ \frac{a_{chl}^3 \cdot a_{alm}^5}{a_{fchl}^3 \cdot a_{prp}^5} \right\} \quad \text{Eq 3.17}$$

The activity of chlorite was calculated using an ideal mixing on sites solution model, which assumes Fe and Al mix randomly over the six octahedrally coordinated sites in the chlorite structure (Bryndzia & Scott, 1987).

$$a_{Cham} = \left[1 / \frac{(5^5 \cdot 1)}{6^6} \right] \cdot \left[\left(\frac{Fe_{VI}^{2+}}{6} \right)^5 \left(\frac{Al_{VI}}{6} \right) \right] = 14.93 \cdot \left[\left(\frac{Fe_{VI}^{2+}}{6} \right)^5 \left(\frac{Al_{VI}}{6} \right) \right] \quad \text{Eq 3.18}$$

(See Appendix 2 for a detailed description of activity models). Garnet activity was calculated using a non-ideal solution model with activity coefficients from Berman (1990). Substituting activity expressions into equation 3.17:

$$\ln K = \ln \left\{ \frac{\left(14.93 \cdot \left[\left(\frac{Mg_{VI}^{2+}}{6} \right)^5 \left(\frac{Al_{VI}}{6} \right) \right] \right)_{chl}^3 \cdot X_{alm}^{15} \cdot \gamma_{alm}^{15}}{\left(14.93 \cdot \left[\left(\frac{Fe_{VI}^{2+}}{6} \right)^5 \left(\frac{Al_{VI}}{6} \right) \right] \right)_{fchl}^3 \cdot X_{prp}^{15} \cdot \gamma_{prp}^{15}} \right\} \quad \text{Eq 3.19}$$

Table 3.16 below summarizes the natural mineral assemblage data (equilibrium temperatures/pressures and the value of the equilibrium constant ($\ln K$)) used to extract chamosite enthalpy and entropy.

A first-order linear regression through the data on Figure 3.16 gives the following best-fit equation: $\Phi = 0.5516851T + 7146.4999$, which by comparison with equation 3.16 yields the following enthalpy and entropy values for chamosite:

$$H_{fchl} = -7146499.9 \text{ J/mol}$$

$$S_{fchl} = 551.69 \text{ J/mol/K}$$

The entropy value obtained from Figure 3.16 is consistent with the chamosite entropy value contained in Holland & Powell (1990), which was also obtained from Fe-Mg partitioning data. However, this value is considerably lower than either the chamosite entropy estimated in section 3.7.2 above (580.7 J/K/mol) or the previously published entropy values summarized in Table 3.15 (with exception of Holland & Powell, 1990). A second linear regression with a fixed slope equal to the estimated chamosite entropy (0.5807 kJ/K/mol) was therefore completed through the data. This regression line, shown in red on Figure 3.16, gives a best-fit equation of $\Phi = 0.5807T + 7123.5$, which by comparison with equation 3.16 yields the following enthalpy and entropy values for chamosite:

$$H_{fchl} = -7123500 \text{ J/mol}$$

$$S_{fchl} = 580.7 \text{ J/mol/K}$$

3.6.4 Discussion of Results

Chamosite thermodynamic properties are summarized in Table 3.17 below. Note Wang & Spear (1990), and Spear & Cheney (1989) are not directly comparable with the rest of the data because both employ a chamosite formula that has half a molecule of tschermaks substitution applied ($Al^{VI} + Al^{IV} = Fe^{2+} + Si$), relative to the chamosite formula used in this study. (The iron-chlorite composition used in these two publications lies halfway between chamosite and Fe-amesite - $Fe_4Al_4Si_2O_{10}(OH)_8$).

TABLE 3.16

Natural Assemblage Data Used to Extract Chamosite Enthalpy and Entropy

Reference	Locality	Sample	T (°C)	P (bars)	lnK
Wang & Spear (1991)	Appalachian Orogen Taconic Range New England USA	#106-3	529	4500	27.609
		#107-1	525	4500	29.027
		#108-1	513	4500	30.302
		#193-1	505	4500	29.554
		#199-1	521	4500	28.294
		#282-2	525	4500	29.738
		#284-2	502	4500	29.820
Lang & Rice (1985)	Snow Peak Northern Idaho, USA	#293-1	460	4500	31.797
		TS29	437	4000	32.533
		TS11	440	4000	31.129
		TS21	423	4000	32.542
		BT144	491	4000	29.306
		BT96	496	4000	29.586
		TS2	440	4000	32.126
		BT91	466	4000	31.866
		BT86	488	4000	29.435
		BC46	455	4000	30.034
		BC41	454	4000	32.902
		BT61	487	4000	28.213
		BT83	496	4000	29.338
Yardley <i>et al.</i> (1980)	Connemara, Ireland	BT174	517	5000	28.607
		BT137	515	5000	27.361
		BT98.2	508	6000	29.966
		BT20.1	478	6000	30.210
		BT41	541	6000	26.945
		BT40	533	6000	27.064
		BT39	542	6000	27.295
		BT28	529	6000	27.339
		ML17	569	6000	26.610
		ML16	535	6000	28.959
		BY 230M	527	5000	29.022
		M.93.4 W	509	5500	29.026
		M.101.1 E	553	5500	27.148
Ashworth & Evirgen (1984)	Menderes Massif Southwestern Turkey	M.69.3 W	509	5500	28.786
		M.76.2 W	647	5500	23.725
		ASC16, g4c1	622	16000	26.963
Vuichard & Ballèvre (1988)	Sesia zone Western Alps	AGN6, g6c8	555	16000	28.450
		AGN6, g7c8	614	16000	26.329

TABLE 3.16

Natural Assemblage Data Used to Extract Chamosite Enthalpy and Entropy

Reference	Locality	Sample	T (°C)	P (bars)	lnK
Droop & Harte (1995)	Stonhaven coast NE Scotland SE Tauern Window Austria	R6	545	4500	26.420
		60031	554	4500	27.522
		81-16	600	4500	25.699
		GD561	518	7000	28.867
		GD825	505	7000	29.933
		GD570	552	7000	27.063
		GD573	454	7000	32.106
		GD572	566	7000	26.911
		GD509	545	7000	27.443
		GD1340	570	7000	27.033
		GD1289E	610	7000	26.088
		GD308A	630	7000	24.937
		GD308C	511	7000	29.869
Ghent <i>et al.</i> (1987)	Tertiary high- pressure belt, Northern New Caledonia	GD725	499	7000	29.711
		GD1296	600	7000	25.033
		GD1297D	530	7000	27.563
		GD1297P	615	7000	24.594
		GD1297Q	565	7000	26.858
		GD50C	530	7000	28.327
		23913	366	11000	37.349
		23915	408	11000	34.496
		23917	455	11000	32.783
		46	500	11000	26.141
		306	464	11000	32.269
		37101	492	11000	30.703
		37102	443	11000	33.401
Thompson & LeClair (1987)	Hastings metamorphic low, Southwestern Grenville Province	37103	550	11000	26.281
		A1	517	4000	27.903
		A2	512	4000	28.270
		B1	500	5500	28.931
		B2	497	5500	28.991
Karabinos (1985)	Appalachian Orogen Southern Vermont USA	333	583	5000	25.904
		118	500	5000	29.044
		559	586	5000	25.579
		120D	574	5000	26.018

Figure 3.16: Plot of Φ/α versus temperature (K) for the chlorite-garnet exchange reaction. Φ is defined as the right-hand side of equation 3.15. α is chamosite stoichiometric coefficient (in this case, $\alpha = -3$). First order linear regression through the data yields the following best-fit line $\Phi = 0.5516851T + 7146.4999$. Comparison with equation 3.16 shows $S_{fchl} = 551.7$ J/K·mol and $H_{fchl} = -7146500$ J/mol.

Table 3.17 shows ~30 J/mol/K difference between the estimated chamosite entropy from section 3.7.2 and the value obtained from Fe-Mg partitioning data above. This difference is larger than expected given that entropy estimation algorithms outlined by Helgeson et al. (1978) and Holland (1989) are both capable of yielding estimated values within approximately 1 to 2% of the calorimetric entropy or ± 6 -12 J/mol/K for chamosite.

The additive component model of Holland (1989) estimates a chamosite (daphnite) entropy value of 542 ± 6 J/mol/K. However, the Holland (1989) value represents only calorimetric and magnetic entropy contributions, and does not include additional entropy caused by crystallographic site disorder, (also known as configurational entropy or S_{config}). Complete disorder on the octahedral and tetrahedral sites in chamosite, which has the following structural formula: $[\text{Fe}_5\text{Al}]^{\text{VI}}[\text{AlSi}_3]^{\text{IV}}\text{O}_{10}(\text{OH})_8$, would add an additional 41.1 J/mol/K to the entropy estimate ($S_{\text{config}} = -6R[5/6\ln(5/6)+1/6\ln(1/6)] + \{-4R[1/4\ln(1/4)+3/4\ln(3/4)]=41.1\}$), resulting in a chamosite entropy value of 583.1 ± 6 J/mol/K. Comparing these results with entropy values summarized in Table 3.17 shows, that completely disordered chamosite has an entropy value similar to the estimated chamosite entropy from section 3.6.2 (580.7 J/K/mol), while the entropy of ordered chamosite (542 ± 6 J/mol/K) is relatively close to the value obtained from Fe-Mg partitioning data (551.7 J/mol/K).

Berman (1988) reported that the entropy of clinocllore derived from phase equilibrium data ($S_{\text{cln}} = 435.15$ J/mol/K) was approximately 38 J/mol/K higher than the calorimetric value (397.6 J/mol/K) measured by Henderson et al. (1983). Berman (1988) proposed that this difference was due to substantial disorder in the clinocllore octahedral and tetrahedral sites. The chamosite entropy value derived using equilibrium 3.9 should contain the same configurational entropy contribution, given that the estimated chamosite entropy value uses the entropy of clinocllore as a reference point.

It is proposed that the difference between the estimated entropy value, and the value obtained from Fe-Mg partitioning data is due primarily to order-disorder phenomenon in the chamosite crystal structure. It is assumed that the amount of disorder observed in clinocllore by Berman (1988) is the same for chamosite. Therefore, the higher entropy value obtained by estimation using equilibrium 3.9 is preferred over the entropy obtained from Fe-Mg partitioning data.

The preferred chamosite entropy value (580.7 J/mol/K) is approximately the same as the value obtained by Saccocia & Seyfried (1993), who also assumed complete disorder in the chamosite crystal structure. The entropy obtained in this study is approximately 2.5% lower than both the value estimated by Helgeson et al. (1978) (largely within the expected error range for entropy estimation), and the value obtained by Bryndzia & Scott (1987) (lying well within the ± 54.4 J/mol/K uncertainty range quoted by these authors). The entropy for daphnite (chamosite) reported in Holland & Powell (1990) (559.0 J/K/mol) is the only previously published value that is significantly different from the entropy value obtained in this study.

The preferred chamosite enthalpy value, -7120.1 kJ/mol, is an intermediate value between the higher (-7094 to -7102 kJ/mol) values obtained by Walshe (1986) and Saccocia & Seyfried (1993) and the lower estimate obtained by Holland & Powell (1990) and Bryndzia & Scott (1987) (-7223 kJ/mol).

TABLE 3.17
Summary and Comparison of Chamosite Thermodynamic Properties

Database	Formula	Enthalpy (J/mol)	Entropy (J/K·mol)	V (J/bar)	k ₀	k ₁	k ₂	k ₃	k ₅	v ₁ ×10 ⁻⁵	v ₂ ×10 ⁻⁵	v ₃ ×10 ⁻⁵	v ₄ ×10 ⁻⁸
Estimated Entropy. Fe-Mg Partitioning Preferred Values‡			580.6575										
	Fe ₅ Al ₂ Si ₃ O ₁₀ (OH) ₈	-7146500	551.69	21.34	1229.233	-10256.46	-12276980	2121507000	0.00	2.6125	0.00	-0.1798	0.00
		-7120000	580.7	21.34	1229.233	-10256.46	-12276980	2121507000	0.00	2.6125	0.00	-0.1798	0.00
S & S† (1993)	Fe ₅ Al ₂ Si ₃ O ₁₀ (OH) ₈	-7101970 ±4170	583.20	21.34	1229.233	-10256.5	-12276900	2121510000					
W & S† (1991)	*Fe _{4.5} Al ₃ Si _{2.5} O ₁₀ (OH) ₈	545.12		21.105	1224.520	-10138.98	-13358350	2256916000					
H & P† (1990) daphnite	Fe ₅ Al ₂ Si ₃ O ₁₀ (OH) ₈	-7148440	559.0	21.34	1237.4	-11250.0	-3743000		0.013594	2.7648	0.00	-0.1781	0.00
S & C† (1990)	*Fe _{4.5} Al ₃ Si _{2.5} O ₁₀ (OH) ₈		554.0	21.52	1224.520	-10138.98	-13358350	2256916000					
B & S† (1987)	Fe ₅ Al ₂ Si ₃ O ₁₀ (OH) ₈	-7222840 ±4600	594.96 ±54.4	21.52	1224.520	-10138.98	-13358350	2256916000					
Helgeson et al. (1978)	Fe ₅ Al ₂ Si ₃ O ₁₀ (OH) ₈		596.22										

‡Linear regression through natural Fe-Mg partitioning data with fixed slope equal to the estimated entropy value.

†Saccoccia & Seyfried (1993), Wang & Spear (1991), Holland & Powell (1990), Spear & Cheney (1989), Bryndzia & Scott (1987)

*Note different formula, halfway between chamosite and Fe-amesite.

3.7 Thermochemical Properties of MagnesioStauroolite

3.7.1 Introduction and Previous Work

The purpose of this section is to derive a set of thermochemical properties for magnesioStauroolite ($\text{Mg}_4\text{Al}_{18}\text{Si}_{7.5}\text{O}_{44}(\text{OH})_4$) consistent with the Berman (1988) database. Several authors including Chopin & Schreyer (1983), Massonne (1995) and Fockenberg (1998) have conducted experimental work on magnesioStauroolite stability. Previously published thermodynamic properties for magnesioStauroolite are summarized in Table 3.20 below:

3.7.2 Estimated MagnesioStauroolite Enthalpy, Entropy, Heat Capacity, Molar Volume, Compressibility and Expansivity

MagnesioStauroolite entropy was estimated using a four-cation Fe-Mg exchange reaction:

Stauroolite and periclase entropy values were taken from Berman (1988). Iron oxide entropy was obtained from Helgeson et al. (1978). The estimated value was adjusted by +4.7 J/cation of exchanged iron (McMullin et al., 1991) to account for entropy contributions from electronic configuration and crystal-field stabilization, resulting in a final magnesioStauroolite entropy estimate of:

$$S_{\text{mst}} = 888.9246 \text{ J/ mol/K}$$

MagnesioStauroolite heat capacity coefficients for equation 3.2 were estimated using the additive oxide component model of Berman & Brown (1985). MagnesioStauroolite molar volume (44.26 J/bar) was obtained from Holland & Powell (1990). Stauroolite compressibility and expansivity values from Berman (1988) were adopted for magnesioStauroolite with the exception of the v_4 term, which was empirically modified (see below). The results of these estimation techniques are summarized in Table 3.20 below.

3.7.3 Magnesiostraurolite –Enthalpy and Entropy by Linear Regression of Experimental Data

Fockenberg (1998) conducted a series of high-pressure experiments designed to outline the P-T stability field of magnesiostraurolite. Data for six magnesiostraurolite-bearing equilibria is provided, although only four (summarized in Table 3.18 below) contain sufficient information to be of use in this exercise (the two remaining reactions have 1 and 1.5 experimental brackets respectively). Note that the reaction stoichiometry in Table 3.18 differs from that in Fockenberg (1998) because reactions have been balanced in accordance with the straurolite formula contained in Berman (1988), rather than the Hawthorne et al. (1993) formula $(\text{Mg}_4\text{Al}_{16}\text{Si}_8\text{O}_{46}(\text{OH})_2)$ used by Fockenberg (1998).

TABLE 3.18
Magnesiostraurolite Enthalpy and Entropy Values by Linear Regression

Equilibrium Number	Equilibrium	Enthalpy (J/mol)	Entropy (J/mol/K)	Enthalpy* if S=888.9
Equil 3.12	6mst = 8prp + 21ky + 25cor + 12H ₂ O	-25168921.9	883.4	-25162555.0
Equil 3.13	8chl + 51ky + 31cor = 10mst + 12H ₂ O	-25121089.3	914.7	-25146265.3
Equil 3.14	2mst = 4en + 7ky + 11cor + 4H ₂ O	-25037826.8	993.7	-25154734.8
Equil 3.15	8mctd + 7ky + 6dsp = 2mst + 7H ₂ O	-25223815.8	800.3	-25141586.3
	Average	-25137913.5	898.0	-25151285.4
	Standard Deviation	78827.1	80.0	9176.8

*Enthalpy assuming estimated entropy from section 3.8.2 above (888.9 J/mol/K) is correct.

Magnesiostraurolite enthalpy and entropy can be retrieved from the experimental data by linear regression, as was done for chloritoid in section 3.3 above. The procedure involves calculating the LHS of equation 3.11 at the pressure and temperature of each experimental point to obtain some real number Φ . If the equilibrium has been bracketed correctly, plotting these values against temperature (the abscissa) should yield a straight line separating the half-brackets. A "best-fit" line with a slope of nS_{Cld} and an ordinate intercept equal to $-nH_{\text{Cld}}$ can be obtained using least squares linear regression.

Initial attempts to fit data for reaction 3.12 yielded poor results. The product and reactant assemblages were not adequately separated by the best-fit line and the entropy value obtained from the slope was exceedingly high (1024 J/mol/K). Furthermore, when the enthalpy and entropy values obtained from the best-fit line were used to plot the reaction in P-T space, the resulting equilibrium line fell outside all of the Fockenberg (1998) experimental brackets. As shown in Figure 3.17, this discrepancy was caused primarily because the reaction did not show significant deflection with increasing pressure until reaching very high pressures. This indicated that the adopted iron staurolite compressibility values were inappropriate, and that the magnesio-staurolite compressibility values required adjustment. The v_1 and v_3 terms were left unaltered, however the v_4 compressibility term was iteratively increased until the reaction 3.12 passed through all of the Fockenberg (1998) experimental brackets (see Figure 3.17). Increasing the v_4 compressibility term to 0.0004×10^{-8} was the minimum amount of adjustment required to satisfy five of the six experimental brackets.

All four Fockenberg (1998) magnesio-staurolite-bearing equilibria were fit by linear regression using this v_4 compressibility term. Molar volume, heat capacity and additional expansivity/compressibility terms were obtained from section 3.8.2 above. The results are illustrated in Figures 3.18 to 3.21. Note that the stoichiometry of each reaction has been normalised to 1 mole of reactant magnesio-staurolite so that $n = -1$ in equation 3.11. The extracted magnesio-staurolite enthalpy and entropy values are summarised in Table 3.18 above.

Figure 3.17: P-T plot of equilibrium 3.12 ($6\text{mst} = 8\text{prp} + 21\text{ky} + 25\text{cor} + 12\text{H}_2\text{O}$) showing the effect different v_4 compressibility coefficients have on the location of the reaction. The Fockenberg (1998) experimental brackets are also shown (filled symbols indicate reactant assemblage is stable). Note that the equilibrium with $v_4 = 0.0004 \times 10^{-8}$ is the first to pass through 5 of the 6 experimental brackets.

Figure 3.18: Linear regression through Fockenberg (1998) experimental data for equilibrium 3.12 - $6\text{mst}+8\text{prp}+21\text{ky}+25\text{cor}+12\text{H}_2\text{O}$ (normalized to 1 mole magnesioस्ताuroilite reactant). Dashed line shows best-fit line through experimental data assuming fixed slope of -0.8889 J/mol/K (assumes the estimated magnesioस्ताuroilite entropy of 888.9 J/mol/K is correct).

Figure 3.19: Linear regression through Fockenberg (1998) experimental data for equilibrium 3.13 - $8\text{chl}+51\text{ky}+31\text{cor}=10\text{mst}+12\text{H}_2\text{O}$ (normalized to 1 mole magnesioस्ताuroilite reactant). Dashed line shows best-fit line through experimental data assuming fixed slope of -0.8889 J/mol/K (assumes the estimated magnesioस्ताuroilite entropy of 888.9 J/mol/K is correct).

Figure 3.20: Linear regression through Fockenberg (1998) experimental data for equilibrium $2mst=4en+7ky+11cor+4H_2O$ (normalized to 1 mole magnesioस्ताuroilite reactant). Dashed line shows best-fit line through experimental data assuming fixed slope of -0.8889 J/mol/K (assumes the estimated magnesioस्ताuroilite entropy of 888.9 J/mol/K is correct).

Figure 3.21: Linear regression through Fockenberg (1998) experimental data for equilibrium $3.15 - 8mctd+7ky+6dsp=2mst+7H_2O$ (normalized to 1 mole magnesioस्ताuroilite reactant). Dashed line shows best-fit line through experimental data assuming fixed slope of -0.8889 J/mol/K (assumes the estimated magnesioस्ताuroilite entropy of 888.9 J/mol/K is correct).

3.7.4 Retrieval of Magnesiohastauriolite Enthalpy and Entropy from Natural Samples

Magnesiohastauriolite enthalpy and entropy were also obtained using natural Fe-Mg partitioning data. The Fe-Mg exchange reaction between hastauriolite and garnet (Equilibrium 3.16 below) was chosen as the most suitable equilibrium because it is vapour-conservative, and the thermodynamic properties of the remaining three phases involved are relatively well known and are already present in the Berman (1988) database.

Equil 3.16

The equilibrium constant for this reaction is given by:

$$\ln K = \ln \left\{ \frac{a_{st}^3 \cdot a_{prp}^4}{a_{mst}^3 \cdot a_{alm}^4} \right\} \quad \text{Eq 3.20}$$

The activity of hastauriolite was calculated using an ideal mixing on sites solution model (see Appendix 2 for a detailed description of activity models used throughout the thesis). Garnet activity was calculated using a non-ideal solution model with activity coefficients from Berman (1990).

Substituting activity expressions into equation 3.20:

$$\ln K = \ln \left\{ \frac{X_{st}^{12} \cdot X_{prp}^{12} \cdot \gamma_{prp}^{12}}{X_{mst}^{12} \cdot X_{alm}^{12} \cdot \gamma_{alm}^{12}} \right\} = 12 \ln \left\{ \frac{X_{st} \cdot X_{prp} \cdot \gamma_{prp}}{X_{mst} \cdot X_{alm} \cdot \gamma_{alm}} \right\} \quad \text{Eq 3.21}$$

Table 3.18 below summarizes the natural mineral assemblage data (equilibrium temperatures/pressures and the value of the equilibrium constant ($\ln K$)) used to extract magnesiohastauriolite enthalpy and entropy.

TABLE 3.19

Natural Assemblage Data Used to Extract Magnesiohastauriolite Enthalpy & Entropy

Reference	Locality	Sample	T (°C)	P (bars)	lnK
Wang & Spear (1991)	Taconic Range New England USA	#106-3	529	4500	-1.305
		#107-1	525	4500	-2.410
Lang & Rice (1985)	Snow Peak Northern Idaho, USA	BT96	500	4000	-3.325
		BT126	485	4000	-7.177
		BT86	490	4000	-6.784
		BT125	430	4000	-7.098
		BC46	455	4000	-5.582
		BC41	455	4000	-4.385
		BT83	500	4000	-6.592
		BT174	517	5000	-2.600
		BT137	515	5000	-1.455
		BT98.2	510	6000	-2.115
		BT20.1	480	6000	-6.610
		BT41	540	6000	-1.775
Yardley <i>et al.</i> (1980)	Connemara, Ireland	BT40	530	6000	-3.198
		BT39	540	6000	-2.208
		BT45	505	6000	-1.973
		BT28	530	6000	-0.978
		ML17	570	6000	-2.206
		BT49	550	6000	-1.594
		BT35	575	6000	-1.594
		BT34	525	6000	-4.019
		BT33	550	6000	-1.746
		BT32	570	6000	-1.827
		BT47.1	515	6000	-3.450
		BY 230M	530	5000	-3.454
Hiroi (1983)	Unazaki Schists Hida Terrane Central Japan	BL 2927B, c	540	5000	-6.525
		BL 2915, rim	560	5000	-5.098
		BY 125S	600	5000	-2.108
		BY 170S	615	5000	-2.272
		CF 3163/2S	640	5000	1.025
		BY 111S	650	5500	-0.070
		BY 299S	650	5500	-0.592
		791111	610	5000	-2.834
		760409	560	5000	-2.615
		750803	665	5000	-0.582
		NA 20	515	4200	-4.311
		NA 24	513	4200	-4.621

Bickle & Archibald (1989)

TABLE 3.18

Natural Assemblage Data Used to Extract Magnesiohastauriolite Enthalpy & Entropy

Reference	Locality	Sample	T (°C)	P (bars)	lnK
Droop & Harte (1995)	Stonchaven coast NE Scotland	60136	555	4500	-3.210
		60031	610	4500	0.046
		81-16	600	4500	-5.238
		5276	595	4500	-3.783
		60027	580	4500	-1.467
		60028	650	4500	-3.827
		A2	540	4500	-5.044
		60001	540	4500	-3.013
		GD308C	510	7000	-1.876
		GD725	500	7000	3.557
		GD1296	600	7000	-2.863
		GD1297D	530	7000	1.555
Dymoke & Sandiford (1992)	Mount Lofty Ranges South Australia	GD1297P	615	7000	-2.380
		GD1297Q	565	7000	-4.603
		GD1297L	580	7000	-4.335
		GD50C	530	7000	-2.961
		474-318	510	3500	-5.945
		474-428	550	3500	-3.528
		185-636/4	550	3500	-3.595
		A281-716	523	3500	-5.782
		A281-215	570	3500	-5.346
		A281-222	555	3500	-1.676
		A281-223	600	3500	-2.685
		A281-715	630	3500	-2.753
Novak & Holdaway (1981)	Augusta quadrangle south-central Maine USA	147	540	3200	-1.898
		77	550	3000	-2.360
		AH-1	530	3000	-2.398
		91	520	3300	-2.938
		41	530	3800	-2.105
		5	560	3700	-1.322
		102	550	3800	-4.035
		EW-3	590	4200	2.947
		77-341a	565	4000	-1.196
		559	586	5000	-1.386
		120D	574	5000	0.391
		#373	630	6500	-0.110
Grambling (1981)	Truchas Peaks, New Mexico	DR-11A	500	7750	1.181
Karabinos (1985)	Appalachian Orogen South-Vermont USA				
Pigage & Greenwood (1982)	Shuswap Complex Western Canada				
Mposkos (1989)	Northern Greece

Figure 3.22: Plot of Φ/α versus temperature (K) for the staurolite-garnet exchange reaction. Φ is defined as the right-hand side of equation 3.15. α is magnesiostaurolite stoichiometric coefficient (in this case, $\alpha=-3$). First order linear regression through the data yields the following best-fit line $\Phi=0.8762268T+25155.9929$. Comparison with equation 3.16 shows $S_{fchl}=876.2$ J/K·mol and $H_{fchl}=-25155993$ J/mol. The second best-fit line in red assumes a fixed slope, equal to the estimated magnesiostaurolite entropy of 888.9 J/mol/K.

A first-order linear regression through the data on Figure 3.22 gives the following best-fit equation: $\Phi = 0.8762268T + 25155.9929$, which by comparison with equation 3.16 yields the following enthalpy and entropy values for magnesioσταυrolite:

$$H_{\text{mst}} = -25155.993 \text{ J/mol}$$

$$S_{\text{mst}} = 876.23 \text{ J/mol/K}$$

The entropy value obtained from Figure 3.22 is approximately 1.5% lower than the magnesioσταυrolite entropy estimated in section 3.7.2 above (888.9 J/K/mol), lying within the 1 to 2% accuracy range for entropy estimation algorithms. A second linear regression with a fixed slope equal to the estimated chamosite entropy (0.8889 kJ/K/mol) was completed through the data. This regression line, shown in red on Figure 3.22, gives a best-fit equation of $\Phi = 0.8889T + 25145.54$, which by comparison with equation 3.16 yields the following enthalpy and entropy values for magnesioσταυrolite:

$$H_{\text{mst}} = -25145.54 \text{ J/mol}$$

$$S_{\text{mst}} = 888.9 \text{ J/mol/K}$$

3.7.5 Discussion of Magnesioσταυrolite Results

Magnesioσταυrolite thermodynamic properties obtained in this study are compared with previously published values in Table 3.18 below. Note that data from Massonne (1995) is not directly comparable because it pertains to magnesioσταυrolite end-members with a different number of hydroxyl groups than the formula used in Berman (1988).

Entropy values obtained in this study compare favourably to published values. The estimated entropy from section 3.7.2 (888.9 J/mol/K) is similar to the value in Holland & Powell (1990); while the entropy from Fe-Mg partitioning data (876.2 J/mol/K) is identical to the value in Spear & Cheney (1990) and is only 3 J/mol/K higher than the value in Wang & Spear (1991). Only the entropy obtained by linear regression through the Fockenberg (1998) experimental data set lies outside the range of published values, and this value only exceeds the Holland & Powell (1990) entropy by 8 J/mol/K.

TABLE 3.20
Summary and Comparison of Magnesiohastaurite Thermodynamic Properties

Database	Formula	Enthalpy (J/mol)	Entropy (J/K·mol)	V (J/bar)	k ₀	k ₁	k ₂	k ₃	k ₅	v ₁ ×10 ⁻⁵	v ₂ ×10 ⁻⁵	v ₃ ×10 ⁻⁵	v ₄ ×10 ⁻⁸
This Study	Linear Regression	-25137914	898.0										
	Mg ₄ Al ₁₈ Si _{7.5} O ₄₄ (OH) ₄												
	Fe-Mg Partitioning	-25155993	876.2	44.26	2502.312	-14572.16	-66804220	9120506500	0.00	2.97390	0.00	-0.06466	0.0004
	Estimated S, Partitioning	-25145544	888.9										
	Mg ₄ Al ₁₈ Si _{7.5} O ₄₄ (OH) ₄												
Massonne (1995)	Mg-Hastaurite	-25299500	860.0	44.260									
	Mg ₄ Al ₁₈ Si ₈ O ₄₆ (OH) ₂												
Wang & Spear (1991)	Mg-Hastaurite	-24832000	1060	44.700						2.4000	0.00	-0.0650	0.00015
	Mg ₄ Al ₁₈ Si ₈ O ₄₂ (OH) ₆												
Holland & Powell (1990)	Mg ₄ Al ₁₈ Si _{7.5} O ₄₄ (OH) ₄	-25118490	890.00	44.26	2820.50	-24126.0	-13774000	0.00	-0.059366	2.7113 ²³	0.00	-0.0723	0.00
	Mg ₄ Al ₁₈ Si _{7.5} O ₄₄ (OH) ₄												
Spear & Cheney (1989)	Mg ₄ Al ₁₈ Si _{7.5} O ₄₄ (OH) ₄		876.00	44.19	2502.311	-14571.04	-66804220	9120506000	0.00				

* Assumes αV factor of 120 for magnesiohastaurite (misprinted as 12.0 in Table 7b, Holland & Powell, 1990)

Magnesiostaurolite enthalpy obtained from linear regression through the Fockenberg (1998) experimental data set is approximately 19.5 kJ/mol less than the value quoted by Holland & Powell (1990). The two values lie within two standard deviations of each other, based on a quoted magnesiostaurolite enthalpy uncertainty of ± 11.14 kJ/mol (Holland & Powell, 1990). Magnesiostaurolite enthalpy values obtained from Fe-Mg partitioning data are approximately 28 to 38 kJ/mol less than the Holland & Powell (1990) value, depending on the entropy value used in the linear regression.

3.7.6 *Comparison of Magnesiostaurolite Thermodynamic Data with Experimental Brackets*

Figures 3.23 and 3.24 compare the Fockenberg (1998) experimental brackets with equilibrium curves plotted using the Berman (1988) database with additional magnesiostaurolite and magnesiochloritoid thermochemical properties derived in this study. Equilibria were located using the program TWQ and the Haar et al. (1984) equation of state for water. Experimental brackets have been widened to account for experimental error (temperature values were adjusted by $\pm 5^\circ\text{C}$, pressure values by $\pm 5\%$). The location of the original published data (unadjusted) is illustrated by the end of short line connected to the bracket symbol, which appears white for the reactant assemblage and black for the product assemblage.

Figure 3.23 compares the highest-pressure experimental brackets from Fockenberg (1998) with equilibrium curves plotted using the three sets of magnesiostaurolite data obtained in this study (linear regression through Fockenberg (1998) data, Fe-Mg partitioning, and Fe-Mg partitioning with estimated entropy). Computed equilibrium curves for all three data sets appear to be relatively consistent with the experimental data for the $\text{mctd} + \text{ky} + \text{dsp} = \text{mst} + \text{H}_2\text{O}$ equilibrium, passing through two of three experimental brackets. However, experimental results for the $\text{mst} = \text{prp} + \text{ky} + \text{cor} + \text{H}_2\text{O}$ equilibrium are all displaced to higher temperatures than the computed equilibrium curves for all three data sets.

Figure 3.24 shows the same comparison for intermediate pressure brackets. The curve computed with magnesiostaurolite thermodynamic data derived by linear regression passes through

all of the experimental brackets for the $\text{chl}+\text{ky}+\text{cor}=\text{mst}+\text{H}_2\text{O}$ equilibrium. Curves plotted using thermodynamic data derived from Fe-Mg partitioning data are less consistent with the experimental data for this equilibrium, passing through either 2 (Fe-Mg partitioning enthalpy with estimated entropy) or 1 of the experimental brackets (Fe-Mg partitioning enthalpy and entropy). None of the computed equilibrium curves pass through the experimental brackets for the $\text{mst}=\text{en}+\text{ky}+\text{cor}+\text{H}_2\text{O}$ equilibrium, although the linear regression/Fockenberg (1998) curve lies closest to the experimental data.

Results of the comparison illustrated in Figures 3.23 and 3.24 favour adoption of magnesio-staurolite thermodynamic properties derived by linear regression in section 3.7.3, since equilibrium curves plotted using this thermodynamic data are more consistent with the Fockenberg (1998) experimental brackets than curves plotted using data from natural Fe-Mg partitioning. (This is perhaps not too surprising given that the linear regression results are derived from the experimental data). Adopting the linear regression thermodynamic properties also avoids arguments of circular logic that arise from using field-based data such as Fe-Mg partitioning, since these results were obtained solely from phase equilibrium experiments

However, the Fockenberg (1998) experiments were conducted on dehydration reactions involving a fluid phase. Therefore, magnesio-staurolite thermodynamic properties obtained from this data rely, in part, on calculated fugacity values whose accuracy can be questioned at the very high-pressures shown on Figure 3.23 (the Haar et al. (1984) equation of state is generally reliable to 30kbar – most of the experimental data on Figure 3.23 was obtained at higher pressure). Magnesio-staurolite compressibility is also poorly defined (adopted staurolite values had to be empirically modified). Incorrect magnesio-staurolite compressibility values should have little effect on derived thermodynamic properties at low pressures where the energy contribution due to solid phase compressibility is generally small; however, these errors will have an increased effect on derived thermodynamic properties at higher pressures.

Uncertainty in the fluid phase fugacity, and magnesio-staurolite compressibility are both a function of increasing pressure. The effect of this uncertainty will be minimal in the magnesio-staurolite thermodynamic data derived from Fe-Mg partitioning since the natural

assemblages used in the derivation were all metamorphosed at mid-crustal levels, where the pressure did not exceed 10kbar. The same cannot be said for the high-pressure Fockenberg (1998) experimental data. Therefore, it is recommended that the magnesiohastatolite thermodynamic data derived from natural Fe-Mg partitioning be adopted, pending measurement of magnesiohastatolite compressibility.

Figure 3.23: High-pressure experimental brackets from Fockenberg (1998). Computed equilibrium curves for the $mctd+ky+6dsp = mst+H_2O$ reaction are relatively consistent with the experimental data (circles). However, none of the data sets can reproduce the experimental results for the $mst=prp+ky+cor+H_2O$ equilibrium (squares).

Figure 3.24: Intermediate-pressure experimental brackets from Fockenberg (1998). Computed equilibrium curves from two of the three data sets (linear regression and Fe-Mg partitioning data with estimated entropy) are relatively consistent with experimental data for the $chl+ky+cor = mst+H_2O$ reaction (squares). However, experimental brackets for the $mst=en+ky+cor+H_2O$ equilibrium (circles) all occur at higher temperature than the computed equilibrium curves.

Chapter 4 - Thermobarometry

4.1 Analytical Techniques

Samples were selected for geothermobarometry based on mineral assemblage and a high modal percentage of biotite (higher biotite content should reduce the effects of re-equilibration during cooling, see Ferry & Spear, 1978). Mineral chemistry was determined using the Geoscience Laboratories JEOL JSM6400 scanning electron microscope in Sudbury, Ontario Canada, which is equipped with an Oxford Instruments eXL LZ4 energy dispersive X-ray spectrometer. Quantitative mineral analysis was completed using the following analytical conditions: accelerating voltage 20kV, beam current 2.5namp, acquisition time of 100 live seconds. For plagioclase, the electron beam was rastered over a 30×30μm area to minimize the loss of sodium. Standards used to analyze various minerals are summarized in Appendix 5.

Garnet zoning was evaluated by completing a traverse of 40 to 60 points across one of the largest garnet crystals in a given polished section. Garnet compositional profiles are summarized in Appendix 6. Garnets from the garnet-chlorite and staurolite-biotite zones typically preserve zoning profiles with bell-shaped Mn-enriched cores. In higher-grade zones, these cores have been re-equilibrated by diffusion. All garnet zoning profiles exhibit a decrease in $Mg/(Fe+Mg)$ ratio close to the garnet rim, which can be attributed to re-equilibration during cooling. The garnet composition with the highest $Mg/(Fe+Mg)$ ratio was generally used in the thermobarometry calculation to estimate peak metamorphic conditions. This point typically occurs within 20 to 100μm of the garnet rim.

The oxidation state of iron cannot be determined by electron probe analysis, and therefore all iron was assumed to be ferrous (Fe^{2+}). This assumption precludes the possibility of a ferric iron component in biotite, resulting in higher temperature estimates than garnet-biotite results calculated with a ferric-biotite end-member. Rathmell et al. (1999) determined that garnet-biotite temperatures decreased by an average of 30°C if 8% of the total iron in biotite was assumed to be ferric (following Guidotti & Dyar, 1991).

4.2 Thermobarometry Methods

Approximately 60 pelites were analyzed for thermobarometry (all were obtained from Flinton Group rocks, with the exception of one sample collected near the Queensborough syncline). Equilibrium pressure and temperature values were estimated for each sample using the program TWQ (TWEEQU – Thermobarometry With Estimation of EQUilibration state; Berman, 1991), a second-generation version of the GeO-Calc program by Berman et al. (1987), and Brown et al. (1988). The following activity models were used in the TWQ calculations (activity models summarized in Appendix 2):

Garnet – Berman (1990)

Biotite – McMullin et al. (1991)

Plagioclase – Fuhrman & Lindsley (1988)

Muscovite – Chatterjee & Froese (1975)

Chloritoid, Staurolite, Chlorite, Margarite, Ilmenite, Rutile – Ideal Mixing on Sites.

The TWQ program, described in detail by Berman (1991), calculates the location of all possible equilibria for a given mineral assemblage in P-T-X space using internally consistent thermodynamic data from Berman (1988). Various auxiliary programs are available to organize graphical output (CLEAN), display and annotate results (PLOT), and calculate an average equilibrium pressure and temperature based on all possible reaction intersections (INTERSX).

It is important to note that the TWQ program calculates reactions amongst mineral end-members (or phase components), rather than actual phases in a rock. Therefore, generally fewer than five (usually only 3) of the equilibria calculated and plotted by TWQ are linearly independent of one another. (The number of linearly independent reactions (# IR) in a system can be calculated by determining the difference between the number of system components (C) and the number of phase components (PC), expressed as $\# \text{ IR} = \text{PC} - \text{C}$). The p-T location of the non-linearly independent reactions is not a function of mineral chemistry or phase component activity, since the location of these reactions can be derived by a linear combination of the independent equilibria in the system. Graphical output from the TWQ program thus appears to over-represent confidence in the derived equilibrium pressure-temperature location, since many of the reactions shown passing through an equilibrium point are typically not independent of each other.

There are however, several advantages to the TWQ approach, which outweigh this limitation. First, calculating every possible reaction in a given mineral assemblage avoids the potential problem of determining an equilibrium pressure and temperature based on an arbitrary set of independent reactions (with each set presumably having a different equilibrium pressure and temperature). Second, this approach allows the user to assess the degree of equilibrium between the various mineral end-members. Poor reaction convergence is generally due to use of non-equilibrium phase compositions (two or more phases are not in chemical equilibrium), or inappropriate volatile phase activity.

TWQ results were compared with temperature estimates from the garnet-chlorite thermometer of Dickenson & Hewitt (1986; with garnet activity from Hodges & Spear, 1982) and the garnet-biotite thermometer of Hodges & Spear (1982).

4.3 Thermobarometry Results – Garnet-Chlorite and Garnet-Chlorite-Chloritoid-Biotite Transition Zone

4.3.1 Madoc-Queensborough area

Graphical TWQ results for the garnet-chlorite zone in the Madoc-Queensborough area (including the garnet-chlorite to chloritoid-biotite transition zone) are shown on Figure 4.1 below. TWQ pressure-temperature values are compared with garnet-chlorite and garnet-biotite thermometry results in Table 4.1.

<div>TABLE 4.1</div> <div>Thermobarometry Results</div> <div>Madoc-Queensborough Area – Grt-Chl Zone and Grt-Chl-Ctd-Bt Transition Zone</div>									
Sample	Mineral Assemblage*	P (bars)	TWQ Results		Garnet-Chlorite		Garnet-Biotite		
			± 2σ (Intersx)	T (°c)	± 2σ (Intersx)	T ₁ @ P=5.0kbar	Δ (T ₁ -T _{TWQ})	T ₂ @ P=5.0kbar	Δ (T ₂ -T _{TWQ})
Madoc-4a-I	Ctd+Ky+Chl+St	5200	1700	505	25				
Madoc-7b2-III	Grt+Chl+Bt			535 [☆]	20	495	-40	500	-35
Madoc-7e2-III	Chl+Ctd			545 [☆]	50				
Madoc-5e-II	Grt+Chl+Ctd			510 [☆]	50	475	-35		
Average Madoc Grt-Chl Zone		5200	1700	525	35	485	-40	500	-25
Madoc-2e-V	Grt+Chl+Bt+St+ (Relict Ctd [†])+Plag	4300	500	530	15	495	-35	515	-15
Queens-1a-I	Grt+Chl+Ctd+Bt+ Plag + trace St [†]	5500	1500	555	30	535	-20	510	-45
Average Grt-Chl-Ctd-Bt Zone		4900	1000	545	25	515	-30	515	-30

- +Ms+Qtz. [☆] Temperature value assumes equilibrium pressure of 5000bars
- [†] Mineral not in equilibrium with remaining assemblage, omitted from TWQ calculation.

Figure 4.1A TWQ results for Madoc-4a-I, an aluminous pelite containing Ctd+Chl+St+Ky+Ms+Qtz. Ky was excluded from the calculation since results indicate it is not in equilibrium with the remaining mineral assemblage.

Figure 4.1B TWQ results for sample Madoc-7b2-III, a typical greenschist facies pelite with Grt and Bt porphyroblasts in a matrix of chlorite and muscovite (Grt+Chl+Bt+Ms+Qtz schist). Calculated temperature assumes equilibrium pressure of 5000 bars.

Figure 4.1C TWQ results for Madoc-2e-V, a Grt+Chl+Bt+St+Ms+Qtz+Plag schist with relict Ctd. Water & Ctd excluded from calculation. Ctd crystals occur as rare coarse-grained porphyroblasts studded with Bt. TWQ results indicate Ctd is not in equilibrium with the remaining mineral assemblage.

Figure 4.1D TWQ results for Queens-1a-I, a Grt+Chl+Ctd+Bt+Qtz+Plag semi-pelite (no muscovite). Sample contains only 2-3 grains of Zn-rich staurolite, which is just starting to nucleate at the contact between Grt and Ctd. St was not used in the calculation-see discussion.

4.3.2 Bishop Corners area

Graphical TWQ results for the garnet-chlorite zone (including the garnet-chlorite to chloritoid-biotite transition zone) are shown on Figures 4.2 and 4.3. TWQ pressure-temperature values are compared with garnet-chlorite and garnet-biotite thermometry results in Table 4.2 below.

TABLE 4.2
Thermobarometry Results
Bishop Corners Area – Grt-Chl Zone and Grt-Chl-Ctd-Bt Transition Zone

Sample	Mineral Assemblage*	TWQ Results				Garnet-Chlorite		Garnet-Biotite	
		P (bars)	$\pm 2\sigma$ (Intersx)	T (°C)	$\pm 2\sigma$ (Intersx)	T ₁ @ P=5.5kbar	Δ (T ₁ -T _{TWQ})	T ₂ @ P=5.5kbar	Δ (T ₂ -T _{TWQ})
90-10d-I	Grt+Chl+Ctd	6000	4000	545	15	505	-40		
90-10g-I	Chl+Ctd			555 [☆]	50				
91-27a-I	Grt+Chl			550 [☆]	50	515	-35		
91-27e-I	Grt+Chl+Ctd	4700	1300	535	10	500	-35		
93-13b-I	Grt+Chl+St [‡] + Relict Ctd			535 [☆]	25	485	-50		
93-16a-II	Grt+Chl+Ilm+Rt	4800	1000	545	50	505	-40		
93-16b-I	Grt+Chl+Ilm+Rt+ Relict Ctd	5000	2400	540	35	515	-25		
93-15d-I	Grt+Chl+Bt+Pl	5900	900	545	10	520	-15	535	0
Average Bishop Corners Grt-Chl Zone		5300	1900	545	30	505	-30	535	0
92-6a-I	Grt+Chl			555 [☆]	50	525	-30		
92-6c-III	Grt+Ctd+Bt + (Retro Chl)			540 [☆]	10			515	-25
92-6f1-II	Grt+Chl+Ctd+Bt [†]	4500	500	555	10	525	-30	485 [§]	
93-26e-I	Grt+Chl+Ctd+Bt [†] +St [‡] +Mrg			540 [☆]	10	500	-40	545	+5
93-26g-I	Grt+Chl+Bt+St [‡] + Mrg+(Ctd incl)			550 [☆]	15	515	-35	510 [§]	-40
93-24a-II	Grt+Chl+Ctd+Mrg	5000	1700	545	15	505	-40		
92-8d-I	Grt+Chl+Ctd+Bt [†] +St [‡] +Mrg	5400	1750	545	45	495	-50	490 [§]	-55
Average Grt-Chl-Ctd-Bt Zone		5000	1300	550	25	515	-35	495	-55

* +Ms+Qtz. [☆] Temperature value assumes equilibrium pressure of 5500bars

[†] Sample contains only a small amount of Bt, which has re-equilibrated during cooling and is not in equilibrium with remaining assemblage – Bt has been omitted from TWQ calculation.

[‡] High Zn staurolite with no appropriate activity model, omitted from TWQ calculation.

[§] Sample contains only a small amount of Bt, assume it has re-equilibrated during cooling.

Figure 4.2A TWQ results for 91-27e-I. Sample is a Grt+Chl+Ctd+Ms+Qtz schist. Ctd porphyroblasts are partially corroded. Elimination of Ctd may be due to continuous reaction, such as equilibrium #3 (pink).

Figure 4.2B TWQ results for sample 90-10d-I, a Grt+Chl+Ms+Qtz Schist. Chloritoid used in the calculation occurs only as inclusions in garnet.

Figure 4.2C TWQ results for 93-16b-I, a Grt+Chl+Ms+Qtz+Ilm+Rut schist. Sample also contains Ctd which occurs as inclusions in garnet, and as relict matrix grains armoured in quartz and muscovite.

Figure 4.2D TWQ results for 93-15d-I, a calcic pelite containing Grt+Chl+Bt+Ms+Qtz+Plag. The three-phase assemblage Grt+Chl+Bt is relatively rare in the Bishop Corners area.

Figure 4.3A TWQ results for 92-6f1-II, a Grt+Chl+Ctd+Bt+Ms+Qtz schist. TWQ results indicate that Bt has re-equilibrated during cooling and is not in equilibrium with the remaining minerals. Note that calculated pressure is too low (in sillimanite field).

Figure 4.3B TWQ results for sample 92-6c-III, a Grt+Ctd+Bt+Ms+Qtz schist. Biotite is more abundant in this sample than 92-6f1-II (previous diagram), producing an estimated temperature (at 5500 bars) that is consistent with results from other samples.

Figure 4.3C TWQ results for 92-24a-II, a Grt+Chl+Ms+Qtz schist with margarite. Chloritoid crystals form abundant inclusions in garnet but are relatively rare in the matrix. Additional samples from the same outcrop contain the assemblage Grt+Chl+Ctd+Bt.

Figure 4.3D TWQ results for 92-8d-I, a Grt+Chl+Ctd+Bt+Ms+Qtz+Mrg+St schist. Bt and St not used in the calculation. Bt appears to have re-equilibrated during cooling, since only a small amount is present. Sample contains only 2-3 grains of Zn-rich staurolite.

4.4 Results - Chloritoid-Biotite Zone and Lower Garnet-Staurolite-Biotite Zone

TWQ results for chloritoid-biotite zone and the lower garnet-staurolite-biotite zone pelites (St-Grt-Bt±Ctd) are shown on Figures 4.4 and 4.5. TWQ pressure-temperature values are compared with garnet-chlorite and garnet-biotite thermometry results in Table 4.3.

Sample	Mineral Assemblage*	TWQ Results				Garnet-Biotite	
		P (bars)	± 2σ (Intersx)	T (°C)	± 2σ (Intersx)	T ₂ @ P=5.5kbar	Δ (T ₂ -T _{TWQ})
92-42c-I	Grt+Ctd+Bt			545 [✱]	10	535	-10
93-18a-I	Grt+Ctd+Bt			535 [✱]	10	510	-25
92-41a-I	Grt+Ctd+Bt			540 [✱]	15	520	-20
92-41d-I	Ctd+Chl+Mrg			575 [✱]	50		
93-20f-I	Grt+Ctd+Bt			540 [✱]	10	520	-20
Average Ctd-Bt Zone				545	20	520	-20
92-10a-II	Ctd+St+Grt+Bt	4400	1150	535	15	535	0
90-19a-I	Ctd+St+Grt+Bt+Plag	5200	800	535	20	550	+15
92-27a-II	Ctd+St+Grt+Bt	5800	1800	555	20	515	-40
93-28a-I	Ctd+St+Grt+Bt	5300	600	550	20	530	-20
Average Lower Grt-St-Bt Zone		5200	1100	545	20	535	-10

* +Ms+Qtz. ✱ Temperature value assumes equilibrium pressure of 5500bars

† only a small amount of Bt in sample, assume it has re-equilibrated during cooling.

Figure 4.4A TWQ results for 93-18a-I. Sample is located on the high-grade side of the Grt+Chl = Ctd-Bt isograd, containing the assemblage Grt+Ctd+Bt+Ms+Qtz (+H₂O).

Figure 4.4B TWQ results for sample 92-41a-I. Sample contains the assemblage: Grt+Ctd+Bt+Ms+Qtz (+H₂O), indicative of the Ctd-Bt zone.

Figure 4.4C TWQ results for 93-20f-I. Sample contains Grt+Ctd+Bt+Ms+Qtz (+H₂O). This sample marks the highest grade occurrence of Ctd+Bt without staurolite.

Figure 4.4D TWQ results for 92-10a-II. Sample marks first appearance of 4-phase assemblage Grt+Ctd+St+Bt with Ms+Qtz (+H₂O), characteristic of the Ctd-out isograd. Magnesio-staurolite omitted from calculation due to large equilibrium scatter.

Figure 4.5A TWQ diagram for sample 90-19a-I. Sample contains Ctd-out assemblage (Ctd+St+Grt+Bt+Ms+Q+Plag). Results indicate Bt is not in equilibrium with the remaining mineral assemblage (ann+phl excluded from the calculation).

Figure 4.5B TWQ results for sample 92-27a-II, a Grt+St+Bt+Ctd+Ms+Qtz schist. Results indicate mst is not in equilibrium with the remaining mineral assemblage (excluded from the calculation).

Figure 4.5C Sample 92-28a-I solid phase equilibria among phase components: mctd, ctd, prp, alm, phl, ann, st, mst, ms and qtz. Sample contains Ctd+Grt+Bt+St+Ms+Q, indicative of the Ctd-out isograd.

Figure 4.5D Previous diagram with the addition of water. P-T equilibrium value estimated, since the number of reactions exceeds the maximum that can be averaged using the Intersx program.

4.5 Thermobarometry Results – Upper Garnet-Staurolite-Biotite Zone

TWQ results for the upper garnet-staurolite-biotite zone, in which pelites typically contain the assemblage Grt+Chl+St±Bt, are shown on Figure 4.6. TWQ pressure-temperature values are compared with garnet-chlorite and garnet-biotite thermometry results in Table 4.4 below.

Sample	Mineral Assemblage*	TWQ Results				Garnet-Chlorite		Garnet-Biotite	
		P (bars)	± 2σ (Intersx)	T (°C)	± 2σ (Intersx)	T ₁ @P=5.5 kbar	Δ (T ₁ -T _{TWQ})	T ₂ @ P=5.5kbar	Δ (T ₂ -T _{TWQ})
92-9i2-II	Grt+Chl+Bt+Plag+Epid	4800	350	545	10	575	+30	545	0
92-26b-I	Grt+Chl+St+Ky+Plag	5500	800	550	10	470	-80		
91-21c2-III	Grt+Chl+St (Cld+Mrg incl)			545 [☆]	15	505	-40		
93-10b-II	Grt+Chl+Bt+St+Plag+(relict Ky)	5200	300	555	10	515	-45	565	+10
92-11-I	Grt+Chl+Bt+St+Plag ‡	5800	750	575	10	550	-25	565	-10
Avg. Upper Grt-St-Bt Zone		5350	550	555	10	525	-30	560	0

* +Ms+Qtz. [☆] Temperature value assumes equilibrium pressure of 5500bars

† Only a small amount of Bt in sample, assume it has re-equilibrated during cooling.

‡ Ore Chimney Formation K-poor pelite (no muscovite).

Figure 4.6A TWQ results for sample 91-21c2-III, a Grt+Chl+St+Ms+Qtz schist. Garnet crystals contain inclusions of chloritoid and margarite.

Figure 4.6B TWQ results for sample 92-9i2-II, a calcic pelite containing Grt+Bt+Chl+Ms+Qtz+Plag+Epid (+Ilm+Rut). Clinocllore (Mg-Chl) & Epidote have been excluded. Addition of Mg-Chl increases scatter with $P=4900\pm2000$, $T=555\pm30$

Figure 4.6C TWQ results for 93-10b-II, a calcic pelite with Grt+Bt+Chl+St+Ms+Qtz+Plag and relict Ky. A water activity of 0.7 produces the tightest reaction intersection. TWQ results indicate Ky and Chl are not in equilibrium with the remaining mineral

Figure 4.6D TWQ results for 92-11-I, a K-poor pelite (no muscovite) from the Ore Chimney Formation. Sample contains Grt+Bt+Chl+St+Qtz+Plag, however using plagioclase in the calculation resulted in unreasonably low equilibrium pressures.

4.6 Thermobarometry Results – Marble Lake Kyanite-Biotite Zone

Figure 4.7 shows TWQ results obtained from a garnet-bearing schist that is interbedded with kyanite-biotite-bearing assemblages near Marble Lake. TWQ pressure-temperature values are compared with garnet-chlorite and garnet-biotite thermometry results in Table 4.5. Low water activities are required to produce unified TWQ equilibrium points within this zone, consistent with the hypothesis that the kyanite-biotite isograd has been depressed in this area due to infiltration of CO₂-rich fluids from adjacent carbonate units.

Sample	Mineral Assemblage*	TWQ Results				Garnet-Biotite	
		P (bars)	$\pm 2\sigma$ (Intersx)	T (°C)	$\pm 2\sigma$ (Intersx)	T ₂ @ P=5.5kbar	Δ (T ₂ -T _{TWQ})
90-1e-I	St+Grt+Bt	5500	600	535	10	520	-15
90-4h-I	St+Grt+Bt+Plag (Ctd incl†)	5500	600	540	35	510	-30
Average Marble Lake Ky-Bt Zone		5500	600	540	25	515	-25

* +Ms+Qtz.

† Mineral not in equilibrium with remaining assemblage, omitted from TWQ calculation.

Figure 4.7: Pressure-temperature path defined by the composition of various staurolite-garnet pairs taken from Bishop Corners Formation Grt+St+Bt+Ms +Qtz schist at Marble Lake (Sample 90-1e-l). Equilibrium point 1 (peak pressure) was derived using the composition of a staurolite inclusion in conjunction with chemistry from the surrounding garnet. A water activity of 0.65 was required to produce a consistent equilibrium point. Equilibrium point 2 represents peak metamorphic temperature conditions, derived using the near-rim garnet composition in conjunction with staurolite porphyroblast chemistry and a water activity of 0.5. Point 3 was derived using the garnet rim composition in conjunction with the composition of a staurolite crystal that is just being engulfed by garnet. Activity of water was reduced to 0.2 to produce the best possible p-T intersection point. See text for additional discussion.

4.7 Thermobarometry Results – Mississagagon Lake Grt-St-Bt Zone

Bishop Corners pelitic schists with coexisting garnet, chlorite and staurolite occur south of Mississagagon Lake. Several of these outcrops were sampled to determine if geothermometry results are consistent with the apparent metamorphic grade reversal indicated by the reappearance of garnet+chlorite+staurolite and the disappearance of co-existing kyanite+biotite. TWQ results for this zone (Mississagagon Lake Garnet-Staurolite-Biotite zone) are shown on Figure 4.8. TWQ pressure-temperature values are compared with garnet-chlorite and garnet-biotite thermometry results in Table 4.6. These results show no temperature variation exists between chlorite-bearing rocks from this area and kyanite-biotite-bearing schists near Marble Lake. This observation is consistent with hypothesis that kyanite-biotite has been stabilized in the Marble Lake area due to CO₂-rich fluid infiltration.

TABLE 4.6
Thermobarometry Results – Mississagagon Lake Garnet-Staurolite-Biotite Zone

Sample	Mineral Assemblage*	TWQ Results				Garnet-Chlorite		Garnet-Biotite	
		P (bars)	± 2σ (Intersx)	T (°C)	± 2σ (Intersx)	T ₁ @ P=5.5 kbar	Δ (T ₁ -T _{TWQ})	T ₂ @ P=5.5kbar	Δ (T ₂ -T _{TWQ})
91-26a-II	Grt+St+Chl			550 [*]	35	535	-15		
91-26e-II	Grt+St+Chl+Bt†			550 [*]	10	510	-40	490‡	-60‡
91-24a-I	Grt+St+Chl+Ky†			540 [*]	40	480	-60		
91-1b2-II	Grt+St+Bt†+Chl+Plag	5600	1200	530	15	510	-20	495‡	-35‡
91-1e-I	Grt+St+Bt+Ky			520 [*]	50			485	-35
Average Mississagagon Lake Grt-St-Bt Zone		5600	1200	540	30	510	-35	490	-45

* +Ms+Qtz.

^{*} Temperature value assumes equilibrium pressure of 5500bars

† Mineral not in equilibrium with remaining assemblage, omitted from TWQ calculation.

‡ Low temperature possibly due to retrograde exchange reaction during cooling

Figure 4.8A TWQ results for sample 90-4h-I, a Grt+St+Bt+Ms+Qtz+Plag schist. Garnet crystals contain armoured inclusions of chloritoid, making this locality the easternmost, highest-grade occurrence of this mineral.

Figure 4.8B TWQ results for sample 91-26e-II, a Grt+Bt+Chl+St+Ms+Qtz schist. A water activity of 0.7 produces the tightest reaction intersection. Biotite excluded from the calculation, since results indicate it is not in equilibrium with the remaining minerals.

Figure 4.8C TWQ results for 91-24a-I, a Ky-bearing Grt+Chl+St+Ms+Qtz pelite. A water activity of 0.7 produces the tightest reaction intersection. TWQ results indicate Ky is not in equilibrium with the remaining minerals (excluded from the calculation).

Figure 4.8D TWQ results for 91-1b2-II. Sample contains the assemblage Grt+Bt+Chl+St+Qtz+Plag. Biotite was excluded from the calculation because it resulted in an unreasonably low equilibrium temperature ($\approx 510^\circ\text{C}$). Diagram assumes a water activity of 0.6.

4.8 Thermobarometry Results - Kyanite-Biotite and Sillimanite-Garnet-Biotite Zones

TWQ results for kyanite-biotite zone and sillimanite-garnet-biotite zone (Grt-Bt-Sill±St) pelites are shown on Figures 4.9 and 4.10. TWQ pressure-temperature values are compared with garnet-biotite thermometry results in Table 4.7 below.

TABLE 4.7							
Thermobarometry Results – Ky-Bt Zone and Sill-Grt-Bt Zone							
Sample	Mineral Assemblage*	TWQ Results				Garnet-Biotite	
		P (bars)	± 2σ (Intersx)	T (°c)	± 2σ (Intersx)	T ₂ @ P=5.5kbar	Δ (T ₂ -T _{TWQ})
Kyanite-Biotite Zone							
91-5b-II	St+Grt+Bt+Ky+Plag+Chl†	6100	200	550	10	510	-40
93-39d-III	Grt+Bt+Ky+Plag	6000	1000	615	50	625	+10
93-44b-II	St+Grt+Bt+Ky†+Plag	4100	600	565	15	580	+15
91-14d-I	St+Grt+Bt+Plag	5700	500	575	15	570	-5
93-45a-I	St+Grt+Bt+Plag	5300	200	580	15	570	-10
94-1a-I	St+Grt+Bt+Plag	5100	200	590	15	575	-15
CR-8b-I	St+Grt+Bt+Plag	5700	300	590	25	585	-5
Sillimanite-Garnet-Biotite Zone							
Ardoc-201-V	St+Grt+Bt+Sill+Plag+(relict Ky)	4900	300	595	10	605	+10
92-34b-I	St+Grt+Bt+Sill+Plag	4900	400	610	15	615	+5
SB-10b	St+Grt+Bt+Sill	5500	400	630	15	640	+10
93-46b-I	Grt+Bt+Sill	5200	1000	650	50	660	+10
R3 301-II	St+Grt+Bt+Sill+Plag ‡	5600	1400	630	50	645	+15
93-40d-I	St+Grt+Bt+Sill	5000	400	630	15	620	-10
CR-4a-I	St+Grt+Bt+Sill+Plag	4800	600	625	20	640	+15
CR-3a-I	Grt+Bt+Plag	5000	1000	610	50	630	+20

* +Ms+Qtz. ✱ Temperature value assumes equilibrium pressure of 5500bars

‡ K-poor pelite (no muscovite).

† Mineral not in equilibrium with remaining assemblage, omitted from TWQ calculation.

Figure 4.9A TWQ results for 93-45a-I. Fluid absent equilibria only - no water. Sample is a Grt+St+Bt+Ms+Qtz+Plag schist. Associated Ky-rich rock contains a small amount of Sill. Note that the resulting equilibrium point falls on the Ky-Sill transition.

Figure 4.9B TWQ results for sample Ardoc 201-V. Sample contains: Grt+St+Bt+Sill+Ms+Qtz+Plag, indicative of the St-out isograd. Plag was omitted from the calculation since all measured compositions resulted in unreasonably high pressure estimates.

Figure 4.9C TWQ results for 92-34b-I, a pelite from the north shore of Mud Lake. This sample contains the St-out univariant assemblage: Grt+St+Bt+Sill+Ms+Qtz+Plag, which has persisted for approximately 2.75km above the location of this isograd.

Figure 4.9D TWQ results for SB-10b-II. Sample contains the St-out univariant assemblage: Grt+St+Bt+Sill+Ms+Qtz, but is located approximately 4.5km above the St-out isograd.

Figure 4.10A TWQ results for CR-8b-I, a Grt+St+Bt+ Ms+Qtz+Plag schist. Fluid-absent equilibria only. The P-T equilibrium point lies close to the Ky-Sill reaction, consistent with the nearby occurrence of the two polymorphs.

Figure 4.10B TWQ results for sample CR-4a-I. Sample contains a mineral assemblage indicative of the St-out isograd: Grt+St+Bt+Sill+Ms+Qtz+Plag.

Figure 4.10C TWQ results for R3 301-II (Kaladar Metasediments). Sample is a K-poor pelite (no muscovite) with Grt+Bt+Sill+Qtz+Plag. Relict staurolite crystals occur in plagioclase porphyroblasts and quartz-rich areas.

Figure 4.10D TWQ results for 93-40a-I (Kaladar Metasediments). Sample contains abundant poikiloblastic staurolite co-existing with garnet, biotite, muscovite and sillimanite (St-out assemblage).

4.9 Discussion

TWQ results obtained with the thermodynamic data derived in chapter 3 generally converged to a single point, at pressure-temperature values consistent with other estimates of the metamorphic grade (such as garnet-biotite thermometry or aluminosilicate mineral assemblage).

Figures 4.11 and 4.12 below show TWQ thermometry and barometry results superimposed on a map of the study area, with isotherms and isobars drawn at 10 degree and 1000 bar intervals. Both figures include additional thermobarometry results from Rathmell (1993), Buckley (1995), Busch (1996), Cureton et al. (1997) and Ford & Skippen (1997, results shown in the southern portion of the Flinton synclinorium west of Kaladar).

The isotherms on figure 4.11 have been drawn to reflect late-stage, post-peak metamorphic movement along the Mooroton shear zone (Easton & Ford, 1991; Ford & Skippen, 1994; Cureton et al., 1997; Carr et al., 2000), resulting in the uplift of the Mazinaw terrane relative to the Elzevir terrane (this study; Cureton et al., 1997). Evidence for late-stage, post-peak metamorphic movement along the Mooroton Shear Zone includes the fracturing and deformation of peak temperature minerals like kyanite and staurolite (see photo 4.1 below) in shear-bands, which are developed in pelites on the outer margin of the shear zone

TWQ thermometry results on figure 4.11 range from 540°C in low-grade areas (Madoc and Bishop-Corners) to 650°C in the highest-grade portions of the study area. The isotherm pattern is generally consistent with the trend of the isograds shown in figure 2.1, with relatively low temperature zones centred on Madoc, Bishop Corners-Cloyne, and the northern portion of Clare River synclinorium south of Kaladar. A high temperature apex has also been mapped in the southern portion of the Flinton syncline (10km west of Kaladar), where Thompson (1973) documented an increased abundance of two- mica granitic pegmatites, which he attributed to partial melting of the Flinton group sediments. In general, peak metamorphic temperatures appear to increase at a relatively steady rate across the study area towards the north and east (with isotherms trending roughly parallel to the Roberson Lake shear zone). Note that the isotherms in southern portion of the map area cannot be continued across the north due to insufficient data.

TWQ barometry results shown on figure 4.12 generally range from 5000 to 5500 bars, with little variation across the map area. Busch et al. (1996) obtained two relatively high-pressure results (8 to 10 kbar) adjacent to the Robertson Lake shear zone, indicating that deeper crustal levels may be exposed next to the shear. A smaller scale pressure increase was noted in the southern portion of the Flinton synclinorium east of Kaladar, adjacent to the Moororton shear zone.

Photo 4.1: Photomicrograph of disaggregated kyanite in shear-band running through a kyanite-biotite-staurolite pelite from locality 93-43b2-II. The sample was obtained from the edge of a swamp, marking the western boundary of the Flinton Synclinorium. The Moororton shear zone is not exposed at this location but presumably runs through the swamp. The assemblage kyanite-biotite represents the peak metamorphic assemblage at this locality. Kyanite from this assemblage has been deformed in the shear band, implying that deformation along the Moororton shear zone post-dates the peak of metamorphism.

Figure 4.11: Contoured TWQ temperature data for the southern Mazinaw terrane and part of the eastern Elzevir terrane (10°C contour interval). Yellow dots indicate TWQ results from this study. Red squares in NE corner are TWQ results from Buckley (1995). Coloured squares indicate garnet-biotite thermometry results (adjusted by +20°C for consistency with TWQ) from the following additional sources: pink – Rathmell et al. (1999), blue – Busch et al. (1996), and green – Cureton et al. (1997). The Mooroton shear zone (MMSZ) and the Robertson Lake shear zone (RLSZ) mark the western and eastern boundaries of the Mazinaw terrane.

Chapter 5 - Summary of Flinton Group Metamorphism

5.1 Metamorphic Zonation in the Mazinaw Terrane and Grimsthorpe Domain, Summary and Comparison with Previous Work

Figure 5.1 shows the distribution of metamorphic zones throughout the southern Mazinaw terrane and southeastern Elzevir terrane (Grimsthorpe domain). The metamorphic zones have been defined using reaction isograds, as advocated by Berman et al. (2000), with one important difference, the upper limit of the greenschist zone has been defined on figure 5.1 using the chloritoid-out isograd (Equil 2.2), rather than the garnet + chlorite + muscovite = staurolite + biotite isograd of Berman et al. (2000). Use of the chloritoid-out isograd is preferable; given the marked effect that manganese partitioning has on the high temperature stability limit of the assemblage garnet-chlorite. (For example see Chapter 2, sections 2.7.3 and 2.8.3, where the assemblage garnet-chlorite persists in magnesian bulk compositions anywhere from 5 to 15 kilometres up-grade of chloritoid-biotite isograd - from Bishop Corners through to the upper garnet-staurolite-biotite zone near Mississagagon Lake).

The distribution of metamorphic facies shown on figure 5.1 appears to be more complex than the simple concentric ringed pattern of higher-grade metamorphic zones surrounding the Madoc-Marmora area described by Carmichael et al. (1978 – see figure 1.2 - the Hastings Metamorphic Low). This difference is caused primarily by the separation of the Madoc and Bishop Corners garnet-chlorite grade pelitic rocks into two distinct nodes, so that metamorphic zonation is described by two metamorphic lows, one centred around Madoc-Marmora (as per the original Hastings Metamorphic Low) and a second low grade node centred around Bishop Corners. This interpretation is based on several observations including:

- 1) The presence of anthophyllite in ultramafic rocks surrounding the Canniff Tonalite (Easton and Ford, 1990) (anthophyllite stability is restricted to the mid-staurolite zone; see Trommsdorff and Evans, 1974).

- 2) The occurrence of coexisting chloritoid-biotite (with chlorite-muscovite and quartz) south of the village of Cooper (reported by Sampson, 1972; his locality 383, the furthest blue square north of Madoc on figure 5.1).

Figure 5.1: Metamorphic zonation in the southern Mazinaw and eastern Elzevir terranes. Isograds are dashed where their location is inferred. Ornaments are on the high-grade side. Metamorphic zones have been defined using isograd reactions consistent with Berman et al., 2000. Flinton Group pelites shown with stippled pattern (see legend on figure 2.1 (pg. 9) for other rock-type fill patterns).

Recognition that isograds have been displaced by late-stage, post-peak metamorphic movement along the Mooroton shear zone (Easton & Ford, 1991; Ford & Skippen, 1994; Cureton et al., 1997; Carr et al., 2000) is the second major difference between the Carmichael et al. (1978) depiction of the Hastings Metamorphic Low and the metamorphic zonation map shown on figure 5.1. This displacement resulted in the uplift of the Mazinaw terrane relative to the Elzevir terrane (see discussion Chapter 4; Cureton et al., 1997). Evidence for late-stage, post-peak metamorphic movement along the Mooroton Shear Zone includes the fracturing and deformation of peak temperature minerals like kyanite and staurolite (see photo 4.1) in shear-bands, which are developed in pelites on the outer margin of the shear zone. This late-stage movement may have been assisted by prolonged fluid-flow through the zone, which also resulted in the formation of garnet-biotite-chlorite schists in the central portion of the shear. These relatively low-grade pelites contain corroded kyanite and staurolite relics, evidence that they were formed by retrograde metamorphism of higher-grade assemblages, a process that requires the presence of a fluid-phase.

Thompson (1972) and Carmichael et al. (1978) concluded that isograds in the area were relatively steeply dipping and crosscut all major structures. However, this geometry is not consistent with the presence of the two low-grade nodes shown on figure 5.1 (greenschist facies node near Bishop Corners and lower amphibolite facies node in the Clare River synclinorium south of Kaladar). It is therefore inferred that the isograds in the study area have been folded, forming a dome and basin interference pattern. Such a pattern is consistent with the structural history of the area. Microstructural evidence shows that most porphyroblast development, and therefore peak metamorphism and isograd formation, occurred either during or after the first deformational event (D1 – major isoclinal folding forming the Flinton Group synclines). Once established, the isograds may have been folded by the two deformational events that post-date D1. Structures related to these two events are oriented perpendicular to each other (D2 axial surfaces strike northeast-southwest, while D3 axial surfaces trend to the northwest), consistent with the formation of a dome and basin structural interference pattern. (Note that this interpretation assumes the original post-D1 isograds were relatively shallow dipping). Doubly plunging refolded isoclinal folds have been identified in the northeast corner of the study area near Ompah (Ford, 1992); however, a similar dome and basin interference pattern has not been identified in the lower-grade part of the study area, and the isograd

folding implied on figure 5.1 is therefore based solely on mineral distribution.

Easton (2000) provides a more recent overview of metamorphic zonation throughout the Ontario portion of the Grenville Province. Comparison of figure 5.1 with his figure 4 (pg. 332) shows several similarities:

- 1) The greenschist facies zone between Madoc and Bishop Corners has been replaced by an area of lower amphibolite facies metamorphism.
- 2) The Mooroton shear zone has resulted in the juxtaposition of upper amphibolite facies rocks from the Mazinaw terrane against lower amphibolite facies rocks from the Grimsthorpe domain.

However, Easton (2000) links the Madoc and Bishop Corners low-grade nodes with a wide band of greenschist facies metamorphism that arcs through the central portion of the Grimsthorpe domain (corresponding to the area west of Cloyne on figure 5.1). Greenschist facies metamorphism may in fact encompass part of the Weslemkoon Tonalite in the northwestern corner of figure 5.1 (locating the exact trace of the greenschist facies north and west of Madoc was beyond the scope of this study), however, the discussion above shows that there is little justification for linking the greenschist facies node at Bishop Corners to any other area of greenschist facies metamorphism.

5.2 Pressure - Temperature Conditions for Metamorphic Isograds in the Study Area

Geothermobarometry results from Chapter 4 have been summarized on figure 5.2 below, plotted in approximate order of increasing metamorphic grade (calculated as perpendicular distance above or below bounding isograds). The five pelitic isograds that have been mapped through the study area are also superimposed on this diagram. Thermobarometry results above and below these isograds can be used to estimate their location in pressure-temperature space.

TWQ geobarometry data in the lower portion of the diagram shows little variation, with most samples recording metamorphic pressures between 5000 and 5500 bars. Estimated isograd pressures in Table 5.1 therefore fall within this limited range. Metamorphic temperatures in the upper portion of the diagram appear to be relatively constant below the Ky-Bt isograd, but increase steadily once this isograd is encountered. Temperature estimates for the three lower-grade isograds reflect this pattern, falling in a relatively restricted temperature range (from 540 to 560°C, see Table 5.1).

TABLE 5.1

Peak-Temperature Estimates for Pelitic Isograds in the Study Area

Metamorphic Isograd	Pressure (bars)	Temperature (°C)
Grt+Chl+Ms = Ctd+Bt (Madoc Area)	5000±500	535±10
Grt+Chl+Ms = Ctd+Bt	5000±500	545±10
Ctd+Ms = Grt+St+Bt	5500±500	550±10
Chl+St+Ms = Ky+Bt	5500±500	555±10
Ky = Sill	5500±500	590±10
St+Ms = Grt+Sill+Bt	5500±500	610±10

Figure 5.2: Geothermobarometry results for Flinton Group pelitic schists, in approximate order of increasing metamorphic grade. Isograd reactions are shown as vertical lines.

5.3 Topology of the Cordierite-Aluminosilicate-Absent Invariant Point: Constraints from Flinton Group Pelites

In the last decade several authors have constructed KFMASH petrogenetic grids for greenschist to amphibolite facies pelites using internally consistent thermodynamic data sets (Spear & Cheney, 1989; Powell & Holland, 1990; Wang & Spear, 1991; Droop & Harte, 1995; Mahar et al., 1997). Each of these grids bears some similarity to the others; however, several have markedly different topologies for chloritoid-bearing equilibria. These differences arise primarily due to variation in the arrangement of reactions around the chloritoid-staurolite-garnet-biotite-chlorite invariant point (typically identified as the cordierite-aluminosilicate-absent invariant point or [Crd,Als]). The topology of this invariant point can be related in each case to one of two possible configurations, shown below in figure 5.3. Powell & Holland (1990), Droop & Harte (1995) and Mahar et al. (1997) favour invariant point configuration A, while Spear & Cheney (1989) and Wang & Spear (1991) use configuration B. Natural assemblage data from the Flinton Group pelites can be used to select the correct topology and place some constraints on the location of this invariant point in pressure-temperature space.

The pattern of metamorphic zonation in the Madoc and Bishop Corners areas shows that the assemblage garnet-chlorite is stable at lower metamorphic grade than the assemblage chloritoid-biotite (for identical manganese bulk compositions). Garnet-chlorite can persist up-grade beyond the stability field of chloritoid-biotite (to the kyanite-biotite isograd), but only in extremely manganese-rich bulk compositions. The metamorphic zonation pattern therefore favours invariant point configuration A, where the assemblage garnet-chlorite is stable at lower-temperatures.

Furthermore, the sequence of isograds surrounding the Bishop Corners low-grade node:

is identical to the sequence of reactions encountered below invariant point A, providing additional evidence that this configuration is the correct topology.

The chloritoid-bearing isograd sequence surrounding the Bishop Corners low-grade node is therefore consistent with a metamorphic field gradient that passes through reactions on the low-pressure side of invariant point configuration A. The field gradient must also pass relatively

Figure 5.3: Alternate arrangement of the cordierite-aluminosilicate-absent invariant point in the KFMASH system (Ford & Skippen, 1996). Variation A has been proposed by Powell & Holland (1990) and Mahar et al. (1997). Variation B has been proposed by Spear & Cheney (1989) and Wang & Spear (1991). Garnet-chlorite stability field is shaded green; chloritoid-biotite stability field is shaded yellow.

close to the invariant point, given the narrow spacing between all three isograds (approximately 500 metres). Field data can also be used to place additional constraints on the location of [Crd,Als] invariant point:

- 1) Chloritoid-bearing assemblages are interbedded with magnesium-rich kyanite-chlorite pelites (section 2.4.5, photos 2.20 and 2.21), indicating that the cordierite-aluminosilicate absent invariant point must be located in the kyanite stability field. (The petrogenetic grid derived by Mahar et al. (1997) is not consistent with this observation, since they located the [Crd,Als] invariant point in the andalusite stability field at a pressure of approximately 4kbars.)
- 2) TWQ thermobarometry results for samples located close to the chloritoid-bearing isograds (see figure 5.2 above near the chloritoid-biotite and garnet-staurolite-biotite isograds, equilibrium 2.1 and 2.3 respectively) show that peak metamorphic pressure- temperature conditions were reached at approximately 5000–5500 bars and 545–550°C. Since the metamorphic field gradient passes relatively close to the [Crd,Als] invariant point on the low-pressure side, the thermobarometry results can be used to estimate the location of the cordierite-aluminosilicate-absent invariant point, which must lie at a pressure of 6000 ± 1000 bars and a temperature of $550 \pm 10^\circ\text{C}$.

Of the many petrogenetic grids calculated to date, only Powell & Holland (1990, with the addition of ferric iron to biotite - their figure 7) is consistent with these results (correct invariant point topology located in the kyanite stability field at 6000 bars and 550°C).

Chapter 6 - Conclusions

- 1) The following five isograds have been mapped through the study area:

- 2) The assemblage Garnet-Chlorite with or without Chloritoid is characteristic of the lowest-grade pelites in the area. This assemblage is found near Madoc and Bishop Corners in two geographically discrete areas of low-grade metamorphism that are not connected. These low-grade areas may have been formed by isograd folding during late-stage deformation (see 3 below).
- 3) Most of the porphyroblast growth associated with the reactions above took place after the development of the primary S1 schistosity, but prior to the later D2 and D3 deformational events. (S1 formed during the main deformational phase (D1), which produced the synclinal structures hosting the Flinton Group sediments). The isograds were initially relatively flat lying, and were refolded by later deformational events about northeast and northwest trending folds, forming a dome and basin interference pattern. This folding is responsible for the occurrence of the Bishop Corners greenschist facies node and the lower amphibolite facies node in the Clare River synclinorium.
- 4) Pelites on the margin the Mooroton shear zone contain kyanite and staurolite that have been fractured and deformed in shear bands. The deformation of these peak temperature minerals indicates that the isograds have been displaced by late-stage (post-peak metamorphic) movement along the Mooroton shear zone, resulting in the uplift of the Mazinaw terrane relative to the Elzevir terrane.

- 5) Pelites near Madoc contain the assemblage Chloritoid-Kyanite-Staurolite-Chlorite, evidence that the following reaction is occurring in magnesium-rich bulk compositions:

This assemblage cannot be mapped in the field area as an isograd since it is preserved only at a single locality. Chloritoid-kyanite is not preserved in the Bishop Corners area, indicating that the Madoc area may be at a slightly lower metamorphic grade.

- 6) Garnet-chlorite pelites in the Bishop Corners area typically contain trace amounts of chloritoid, either as inclusions in garnet or as xenoblastic relics armoured in matrix quartz grains. This evidence indicates that chloritoid is unstable in the presence of garnet and chlorite, possibly due to the following continuous reaction in the KFLASH system:

- 7) Preferential manganese partitioning stabilizes garnet throughout the low and medium-grade portions of the study area (into the garnet-staurolite-biotite zone) however; the occurrence of manganese-poor garnet with chlorite and biotite in a pelite sample from the Madoc area implies that the low-grade stability of garnet-chlorite is not a function of manganese bulk composition.
- 8) Infiltrating carbon dioxide-rich fluids depressed the equilibrium temperature of the kyanite-biotite isograd near Marble Lake, forming a relatively high-grade dome along the south shore of the lake where the assemblage kyanite-biotite is stable. This dome is surrounded by staurolite-chlorite-bearing pelites.
- 9) The Kyanite – sillimanite isograd (Equil 2.4) is located near outcrop 93-45, approximately 3.5 kilometres down-grade of the Staurolite-out isograd (Equil 2.5), confirming that Staurolite breakdown occurs in the sillimanite stability field and that the area lies in bathozone 4 of Carmichael (1978).
- 10) The electron microprobe was used to measure changes in ferromagnesian silicate chemistry, which varied in a smooth and continuous manner between reaction isograds as a function of metamorphic grade.

- 11) A set of thermodynamic data for chloritoid, magnesiochloritoid, chamosite (iron chlorite) and magnesiostauroilite was derived using published experimental data and Fe-Mg partitioning data from natural assemblages. The dataset (summarized in Table 6.1 below) is consistent with the Berman (1988) database.
- 12) The thermodynamic data in table 6.1 was used in conjunction with the TWQ program (Berman, 1991) to estimate peak metamorphic temperature and pressure conditions for samples located throughout the study area. TWQ diagrams produced with the new thermodynamic data generally converged to a single point, at pressure-temperature values consistent with other estimates of the metamorphic grade (such as garnet-biotite thermometry or aluminosilicate mineral assemblage).
- 13) Calculated metamorphic temperatures range from 540°C in low-grade areas (Madoc and Bishop-Corners) to 650°C in the highest-grade portions of the study area. Metamorphic pressure data showed little variation across the map area, ranging from 5000 to 5500 bars. TWQ thermometry results were plotted on a map of the area and contoured, the resulting isotherm pattern is generally consistent with the trend of the isograds; relatively low temperature zones are centred on Madoc, Bishop Corners-Cloyne, and the northern portion of Clare River synclinorium south of Kaladar. A high temperature apex was also mapped in the southern portion of the Flinton syncline west of Kaladar.
- 14) The distribution of metamorphic facies throughout the southern Mazinaw terrane appears to be more complex than the concentric ringed pattern of higher-grade metamorphic zones described by Carmichael et al. (1978 – the Hastings Metamorphic Low). This difference is caused primarily by the separation of the Madoc and Bishop Corners garnet-chlorite grade pelitic rocks into two distinct nodes, so that metamorphic zonation is described by two metamorphic lows, one centred around Madoc-Marmora (as per the original Hastings Metamorphic Low) and a second low grade node centred around Bishop Corners. This zonation pattern bears some similarity to the pattern described by Easton (2000).

TABLE 6.1
Summary of Preferred Thermodynamic Properties for Chloritoid, Magnesiochloritoid, Chamosite and Magnesiochaunite

Mineral	Enthalpy (J/mol)	Entropy (J/K·mol)	V (J/bar)	k ₀	k ₁	k ₂	k ₃	$\nu_1 \times 10^{-5}$	$\nu_2 \times 10^{-5}$	$\nu_3 \times 10^{-5}$	$\nu_4 \times 10^{-8}$
Chloritoid	-3211482.5	160.9879	6.98	426.537	-3182.8	-7219860	1099977000	2.7869	0	-0.0863	0
Magnesiochloritoid	-3556491.6	133.2477	6.875	407.697	-2759.53	-8624440	1207092000	2.9739	0	-0.06466	0
Chamosite	-7120000	580.7	21.34	1229.233	-10256.46	-12276980	2121507000	2.6124	0	-0.1798	0
Magnesiochaunite	-25156000	876.2	44.26	2502.312	-14572.16	-66804220	9120506500	1.8000	0.0009	-0.0800	0.0004

- 15) TWQ pressure-temperature results were used to estimate peak temperature equilibrium conditions of the metamorphic isograds in the study area. All five isograds equilibrated in a relatively limited pressure range, from 5000 to 5500 bars. Temperature estimates for the three lower-grade isograds (Equil 2.1 to 2.3) fall in a relatively narrow temperature range from 540 to 560°C. The remaining two isograds equilibrated at higher temperatures, summarized below:

Metamorphic Isograd	Pressure (bars)	Temperature (°C)
Grt+Chl+Ms = Ctd+Bt (Madoc Area)	5000±500	535±10
Grt+Chl+Ms = Ctd+Bt	5000±500	545±10
Ctd+Ms = Grt+St+Bt	5500±500	550±10
Chl+St+Ms = Ky+Bt	5500±500	555±10
Ky = Sill	5500±500	590±10
St+Ms = Grt+Sill+Bt	5500±500	610±10

- 16) Two possible topologies (A and B) for the cordierite-aluminosilicate-absent invariant point in the KFMASH system were compared with natural assemblage data from the study area. Garnet-chlorite appears to be stable at lower metamorphic grade than chloritoid-biotite in both the Madoc and Bishop Corners areas. This zonal sequence is consistent with invariant point configuration A (see figure 5.3, Powell & Holland, 1990; Droop & Harte, 1995; and Mahar et al., 1997). In addition, the sequence of isograds surrounding the Bishop Corners low-grade node was found to be identical to the sequence of reactions encountered on the low-pressure side of the invariant point. This observation was used, in conjunction with TWQ thermobarometry results, to estimate the location of the cordierite-aluminosilicate-absent invariant point, which appears to be located in the kyanite stability field at a pressure of 6000±1000 bars and a temperature of 550±10°C.

REFERENCES

- Ashworth, J.R., & Evirgen, M.M., 1984. Garnet and associated minerals in the southern margin of the Menderes Massif, southwest Turkey. *Geological Magazine*, **4**, 323-337.
- Berman, R.G., 1988. Internally-consistent thermodynamic data for minerals in the system Na₂O-K₂O-CaO-MgO-FeO-Fe₂O₃-Al₂O₃-SiO₂-TiO₂-H₂O-CO₂. *Journal of Petrology*, **29**, 445-522.
- Berman, R.G., 1990. Mixing properties of Ca-Mg-Fe-Mn garnets. *American Mineralogist*, **75**, 328-344.
- Berman, R.G., 1991. Thermobarometry using multiequilibrium calculations: a new technique with petrologic applications. *Canadian Mineralogist*, **29**, 833-855.
- Berman, R.G., & Brown, T.H., 1985. The heat capacity of minerals in the system K₂O-Na₂O-CaO-MgO-FeO-Fe₂O₃-Al₂O₃-SiO₂-TiO₂-H₂O-CO₂; Representation, estimation, and high temperature extrapolation. *Contributions to Mineralogy and Petrology*, **89**, 168-183.
- Berman, R.G., Brown, T.H., & Perkins, E.H., 1987. GE0-CALC: software for calculation and display of pressure-temperature-composition phase diagrams. *American Mineralogist*, **72**, 861-862.
- Berman, R.G., Easton, R.M., & Nadeau, L., 2000. A New Tectonometamorphic Map of the Canadian Shield: Introduction. *Canadian Mineralogist*, **38**, 277-285.
- Bickle, M.J., & Archibald, N.J., 1984. Chloritoid and staurolite stability: implications for metamorphism in the Archaean Yilgarn Block, Western Australia. *Journal of Metamorphic Geology*, **2**, 179-203.
- Brown, T.H., Berman, R.G., & Perkins, E.H., 1988. Ge0-Calc: software package for calculation and display of pressure-temperature-composition phase diagrams using an IBM or compatible personal computer. *Computers and Geosciences*, **14**, 279-289.
- Bryndzia, L.T., & Scott, S.D., 1987. The composition of chlorite as a function of sulfur and oxygen fugacity: An experimental study. *American Journal of Science*, **287**, 50-76.
- Buckley, S.G., 1995. The petrology of pelitic schists from the Green Lake outlier. Unpublished Bachelors thesis, Carleton University, Ottawa, Ontario
- Busch, J.P., van der Pluijm, B.A., Hall, C.M., & Essene, E.J., 1996. Listric normal faulting during postorogenic extension revealed by ⁴⁰Ar/³⁹Ar thermochronology near the Robertson Lake shear zone, Grenville Orogen, Canada. *Tectonics*, **15**, 387-402.
- Carmichael, D.M., 1970. Intersecting isograds in the Whetstone Lake area Ontario. *Journal of Petrology*, **11**, 147-181.
- Carmichael, D.M., 1978. Metamorphic bathozones and bathograds: a measure of the depth of post-metamorphic uplift and erosion on a regional scale. *American Journal of Science*, **278**, 769-797.
- Carmichael, D.M., Moore, J.M. Jr., & Skippen, G.B., 1978. Isograds around the Hastings metamorphic "low". In: A.L. Currie and W.O. Mackasey (Eds.), *Toronto '78 Field Trips Guidebook*, Geol. Assoc. Canada, Annual Meeting, Toronto Ontario, 1978. 325-346.
- Carr, S.D., Easton, R.M. Jamieson, R.A., & Culshaw, N.G., 2000. Geologic Transect Across the Grenville Orogen of Ontario and New York. *Canadian Journal of Earth Sciences*, **37**, 193-216.

- Chappell, J.F., 1978. The Clare River structure and its tectonic setting. Unpublished Doctoral thesis, Carleton University, Ottawa, Ontario
- Chatterjee, N.D., & Froese, E., 1975. A thermodynamic study of the pseudobinary join muscovite – paragonite in the system $\text{KAlSi}_3\text{O}_8 - \text{NaAlSi}_3\text{O}_8 - \text{Al}_2\text{O}_3 - \text{SiO}_2 - \text{H}_2\text{O}$. *American Mineralogist*, **60**, 985-993.
- Chopin, C. 1983. Magnesiochloritoid, a key-mineral for the petrogenesis for high-grade pelitic blueschists. *Bulletin de Minéralogie*. **106**, 715-717.
- Chopin, C., & Monié, P. 1984. A unique magnesiochloritoid-bearing high-pressure assemblage from the Monte Rosa, Western Alps: petrologic and ^{40}Ar - ^{39}Ar radiometric study. *Contributions to Mineralogy and Petrology*. **87**, 388-398.
- Chopin, C., & Schreyer, W. 1983. Magnesiochloritoid and magnesiochloritoid: two index minerals of pelitic blueschists and their preliminary phase relations in the model system $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$. *American Journal of Science, Orville volume*. **283A**, 72-96.
- Comodi, P., Mellini, M., & Zanazzi, P.F., 1992. Magnesiochloritoid: compressibility and high pressure structure refinement. *Physics and Chemistry of Minerals*. **18**, 483-490.
- Connelly, J.N., 1985. The Elzevir batholith: emplacement history with respect to the Grenville Supergroup and Flinton Group, southeastern Ontario. In: *Current Research, part B*, Geological Survey of Canada, Paper 85-1B, 161-167.
- Corfu, F., & Easton, R.M., 1995. U-Pb geochronology of the Mazinaw terrane, an imbricate segment of the Central Metasedimentary Belt, Grenville Province, Ontario. *Canadian Journal of Earth Sciences*, **32**, 959-976.
- Cureton, J.S., van der Pluijm, B.A., & Essene, E.J., 1997. Nature of the Elzevir-Mazinaw domain boundary, Grenville Orogen, Ontario. *Canadian Journal of Earth Sciences*, **34**, 976-991.
- Davidson, A., Carmichael, D.M., & Pattison, D.R.M., 1990. Metamorphism and geodynamics of the southwestern Grenville Province, Ontario. *International Geological Correlation Program, Project 235-304, Field Trip Guidebook 1*.
- Dickenson, M.P., III, & Hewitt, D.A., 1986. A garnet-chlorite geothermometer. Geological Society of America, Abstract with Program, **18**, 584.
- Donnay, J.D.H., & Ondik, H.M., 1973. Crystal data determinative tables, 3rd edition. U.S. Department of Commerce, National Bureau of Standards, Joint Commission on Powder Diffraction Standards, volume 2, 1580 pgs.
- Droop, G.T.R., & Bucher-Nurminen, K, 1984. Reaction textures and metamorphic evolution of sapphirine-bearing granulites from the Gruf complex, Italian central Alps. *Journal of Petrology*, **25**, 766-803.
- Droop, G.T.R., & Harte, B., 1995. The effect of Mn on the phase relations of medium-grade pelites: Constraints from natural assemblages on petrogenetic grid topology. *Journal of Petrology*, **36**, 1549-1578.
- Dymoke, P., & Sandiford, M., 1992. Phase relationships in Buchan facies series pelitic assemblages: calculations with application to andalusite-staurolite parageneses in the Mount Lofty Ranges, South Australia. *Contributions to Mineralogy and Petrology*, **110**, 121-132.

- Easton, R.M., 1988. Precambrian geology of the Darling area, Frontenac and Renfrew counties. Ontario Geological Survey, Open File Report 5693.
- Easton, R.M., 1992. The Grenville Province. In: Thurston, P. (Ed.) *Geology of Ontario*, Ontario Geological Survey, Special Volume 4, Part 2: 713-904.
- Easton, R.M., 2000. Metamorphism of the Canadian Shield, Ontario, Canada. II. Proterozoic Metamorphic History. *Canadian Mineralogist*, **38**, 319-344.
- Easton, R.M., & Ford, F.D., 1990. Geology of the Grimsthorpe Area (Project Unit 90-19). In: *Summary of fieldwork and other activities 1990*, Ontario Geological Survey, Miscellaneous Paper 151, 99-110.
- Easton, R.M., & Ford, F.D., 1991. Geology of the Mazinaw Area (Project Unit 91-08). In: *Summary of fieldwork and other activities 1991*, Ontario Geological Survey, Miscellaneous Paper 157, 95-106.
- El-Shazly, A.K., & Liou, J.G., 1991. Glaucophane chloritoid-bearing assemblages from NE Oman: petrologic significance and a petrogenetic grid for high P metapelites. *Contributions to Mineralogy and Petrology*, **107**, 180-201.
- Ferry, J.M., & Spear, F.S., 1978. Experimental calibration of the partitioning of Fe and Mg between biotite and garnet. *Contributions to Mineralogy and Petrology*, **66**, 113-117.
- Fletcher, C.J.N., & Greenwood, H.J., 1979. Metamorphism and structure of Penfold Creek area, near Quesnel Lake, British Columbia. *Journal of Petrology*, **20**, 743-794.
- Ford, F.D., 1992. Geology of the Fernleigh and Ompah "synclines", Palmerston Lake Area. In: *Summary of fieldwork and other activities 1992*, Ontario Geological Survey, Miscellaneous Paper 160, 41-46.
- Ford, F.D., & Skippen, G.B., 1994. Shear Zone Associated, Late-Stage Deformation and Retrograde Metamorphism on the Western Margin of the Flinton Synclinorium. In: *Geological Association of Canada / Mineralogical Association of Canada, Program with Abstracts*, **19**, A37.
- Ford, F.D., & Skippen, G.B., 1996. Analysis of Chloritoid-Garnet-Biotite-Chlorite Pelitic Schists from the Flinton Group, Grenville Province, Eastern Ontario. In: *Geological Association of Canada / Mineralogical Association of Canada, Program with Abstracts*, **21**, A30.
- Ford, F.D., & Skippen, G.B., 1997. Petrology of the Flinton Creek Metaperidotites: Enstatite-Magnesite and Anthophyllite-Magnesite Assemblages from the Grenville Province. *Canadian Mineralogist*, **35**, 1221-1236.
- Fockenberg, T., 1998. An experimental investigation on the P-T stability of Mg-staurolite in the system $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$. *Contributions to Mineralogy and Petrology*, **130**, 187-198.
- Fuhrman, M.L., & Lindsley, D.H., 1988. Ternary-feldspar modelling and thermometry. *American Mineralogist*, **73**, 201-215.
- Gal, L.P. & Ghent, E.D., 1991. Margarite-bearing pelites from the western Rocky Mountains, Northwest of Golden, British Columbia. *Canadian Mineralogist*, **29**, 11-19.
- Ganguly, J., 1969. Chloritoid stability and related parageneses: Theory, experiments, and applications. *American Journal of Science*, **267**, 910-944.
- Ghent, E.D., 1976. Plagioclase-garnet- Al_2SiO_5 -quartz: a potential geobarometer-geothermometer. *American Mineralogist*, **61**, 710-714.

- Ghent, E.D., Stout, M.Z., Black, P.M., & Brothers, R.N., 1987. Chloritoid-bearing rocks associated with blueschists and eclogites, northern New Caledonia. *Journal of Metamorphic Geology*, **5**, 239-254.
- Grambling, J.A., 1981. Kyanite, andalusite, sillimanite, and related mineral assemblages in the Truchas Peaks region, New Mexico. *American Mineralogist*, **66**, 702-722.
- Guidotti, C.V., 1970. The mineralogy and petrology of the transition from the lower to the upper sillimanite zone in the Oquossoc area, Maine. *Journal of Petrology*, **11**, 277-336.
- Guidotti, C.V., & Dyar M.D., 1991. Ferric iron in metamorphic biotite and its petrologic and crystallochemical implications. *American Mineralogist*, **76**, 161-175.
- Haar, L., Gallagher, J. S., & Kell, G. S., 1984. NBS/NRC Steam Tables, Hemisphere Publ. Corp., Washington, DC and McGraw-Hill International Book Company
- Hawthorne, F.C., Ungaretti, L., Oberti, R., Caucia, F., & Callegari, A., 1993. The crystal chemistry of staurolite. I. Crystal structure and site populations. *Canadian Mineralogist*, **31**, 551-582.
- Helgeson, H.C., Delaney, J.M., Nesbitt, H.W., & Bird, D.C., 1978. Summary and critique of the thermodynamic properties of rock forming minerals. *American Journal of Science*, **278A**, 1-229.
- Hemingway, B.S., Haas, J.L., & Robinson, G.R., 1982. Thermodynamic properties of selected minerals in the system $\text{Al}_2\text{O}_3\text{-CaO-SiO}_2\text{-H}_2\text{O}$ at 298.15K and 1 bar (10^5 pascals) pressure and at higher temperatures. United States Geological Survey Bulletin 1544, 70 pgs.
- Henderson, C.E., Essene, E.J., Anovitz, L.M., Westrum, E.F., Jr., Hemingway, B.S., & Bowman, J.R., 1983. Thermodynamics and phase equilibria of chlinochlore, $(\text{Mg}_5\text{Al})(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_8$. *Transactions of the American Geophysical Union*, **64**, 466.
- Hey, M.H., 1954. A new review of the chlorites. *Mineralogical Magazine*, **30**, 277-292.
- Hiroi, Y., 1983. Progressive metamorphism of the Unazuki pelitic schists in the Hida Terrane, Central Japan. *Contributions to Mineralogy and Petrology*, **82**, 334-350.
- Hodges, K.V., & Spear, F.S., 1982. Geothermometry, geobarometry and the Al_2SiO_5 triple point at Mt. Moosilauke, New Hampshire. *American Mineralogist*, **67**, 1118-1134.
- Holdaway, M.J., 1971. Stability of andalusite and the aluminum silicate phase diagram. *American Journal of Science*, **271**, 97-131.
- Hollister, L.S., 1966. Garnet zoning: an interpretation based on the Rayleigh fractionation model. *Science*, **154**, 1647-1651.
- Holland, T.J.B., 1989. Dependence of entropy on volume for silicate and oxide minerals: A review and predictive model. *American Mineralogist*, **74**, 5-13.
- Holland, T.J.B., & Powell, R., 1990. An enlarged and updated internally consistent thermodynamic dataset with uncertainties and correlations: The system $\text{K}_2\text{O-Na}_2\text{O-CaO-MgO-MnO-FeO-Fe}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-TiO}_2\text{-SiO}_2\text{-C-H}_2\text{-O}_2$. *Journal of Metamorphic Geology*, **8**, 89-124.
- Hounslow, A.W., & Moore, J.M., Jr., 1967. Chemical petrology of Grenville schists near Fernleigh, Ontario. *Journal of Petrology*, **8**, 1-28.

- Hutcheon, I.E., & Moore, J.M., Jr., 1973. The tremolite isograds near Marble Lake, Ontario. *Canadian Journal of Earth Sciences*, **10**, 936-947.
- Ivaldi, G., Catti, M., & Ferraris, G., 1988. Crystal structure at 25 and 700°C of magnesiochloritoid from a high-pressure assemblage (Monte Rosa). *American Mineralogist*, **73**, 358-364.
- James, R.S., Turnock, A.C., & Fawcett, J.J., 1976. The stability and phase relations of iron chlorite below 8.5kb pH₂O. *Contributions to Mineralogy and Petrology*, **56**, 1-25.
- Jarosewich, E., Nelen, J.A., Norberg, J.A., 1979. Electron Microprobe Reference Samples for Mineral Analyses. In: *Smithsonian Institution Contributions to the Earth Sciences, Number 22*, Smithsonian Institution Press, Washington, D.C., pp. 68-72.
- Karabinos, P., 1985. Garnet and staurolite producing reactions in a chlorite-chloritoid schist. *Contributions to Mineralogy and Petrology*, **90**, 262-275.
- Kerrick, D.M., & Darken, L.S., 1975. Statistical thermodynamic models for ideal oxide and silicate solid solutions, with application to plagioclase. *Geochimica et Cosmochimica Acta*, **39**, 1431-1442.
- Kienast, J.R., & Messiga, B., 1987. Cr-rich Mg-chloritoid, a first record in high-pressure metagabbros from Monviso (Cottian Alps), Italy. *Mineralogical Magazine*, **51**, 681-687.
- Kienast, J.R., & Pognante, U., 1988. Chloritoid-bearing assemblages in eclogitized metagabbros of the Lanzo peridotite body (western Italian Alps). *Lithos*, **21**, 1-11.
- Koziol, A.M., & Newton, R.C., 1988. Redetermination of the anorthite breakdown reaction and improvement of the plagioclase-garnet-Al₂SiO₅ geobarometer. *American Mineralogist*, **73**, 216-223.
- Lang, H.M., & Rice, J.M., 1985. Geothermometry, geobarometry and T-X(Fe-Mg) relations in metapelites, Snow Peak, Northern Idaho. *Journal of Petrology*, **26**, 889-924.
- Mahar, E.M., Baker, J.M., Powell, R., Holland, T.J.B., & Howell, N., 1997. The Effect of Mn on Mineral Stability in Metapelites. *Journal of Metamorphic Geology*, **15**, 223-238.
- Massonne, H.J., 1995. Experimental and petrogenetic study of UHPM. In: R.G. Coleman and X. Wang (Eds.) *Ultrahigh pressure metamorphism*, Cambridge University Press, Cambridge, pp. 33-95.
- Massonne, H.J., Mirwald, P.W., & Schreyer, W., 1981. Experimentelle Überprüfung der Reaktionskurve Chlorit + Quarz = Talk + Disthen im System MgO-Al₂O₃-SiO₂-H₂O. *Fortschr Mineral*, **59**, 122-123.
- McMullin, D.W.A., Berman, R.G., & Greenwood, H.J., 1991. Calibration of the SGAM thermobarometer for pelitic rocks using data from phase-equilibrium experiments and natural assemblages. *Canadian Mineralogist*, **29**, 889-908.
- McOnie, A.W., Fawcett, J.J., & James, R.S., 1975. The stability of intermediate chlorites of the clinocllore-daphnite solid solution series at 2kb water pressure. *American Mineralogist*, **60**, 1047-1062.
- Messiga, B., Kienast, J.R., Rebay, G., Riccardi, M.P., & Tribuzio, R., 1999. Cr-rich magnesiochloritoid eclogites from the Monviso ophiolites (Western Alps, Italy). *Journal of Metamorphic Geology*, **17**, 287-299.

- Moore, J.M., Jr., & Thompson, P.H., 1980. The Flinton Group: A late Precambrian metasedimentary succession in the Grenville Province of eastern Ontario. *Canadian Journal of Earth Sciences*, **17**, 1695-1707.
- Mposkos, E., 1989. High-pressure metamorphism in gneisses and pelitic schists in the East Rhodope Zone (N. Greece). *Mineralogy and Petrology*, **41**, 25-39.
- Newton, R.C., & Haselton, H.T., 1981. Thermodynamics of the plagioclase- Al_2SiO_5 -quartz geobarometer. In: R.C. Newton, A. Navrotsky, and B.J. Wood (Eds.) *Thermodynamics of mineral and melts, Advances in physical geochemistry*, vol. 1, Springer-Verlag, New York, pp. 131-148.
- Nordstrom, D.K., & Munoz, J.L., 1986. *Geochemical Thermodynamics*, Blackwell Scientific Publications, Palo Alto, California, U.S.A.
- Novak, J.M., & Holdaway, M.J., 1981. Metamorphic petrology, mineral equilibria, and polymetamorphism in the Augusta quadrangle, south-central Maine. *American Mineralogist*, **66**, 51-69.
- Pigage, L.C., & Greenwood, H.J., 1982. Internally consistent estimates of pressure and temperature: The staurolite problem. *American Journal of Science*, **282**, 943-969.
- Powell, R. and Holland, T.J.B., 1990. Calculated mineral equilibria in the pelite system, KFMASH (K_2O - FeO - MgO - Al_2O_3 - SiO_2 - H_2O). *American Mineralogist*, **75**, 367-380.
- Rathmell, M.A., Streepey, M.M., Essene, E.J., & van der Pluijm, B.A., 1999. Comparison of garnet-biotite, calcite-graphite, and calcite-dolomite thermometry in the Grenville Orogen; Ontario, Canada. *Contributions to Mineralogy and Petrology*, **134**, 217-231.
- Rao, B.B., & Johannes, W., 1979. Further data on the stability of staurolite + quartz and related assemblages. *Neuers Jahrb Mineral Monatsh*, **10**, 437-447.
- Rivers T., (1976). Structures and textures of metamorphic rocks, Ompah area, Grenville Province, Ontario. Unpublished Doctoral thesis, University of Ottawa, Ottawa, Ontario.
- Saccoccia, P.J., & Seyfried, W.E., Jr., 1993. A resolution of discrepant thermodynamic properties for chamosite retrieved from experimental and empirical techniques. *American Mineralogist*, **78**, 607-611.
- Sager-Kinsman, E.A., & Parrish, R.R., 1993. Geochronology of detrital zircons from the Elzevir and Frontenac terranes, Central Metasedimentary Belt, Grenville Province, Ontario. *Canadian Journal of Earth Sciences*, **30**, 465-473.
- Sampson G.A., 1972. Petrology of some Grenville Volcanic and Pelitic Rocks from Near Madoc, Southeastern Ontario. Unpublished Doctoral thesis, University of Toronto, Toronto, Ontario, 218 pgs.
- Schreyer, W., 1988. Experimental studies on metamorphism of crustal rocks under mantle pressures. *Mineralogical Magazine*, **52**, 1-26.
- Sethuraman, K., & Moore, J.M., Jr., 1973. Petrology of metavolcanics rocks in the Bishop Corners – Donaldson area, Grenville Province, Ontario. *Canadian Journal of Earth Sciences*, **10**, 589-614.
- Spear, F.S., 1993. *Metamorphic Phase Equilibria and Pressure-Temperature-Time Paths*, Mineralogical Society of America Monograph, Washington, D.C.

- Spear, F.S., & Cheney, J.T., 1989. A petrogenetic grid for pelitic schists in the system $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-FeO-MgO-K}_2\text{O-H}_2\text{O}$. *Contributions to Mineralogy and Petrology*, **101**, 149-164.
- Sverjensky, D.A., 1985. The distribution of divalent trace elements between sulfides, oxides, silicates and hydrothermal solutions. I. Thermodynamic basis. *Geochimica et Cosmochimica Acta*, **49**, 853-864.
- Thompson, J.B., Jr., 1957. The graphical analysis of mineral assemblages in pelitic schists. *American Mineralogist*, **42**, 842-858.
- Thompson, J.B., Jr., 1967. Thermodynamic properties of simple solutions. In: P.H. Abelson (Ed.) *Researches in geochemistry*, vol. 2, Wiley, pp. 340-361.
- Thompson, P.H., 1972. Stratigraphy, structure and metamorphism of the Flinton Group in the Bishop Corners-Madoc area, Grenville Province, eastern Ontario. Unpublished Doctoral thesis, Carleton University, Ottawa, Ontario.
- Thompson, P.H., 1973. Mineral zones and isograds in "impure" calcareous rocks, an alternative means of evaluating metamorphic grade. *Contributions to Mineralogy and Petrology*, **42**, 63-80.
- Thompson, P.H., & LeClair, A.D., 1987. Chloritoid-hornblende assemblages in quartz-muscovite pelitic rocks of the Central Metasedimentary Belt, Grenville Province, Canada. *Journal of Metamorphic Geology*, **5**, 415-436.
- Trommsdorff, V., & Evans, B.W., 1974. Alpine Metamorphism of Peridotitic Rocks. *Schweizerische Mineralogische und Petrographische Mitteilungen*, **54**, 333-354.
- Turnock, A.C., 1960. The stability of iron chlorites. *Carnegie Institute of Washington Year Book*, **59**, 98-103.
- Vidal, O., Theye, T., & Chopin, C., 1994. Experimental study of chloritoid stability at high pressure and various $f\text{O}_2$ conditions. *Contributions to Mineralogy and Petrology*, **118**, 256-270.
- Vuichard, J.P., & Ballèvre, M., 1988. Garnet-chloritoid equilibria in eclogitic pelitic rocks from the Sesia zone (western Alps): their bearing on phase relations in high pressure metapelites. *Journal of Metamorphic Geology*, **6**, 135-157.
- Walshe, J.L., 1986. A six-component chlorite solid solution model and the conditions of chlorite formation in hydrothermal and geothermal systems. *Economic Geology*, **81**, 681-703.
- Wang, P., & Spear, F.S., 1991. A field and theoretical analysis of garnet+chlorite+chloritoid+ biotite assemblages from the tri-state (MA, CT, NY) area, USA. *Contributions to Mineralogy and Petrology*, **106**, 217-235.
- Wynne-Edwards, H.R., 1972. The Grenville Province. In Price, R.A. & Douglas, R.J.W. (eds.) *Variations in Tectonic Styles in Canada*. Geological Association of Canada Special Paper, **11**, 263-334.
- Yardley, B.W.D., Leake, B.E., & Farrow, C.M., 1980. The metamorphism of Fe-rich pelites from Connemara, Ireland. *Journal of Petrology*, **21**, 365-399.

Appendix 1 - Mineral Abbreviations

TABLE A1.1

Mineral Abbreviations

Mineral	Abbreviation	Phase Component	Abbreviation	Formula
Aluminosilicate	Als	andalusite	and	Al_2SiO_5
		kyanite	ky	Al_2SiO_5
		sillimanite	sill	Al_2SiO_5
Biotite	Bt	annite	ann	$\text{KFe}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$
		phlogopite	phl	$\text{KMg}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$
Chlorite	Chl	chamosite	fchl	$\text{Fe}_5\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_8$
		clinochlore	chl	$\text{Mg}_5\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_8$
Chloritoid	Ctd	chloritoid	fctd	$\text{FeAl}_2\text{SiO}_5(\text{OH})_2$
		magnesiochloritoid	mctd	$\text{MgAl}_2\text{SiO}_5(\text{OH})_2$
Corundum	Cor	corundum	cor	Al_2O_3
Diaspore	Dsp	diaspore	dsp	$\text{AlO}(\text{OH})$
Garnet	Grt	almandine	alm	$\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$
		grossular	grs	$\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$
		pyrope	prp	$\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$
		spessartine	sps	$\text{Mn}_3\text{Al}_2\text{Si}_3\text{O}_{12}$
Muscovite	Ms	muscovite	ms	$\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$
Margarite	Mrg	margarite	mrg	$\text{CaAl}_2\text{Al}_2\text{Si}_2\text{O}_{10}(\text{OH})_2$
Plagioclase	Plag	anorthite	an	$\text{CaAl}_2\text{Si}_2\text{O}_8$
		albite	ab	$\text{NaAlSi}_3\text{O}_8$
Quartz	Qtz	alpha-quartz	aqtz	SiO_2
Staurolite	St	staurolite	st	$\text{Si}_{7.5}\text{Fe}_4\text{Al}_{18}\text{O}_{44}(\text{OH})_4$
		magnesio-staurolite	mst	$\text{Si}_{7.5}\text{Mg}_4\text{Al}_{18}\text{O}_{44}(\text{OH})_4$
Talc	Tlc	talc	tlc	$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$
Water Vapour	H_2O or V	water vapour		H_2O

Appendix 2 - Solid Solution Models used for Various Minerals

The following solution models were used in various calculations throughout the thesis:

Garnet - Berman (1990),
 Plagioclase - Fuhrman & Lindsley (1988),
 Biotite - McMullin et al. (1991), and
 Muscovite - Chatterjee & Froese (1975).

Ideal solution models were used for kyanite, chlorite (clinochlore and chamosite from Bryndzia & Scott, 1987), chloritoid, magnesiochloritoid, staurolite and magnesio-staurolite. The PTDiag spreadsheet used to derive thermodynamic properties in Chapter 3 (described in Appendix 3 below) includes non-ideal garnet and plagioclase solution models, which have therefore been listed in a more explicit form below.

The thermodynamics of geological solutions has been extensively reviewed by many authors (Nordstrom and Munoz, 1986; Spear, 1993). The approach taken by many of these authors is to break geological solutions into ideal and non-ideal components so that:

$$G_{\text{solid solution}} = G_{\text{ideal}} + G_{\text{excess}}$$

The ideal term in this equation can be calculated as

$$G_{\text{ideal}} = G_i^\circ + RT \ln a_i$$

where a_i is the activity of component i . This is readily calculated since, by definition, the activity of a phase in an ideal solution is equal to the mole fraction of the solution:

$$a_i^{\text{ideal}} = X_i^\alpha$$

Where X_i is the mole fraction of the cation on a crystallographic site and α is the site multiplicity (the number of cations in a particular crystallographic site).

In the geological literature, G_{excess} has generally been approximated by a polynomial expansion (termed a Margules model; Thompson, 1967).

$$G_{\text{excess}} = A + BX_i + CX_i^2 + DX_i^3 + \dots$$

Simplification of this expression leads to the formulation of Margules parameters (identified as W_{ijk}).

G_{excess} is related to the activity coefficient, γ by the following expression:

$$G_{\text{excess}} = G_i^{\circ} + RT \ln \gamma_i$$

A2.1.1 Garnet – Ideal Solution Model

$$a_{\text{Alm}}^{\text{ideal}} = (X_{\text{Fe}}^{\text{Grt}})^3, \text{ where } X_{\text{Fe}}^{\text{Grt}} = \frac{\text{Fe}}{\text{Fe} + \text{Mn} + \text{Mg} + \text{Ca}}$$

$$a_{\text{Grs}}^{\text{ideal}} = (X_{\text{Ca}}^{\text{Grt}})^3, \text{ where } X_{\text{Ca}}^{\text{Grt}} = \frac{\text{Ca}}{\text{Fe} + \text{Mn} + \text{Mg} + \text{Ca}}$$

$$a_{\text{Sps}}^{\text{ideal}} = (X_{\text{Mn}}^{\text{Grt}})^3, \text{ where } X_{\text{Mn}}^{\text{Grt}} = \frac{\text{Mn}}{\text{Fe} + \text{Mn} + \text{Mg} + \text{Ca}}$$

$$a_{\text{Prp}}^{\text{ideal}} = (X_{\text{Mg}}^{\text{Grt}})^3, \text{ where } X_{\text{Mg}}^{\text{Grt}} = \frac{\text{Mg}}{\text{Fe} + \text{Mn} + \text{Mg} + \text{Ca}}$$

A2.1.2 Garnet Non-Ideal Solution Model – Berman (1990)

Margules parameters are listed in Table 4, Berman (1990). Activity coefficients are calculated using the following equations from Appendix 1, Berman (1990):

$$\begin{aligned} 3RT \ln \gamma_{\text{Alm}} = & W_{112}(-2X_{\text{Grs}}^2 X_{\text{Prp}}) + W_{122}(-2X_{\text{Grs}} X_{\text{Prp}}^2) \\ & + W_{113}(X_{\text{Grs}}^2 - 2X_{\text{Grs}}^2 X_{\text{Alm}}) + W_{133}(2X_{\text{Grs}} X_{\text{Alm}} - 2X_{\text{Grs}} X_{\text{Alm}}^2) \\ & + W_{223}(X_{\text{Prp}}^2 - 2X_{\text{Prp}}^2 X_{\text{Alm}}) + W_{233}(2X_{\text{Prp}} X_{\text{Alm}} - 2X_{\text{Prp}} X_{\text{Alm}}^2) \\ & + W_{123}(X_{\text{Grs}} X_{\text{Prp}} - 2X_{\text{Grs}} X_{\text{Prp}} X_{\text{Alm}}) + W_{124}(-2X_{\text{Grs}} X_{\text{Prp}} X_{\text{Sps}}) \\ & + W_{134}(X_{\text{Grs}} X_{\text{Sps}} - 2X_{\text{Grs}} X_{\text{Alm}} X_{\text{Sps}}) + W_{234}(X_{\text{Prp}} X_{\text{Sps}} - 2X_{\text{Prp}} X_{\text{Alm}} X_{\text{Sps}}) \end{aligned}$$

$$\begin{aligned} 3RT \ln \gamma_{\text{Prp}} = & W_{112}(X_{\text{Grs}}^2 - 2X_{\text{Grs}}^2 X_{\text{Prp}}) + W_{122}(2X_{\text{Grs}} X_{\text{Prp}} - 2X_{\text{Grs}} X_{\text{Prp}}^2) \\ & + W_{113}(-2X_{\text{Grs}}^2 X_{\text{Alm}}) + W_{133}(-2X_{\text{Grs}} X_{\text{Alm}}^2) \\ & + W_{223}(2X_{\text{Prp}} X_{\text{Alm}} - 2X_{\text{Prp}}^2 X_{\text{Alm}}) + W_{233}(X_{\text{Alm}}^2 - 2X_{\text{Prp}} X_{\text{Alm}}^2) \\ & + W_{123}(X_{\text{Grs}} X_{\text{Alm}} - 2X_{\text{Grs}} X_{\text{Prp}} X_{\text{Alm}}) + W_{124}(X_{\text{Grs}} X_{\text{Sps}} - 2X_{\text{Grs}} X_{\text{Prp}} X_{\text{Sps}}) \\ & + W_{134}(-2X_{\text{Grs}} X_{\text{Alm}} X_{\text{Sps}}) + W_{234}(X_{\text{Alm}} X_{\text{Sps}} - 2X_{\text{Prp}} X_{\text{Alm}} X_{\text{Sps}}) \end{aligned}$$

$$\begin{aligned} 3RT \ln \gamma_{\text{Grs}} = & W_{112}(2X_{\text{Grs}} X_{\text{Prp}} - 2X_{\text{Grs}}^2 X_{\text{Prp}}) + W_{122}(X_{\text{Prp}}^2 - 2X_{\text{Grs}} X_{\text{Prp}}^2) \\ & + W_{113}(2X_{\text{Grs}} X_{\text{Alm}} - 2X_{\text{Grs}}^2 X_{\text{Alm}}) + W_{133}(X_{\text{Alm}}^2 - 2X_{\text{Grs}} X_{\text{Alm}}^2) \\ & + W_{223}(-2X_{\text{Prp}}^2 X_{\text{Alm}}) + W_{233}(-2X_{\text{Prp}} X_{\text{Alm}}^2) \\ & + W_{123}(X_{\text{Prp}} X_{\text{Alm}} - 2X_{\text{Grs}} X_{\text{Prp}} X_{\text{Alm}}) + W_{124}(X_{\text{Prp}} X_{\text{Sps}} - 2X_{\text{Grs}} X_{\text{Prp}} X_{\text{Sps}}) \\ & + W_{134}(X_{\text{Alm}} X_{\text{Sps}} - 2X_{\text{Grs}} X_{\text{Alm}} X_{\text{Sps}}) + W_{234}(-2X_{\text{Prp}} X_{\text{Alm}} X_{\text{Sps}}) \end{aligned}$$

A2.1.3 Plagioclase– Ideal Solution Model

Ideal plagioclase activity was calculated using the aluminium-avoidance model of Kerrick & Darken (1975):

$$a_{An}^{ideal} = 0.25 X_{Ca}^{Pl} (1 + X_{Ca}^{Pl})^2, \text{ where } X_{Ca}^{Pl} = \frac{Ca}{Ca + Na + K}$$

A2.1.4 Plagioclase Non-Ideal Solution Model – Fuhrman & Lindsley (1988)

$$\begin{aligned} RT \ln \gamma_{An} = & W_{OrAb} [X_{Ab} X_{Or} (0.5 - X_{An} - 2X_{Ab})] \\ & + W_{AbOr} [X_{Ab} X_{Or} (0.5 - X_{An} - 2X_{Or})] \\ & + W_{OrAn} [2X_{Or} X_{An} (1 - X_{An}) + X_{Ab} X_{Or} (0.5 - X_{An})] \\ & + W_{AnOr} [X_{Or}^2 (1 - 2X_{An}) + X_{Ab} X_{Or} (0.5 - X_{An})] \\ & + W_{AbAn} [2X_{Ab} X_{An} (1 - X_{An}) + X_{Ab} X_{Or} (0.5 - X_{An})] \\ & + W_{AnAb} [X_{Ab}^2 (1 - 2X_{An}) + X_{Ab} X_{Or} (0.5 - X_{An})] \\ & + W_{OrAbAn} [X_{Or} X_{Ab} (1 - 2X_{An})] \end{aligned}$$

A2.1.5 Ideal Solution Models

$$a_{Ky}^{ideal} = (X_{Al}^{Ky})^2, \text{ where } X_{Al}^{Ky} = \frac{Al}{Al + Fe^{3+} + Cr + Ti}$$

$$a_{Cln}^{ideal} = 14.93 \left(\frac{X_{Mg}^{Chl}}{6} \right)^5 \left(\frac{X_{Al}^{Chl}}{6} \right), \text{ where } X_{Mg}^{Chl} = \frac{Mg}{Al_{VI} + Ti + Fe + Mn + Mg}$$

$$X_{Al}^{Chl} = \frac{Al_{VI}}{Al_{VI} + Ti + Fe + Mn + Mg}$$

$$a_{Chm}^{ideal} = 14.93 \left(\frac{X_{Fe}^{Chl}}{6} \right)^5 \left(\frac{X_{Al}^{Chl}}{6} \right), \text{ where } X_{Fe}^{Chl} = \frac{Fe}{Al_{VI} + Ti + Fe + Mn + Mg}$$

$$a_{Ctd}^{ideal} = (X_{Fe}^{Ctd})^2, \text{ where } X_{Fe}^{Ctd} = \frac{Fe}{Ti + Fe + Mn + Mg}$$

$$a_{mCtd}^{ideal} = (X_{Mg}^{Ctd})^2, \text{ where } X_{Mg}^{Ctd} = \frac{Fe}{Ti + Fe + Mn + Mg}$$

$$a_{St}^{ideal} = (X_{Fe}^{St})^4, \text{ where } X_{Fe}^{St} = \frac{Fe}{Fe + Mg + Mn + Zn}$$

$$a_{mSt}^{ideal} = (X_{Mg}^{St})^4, \text{ where } X_{Mg}^{St} = \frac{Mg}{Fe + Mg + Mn + Zn}$$

Appendix 3 - Thermodynamic Calculations with Excel Spreadsheet PTDiag

A3.1 Spreadsheet Layout

All thermodynamic calculations were completed using a Microsoft Excel spreadsheet titled PTDiag (Pressure-Temperature Diagram). The general layout of this spreadsheet is presented in Figures A3.1 and A3.2 (the garnet-chlorite exchange reaction for sample 284-2 from Wang and Spear (1991) is shown as an example). The spreadsheet has been divided into five sections based on functionality: data input, thermodynamic constant storage, mineral chemistry and equilibrium constant calculation, free energy calculation and results plotting. (These have been coloured differently for illustration).

Equilibrium input and thermodynamic data retrieval are completed in the data input section, shown in yellow. The user enters abbreviations for various phases involved in the reaction in Column B (to a maximum of 10, five reactants and five products) and balanced stoichiometric coefficients in column C. Thermodynamic data retrieval is accomplished by selecting one of several interactive buttons, located immediately below the data input section. These buttons invoke a search routine which obtains the required thermodynamic data from one of three sources: Berman (1988 – Jun92.GSC version), Holland & Powell (1990) or Helgeson et al. (1978). Two additional buttons, Clear All and Clear Data, are available to remove data from the worksheet. Clear All deletes the contents of the entire data input section. Clear Data removes only the thermodynamic data (this facilitates the selection an alternative thermodynamic data source since user input – phase identity and stoichiometry, is left intact). Thermodynamic data for each phase involved in the reaction is retrieved from the selected database and displayed in the following columns: enthalpy -column D, entropy - column E, molar volume - column F, heat capacity coefficients - columns G through M, expansivity/compressibility data - columns N through Q and disorder data - columns V through AC (not shown). Change in the thermodynamic properties of the system, caused by the reaction, are calculated and displayed as delta values in row 16

A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q
1	Mineral	Stoi. Coeff.	Enthalpy H	Entropy S	Volume V	a	e	e	f	g	b	d				
2																
3																
4	Reactant 1	5	-6286547.62	266.3591	11.316	(l)	(T ^h -5)	(T ^h -2)	(T ^h -3)	(T ^h -1)	(T)	(T ^h -2)	v1	v2	v3	v4
5	Reactant 2															
6	Reactant 3	3	-7120000	580.7	21.34	1229.233	-10256.46	-12276980	2121507000	0	0	0	2.25186544	0.00037044	-0.0576209	0.0000442
7	Reactant 4												2.6124541	0	-0.1798471	0
8	Reactant 5															
9																
10	Product 1	5	-5267216.0	340.007	11.511	573.96191	-1483.127	-29291968	5022076928							
11	Product 2	3	-8909589.84	435.1545	21.147	1214.38442	-11217.129	0	-1.250E+09				1.86123012	0.00074539	-0.05577832	0.00003211
12	Product 3												2.64515406	0	-0.18194707	0
13	Product 4															
14	Product 5															
15																
16	DELTA															
17			-272111.42	-68.397	0.396	-378.63604	12412.708	-86119400	1.4977E+10	0	0	0	-1.85497672	0.00187475	0.00291299	-0.00006045
18	Clear All	Clear Data														
19																
20																
21																
22																
23																
24																
25																
26																
27																
28																
29																

Figure A3.1 – First page of PTDiag spreadsheet. Data input section shown in yellow, Thermodynamic Constants in Red, and the Mineral Chemistry/Equilibrium Constant section in green.

[illegible]

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Figure A3.2 – Second page of PTDiag spreadsheet. The Free energy calculation section is shown in blue, the reaction plotting section in purple.

A small portion of the spreadsheet, shown in red, is used to store the value of various thermodynamic constants including the gas constant (R), and the reference pressure (P_r) and reference temperature (T_r) for the thermodynamic data sets.

The equilibrium constant is calculated in the third section of the spreadsheet, shown in green. This calculation requires the user to specify a non-unit activity value for all phases or phase components in the reaction that are impure, relative to tabulated compositions in the thermodynamic database. In most cases, the user must manually calculate the required activities with an appropriate activity model and enter these values in the activity-input cells (H21 through L24). These cells have unit activity by default, and do not have to be adjusted for pure phases of constant composition. The activity-input cells are arranged in the same manner as an equilibrium constant expression, with product phases in the numerator (top) and reactant phases in the denominator (bottom).

The current version of the spreadsheet will calculate the activity of the four garnet phase components (almandine, spessartine, pyrope and grossular) directly from mineral chemistry. The activity model used is an ideal mixing on sites model listed in Appendix 2.

Results of this calculation are displayed in cells E22 to F25; however, required activity values must still be manually transferred to the activity-input cells (H21 to L24). Garnet mineral chemistry can be entered either as calculated mole fraction (for almandine, spessartine, pyrope and grossular in cells M26 through M29) or as the 8-fold site population in the garnet mineral formula (in cells J26 through J29 – formula should be calculated on the basis of 12 oxygens).

The spreadsheet will also calculate the ideal activity of anorthite plagioclase directly from mole fraction data (entered in cells C27 through D29).

Equilibrium conditions for the reaction are calculated in the fourth section of the spreadsheet, shown in light blue. Column B displays the Gibbs free energy of reaction for 21 user-defined pressure values, which are entered in column A from rows 35 to 55. The free energy of reaction (ΔG) is calculated by the summing columns C through M, which display the energy contribution (in J/mol) of various component functions of the Gibbs free energy equation. Table A3.1 below summarizes these functions and lists the excel formulas used to calculate their value.

Equilibrium conditions for the reaction are calculated by determining the pressure and

temperature where the Gibbs free energy of the reactant assemblage is equal to that of the product assemblage, or where the free energy change of reaction ΔG_R is equal to zero ($\Delta G_R = G_{\text{prod}} - G_{\text{react}}$).

Equilibrium temperature values in column O are calculated automatically by the spreadsheet using the Microsoft Excel Solver application. Solver uses numerical methods to minimize the value of ΔG_R (column B) by varying the temperature in column O. The interactive button labelled Calc. Equil. launches the Solver routine and steps it through rows 35 to 55 to calculate ΔG_R at each user defined pressure.

The final section of the spreadsheet shown in purple plots the trace of the reaction through P-T space and determines reaction facing. (Reaction facing is determined by the spreadsheet so that the user does not need to know which mineral assemblage (product or reactant) is stable on the high temperature side of the reaction, in fact, the phase input cells in section 1 are labelled reactant and product only for the purpose of separating the two mineral assemblages). Reaction facing is calculated and displayed in cells B58 through C64 by determining which mineral assemblage has the highest entropy. This assemblage must be the reactant assemblage, which is stable on the high-temperature side of the reaction, since the second law of thermodynamics postulates that reactions can only proceed spontaneously with increasing entropy.

TABLE A3.1
Thermodynamic Functions in PTDiag Spreadsheet

Column	Function	Column Title	Excel Formula for Row 35
C	ΔH reaction	dH	=dH dH is a named cell which refers to D16
D	ΔS reaction	-TdS	=(N35*dS) dS is a named cell which refers to E16
E	ΔV reaction	+VdP	=dV*(A35-Pr) Named cells are defined as: dV=F16, and Pr=B23
F	Heat Capacity	+C _p dT	=(dk_0*(N35-Tr+N35*LN(Tr/N35)))+(dk_1*(4*SQRT(N35)-2*SQRT(Tr)-2*N35/SQRT(Tr))) +(dk_2*(1/Tr)-N35/(2*Tr^2)-1/(2*N35)))+(dk_3*(1/(2*Tr^2)-N35/(3*Tr^3))-1/(6*N35^2)) +(dk_4*(LN(N35)-LN(Tr)-N35/Tr)+1)+dk_5*(N35*Tr)-((Tr^2/2)-(N35^2/2))) Named cells are defined as: dk_0=G16, dk_1=H16, dk_2=I16, dk_3=J16, dk_4=K16, dk_5=L16, and Tr=B22
G	Expansivity / Compressibility	+a.b	=(((-dv_3+dv_4+dv_1*(N35-Tr)+dv_2*(N35-Tr)^2)*(A35-1)))+(dv_3/2-dv_4)*(A35^2-1))+(dv_4/3*((A35^3-1))) Named cells are defined as: dv_1=R16, dv_2=S16, dv_3=T16, dv_4=U16, Tr=B22 and Pr=B23
H	Equilibrium Constant	+RTlnK	=(R_*N35*ln_K) Named cells are defined as: R_=B24, and ln_K=P23
I	Fluid Fugacity	+nRTlnf	=IF(OR(\$B\$4="W", \$B\$5="W", \$B\$6="W", \$B\$7="W", \$B\$8="W"), \$B\$25*(B99+(D99*N35)+(F99*N35^2))*1000, IF(OR(\$B\$10="W", \$B\$11="W", \$B\$12="W", \$B\$13="W", \$B\$14="W", \$B\$25*(B99+(D99*N35)+(F99*N35^2))*1000, 0)) Cell B25 is the moles of water involved in the reaction. Fluid phase fugacity equation from Holland and Powell (1990): $RT \ln f = a + bT + cT^2$ (T in Kelvin, P in kilobars) Cell references are to fit coefficients as follows: B99 = a, D99 = b and F99 = c
J	Dolomite Disorder	+Gdis	=E72-N35*F72+G72*(A35-Pr) Free energy of disorder from Berman (1988): $\Delta_d G = \Delta_d H - T \Delta_d S + \Delta_d V (P - P_f)$ Cell references are as follows: E72 = $\Delta_d H$, F72 = $\Delta_d S$ and G72 = $\Delta_d V$

TABLE A3.1-Continued

Thermodynamic Functions in PTDiag Spreadsheet

Column	Function	Column Title	Excel Formula for Row 35
K	Pyrope Activity	+RTln γ_{Prp}	<p>$\text{=IF(OR(\\$B\\$4="Prp",\\$B\\$5="Prp",\\$B\\$6="Prp",\\$B\\$7="Prp",\\$B\\$8="Prp"),\\$B\\$27*T150,IF(OR(\\$B\\$10="Prp",\\$B\\$11="Prp",\\$B\\$12="Prp",\\$B\\$13="Prp",\\$B\\$14="Prp"),\\$B\\$27*T150,0))}$</p> <p>Cell B27 is # of moles of pyrope in the reaction. Cell T150 is the pyrope activity coefficient from Berman (1990), calculated as:</p> $T150 = \$C150*(\text{Grs}^2-2*\text{Grs}^2*\text{Prp})+\$D150*(2*\text{Grs}*\text{Prp}-2*\text{Grs}*\text{Prp}^2)+\$E150*(-2*\text{Grs}^2*\text{Alm})+\$F150*(-2*\text{Grs}*\text{Alm}^2)+\$I150*(2*\text{Prp}*\text{Alm}-2*\text{Prp}^2*\text{Alm})+(\$J150*(\text{Alm}^2-2*\text{Prp}*\text{Alm}^2)+\$O150*(\text{Grs}*\text{Alm}-2*\text{Grs}*\text{Prp}*\text{Alm})+\$P150*(\text{Grs}*\text{Sps}-2*\text{Grs}*\text{Prp}*\text{Sps})+\$Q150*(-2*\text{Grs}*\text{Alm}*\text{Sps})+\$R150*(\text{Alm}*\text{Sps}-2*\text{Prp}*\text{Alm}*\text{Sps})$ <p>Named cells are defined as: Alm=D22, Sps=D23, Prp=D24, and Grs=D25. The following cells refer to Margules parameters: C150=W112, D150=W122, E150=W133, F150=W133, I150=W223, J150=W233, O150=W123, P150=W124, Q150=W134 and R150=W234.</p>
L	Almandine Activity	+RTln γ_{Alm}	<p>$\text{=IF(OR(\\$B\\$4="Alm",\\$B\\$5="Alm",\\$B\\$6="Alm",\\$B\\$7="Alm",\\$B\\$8="Alm"),\\$B\\$26*U150,IF(OR(\\$B\\$10="Alm",\\$B\\$11="Alm",\\$B\\$12="Alm",\\$B\\$13="Alm",\\$B\\$14="Alm"),\\$B\\$26*U150,0))}$</p> <p>Cell B26 is # of moles of almandine in the reaction. Cell U150 is the almandine activity coefficient from Berman (1990), calculated as:</p> $U150 = \$C150*(-2*\text{Grs}^2*\text{Prp})+\$D150*(-2*\text{Grs}*\text{Prp}^2)+\$E150*(\text{Grs}^2-2*\text{Grs}^2*\text{Alm})+\$F150*(2*\text{Grs}*\text{Alm}-2*\text{Grs}*\text{Alm}^2)+\$I150*(\text{Prp}^2-2*\text{Prp}^2*\text{Alm})+\$J150*(2*\text{Prp}*\text{Alm}-2*\text{Prp}^2*\text{Alm}^2)+\$O150*(\text{Grs}*\text{Prp}-2*\text{Grs}*\text{Prp}*\text{Alm})+\$P150*(-2*\text{Grs}*\text{Prp}*\text{Sps})+\$Q150*(\text{Grs}*\text{Sps}-2*\text{Grs}*\text{Alm}*\text{Sps})+\$R150*(\text{Prp}*\text{Sps}-2*\text{Prp}*\text{Alm}*\text{Sps})$ <p>Named cells are defined as: Alm=D22, Sps=D23, Prp=D24, and Grs=D25. The following cells refer to Margules parameters: C150=W112, D150=W122, E150=W133, F150=W133, I150=W223, J150=W233, O150=W123, P150=W124, Q150=W134 and R150=W234.</p>
M	Grossular Activity	+RTln γ_{Grs}	<p>$\text{=IF(OR(\\$B\\$4="Grs",\\$B\\$5="Grs",\\$B\\$6="Grs",\\$B\\$7="Grs",\\$B\\$8="Grs"),\\$B\\$28*V150,IF(OR(\\$B\\$10="Grs",\\$B\\$11="Grs",\\$B\\$12="Grs",\\$B\\$13="Grs",\\$B\\$14="Grs"),\\$B\\$28*V150,0))}$</p> <p>Cell B28 is # of moles of grossular in the reaction. Cell V150 is the grossular activity coefficient from Berman (1990), calculated as:</p> $V150 = \$C150*(2*\text{Grs}*\text{Prp}-2*\text{Grs}^2*\text{Prp})+\$D150*(\text{Prp}^2-2*\text{Grs}*\text{Prp}^2)+\$E150*(2*\text{Grs}*\text{Alm}-2*\text{Grs}^2*\text{Alm})+\$F150*(\text{Alm}^2-2*\text{Grs}*\text{Alm}^2)+\$I150*(-2*\text{Prp}^2*\text{Alm})+\$J150*(-2*\text{Prp}*\text{Alm}^2)+\$O150*(\text{Prp}*\text{Alm}-2*\text{Grs}*\text{Prp}*\text{Alm})+\$P150*(\text{Prp}*\text{Sps}-2*\text{Grs}*\text{Prp}*\text{Sps})+\$Q150*(\text{Alm}*\text{Sps}-2*\text{Grs}*\text{Alm}*\text{Sps})+\$R150*(\text{Prp}*\text{Alm}*\text{Sps})$ <p>Named cells are defined as: Alm=D22, Sps=D23, Prp=D24, and Grs=D25. The following cells refer to Margules parameters: C150=W112, D150=W122, E150=W133, F150=W133, I150=W223, J150=W233, O150=W123, P150=W124, Q150=W134 and R150=W234.</p>

TABLE A3.1-Continued
Thermodynamic Functions in PTDiag Spreadsheet

Excel Formula for Row 35		
Column	Function	Column Title
L	Anorthite Activity	+RTlnγ _{An}
		<p> $=IF(OR(\\$B\\$4="An", \\$B\\$5="An", \\$B\\$6="An", \\$B\\$7="An", \\$B\\$8="An"), -$ $\\$B\\$29*\\$K256, IF(OR(\\$B\\$10="An", \\$B\\$11="An", \\$B\\$12="An", \\$B\\$13="An", \\$B\\$14="An", \\$B\\$29*\\$K256, 0))$ Cell B29 is # of moles of anorthite in the reaction. Cell K256 is the anorthite activity coefficient from Fuhrman & Lindsley (1988), calculated as: $K256 = D256*(Ab*Or*(0.5-An-2*Ab)) + C256*(Ab*Or*(0.5-An-2*Or)) + H256*(2*Or*An*(1-An) + Ab*Or*(0.5-An)) + G256*(Or^2*(1-2*An) + Ab*Or*(0.5-An)) + E256*(2*Ab*An*(1-An) + Ab*Or*(0.5-An)) + F256*(Ab^2*(1-2*An) + I256*(Or*Ab*(1-2*An)))$ Named cells are defined as: An=D27, Ab=D28 and Or=D29. The following cells refer to Margules parameters: C256=WAbOr, D256=WOrAb, E256=WAbAn, F256=WAnAb, G256=WAnOr, H256=WOrAn and I256=WOrAbAn. </p>

A3.2 Testing and Verifying PTDiag Spreadsheet

PTDiag was empirically tested by comparing pressure-temperature results from the spreadsheet with those obtained using the program TWQ (Berman, 1990). Using both dehydration and solid phase reactions, involving a wide variety of phases including garnet, plagioclase and dolomite, tested all aspects of the spreadsheet. Test conditions for four of these tests are summarized below in Table A2.2.

TABLE A3.2
Testing Data for PTDiag Spreadsheet

Test Number	Data Source:	Sample	Equilibrium	Phase	Mole Fraction	Ideal Activity
1	Wang & Spear (1991)	293-1	Garnet-Chlorite Exchange Reaction: $5\text{Prp} + 3\text{fChl} = 5\text{Alm} + 3\text{Chl}$	Alm	0.638	2.591E-01
				Sps	0.251	1.586E-02
				Prp	0.052	1.366E-04
				Grs	0.060	2.134E-04
				fChl	0.546	0.041
				Chl	0.454	0.0164
2	Gal & Ghent (1991)	LG426	Mrg+Grt+Qtz out Reaction $15\text{aQtz} + 5\text{Prp} + 12\text{Mrg} + 7\text{Grs} = 33\text{An} + 3\text{Chl}$	Alm	0.671	3.016E-01
				Sps	0.032	3.338E-05
				Prp	0.151	3.442E-03
				Grs	0.146	3.123E-03
				Chl	0.637	0.096
				Mrg	0.729	0.729
3	Fletcher & Greenwood (1979)	#6	GASP geobarometer: $\text{aQtz} + \text{Ky} + \text{Grs} = 3\text{An}$	An	0.362	0.168†
				Alm	0.758	4.362E-01
				Sps	0.042	7.375E-05
				Prp	0.124	1.921E-03
				Grs	0.075	4.284E-04
				Ky		0.98
4	Wang & Spear (1991)	284-2	Dehydration Reaction: $\text{fChl} + \text{fCtd} + 2\text{aQtz} = 2\text{Alm} + 5\text{H}_2\text{O}$	An	0.292	0.122†
				Alm	0.638	2.591E-01
				Sps	0.251	1.586E-02
				Prp	0.052	1.366E-04
				Grs	0.060	2.134E-04
				fChl	0.546	0.041
				Chl	0.454	0.0164

† Ideal activity of anorthite calculated the Al-avoidance model of Kerrich and Darken (1975): $a_{\text{An}} = 1/4X_{\text{Ca}}(1+X_{\text{Ca}})^2$

Results of these comparison tests are listed in Table A3.3. Pressure values were taken from the TWQ Plot.dat file and transferred to the PTDiag spreadsheet prior to running Solver. Note that the average deviation between temperatures obtained using TWQ and those obtained from PTDiag is typically on the order of one to two degrees (testing on additional equilibria produced similar results). This similarity confirms the validity of the formulas used in the spreadsheet calculations, and the overall reliability of the PTDiag spreadsheet.

TABLE A3.3

Testing Results for PTDiag Spreadsheet

Test 1 5Prp+3fchl = 5Alm+3Chl				Test 2 15oQtz+5Prp+12Mrp+7Grp= 33An+3Chl				Test 3 oQtz+Ky+Grp = 3An				Test 4 fchl+Cld+2oQtz = 2Alm+5H ₂ O			
P _{TWQ} (bars)	T _{TWQ} (°C)	T _{PTDiag} (°C)	T _{PTDiag} - T _{TWQ}	P _{TWQ} (bars)	T _{TWQ} (°C)	T _{PTDiag} (°C)	T _{PTDiag} - T _{TWQ}	P _{TWQ} (bars)	T _{TWQ} (°C)	T _{PTDiag} (°C)	T _{PTDiag} - T _{TWQ}	P _{TWQ} (bars)	T _{TWQ} (°C)	T _{PTDiag} (°C)	T _{PTDiag} - T _{TWQ}
10000	491.6	489.5	-2.13	9441.6	700	698.5	-1.54	8162.6	700.0	697.8	-2.20	10000	517.9	519.7	1.82
9224.2	492.0	489.9	-2.13	8667.0	647.1	646.0	-1.13	8085.2	696.0	693.9	-2.18	9265	520.0	521.8	1.79
7640.8	492.8	490.7	-2.14	7217.3	547.1	546.5	-0.61	6950.0	637.7	635.8	-1.91	8515	521.7	523.5	1.83
6057.5	493.7	491.5	-2.14	5780.5	447.1	446.8	-0.33	5822.4	579.4	577.7	-1.67	7765	522.8	524.7	1.92
5449.5	494.0	491.8	-2.14	5230.5	408.7	408.5	-0.27	5391.3	557.0	555.4	-1.59	6265	523.4	525.5	2.16
5297.5	494.0	491.9	-2.14	5093.0	399.1	398.9	-0.26	5283.6	551.4	549.8	-1.57	5689	522.9	525.1	2.24
5259.5	494.1	491.9	-2.14	5058.6	396.7	396.5	-0.25	5256.7	550.0	548.4	-1.56	5545	522.7	524.9	2.25
5250.0	494.1	491.9	-2.14	5050.0	396.1	395.9	-0.25	5250.0	549.6	548.1	-1.56	5509	522.6	524.9	2.26
5240.5	494.1	491.9	-2.14	5041.4	395.5	395.3	-0.25	5243.3	549.3	547.7	-1.56	5500	522.6	524.9	2.26
5202.5	494.1	492.0	-2.14	5007.0	393.1	392.9	-0.25	5216.4	547.9	546.3	-1.56	5491	522.6	524.8	2.26
5050.5	494.2	492.0	-2.14	4869.6	383.5	383.3	-0.24	5108.8	542.3	540.7	-1.54	5455	522.5	524.8	2.26
4442.5	494.5	492.3	-2.14	4319.4	345.1	344.9	-0.20	4679.1	519.9	518.4	-1.46	5311	522.3	524.5	2.26
2859.2	495.3	493.1	-2.14	2882.7	245.1	245.0	-0.15	3563.8	461.5	460.2	-1.29	4735	521.0	523.2	2.24
1275.8	496.1	493.9	-2.14	1436.9	145.1	145.0	-0.12	2452.8	403.2	402.1	-1.14	3985	518.4	520.4	2.01
500	496.5	494.3	-2.14	782.2	100	99.9	-0.10	1442.3	350	349.0	-1.03	3235	514.6	516.0	1.41
Average Temp. Difference 2σ Standard Deviation				Average Temp. Difference 2σ Standard Deviation				Average Temp. Difference 2σ Standard Deviation				Average Temp. Difference 2σ Standard Deviation			
-2.14 0.01				-0.40 0.81				-1.59 0.65				1.06 4.47			

Appendix 4 -

Sample Location UTM Coordinates and Maps

Table A4.1: Sample Location UTM Coordinates
Grid Zone Designation: 18T

Sample Location	UTM Northing	UTM Easting	Sample Location	UTM Northing	UTM Easting
89R101	4985 575	356 925	91-11		
89R201	4976 750	347 680	91-12		
89R208	4976 560	347 830	91-13		
90R303	4948 000	330 315	91-14	4974 475	343 230
90R308	4966 700	331 105	91-15	4967 170	331 955
			91-16	4962 890	329 555
90-1	4966 700	331 105	91-17	4976 760	340 630
90-2	4966 770	331 170	91-18		
90-3	4970 280	336 875	91-19	4964 860	330 127
90-4	4967 660	332 490	91-20	4964 920	330 260
90-5	4970 275	336 810	91-21	4965 200	330 025
90-6	4971 040	338 160	91-22	4965 270	330 055
90-7			91-23	4965 145	329 970
90-8			91-24	4969 865	336 055
90-9			91-25	4969 500	335 290
90-10	4960 200	327 480	91-26	4969 190	334 710
90-11	4965 080	330 005	91-27	4960 010	327 430
90-12	4965 120	330 050	91-28	4959 985	327 415
90-13			91-29	4958 940	326 435
90-14			91-30		
90-15			91-31		
90-16			91-32	4964 130	330 303
90-18	4961 915	329 015	91-33		
90-19	4961 890	329 065			
90-20	4962 930	329 575	92-1	4959 815	329 700
90-21	4968 570	334 370	92-2	4961 830	329 045
90-22	4968 440	333 920	92-3	4961 910	329 055
90-23	4962 665	328 720	92-4	4961 960	329 085
90-24	4962 575	328 760	92-5	4960 170	327 860
90-25	4962 590	328 725	92-6	4960 265	327 885
90-26	4965 450	330 440	92-7	4960 660	327 925
			92-8	4961 140	327 850
91-1	4970 695	337 410	92-9	4964 650	329 690
91-2	4970 685	337 380	92-10	4961 050	328 235
91-3	4970 660	337 400	92-11	4959 680	328 095
91-4	4970 025	336 420	92-12	4961 090	328 675
91-5	4971 820	338 800	92-13	4961 070	328 590
91-6	4971 625	338 560	92-14	4961 145	328 345
91-7	4972 750	340 005	92-15	4965 740	330 300
91-8			92-16	4966 580	330 965
91-9			92-17	4966 525	330 875
91-10	4968 400	333 735	92-18	4962 700	329 580

Table A4.1 Continued: Sample Location UTM Coordinates
Grid Zone Designation: 18T

Sample Location	UTM Northing	UTM Easting	Sample Location	UTM Northing	UTM Easting
92-19	4960 215	327 880	93-20	4960 975	328 135
92-20	4963 000	329 840	93-21	4960 920	328 050
92-21	4979 070	352 085	93-22	4960 820	327 675
92-22	4978 400	350 530	93-23	4960 980	327 785
92-23	4963 740	330 090	93-24	4960 900	327 750
92-24	4963 755	330 100	93-25	4960 925	328 460
92-25	4964 185	330 285	93-26	4960 385	327 890
92-26	4964 345	330 330	93-27	4960 550	327 905
92-27	4963 120	329 875	93-28	4961 520	328 830
92-28	4963 180	329 920	93-29	4961 600	328 900
92-29	4963 205	329 920	93-30	4961 750	328 955
92-30	4963 310	329 965	93-31	4961 775	328 980
92-31	4968 305	333 340	93-32	4962 560	328 755
92-32	4965 610	330 740	93-33	4962 580	328 735
92-33	4977 485	348 930	93-34	4962 610	328 700
92-34	4978 125	350 095	93-35	4959 400	329 195
92-35	4978 165	350 155	93-36	4940 920	322 965
92-36	4965 390	330 110	93-37	4940 845	322 865
92-37	4982 410	354 670	H.A.	4944 750	324 355
92-38	4982 455	355 040	93-38	4944 680	324 350
92-39	4984 405	356 185	93-39	4973 820	336 240
92-40	4981 510	354 045	93-40	4947 980	330 275
92-41	4959 060	327 480	93-41	4973 790	336 145
92-42	4959 205	327 480	93-42	4947 410	324 965
92-43			93-43	4947 345	324 935
92-44	4983 725	356 335	93-44	4975 895	340 350
92-45			93-45	4975 010	344 470
93-1	4967 025	331 780	93-46	4985 625	357 060
93-2	4967 445	331 940			
93-3	4967 535	332 155	Madoc-01	4930 630	301 200
93-4	4967 515	331 960	Madoc-02	4932 940	302 300
93-5	4967 100	332 385	Madoc-03	4932 800	302 310
93-6	4965 510	330 260	Madoc-04	4931 650	301 540
93-7	4968 000	333 300	Madoc-05	4931 350	301 610
93-8	4966 940	331 370	Madoc-06	4931 340	301 520
93-9	4967 035	331 490	Madoc-07	4931 175	302 520
93-10	4960 115	329 760	Queens-1	4938 340	308 000
93-11	4960 215	329 780	CR-01	4933 575	325 650
93-12	4960 595	330 465	CR-02	4934 520	326 280
93-13	4959 920	327 410	CR-03	4934 840	326 440
93-14	4967 900	333 750	CR-04	4937 520	327 870
93-15	4959 475	327 485	CR-05	4932 330	324 885
93-16	4959 495	327 295	CR-06	4940 740	329 475
93-17	4958 560	327 510	CR-07	4940 610	329 365
93-18	4959 130	327 460	CR-08	4941 200	329 285
93-19	4960 855	328 055	94-01	4976 110	346 400
			94-02	4976 280	346 770

Appendix 5 - Mineral Chemistry

A5.1 Analytical Conditions

Mineral chemistry was determined using a JEOL JSM6400 scanning electron microscope at the Geoscience Laboratories in Sudbury, Ontario Canada, equipped with an Oxford Instruments eXL LZ4 energy dispersive X-ray spectrometer. Quantitative mineral analysis was completed using the following analytical conditions: accelerating voltage - 20kV, beam current - 2.5namp, acquisition time - 100 live seconds. For plagioclase, the electron beam was rastered over a 30×30µm area to minimize the loss of sodium. Analytical routines were standardized using pure oxides, compounds, and well-characterized minerals (mostly from Jarosewich et al, 1979), summarized in Table A5.1 and Table A5.2 below.

	Na	Mg	Al	Si	Cl	K	Ca	Ti	Cr	Mn	Fe	Zn	Ba
garnet, staurolite, chloritoid		MgO	G87375*	G87375			WDi*	MnTiO ₃	Cr ₂ O ₃	MnTiO ₃	Fe ₂ O ₃	Will*	
biotite, muscovite margarite	Bery*	MgO	Kakhb*	Kakhb	NaCl	Micro*	WDi	MnTiO ₃		MnTiO ₃	Fe ₂ O ₃		BaF ₂
plagioclase		MgO	Alb*	Alb		Micro	WDi	MnTiO ₃		MnTiO ₃	Fe ₂ O ₃		BaF ₂

	Si	Al	Cr	V	Ti	Zn	Cu	Ni	Co	Mn	Fe	Mg	Ca
ilmenite, rutile, magnetite	SiO ₂	Al ₂ O ₃	Cr ₂ O ₃	V	MnTiO ₃	ZnS	Cu	Ni	Co	MnTiO ₃	Fe ₂ O ₃	MgO	WDi*

* Mineral Standard Abbreviations:

Bery – Beryllonite

G87375 – Smithsonian Museum Garnet Standard (Jarosewich et al., 1979)

Kakhb – Kakanui Hornblende (Jarosewich et al., 1979)

Micro – Smithsonian Microcline

WDi – Wakefield Diopside (G. Skippen, pers. comm.)

Alb – Albite var. Clevelandite (Maine, pers collection)

Will – Willemite (pers collection)

Instrument calibration was monitored by analysis of Smithsonian Museum mineral standards.

Results are shown in Table A5.3 below:

	Arenal Hornblende USNM111356				Roberts Victor Garnet USNM110752				Kakanui Pyrope USNM143968			
	Avg. n=27	St. Dev (2σ)	Rec. Comp.*	Rel. Error (%)	Avg. n=70	St. Dev (2σ)	Rec. Comp.*	Rel. Error (%)	Avg. n=30	St. Dev (2σ)	Rec. Comp.*	Rel. Error (%)
SiO ₂	42.09	0.83	41.46	1.5	40.05	0.60	40.16	-0.3	41.40	0.65	46.46	-0.1
TiO ₂	1.45	0.15	1.41	2.6	0.40	0.09	0.35	13.6	0.47	0.07	0.47	-0.2
Al ₂ O ₃	14.82	0.46	15.47	-4.2	22.62	0.46	22.77	-0.4	23.31	0.45	23.73	-1.8
Cr ₂ O ₃	b.d.		b.d.		b.d.		b.d.		b.d.		b.d.	
FeO	11.46	0.27	11.47	-0.1	11.65	0.25	11.31	3.0	10.65	0.17	10.68	-0.3
MnO	0.14	0.08	0.15	-5.2	0.17	0.09	0.19	-8.5	0.32	0.08	0.28	14
MgO	14.56	0.51	14.24	2.2	7.38	0.26	7.17	2.9	18.59	0.37	18.51	0.5
CaO	11.46	0.19	11.55	-0.8	18.02	0.15	18.12	-0.5	5.18	0.11	5.17	0.2
Na ₂ O	2.19	0.29	1.91	14.5	b.d.		b.d.		b.d.		b.d.	
K ₂ O	0.21	0.05	0.21	0.6	b.d.		b.d.		b.d.		b.d.	
Cl	b.d.		b.d.		b.d.		b.d.		b.d.		b.d.	
Sum	98.38		97.87		100.29		100.0		99.92		100.3	

* Smithsonian Recommended Composition (Jarosewich et al., 1979)

b.d. – below limit of detection

A5.2 Mineral Chemistry Results

Microbeam analysis results for various minerals are reported below in the following tables:

Mineral	Table	Page
Chlorite	A5.4	237
Chloritoid	A5.5	243
Garnet	A5.6	248
Biotite	A5.7	262
Staurolite	A5.8	269
Muscovite	A5.9	275
Margarite	A5.10	283
Plagioclase	A5.11	285
Aluminosilicate	A5.12	290
Ilmenite	A5.13	292
Rutile	A5.14	293

Table A5.4: Representative Chlorite Analyses

	Madoc-4a-I		Madoc-7b2-III		Madoc-7e2-III		Madoc-5e-II		Madoc-2e-V		Queens-1a-I	
	Ctd+Ky+Chl+St intgrn w porph		Grt+Chl+Bt chl-rich area		Chl+Ctd chl-rich area		Grt+Chl+Ctd matrix, pll. fol.		Grt+Chl+Bt+St+Ctd chl area adj. plag		Grt+Chl+Ctd+Bt+(St) matrix Chl	
	(5,2)	(2σ)	(3,1)	(2σ)	(3,1)	(2σ)	(10,3)	(2σ)	(3,1)	(2σ)	(6,3)	(2σ)
SiO ₂	25.51	0.39	23.85	0.37	23.94	0.76	24.15	0.44	24.94	0.26	23.34	0.47
Al ₂ O ₃	24.92	0.38	22.23	0.11	23.09	0.37	23.62	0.53	23.05	0.36	23.87	1.13
Cr ₂ O ₃	0.03	0.06	0.01	0.02	0.03	0.06	0.01	0.04	0.06	0.02	0.02	0.05
TiO ₂	0.07	0.05	0.06	0.04	0.05	0.03	0.04	0.06	0.12	0.09	0.02	0.05
FeO	19.87	0.42	30.73	0.56	27.14	0.25	26.43	0.49	24.66	0.45	30.08	0.67
MnO	0.29	0.03	0.02	0.06	0.24	0.05	0.04	0.05	0.10	0.08	0.03	0.06
MgO	17.79	0.29	10.37	0.29	11.84	0.38	13.30	0.34	14.51	0.23	10.79	0.18
CaO	0.02	0.04	0.02	0.02	0.03	0.05	0.02	0.04	0.04	0.04	0.03	0.04
Na ₂ O	0.16	0.15	0.12	0.31	0.13	0.20	0.13	0.23	0.15	0.17	0.28	0.37
K ₂ O	0.04	0.06	0.02	0.03	0.00	0.02	0.01	0.03	0.05	0.03	0.01	0.01
TOTAL	88.71	0.70	87.43	1.80	86.48	0.34	87.75	0.73	87.66	0.81	88.48	1.09
<i>Cation proportions on the basis of 14 oxygens</i>												
Si	2.573	0.032	2.600	0.023	2.588	0.070	2.557	0.046	2.617	0.026	2.504	0.069
Al (IV)	1.427	0.032	1.400	0.023	1.412	0.070	1.443	0.046	1.383	0.026	1.496	0.069
Sum	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000
Al (VI)	1.535	0.025	1.457	0.019	1.529	0.036	1.504	0.025	1.467	0.016	1.521	0.061
Cr	0.003	0.005	0.001	0.002	0.002	0.005	0.001	0.003	0.005	0.001	0.002	0.005
Ti	0.005	0.003	0.005	0.003	0.004	0.002	0.004	0.005	0.009	0.007	0.002	0.004
Fe	1.676	0.042	2.801	0.033	2.453	0.029	2.340	0.043	2.164	0.035	2.699	0.066
Mn	0.024	0.002	0.002	0.005	0.022	0.005	0.004	0.005	0.009	0.007	0.003	0.006
Mg	2.675	0.031	1.685	0.032	1.908	0.055	2.098	0.052	2.270	0.036	1.726	0.037
Ca	0.002	0.005	0.002	0.003	0.003	0.006	0.002	0.004	0.004	0.004	0.004	0.004
Na	0.032	0.029	0.026	0.065	0.027	0.041	0.026	0.046	0.030	0.034	0.059	0.076
K	0.005	0.008	0.002	0.004	0.001	0.002	0.001	0.004	0.006	0.004	0.001	0.001
Sum	5.958	0.029	5.981	0.048	5.950	0.045	5.980	0.041	5.964	0.021	6.015	0.049
Fe/(Fe+Mg)	0.385	0.007	0.624	0.006	0.563	0.007	0.527	0.010	0.488	0.001	0.610	0.005
Mg/(Fe+Mg)	0.615	0.007	0.376	0.006	0.437	0.007	0.473	0.010	0.512	0.001	0.390	0.005
<i>Cation proportions on the basis of 10 cations</i>												
Si	2.594	0.039	2.613	0.019	2.609	0.079	2.570	0.049	2.637	0.036	2.516	0.072
Al	1.406	0.039	1.387	0.019	1.391	0.079	1.430	0.049	1.363	0.036	1.484	0.072
Sum	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000
Al	1.581	0.040	1.484	0.029	1.575	0.060	1.532	0.029	1.509	0.039	1.548	0.077
Fe ³⁺	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Cr	0.003	0.005	0.001	0.002	0.002	0.005	0.001	0.003	0.005	0.001	0.002	0.005
Ti	0.006	0.004	0.005	0.003	0.004	0.002	0.004	0.005	0.009	0.007	0.002	0.004
Fe ²⁺	1.690	0.039	2.816	0.027	2.473	0.022	2.352	0.042	2.180	0.026	2.712	0.057
Mn	0.025	0.002	0.002	0.005	0.023	0.004	0.004	0.005	0.009	0.007	0.003	0.006
Mg	2.697	0.027	1.693	0.032	1.923	0.049	2.109	0.051	2.287	0.027	1.734	0.032
Ca	0.002	0.005	0.002	0.003	0.003	0.006	0.002	0.004	0.004	0.004	0.004	0.004
Na	0.032	0.029	0.027	0.065	0.027	0.041	0.027	0.047	0.030	0.035	0.059	0.077
K	0.005	0.008	0.002	0.004	0.001	0.002	0.001	0.004	0.006	0.004	0.001	0.001
Sum	6.039	0.029	6.031	0.069	6.031	0.036	6.030	0.048	6.040	0.038	6.064	0.076
Fe/(Fe+Mg)	0.385	0.007	0.624	0.006	0.563	0.007	0.527	0.010	0.488	0.001	0.610	0.005
Mg/(Fe+Mg)	0.615	0.007	0.376	0.006	0.437	0.007	0.473	0.010	0.512	0.001	0.390	0.005

Table A5.4 Continued: Representative Chlorite Analyses

	91-27a-I		91-27e-I		93-13b-I		90-10d-I		90-10g-I		93-15d-I	
	Grt+Chl matrix laths		Grt+Chl+Ctd matrix, pll. fol.		Grt+Chl+St+(Ctd) Crs Chl in Pseudo		Grt+Chl+Ctd matrix, pll. fol.		Ctd+Chl chl. agglom.		Grt+Chl+Bt+Pl matrix Chl	
	(9,3)	(2σ)	(6,2)	(2σ)	(7,2)	(2σ)	(10,3)	(2σ)	(11,3)	(2σ)	(8,3)	(2σ)
SiO ₂	23.79	0.51	23.91	0.27	24.42	0.35	23.89	0.22	23.29	0.67	24.02	0.79
Al ₂ O ₃	23.78	0.36	23.20	0.41	24.30	0.42	23.73	0.42	23.83	0.74	23.85	0.84
Cr ₂ O ₃	0.04	0.07	0.03	0.08	0.02	0.05	0.02	0.04	0.02	0.04	0.24	0.07
TiO ₂	0.07	0.08	0.02	0.04	0.06	0.07	0.07	0.07	0.07	0.09	0.09	0.07
FeO	26.84	0.51	28.82	0.34	22.33	0.24	25.84	0.53	28.34	0.43	24.77	0.34
MnO	0.12	0.06	0.15	0.05	0.43	0.08	0.15	0.09	0.09	0.07	0.22	0.07
MgO	12.83	0.21	11.48	0.16	15.36	0.14	13.08	0.21	11.57	0.30	14.04	0.34
CaO	0.05	0.07	0.01	0.02	0.01	0.02	0.01	0.03	0.01	0.03	0.01	0.04
Na ₂ O	0.15	0.24	0.06	0.12	0.21	0.23	0.18	0.22	0.09	0.20	0.08	0.17
K ₂ O	0.01	0.04	0.02	0.05	0.01	0.02	0.02	0.04	0.01	0.03	0.05	0.05
TOTAL	87.69	0.85	87.70	0.60	87.15	0.48	87.00	1.03	87.34	1.39	87.36	1.12
<i>Cation proportions on the basis of 14 oxygens</i>												
Si	2.530	0.037	2.568	0.020	2.550	0.030	2.545	0.034	2.508	0.038	2.537	0.059
Al (IV)	1.470	0.037	1.432	0.020	1.450	0.030	1.455	0.034	1.492	0.038	1.463	0.059
Sum	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000
Al (VI)	1.510	0.031	1.505	0.032	1.540	0.024	1.524	0.037	1.533	0.047	1.505	0.056
Cr	0.004	0.006	0.003	0.007	0.002	0.004	0.001	0.003	0.002	0.004	0.020	0.006
Ti	0.006	0.006	0.002	0.003	0.005	0.005	0.006	0.006	0.006	0.007	0.007	0.005
Fe	2.387	0.047	2.589	0.032	1.950	0.021	2.302	0.040	2.553	0.075	2.188	0.044
Mn	0.011	0.005	0.014	0.005	0.038	0.007	0.014	0.008	0.008	0.006	0.019	0.007
Mg	2.033	0.033	1.839	0.019	2.392	0.020	2.078	0.030	1.858	0.030	2.210	0.044
Ca	0.005	0.008	0.001	0.002	0.001	0.002	0.001	0.003	0.001	0.003	0.001	0.004
Na	0.032	0.050	0.011	0.025	0.043	0.046	0.037	0.046	0.020	0.041	0.016	0.034
K	0.002	0.005	0.003	0.007	0.001	0.002	0.003	0.005	0.002	0.004	0.006	0.007
Sum	5.989	0.035	5.967	0.016	5.972	0.027	5.966	0.047	5.983	0.051	5.973	0.036
Fe/(Fe+Mg)	0.540	0.003	0.585	0.003	0.449	0.004	0.526	0.004	0.579	0.008	0.497	0.007
Mg/(Fe+Mg)	0.460	0.003	0.415	0.003	0.551	0.004	0.474	0.004	0.421	0.008	0.503	0.007
<i>Cation proportions on the basis of 10 cations</i>												
Si	2.543	0.046	2.581	0.025	2.569	0.035	2.561	0.039	2.518	0.043	2.549	0.064
Al	1.457	0.046	1.419	0.025	1.431	0.035	1.439	0.039	1.482	0.043	1.451	0.064
Sum	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000
Al	1.538	0.047	1.532	0.040	1.582	0.021	1.559	0.050	1.556	0.064	1.533	0.060
Fe ³⁺	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Cr	0.004	0.006	0.003	0.007	0.002	0.004	0.001	0.003	0.002	0.004	0.020	0.006
Ti	0.006	0.006	0.002	0.003	0.005	0.005	0.006	0.006	0.006	0.007	0.007	0.005
Fe ²⁺	2.399	0.038	2.602	0.028	1.965	0.022	2.317	0.035	2.563	0.068	2.199	0.040
Mn	0.011	0.005	0.014	0.005	0.038	0.007	0.014	0.008	0.008	0.006	0.019	0.007
Mg	2.043	0.026	1.848	0.015	2.409	0.020	2.090	0.026	1.865	0.028	2.221	0.045
Ca	0.005	0.008	0.001	0.002	0.001	0.002	0.001	0.003	0.001	0.003	0.001	0.004
Na	0.032	0.050	0.012	0.026	0.044	0.047	0.038	0.046	0.020	0.041	0.016	0.035
K	0.002	0.005	0.003	0.007	0.001	0.002	0.003	0.005	0.002	0.004	0.006	0.007
Sum	6.039	0.047	6.015	0.026	6.046	0.045	6.029	0.047	6.023	0.041	6.023	0.034
Fe/(Fe+Mg)	0.540	0.003	0.585	0.003	0.449	0.004	0.526	0.004	0.579	0.008	0.497	0.007
Mg/(Fe+Mg)	0.460	0.003	0.415	0.003	0.551	0.004	0.474	0.004	0.421	0.008	0.503	0.007

Table A5.4 Continued: Representative Chlorite Analyses

	93-16a-II		93-16b-I				92-6a-I		92-6f1-II		93-26e-I	
	Grt+Chl		Grt+Chl+(Relict Ctd)				Grt+Chl		Grt+Chl+Ctd+Bt		Grt+Chl+Ctd+Bt+St+Mgr	
	matrix, fol.		matrix		vein & matrix		matrix Chl		matrix Chl pfl-fol		matrix Chl	
	(7,2)	(2σ)	(7,2)	(2σ)	(7,2)	(2σ)	(10,3)	(2σ)	(7,4)	(2σ)	(8,2)	(2σ)
SiO ₂	24.27	0.90	24.14	0.46	24.29	0.53	24.06	0.33	23.27	0.23	23.40	0.12
Al ₂ O ₃	23.23	0.67	23.41	0.30	23.77	0.24	23.50	0.20	23.61	0.44	23.47	0.41
Cr ₂ O ₃	0.02	0.03	0.03	0.07	0.03	0.05	0.03	0.07	0.03	0.07	0.04	0.06
TiO ₂	0.12	0.09	0.06	0.03	0.06	0.07	0.08	0.07	0.07	0.07	0.07	0.12
FeO	26.98	0.48	26.28	0.35	25.77	0.28	26.52	0.34	29.25	0.33	28.28	0.25
MnO	0.07	0.09	0.15	0.09	0.14	0.05	0.06	0.06	0.05	0.05	0.16	0.06
MgO	12.40	0.18	12.43	0.29	13.14	0.23	12.46	0.34	10.72	0.17	11.63	0.22
CaO	0.02	0.04	0.03	0.06	0.01	0.04	0.04	0.05	0.01	0.02	0.02	0.04
Na ₂ O	0.13	0.22	0.10	0.20	0.19	0.21	0.21	0.21	0.12	0.11	0.13	0.28
K ₂ O	0.03	0.04	0.06	0.05	0.05	0.06	0.07	0.08	0.03	0.05	0.02	0.04
TOTAL	87.27	0.70	86.71	0.77	87.45	0.48	87.03	0.69	87.15	0.50	87.21	0.71
<i>Cation proportions on the basis of 14 oxygens</i>												
Si	2.592	0.090	2.588	0.042	2.572	0.041	2.573	0.024	2.524	0.015	2.525	0.025
Al (IV)	1.408	0.090	1.412	0.042	1.428	0.041	1.427	0.024	1.476	0.015	1.475	0.025
Sum	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000
Al (VI)	1.517	0.037	1.545	0.026	1.539	0.022	1.535	0.033	1.543	0.030	1.511	0.022
Cr	0.002	0.003	0.003	0.006	0.002	0.004	0.002	0.006	0.002	0.006	0.003	0.005
Ti	0.010	0.007	0.005	0.002	0.005	0.005	0.007	0.005	0.006	0.005	0.005	0.009
Fe	2.410	0.047	2.356	0.032	2.282	0.026	2.372	0.034	2.654	0.046	2.552	0.027
Mn	0.006	0.008	0.014	0.008	0.013	0.005	0.005	0.006	0.005	0.005	0.015	0.005
Mg	1.973	0.038	1.986	0.035	2.074	0.045	1.986	0.044	1.734	0.025	1.872	0.031
Ca	0.002	0.004	0.004	0.007	0.001	0.004	0.004	0.006	0.001	0.002	0.002	0.005
Na	0.026	0.046	0.021	0.042	0.039	0.044	0.043	0.044	0.026	0.024	0.028	0.059
K	0.004	0.005	0.009	0.007	0.006	0.009	0.009	0.011	0.004	0.007	0.002	0.006
Sum	5.950	0.074	5.942	0.040	5.961	0.040	5.964	0.045	5.975	0.007	5.990	0.044
Fe/(Fe+Mg)	0.550	0.005	0.543	0.006	0.524	0.007	0.544	0.008	0.605	0.005	0.577	0.006
Mg/(Fe+Mg)	0.450	0.005	0.457	0.006	0.476	0.007	0.456	0.008	0.395	0.005	0.423	0.006
<i>Cation proportions on the basis of 10 cations</i>												
Si	2.614	0.101	2.611	0.047	2.594	0.047	2.597	0.028	2.539	0.018	2.536	0.024
Al	1.386	0.101	1.389	0.047	1.406	0.047	1.403	0.028	1.461	0.018	1.464	0.024
Sum	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000
Al	1.562	0.054	1.596	0.037	1.587	0.035	1.587	0.039	1.574	0.042	1.534	0.022
Fe ³⁺	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Cr	0.002	0.003	0.003	0.006	0.002	0.004	0.002	0.006	0.002	0.006	0.003	0.005
Ti	0.010	0.007	0.005	0.002	0.005	0.005	0.007	0.005	0.006	0.005	0.005	0.009
Fe ²⁺	2.430	0.037	2.378	0.027	2.302	0.026	2.394	0.033	2.669	0.040	2.563	0.024
Mn	0.007	0.009	0.014	0.008	0.013	0.005	0.005	0.006	0.005	0.005	0.015	0.005
Mg	1.990	0.034	2.004	0.033	2.091	0.040	2.004	0.044	1.744	0.023	1.879	0.032
Ca	0.002	0.004	0.004	0.007	0.001	0.004	0.004	0.006	0.001	0.002	0.002	0.005
Na	0.026	0.047	0.021	0.042	0.039	0.045	0.044	0.045	0.026	0.024	0.028	0.060
K	0.004	0.005	0.009	0.007	0.006	0.009	0.009	0.012	0.004	0.007	0.002	0.006
Sum	6.032	0.050	6.034	0.045	6.047	0.047	6.057	0.043	6.031	0.025	6.032	0.063
Fe/(Fe+Mg)	0.550	0.005	0.543	0.006	0.524	0.007	0.544	0.008	0.605	0.005	0.577	0.006
Mg/(Fe+Mg)	0.450	0.005	0.457	0.006	0.476	0.007	0.456	0.008	0.395	0.005	0.423	0.006

Table A5.4 Continued: Representative Chlorite Analyses

	93-26g-I		93-24a-II		92-8d-I		92-41d-I		92-912-II		92-26b-I	
	Grt+Chl+Bt+St+Mrg matrix Chl		Grt+Chl+Ctd+Mrg matrix, pli-fol		Grt+Chl+Ctd+Bt+St+Mrg matrix Chl		Chl+Ctd+Mrg matrix Chl		Grt+Chl+Bt+Pl+Ep matrix Chl		Grt+Chl+St+Ky+Pl Chl-rich seg.	
	(8,3)	(2σ)	(3,1)	(2σ)	(6,3)	(2σ)	(7,2)	(2σ)	(6,2)	(2σ)	(11,3)	(2σ)
SiO ₂	24.71	0.40	24.78	0.26	24.40	0.43	23.27	0.23	24.85	0.30	26.11	0.74
Al ₂ O ₃	23.78	0.34	23.75	0.76	23.79	0.41	23.17	1.05	23.73	0.26	24.63	0.75
Cr ₂ O ₃	0.01	0.03	0.02	0.05	0.04	0.07	0.04	0.07	0.06	0.06	0.01	0.03
TiO ₂	0.08	0.06	0.08	0.06	0.13	0.12	0.07	0.11	0.09	0.10	0.05	0.07
FeO	25.35	0.55	25.16	0.40	25.03	0.30	30.01	0.56	21.81	0.35	14.54	0.38
MnO	0.06	0.06	0.08	0.03	0.17	0.06	0.06	0.08	0.21	0.14	0.35	0.09
MgO	13.90	0.29	13.95	0.37	14.03	0.31	10.40	0.20	16.59	0.30	20.92	0.42
CaO	0.01	0.03	0.04	0.05	0.03	0.03	0.01	0.04	0.00	0.02	0.02	0.04
Na ₂ O	0.31	0.18	0.05	0.14	0.09	0.11	0.11	0.15	0.14	0.18	0.07	0.16
K ₂ O	0.09	0.11	0.10	0.08	0.07	0.05	0.03	0.03	0.03	0.05	0.02	0.05
TOTAL	88.28	1.10	88.02	1.72	87.77	1.28	87.18	1.85	87.52	1.06	86.72	1.43
<i>Cation proportions on the basis of 14 oxygens</i>												
Si	2.583	0.019	2.594	0.026	2.564	0.039	2.536	0.053	2.574	0.026	2.619	0.051
Al (IV)	1.417	0.019	1.406	0.026	1.436	0.039	1.464	0.053	1.426	0.026	1.381	0.051
Sum	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000
Al (VI)	1.513	0.033	1.523	0.008	1.510	0.021	1.513	0.028	1.470	0.032	1.530	0.042
Cr	0.001	0.002	0.002	0.004	0.003	0.006	0.004	0.006	0.005	0.005	0.001	0.002
Ti	0.006	0.005	0.006	0.005	0.010	0.009	0.006	0.009	0.007	0.008	0.004	0.005
Fe	2.216	0.031	2.202	0.035	2.200	0.016	2.736	0.031	1.889	0.021	1.220	0.034
Mn	0.005	0.005	0.007	0.003	0.015	0.005	0.006	0.007	0.019	0.012	0.030	0.008
Mg	2.166	0.033	2.177	0.014	2.198	0.022	1.690	0.012	2.562	0.032	3.127	0.044
Ca	0.001	0.003	0.005	0.006	0.003	0.004	0.001	0.004	0.001	0.003	0.002	0.004
Na	0.063	0.036	0.010	0.027	0.018	0.022	0.024	0.031	0.029	0.036	0.014	0.030
K	0.012	0.014	0.013	0.011	0.009	0.006	0.004	0.005	0.004	0.007	0.002	0.007
Sum	5.983	0.022	5.946	0.013	5.965	0.028	5.982	0.021	5.985	0.040	5.930	0.037
Fe/(Fe+Mg)	0.506	0.005	0.503	0.005	0.500	0.003	0.618	0.001	0.424	0.004	0.281	0.006
Mg/(Fe+Mg)	0.494	0.005	0.497	0.005	0.500	0.003	0.382	0.001	0.576	0.004	0.719	0.006
<i>Cation proportions on the basis of 10 cations</i>												
Si	2.607	0.021	2.615	0.029	2.581	0.045	2.548	0.058	2.586	0.029	2.642	0.057
Al	1.393	0.021	1.385	0.029	1.419	0.045	1.452	0.058	1.414	0.029	1.358	0.057
Sum	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000
Al	1.565	0.041	1.569	0.014	1.546	0.028	1.539	0.036	1.497	0.036	1.579	0.053
Fe ³⁺	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Cr	0.001	0.002	0.002	0.004	0.003	0.006	0.004	0.006	0.005	0.005	0.001	0.002
Ti	0.006	0.005	0.006	0.005	0.010	0.009	0.006	0.009	0.007	0.008	0.004	0.005
Fe ²⁺	2.237	0.029	2.221	0.032	2.214	0.013	2.749	0.026	1.898	0.020	1.231	0.031
Mn	0.005	0.005	0.007	0.003	0.015	0.005	0.006	0.007	0.019	0.012	0.030	0.008
Mg	2.186	0.029	2.195	0.014	2.212	0.019	1.697	0.010	2.574	0.029	3.155	0.040
Ca	0.001	0.004	0.005	0.006	0.003	0.004	0.001	0.004	0.001	0.003	0.002	0.004
Na	0.063	0.037	0.010	0.028	0.019	0.022	0.024	0.032	0.029	0.036	0.014	0.031
K	0.012	0.014	0.013	0.011	0.009	0.006	0.004	0.005	0.004	0.007	0.002	0.007
Sum	6.077	0.037	6.029	0.035	6.030	0.020	6.029	0.035	6.033	0.033	6.018	0.033
Fe/(Fe+Mg)	0.506	0.005	0.503	0.005	0.500	0.003	0.618	0.001	0.424	0.004	0.281	0.006
Mg/(Fe+Mg)	0.494	0.005	0.497	0.005	0.500	0.003	0.382	0.001	0.576	0.004	0.719	0.006

Table A5.4 Continued: Representative Chlorite Analyses

	91-21c2-III		93-10b-II		92-11-I		91-26a-II		91-26e-II		91-24a-I	
	Grt+Chl+St (Mrg+Cld)		Grt+Chl+St+Bt+Pl+Ky		Grt+Chl+St+Bt+Pl		Grt+Chl+St		Grt+Chl+St+Bt		Grt+St+Chl+Ky	
	matrix Chl		matrix Chl		matrix Chl		matrix Chl		Chl-rich area		matrix Chl	
	(5,2)	(2 σ)	(4,1)	(2 σ)	(8,2)	(2 σ)	(8,3)	(2 σ)	(4,1)	(2 σ)	(7,2)	(2 σ)
SiO ₂	24.38	0.34	25.66	0.11	24.65	0.39	25.05	0.39	24.59	0.36	25.26	0.37
Al ₂ O ₃	23.66	0.64	24.06	0.49	23.89	0.59	24.55	0.76	24.01	0.40	24.57	0.56
Cr ₂ O ₃	0.00	0.01	0.04	0.07	0.06	0.07	0.02	0.06	0.03	0.06	0.03	0.06
TiO ₂	0.04	0.07	0.07	0.04	0.09	0.06	0.08	0.03	0.10	0.04	0.05	0.06
FeO	22.62	0.20	16.20	0.07	23.56	0.85	17.59	0.16	22.58	0.19	17.30	0.33
MnO	0.10	0.03	0.22	0.16	0.08	0.07	0.30	0.11	0.02	0.07	0.25	0.06
MgO	15.69	0.32	20.42	0.44	15.52	0.68	18.94	0.70	15.99	0.43	19.62	0.53
CaO	0.01	0.03	0.01	0.03	0.02	0.05	0.01	0.05	0.01	0.04	0.01	0.03
Na ₂ O	0.10	0.22	0.15	0.34	0.20	0.24	0.15	0.22	0.11	0.31	0.10	0.20
K ₂ O	0.01	0.02	0.02	0.05	0.01	0.03	0.01	0.02	0.03	0.02	0.02	0.03
TOTAL	86.61	1.35	86.85	0.68	88.09	0.85	86.71	1.87	87.47	1.05	87.21	1.50
<i>Cation proportions on the basis of 14 oxygens</i>												
Si	2.564	0.016	2.597	0.019	2.559	0.043	2.560	0.024	2.556	0.024	2.560	0.035
Al (IV)	1.436	0.016	1.403	0.019	1.441	0.043	1.440	0.024	1.444	0.024	1.440	0.035
Sum	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000
Al (VI)	1.496	0.037	1.466	0.055	1.481	0.038	1.516	0.037	1.498	0.035	1.495	0.026
Cr	0.000	0.001	0.003	0.006	0.005	0.006	0.002	0.005	0.002	0.005	0.002	0.005
Ti	0.003	0.005	0.005	0.003	0.007	0.005	0.006	0.002	0.008	0.003	0.004	0.004
Fe	1.989	0.029	1.371	0.007	2.046	0.072	1.504	0.033	1.963	0.020	1.467	0.024
Mn	0.009	0.002	0.019	0.013	0.007	0.006	0.026	0.009	0.002	0.006	0.022	0.005
Mg	2.459	0.029	3.080	0.057	2.402	0.102	2.885	0.055	2.477	0.055	2.965	0.050
Ca	0.002	0.004	0.001	0.003	0.002	0.005	0.001	0.005	0.001	0.004	0.001	0.003
Na	0.020	0.045	0.028	0.067	0.041	0.049	0.029	0.044	0.023	0.063	0.019	0.039
K	0.001	0.002	0.002	0.006	0.002	0.003	0.001	0.002	0.004	0.002	0.002	0.004
Sum	5.978	0.043	5.977	0.070	5.992	0.044	5.970	0.040	5.977	0.043	5.977	0.044
Fe/(Fe+Mg)	0.447	0.004	0.308	0.004	0.460	0.018	0.343	0.009	0.442	0.006	0.331	0.006
Mg/(Fe+Mg)	0.553	0.004	0.692	0.004	0.540	0.018	0.657	0.009	0.558	0.006	0.669	0.006
<i>Cation proportions on the basis of 10 cations</i>												
Si	2.575	0.015	2.611	0.021	2.572	0.046	2.576	0.023	2.569	0.022	2.572	0.038
Al	1.425	0.015	1.389	0.021	1.428	0.046	1.424	0.023	1.431	0.022	1.428	0.038
Sum	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000
Al	1.521	0.042	1.497	0.054	1.510	0.047	1.550	0.038	1.526	0.044	1.520	0.036
Fe ³⁺	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Cr	0.000	0.001	0.003	0.006	0.005	0.006	0.002	0.005	0.002	0.005	0.002	0.005
Ti	0.003	0.005	0.006	0.003	0.007	0.005	0.006	0.002	0.008	0.003	0.004	0.004
Fe ²⁺	1.998	0.026	1.379	0.008	2.057	0.074	1.513	0.031	1.973	0.016	1.473	0.024
Mn	0.009	0.002	0.019	0.013	0.007	0.006	0.026	0.009	0.002	0.006	0.022	0.005
Mg	2.469	0.029	3.096	0.057	2.414	0.097	2.903	0.057	2.489	0.051	2.978	0.046
Ca	0.002	0.004	0.001	0.003	0.002	0.005	0.001	0.005	0.001	0.004	0.001	0.004
Na	0.020	0.045	0.029	0.067	0.041	0.050	0.029	0.044	0.023	0.063	0.019	0.039
K	0.001	0.002	0.002	0.006	0.002	0.003	0.001	0.002	0.004	0.002	0.002	0.004
Sum	6.023	0.048	6.032	0.071	6.045	0.049	6.031	0.048	6.028	0.068	6.022	0.043
Fe/(Fe+Mg)	0.447	0.004	0.308	0.004	0.460	0.018	0.343	0.009	0.442	0.006	0.331	0.006
Mg/(Fe+Mg)	0.553	0.004	0.692	0.004	0.540	0.018	0.657	0.009	0.558	0.006	0.669	0.006

Table A5.4 Continued: Representative Chlorite Analyses

	91-1b2-II		91-5b-II	
	Grt+Chl+St+Bt+Pl		St+Grt+Bt+Ky+Pl+Chl	
	matrix Chl		lrg. porph.	
	(3,1)	(2 σ)	(4,1)	(2 σ)
SiO ₂	24.59	0.52	25.81	0.43
Al ₂ O ₃	25.00	0.81	24.24	0.23
Cr ₂ O ₃	0.02	0.04	0.01	0.06
TiO ₂	0.17	0.32	0.02	0.04
FeO	17.17	0.56	14.99	0.39
MnO	0.25	0.10	0.32	0.07
MgO	19.23	0.80	21.48	0.13
CaO	0.02	0.05	0.01	0.02
Na ₂ O	0.10	0.09	0.11	0.17
K ₂ O	0.00	0.01	0.00	0.00
TOTAL	86.54	2.04	87.00	0.54
<i>Cation proportions on the basis of 14 oxygens</i>				
Si	2.513	0.016	2.591	0.028
Al (IV)	1.487	0.016	1.409	0.028
Sum	4.000	0.000	4.000	0.000
Al (VI)	1.524	0.090	1.458	0.011
Cr	0.002	0.003	0.001	0.005
Ti	0.013	0.025	0.002	0.003
Fe	1.467	0.019	1.258	0.034
Mn	0.021	0.009	0.027	0.006
Mg	2.930	0.068	3.215	0.017
Ca	0.002	0.006	0.001	0.002
Na	0.019	0.017	0.022	0.033
K	0.000	0.002	0.000	0.000
Sum	5.978	0.031	5.984	0.008
Fe/(Fe+Mg)	0.334	0.002	0.281	0.006
Mg/(Fe+Mg)	0.666	0.002	0.719	0.006
<i>Cation proportions on the basis of 10 cations</i>				
Si	2.524	0.019	2.601	0.035
Al	1.476	0.019	1.399	0.035
Sum	4.000	0.000	4.000	0.000
Al	1.548	0.093	1.480	0.018
Fe ³⁺	0.000	0.000	0.000	0.000
Cr	0.002	0.004	0.001	0.005
Ti	0.013	0.025	0.002	0.003
Fe ²⁺	1.474	0.018	1.263	0.033
Mn	0.021	0.009	0.027	0.006
Mg	2.942	0.066	3.227	0.018
Ca	0.002	0.006	0.001	0.002
Na	0.019	0.017	0.022	0.034
K	0.000	0.002	0.000	0.000
Sum	6.021	0.022	6.023	0.036
Fe/(Fe+Mg)	0.334	0.002	0.281	0.006
Mg/(Fe+Mg)	0.666	0.002	0.719	0.006

Table A5.5: Representative Chloritoid Analyses

	Madoc-4a-I		Madoc-7e2-III				Madoc-5e-II		Madoc-2e-V		Queens1a-I	
	Ctd+Ky+Chl+St corroded porph.		Chl+Ctd				Grt+Chl+Ctd relict Ctd adj. Grt		Grt+Chl+Bt+St+Ctd lrg. porph.		Grt+Chl+Ctd+Bt+(St) lrg. poik.	
	(7,3)	(2σ)	(2,1)	(2σ)	(2,1)	(2σ)	(4,1)	(2σ)	(3,1)	(2σ)	(8,2)	(2σ)
SiO ₂	24.95	0.25	23.43	0.17	23.46	0.00	23.81	0.28	24.25	0.15	23.92	0.88
Al ₂ O ₃	40.51	0.48	39.46	0.53	39.38	0.84	39.87	0.15	39.87	0.33	39.74	0.93
Cr ₂ O ₃	0.02	0.03	0.04	0.02	0.06	0.17	0.03	0.06	0.03	0.05	0.03	0.08
TiO ₂	0.09	0.33	0.00	0.01	0.02	0.05	0.01	0.02	0.08	0.05	0.02	0.04
FeO (total)	21.35	0.51	24.74	0.32	24.08	0.55	24.95	0.08	24.16	0.07	25.31	0.65
Fe ₂ O ₃ (calc)	0.01	0.05	1.17	0.45	1.06	0.31	1.65	0.42	0.81	0.56	0.85	0.88
FeO (calc)	21.34	0.48	23.69	0.07	23.13	0.27	23.47	0.45	23.43	0.50	24.55	0.60
MnO	1.28	0.16	0.86	0.07	0.75	0.10	0.14	0.04	0.52	0.08	0.05	0.07
MgO	3.74	0.14	1.93	0.26	2.31	0.03	2.72	0.14	2.85	0.18	2.16	0.13
CaO	0.01	0.01	0.02	0.06	0.06	0.06	0.01	0.04	0.02	0.05	0.02	0.03
TOTAL	91.94	0.72	90.50	1.14	90.12	0.26	91.54	0.31	91.77	0.04	91.24	1.48
<i>Cation proportions on the basis of 6 oxygens</i>												
Si	1.024	0.011	0.997	0.006	0.999	0.006	0.998	0.008	1.010	0.006	1.007	0.032
Al (IV)	0.000	0.000	0.003	0.006	0.002	0.004	0.003	0.007	0.000	0.000	0.002	0.005
Sum	1.024	0.011	1.000	0.000	1.001	0.001	1.000	0.001	1.010	0.006	1.008	0.030
Al (VI)	1.960	0.016	1.976	0.006	1.975	0.024	1.966	0.006	1.957	0.014	1.969	0.028
Cr	0.001	0.001	0.002	0.001	0.002	0.006	0.001	0.002	0.001	0.002	0.001	0.003
Ti	0.003	0.010	0.000	0.000	0.001	0.001	0.000	0.001	0.002	0.001	0.001	0.001
Sum	1.963	0.008	1.978	0.007	1.977	0.017	1.968	0.004	1.960	0.015	1.971	0.028
Ti	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Fe	0.733	0.017	0.880	0.000	0.858	0.024	0.874	0.003	0.842	0.003	0.891	0.021
Mn	0.045	0.006	0.031	0.003	0.027	0.003	0.005	0.001	0.019	0.003	0.002	0.002
Mg	0.229	0.008	0.123	0.016	0.147	0.001	0.170	0.008	0.177	0.011	0.136	0.008
Ca	0.000	0.001	0.001	0.003	0.003	0.003	0.001	0.002	0.001	0.002	0.001	0.001
Sum	1.006	0.023	1.035	0.010	1.034	0.017	1.050	0.007	1.038	0.016	1.029	0.020
Fe/(Fe+Mg)	0.762	0.006	0.878	0.014	0.854	0.005	0.837	0.007	0.827	0.008	0.868	0.008
Mg/(Fe+Mg)	0.238	0.006	0.122	0.014	0.146	0.005	0.163	0.007	0.173	0.008	0.132	0.008
<i>Cation proportions on the basis of 4 cations</i>												
Si	1.025	0.014	0.994	0.006	0.996	0.006	0.994	0.009	1.008	0.007	1.005	0.037
Al (IV)	0.000	0.000	0.006	0.006	0.004	0.006	0.007	0.009	0.000	0.000	0.003	0.007
Sum	1.025	0.014	1.000	0.000	1.000	0.000	1.000	0.000	1.008	0.007	1.008	0.033
Al (VI)	1.963	0.013	1.967	0.006	1.967	0.024	1.954	0.007	1.953	0.015	1.964	0.018
Fe ₃₊	0.000	0.002	0.038	0.013	0.034	0.011	0.052	0.013	0.025	0.017	0.027	0.028
Cr	0.001	0.001	0.002	0.001	0.002	0.006	0.001	0.002	0.001	0.002	0.001	0.003
Ti	0.003	0.010	0.000	0.000	0.001	0.001	0.000	0.000	0.002	0.001	0.000	0.001
Sum	1.967	0.009	2.006	0.006	2.003	0.006	2.007	0.009	1.982	0.015	1.992	0.045
Ti	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.001
Fe ₂₊	0.734	0.013	0.840	0.014	0.821	0.014	0.819	0.016	0.815	0.018	0.862	0.022
Mn	0.045	0.005	0.031	0.003	0.027	0.003	0.005	0.001	0.019	0.003	0.002	0.002
Mg	0.229	0.008	0.122	0.014	0.146	0.000	0.169	0.008	0.177	0.011	0.135	0.008
Ca	0.000	0.001	0.001	0.003	0.003	0.001	0.001	0.002	0.001	0.002	0.001	0.001
Sum	1.008	0.018	0.994	0.006	0.997	0.010	0.994	0.010	1.011	0.007	1.000	0.017
Fe/(Fe+Mg)	0.762	0.006	0.873	0.015	0.849	0.002	0.829	0.009	0.822	0.012	0.865	0.009
Mg/(Fe+Mg)	0.238	0.006	0.127	0.015	0.151	0.002	0.171	0.009	0.178	0.012	0.135	0.009

Table A5.5 Continued: Representative Chloritoid Analyses

	91-27e-I		93-13b-I		90-10d-I		90-10g-I		93-16b-I			
	Grt+Chl+Ctd		Grt+Chl+St+(Ctd)		Grt+Chl+Ctd		Ctd+Chl		Grt+Chl+(Relict Ctd)			
	corroded matrix Ctd		relict matrix Ctd		Ctd incl in Grt		porph. core		relict matrix Ctd		lrg. armoured XI	
	(3,1)	(2σ)	(9,3)	(2σ)	(2,1)	(2σ)	(2,1)	(2σ)	(3,1)	(2σ)	(4,1)	(2σ)
SiO ₂	23.66	0.12	24.96	2.60	23.39	0.03	23.65	0.02	24.63	0.10	24.51	0.39
Al ₂ O ₃	39.56	0.53	39.55	1.82	39.49	0.49	39.58	0.09	39.57	0.15	40.28	0.41
Cr ₂ O ₃	0.02	0.06	0.02	0.05	0.03	0.03	0.06	0.04	0.07	0.04	0.04	0.05
TiO ₂	0.02	0.03	0.04	0.06	0.03	0.02	0.05	0.09	0.02	0.02	0.02	0.04
FeO (total)	25.15	0.25	21.93	1.17	23.85	0.11	25.10	0.24	23.71	0.16	23.86	0.34
Fe ₂ O ₃ (calc)	1.16	0.54	0.30	0.75	1.97	0.40	1.17	0.58	0.00	0.00	0.14	0.35
FeO (calc)	24.10	0.28	21.66	0.97	22.08	0.25	24.06	0.27	23.71	0.17	23.73	0.11
MnO	0.46	0.13	1.55	0.15	1.20	0.03	0.26	0.17	0.52	0.15	0.48	0.07
MgO	2.08	0.03	3.01	0.24	2.60	0.17	2.24	0.09	2.58	0.19	2.79	0.15
CaO	0.02	0.05	0.02	0.03	0.05	0.01	0.01	0.00	0.00	0.01	0.03	0.06
TOTAL	90.97	0.77	91.08	1.30	90.64	0.71	90.95	0.52	91.09	0.25	92.00	0.81
<i>Cation proportions on the basis of 6 oxygens</i>												
Si	1.001	0.010	1.039	0.101	0.992	0.007	1.000	0.004	1.030	0.002	1.015	0.011
Al (IV)	0.002	0.006	0.000	0.000	0.009	0.007	0.001	0.003	0.000	0.000	0.000	0.000
Sum	1.002	0.004	1.039	0.101	1.000	0.000	1.001	0.001	1.030	0.002	1.015	0.011
Al (VI)	1.970	0.006	1.941	0.098	1.965	0.001	1.971	0.013	1.951	0.005	1.967	0.013
Cr	0.001	0.002	0.001	0.001	0.001	0.000	0.002	0.001	0.002	0.001	0.002	0.001
Ti	0.001	0.001	0.001	0.002	0.001	0.000	0.002	0.003	0.000	0.001	0.001	0.001
Sum	1.972	0.008	1.943	0.096	1.967	0.001	1.974	0.008	1.954	0.006	1.969	0.012
Ti	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Fe	0.889	0.006	0.764	0.043	0.846	0.004	0.887	0.006	0.829	0.003	0.827	0.013
Mn	0.017	0.005	0.055	0.005	0.043	0.000	0.009	0.006	0.018	0.005	0.017	0.003
Mg	0.131	0.002	0.187	0.015	0.165	0.010	0.141	0.006	0.161	0.012	0.173	0.009
Ca	0.001	0.002	0.001	0.001	0.003	0.001	0.001	0.000	0.000	0.000	0.001	0.003
Sum	1.038	0.010	1.007	0.059	1.056	0.004	1.038	0.017	1.008	0.010	1.017	0.009
Fe/(Fe+Mg)	0.872	0.002	0.803	0.007	0.837	0.009	0.863	0.004	0.837	0.010	0.827	0.009
Mg/(Fe+Mg)	0.128	0.002	0.197	0.007	0.163	0.009	0.137	0.004	0.163	0.010	0.173	0.009
<i>Cation proportions on the basis of 4 cations</i>												
Si	0.998	0.012	1.042	0.116	0.986	0.008	0.996	0.006	1.032	0.002	1.015	0.012
Al (IV)	0.003	0.010	0.000	0.001	0.014	0.008	0.004	0.006	0.000	0.000	0.000	0.000
Sum	1.001	0.001	1.043	0.116	1.000	0.000	1.000	0.000	1.032	0.002	1.015	0.012
Al (VI)	1.963	0.007	1.946	0.074	1.949	0.001	1.962	0.018	1.954	0.008	1.966	0.011
Fe ₃₊	0.037	0.017	0.009	0.023	0.063	0.013	0.037	0.017	0.000	0.000	0.004	0.011
Cr	0.001	0.002	0.001	0.001	0.001	0.000	0.002	0.001	0.002	0.001	0.002	0.001
Ti	0.000	0.001	0.001	0.002	0.000	0.000	0.002	0.001	0.000	0.001	0.001	0.001
Sum	2.001	0.009	1.958	0.087	2.012	0.011	2.002	0.001	1.957	0.009	1.972	0.019
Ti	0.000	0.001	0.000	0.001	0.001	0.000	0.001	0.001	0.000	0.000	0.000	0.000
Fe ₂₊	0.850	0.013	0.756	0.027	0.779	0.016	0.848	0.013	0.831	0.003	0.822	0.003
Mn	0.017	0.005	0.055	0.005	0.043	0.001	0.009	0.006	0.018	0.005	0.017	0.003
Mg	0.131	0.002	0.188	0.013	0.164	0.010	0.141	0.004	0.161	0.012	0.173	0.009
Ca	0.001	0.002	0.001	0.001	0.003	0.001	0.001	0.000	0.000	0.000	0.001	0.003
Sum	0.999	0.009	1.000	0.036	0.988	0.008	0.999	0.001	1.010	0.008	1.013	0.008
Fe/(Fe+Mg)	0.867	0.000	0.801	0.010	0.826	0.012	0.858	0.006	0.837	0.010	0.827	0.008
Mg/(Fe+Mg)	0.133	0.000	0.199	0.010	0.174	0.012	0.142	0.006	0.163	0.010	0.173	0.008

Table A5.5 Continued: Representative Chloritoid Analyses

	92-6c-III		92-6f1-II		93-26e-I		93-26g-I		93-24a-II		92-8d-I	
	Grt+Cld+Bt+(Chi) crs-gr. porphs.		Grt+Chi+Cld+Bt porph. sub-pll-fol.		Grt+Chi+Cld+Bt+St+Mrg med-gr. Cld porph.		Grt+Chi+Bt+St+Mrg incl in Grt		Grt+Chi+Cld+Mrg hi-Fe matrix Cld		Grt+Chi+Cld+Bt+St+Mrg matrix Cld in Qtz	
	(13,3)	(2σ)	(3,1)	(2σ)	(3,1)	(2σ)	(4,1)	(2σ)	(4,2)	(2σ)	(3,1)	(2σ)
SiO ₂	24.69	0.35	23.77	0.41	23.43	0.13	24.08	0.25	24.47	0.41	24.10	0.46
Al ₂ O ₃	40.06	0.32	40.68	0.14	39.69	0.47	39.66	0.18	39.65	0.45	40.41	0.22
Cr ₂ O ₃	0.03	0.07	0.03	0.03	0.06	0.05	0.05	0.08	0.03	0.05	0.03	0.07
TiO ₂	0.03	0.06	0.02	0.04	0.01	0.02	0.04	0.08	0.03	0.06	0.04	0.05
FeO (total)	25.94	0.38	25.38	0.34	24.95	0.44	25.25	0.42	23.88	0.37	23.69	0.17
Fe ₂ O ₃ (calc)	0.05	0.19	0.76	0.99	1.47	0.30	0.91	0.69	0.04	0.10	0.86	0.36
FeO (calc)	25.89	0.32	24.70	0.58	23.62	0.23	24.44	0.34	23.85	0.40	22.92	0.48
MnO	0.12	0.07	0.10	0.05	0.53	0.15	0.83	0.16	0.35	0.20	0.67	0.07
MgO	1.75	0.12	2.03	0.19	2.17	0.07	1.93	0.09	2.77	0.07	2.94	0.03
CaO	0.06	0.10	0.01	0.03	0.00	0.00	0.09	0.05	0.03	0.04	0.02	0.04
TOTAL	92.67	0.73	92.03	0.56	90.83	0.34	91.93	0.19	91.20	0.79	91.89	0.81
<i>Cation proportions on the basis of 6 oxygens</i>												
Si	1.023	0.012	0.991	0.015	0.992	0.003	1.009	0.009	1.023	0.013	1.001	0.010
Al (IV)	0.000	0.000	0.009	0.015	0.008	0.003	0.000	0.000	0.000	0.000	0.002	0.006
Sum	1.023	0.012	1.000	0.000	1.000	0.000	1.009	0.009	1.023	0.013	1.002	0.005
Al (VI)	1.957	0.010	1.991	0.010	1.974	0.011	1.959	0.009	1.954	0.020	1.976	0.011
Cr	0.001	0.003	0.001	0.000	0.002	0.002	0.002	0.003	0.001	0.002	0.001	0.002
Ti	0.001	0.002	0.000	0.001	0.000	0.001	0.001	0.003	0.001	0.002	0.001	0.001
Sum	1.959	0.011	1.992	0.009	1.976	0.009	1.962	0.012	1.955	0.019	1.978	0.010
Ti	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Fe	0.899	0.012	0.885	0.012	0.884	0.019	0.885	0.016	0.835	0.008	0.823	0.002
Mn	0.004	0.003	0.004	0.002	0.019	0.005	0.030	0.006	0.012	0.008	0.023	0.002
Mg	0.108	0.007	0.126	0.011	0.137	0.004	0.121	0.006	0.173	0.004	0.182	0.000
Ca	0.002	0.004	0.000	0.001	0.000	0.000	0.004	0.003	0.001	0.002	0.001	0.002
Sum	1.014	0.014	1.015	0.020	1.039	0.012	1.039	0.017	1.021	0.009	1.029	0.002
Fe/(Fe+Mg)	0.893	0.007	0.875	0.008	0.866	0.005	0.880	0.006	0.829	0.002	0.819	0.000
Mg/(Fe+Mg)	0.107	0.007	0.125	0.008	0.134	0.005	0.120	0.006	0.171	0.002	0.181	0.000
<i>Cation proportions on the basis of 4 cations</i>												
Si	1.024	0.013	0.989	0.017	0.988	0.003	1.007	0.010	1.023	0.014	0.998	0.011
Al (IV)	0.000	0.000	0.011	0.017	0.012	0.003	0.000	0.000	0.000	0.000	0.003	0.009
Sum	1.024	0.013	1.000	0.000	1.000	0.000	1.007	0.010	1.023	0.014	1.001	0.003
Al (VI)	1.959	0.009	1.985	0.017	1.962	0.013	1.955	0.011	1.954	0.019	1.970	0.006
Fe ³⁺	0.002	0.006	0.024	0.031	0.047	0.010	0.029	0.022	0.001	0.003	0.027	0.011
Cr	0.001	0.003	0.001	0.000	0.002	0.002	0.002	0.003	0.001	0.002	0.001	0.002
Ti	0.001	0.002	0.000	0.000	0.000	0.000	0.001	0.003	0.001	0.002	0.001	0.002
Sum	1.962	0.012	2.010	0.014	2.011	0.002	1.986	0.019	1.957	0.020	1.999	0.013
Ti	0.000	0.000	0.000	0.001	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.001
Fe ²⁺	0.898	0.010	0.860	0.023	0.833	0.011	0.854	0.012	0.834	0.008	0.794	0.011
Mn	0.004	0.003	0.004	0.002	0.019	0.005	0.030	0.006	0.012	0.008	0.023	0.002
Mg	0.108	0.007	0.126	0.011	0.137	0.004	0.120	0.006	0.173	0.004	0.181	0.001
Ca	0.002	0.004	0.000	0.001	0.000	0.000	0.004	0.003	0.001	0.002	0.001	0.002
Sum	1.013	0.008	0.991	0.014	0.989	0.003	1.008	0.009	1.020	0.009	1.000	0.011
Fe/(Fe+Mg)	0.893	0.007	0.872	0.013	0.859	0.005	0.877	0.007	0.829	0.003	0.814	0.002
Mg/(Fe+Mg)	0.107	0.007	0.128	0.013	0.141	0.005	0.123	0.007	0.171	0.003	0.186	0.002

Table A5.5 Continued: Representative Chloritoid Analyses

	92-42c-I		93-18a-I		92-41a-I		92-41d-I		93-20f-I		92-10a-II	
	Grt+Ctd+Bt matrix Ctd		Grt+Ctd+Bt matrix Ctd		Grt+Ctd+Bt matrix Ctd		Chl+Ctd+Mrg Ctd porphs.		Grt+Ctd+Bt matrix Ctd		Ctd+St+Grt+Bt Ctd porph rim	
	(6,2)	(2 σ)	(4,1)	(2 σ)	(6,2)	(2 σ)	(11,3)	(2 σ)	(9,3)	(2 σ)	(4,2)	(2 σ)
SiO ₂	24.18	0.30	24.45	0.20	23.75	0.46	23.67	0.40	24.43	0.29	23.75	0.95
Al ₂ O ₃	40.09	0.41	39.79	0.84	40.12	0.26	40.04	0.44	40.00	0.34	40.20	0.73
Cr ₂ O ₃	0.02	0.03	0.02	0.05	0.05	0.07	0.04	0.05	0.04	0.07	0.03	0.07
TiO ₂	0.04	0.04	0.04	0.07	0.00	0.01	0.01	0.05	0.02	0.06	0.02	0.04
FeO (total)	25.31	0.13	25.34	0.26	25.09	0.46	25.53	0.50	26.15	0.30	25.96	0.42
Fe ₂ O ₃ (calc)	0.11	0.20	0.00	0.00	0.66	0.71	1.18	0.98	0.00	0.00	0.76	1.62
FeO (calc)	25.21	0.14	25.34	0.26	24.50	0.39	24.47	0.48	26.15	0.30	25.28	1.30
MnO	0.08	0.08	0.30	0.08	0.10	0.07	0.18	0.08	0.01	0.03	0.20	0.08
MgO	2.03	0.07	1.79	0.07	2.11	0.13	2.04	0.11	1.40	0.08	1.62	0.04
CaO	0.02	0.04	0.00	0.00	0.02	0.03	0.01	0.03	0.02	0.03	0.03	0.05
TOTAL	91.78	0.62	91.74	1.17	91.23	0.83	91.53	0.85	92.07	0.63	91.83	1.46
<i>Cation proportions on the basis of 6 oxygens</i>												
Si	1.010	0.008	1.023	0.011	0.999	0.014	0.995	0.016	1.021	0.009	0.997	0.021
Al (IV)	0.000	0.000	0.000	0.000	0.004	0.007	0.006	0.011	0.000	0.000	0.006	0.015
Sum	1.010	0.008	1.023	0.011	1.002	0.009	1.001	0.008	1.021	0.009	1.003	0.006
Al (VI)	1.974	0.012	1.962	0.015	1.984	0.013	1.977	0.007	1.969	0.014	1.982	0.009
Cr	0.001	0.001	0.001	0.002	0.002	0.002	0.001	0.002	0.002	0.002	0.001	0.003
Ti	0.001	0.002	0.001	0.002	0.000	0.000	0.000	0.002	0.001	0.002	0.001	0.002
Sum	1.976	0.011	1.964	0.015	1.986	0.012	1.979	0.007	1.971	0.015	1.984	0.007
Ti	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Fe	0.885	0.007	0.887	0.011	0.882	0.012	0.897	0.016	0.913	0.006	0.911	0.024
Mn	0.003	0.003	0.011	0.003	0.004	0.003	0.006	0.003	0.000	0.001	0.007	0.003
Mg	0.126	0.004	0.112	0.003	0.132	0.008	0.128	0.007	0.087	0.004	0.102	0.004
Ca	0.001	0.002	0.000	0.000	0.001	0.002	0.000	0.002	0.001	0.002	0.002	0.003
Sum	1.014	0.006	1.009	0.012	1.019	0.017	1.032	0.019	1.002	0.010	1.022	0.032
Fe/(Fe+Mg)	0.875	0.004	0.888	0.002	0.870	0.006	0.875	0.005	0.913	0.004	0.900	0.002
Mg/(Fe+Mg)	0.125	0.004	0.112	0.002	0.130	0.006	0.125	0.005	0.087	0.004	0.100	0.002
<i>Cation proportions on the basis of 4 cations</i>												
Si	1.010	0.009	1.024	0.012	0.997	0.016	0.992	0.018	1.022	0.010	0.995	0.025
Al (IV)	0.000	0.000	0.000	0.000	0.005	0.010	0.009	0.013	0.000	0.000	0.008	0.019
Sum	1.010	0.009	1.024	0.012	1.002	0.009	1.001	0.008	1.022	0.010	1.003	0.006
Al (VI)	1.974	0.011	1.964	0.015	1.980	0.012	1.968	0.012	1.972	0.014	1.976	0.021
Fe ³⁺	0.004	0.006	0.000	0.000	0.021	0.022	0.037	0.031	0.000	0.000	0.024	0.051
Cr	0.001	0.001	0.001	0.002	0.002	0.002	0.001	0.002	0.002	0.002	0.001	0.003
Ti	0.001	0.002	0.001	0.002	0.000	0.000	0.000	0.000	0.001	0.002	0.001	0.002
Sum	1.979	0.013	1.966	0.015	2.002	0.020	2.006	0.022	1.974	0.015	2.002	0.032
Ti	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.002	0.000	0.000	0.000	0.001
Fe ²⁺	0.881	0.004	0.887	0.010	0.860	0.014	0.857	0.020	0.915	0.006	0.886	0.033
Mn	0.003	0.003	0.011	0.003	0.004	0.003	0.006	0.003	0.000	0.001	0.007	0.003
Mg	0.126	0.004	0.112	0.003	0.132	0.007	0.127	0.006	0.088	0.005	0.101	0.003
Ca	0.001	0.002	0.000	0.000	0.001	0.002	0.000	0.002	0.001	0.002	0.002	0.003
Sum	1.010	0.006	1.010	0.011	0.996	0.013	0.992	0.016	1.004	0.009	0.996	0.025
Fe/(Fe+Mg)	0.875	0.004	0.888	0.003	0.867	0.007	0.871	0.007	0.913	0.005	0.897	0.006
Mg/(Fe+Mg)	0.125	0.004	0.112	0.003	0.133	0.007	0.129	0.007	0.087	0.005	0.103	0.006

Table A5.5 Continued: Representative Chloritoid Analyses

	90-19a-I		92-27a-II		92-28a-I		91-21c2-III				90-4h-I	
	Ctd+St+Grt+Bt+Pl lrg. porph. - Grt.		Ctd+St+Grt+Bt rim lrg. poik.		Ctd+St+Grt+Bt lrg. porph.		Grt+Chl+St (Mrg+Ctd incl)				St+Grt+Bt+Pl+(Ctd) incl in Grt	
	(8,1)	(2σ)	(3,1)	(2σ)	(8,1)	(2σ)	(2,1)	(2σ)	(2,1)	(2σ)	n=3	(2σ)
SiO ₂	23.62	0.16	23.67	0.26	23.75	0.31	23.76	0.04	23.62	0.03	24.04	0.43
Al ₂ O ₃	39.87	0.30	40.41	0.33	39.71	0.47	40.09	0.04	40.29	1.09	39.95	0.32
Cr ₂ O ₃	n.d.	n.d.	0.04	0.07	0.02	0.05	0.05	0.01	0.07	0.04	n.d.	n.d.
TiO ₂	0.05	0.09	0.01	0.03	0.02	0.05	0.01	0.02	0.03	0.01	0.07	0.12
FeO (total)	25.55	0.47	25.55	0.09	25.03	0.26	22.55	0.20	22.79	0.16	23.37	0.13
Fe ₂ O ₃ (calc)	1.24	0.65	0.82	0.28	0.69	0.50	1.75	0.04	1.46	0.13	1.79	0.70
FeO (calc)	24.44	0.38	24.81	0.16	24.41	0.36	20.98	0.16	21.48	0.04	21.76	0.50
MnO	0.22	0.11	0.02	0.05	0.04	0.06	0.58	0.07	0.78	0.03	0.87	0.12
MgO	2.04	0.10	1.94	0.03	2.22	0.12	3.78	0.00	3.32	0.03	3.43	0.04
CaO	0.00	0.01	0.02	0.04	0.01	0.03	0.09	0.04	0.07	0.01	0.04	0.06
TOTAL	91.35	0.75	91.66	0.30	90.81	0.77	90.90	0.07	90.95	1.15	91.77	0.23
<i>Cation proportions on the basis of 6 oxygens</i>												
Si	0.995	0.001	0.992	0.008	1.003	0.009	0.994	0.001	0.989	0.014	1.000	0.014
Al (IV)	0.005	0.001	0.008	0.008	0.001	0.002	0.007	0.001	0.011	0.014	0.003	0.005
Sum	1.000	0.000	1.000	0.000	1.004	0.008	1.000	0.000	1.000	0.000	1.003	0.009
Al (VI)	1.975	0.011	1.989	0.008	1.976	0.009	1.969	0.001	1.977	0.013	1.956	0.016
Cr	n.d.	n.d.	0.001	0.002	0.001	0.002	0.002	0.000	0.003	0.001	n.d.	n.d.
Ti	0.002	0.003	0.000	0.001	0.001	0.002	0.000	0.000	0.001	0.000	0.002	0.004
Sum	1.977	0.012	1.990	0.005	1.978	0.010	1.971	0.001	1.980	0.011	1.958	0.013
Ti	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Fe	0.901	0.014	0.895	0.008	0.884	0.012	0.789	0.007	0.798	0.006	0.813	0.008
Mn	0.008	0.003	0.001	0.002	0.001	0.002	0.021	0.001	0.028	0.001	0.031	0.004
Mg	0.128	0.006	0.121	0.002	0.140	0.007	0.236	0.000	0.208	0.004	0.213	0.003
Ca	0.000	0.000	0.001	0.002	0.001	0.001	0.004	0.001	0.003	0.000	0.002	0.002
Sum	1.036	0.018	1.018	0.008	1.026	0.010	1.049	0.004	1.036	0.011	1.058	0.005
Fe/(Fe+Mg)	0.876	0.004	0.881	0.002	0.863	0.007	0.770	0.002	0.794	0.002	0.793	0.001
Mg/(Fe+Mg)	0.124	0.004	0.119	0.002	0.137	0.007	0.230	0.002	0.206	0.002	0.207	0.001
<i>Cation proportions on the basis of 4 cations</i>												
Si	0.992	0.002	0.990	0.009	1.001	0.010	0.989	0.001	0.985	0.014	0.995	0.016
Al (IV)	0.008	0.002	0.010	0.009	0.001	0.004	0.012	0.001	0.015	0.014	0.006	0.011
Sum	1.000	0.000	1.000	0.000	1.003	0.007	1.000	0.000	1.000	0.000	1.001	0.005
Al (VI)	1.965	0.016	1.982	0.010	1.972	0.007	1.955	0.001	1.966	0.013	1.943	0.007
Fe ³⁺	0.039	0.020	0.026	0.009	0.022	0.016	0.055	0.001	0.046	0.004	0.056	0.021
Cr	n.d.	n.d.	0.001	0.002	0.001	0.002	0.002	0.000	0.003	0.001	n.d.	n.d.
Ti	0.000	0.000	0.000	0.000	0.001	0.002	0.000	0.000	0.000	0.000	0.001	0.005
Sum	2.004	0.006	2.009	0.006	1.995	0.016	2.011	0.000	2.014	0.016	2.000	0.022
Ti	0.002	0.003	0.000	0.001	0.000	0.000	0.000	0.000	0.001	0.000	0.001	0.003
Fe ²⁺	0.858	0.010	0.868	0.002	0.861	0.011	0.730	0.006	0.749	0.008	0.754	0.016
Mn	0.008	0.003	0.001	0.002	0.001	0.002	0.021	0.001	0.028	0.001	0.031	0.004
Mg	0.128	0.006	0.121	0.002	0.140	0.007	0.235	0.000	0.207	0.004	0.211	0.003
Ca	0.000	0.000	0.001	0.002	0.001	0.001	0.004	0.001	0.003	0.000	0.002	0.002
Sum	0.996	0.008	0.991	0.007	1.002	0.010	0.989	0.003	0.987	0.014	0.998	0.019
Fe/(Fe+Mg)	0.870	0.007	0.877	0.002	0.860	0.007	0.756	0.001	0.784	0.002	0.781	0.006
Mg/(Fe+Mg)	0.130	0.007	0.123	0.002	0.140	0.007	0.244	0.001	0.216	0.002	0.219	0.006

Table A5.6: Representative Garnet Analyses

	Madoc-7b2-III Grt+Chl+Bt				Madoc-5a-II Grt+Chl+Ctd				Madoc-2a-V Grt+Chl+Bt+St+Pl+(Rel.Ctd)				Queens-1a-I Grt+Chl+Ctd+Bt+Pl+tr.St			
	Rim		Core		Rim		Core		Rim		Core		Rim		Core	
	n=2	(2σ)	n=2	(2σ)	n=2	(2σ)	n=4	(2σ)	n=2	(2σ)	n=3	(2σ)	n=2	(2σ)	n=4	(2σ)
SiO ₂	36.35	0.21	35.95	0.28	36.70	0.08	36.58	0.20	36.87	0.29	36.58	0.15	36.45	0.05	36.53	0.41
Al ₂ O ₃	20.67	0.50	20.62	0.27	20.66	0.08	20.58	0.28	21.19	0.39	20.89	0.25	20.82	0.25	20.61	0.27
Cr ₂ O ₃	0.01	0.02	0.02	0.06	0.01	0.01	0.04	0.07	0.07	0.10	0.05	0.02	0.06	0.01	0.01	0.03
TiO ₂	0.00	0.00	0.13	0.17	0.04	0.00	0.09	0.02	0.01	0.00	0.06	0.09	0.03	0.01	0.07	0.05
FeO	39.54	0.63	29.10	1.11	36.40	0.34	22.66	1.06	33.40	1.06	30.71	0.33	38.08	0.38	34.55	2.09
MnO	0.08	0.15	8.44	0.05	1.95	0.32	15.77	0.07	5.64	0.27	8.21	0.22	0.65	0.01	2.97	0.08
MgO	1.46	0.07	0.69	0.07	1.82	0.05	0.69	0.12	2.17	0.09	1.27	0.09	1.67	0.06	1.21	0.20
CaO	2.29	0.06	4.58	0.12	2.86	0.36	4.15	1.17	2.02	0.18	2.74	0.02	2.83	0.04	4.41	1.91
TOTAL	100.39	1.62	99.53	1.69	100.44	1.25	100.55	0.14	101.37	1.26	100.51	0.76	100.59	0.67	100.34	0.55
<i>Cation proportions on the basis of 12 oxygens</i>																
Si	2.967	0.015	2.955	0.017	2.979	0.010	2.976	0.015	2.961	0.011	2.972	0.017	2.961	0.012	2.971	0.015
Al	0.033	0.015	0.045	0.017	0.021	0.010	0.024	0.015	0.039	0.011	0.028	0.017	0.039	0.012	0.029	0.015
Sum	3.000	0.000	3.000	0.000	3.000	0.000	3.000	0.000	3.000	0.000	3.000	0.000	3.000	0.000	3.000	0.000
Al	1.956	0.012	1.952	0.018	1.954	0.020	1.949	0.016	1.967	0.002	1.972	0.005	1.954	0.000	1.947	0.012
Cr	0.000	0.001	0.001	0.004	0.000	0.001	0.002	0.004	0.005	0.007	0.003	0.001	0.004	0.001	0.001	0.002
Ti	0.000	0.000	0.008	0.011	0.003	0.000	0.005	0.001	0.001	0.000	0.004	0.005	0.002	0.001	0.004	0.003
Sum	1.956	0.013	1.962	0.025	1.957	0.021	1.957	0.019	1.972	0.004	1.979	0.006	1.960	0.002	1.951	0.010
Fe	2.699	0.015	2.000	0.049	2.471	0.020	1.542	0.072	2.243	0.045	2.086	0.012	2.587	0.011	2.350	0.159
Mn	0.006	0.010	0.587	0.011	0.134	0.022	1.087	0.005	0.384	0.023	0.565	0.012	0.044	0.001	0.204	0.007
Mg	0.177	0.010	0.085	0.007	0.220	0.006	0.084	0.014	0.260	0.008	0.154	0.011	0.202	0.008	0.147	0.025
Ca	0.200	0.007	0.404	0.006	0.249	0.031	0.362	0.102	0.174	0.018	0.238	0.004	0.246	0.002	0.384	0.164
Sum Fe to Ca	3.082	0.013	3.075	0.051	3.074	0.036	3.074	0.025	3.061	0.012	3.044	0.019	3.079	0.004	3.085	0.015
Fe/(Fe+Mg)	0.938	0.004	0.959	0.002	0.918	0.002	0.948	0.007	0.896	0.001	0.931	0.004	0.928	0.003	0.941	0.008
Mg/(Fe+Mg)	0.062	0.004	0.041	0.002	0.082	0.002	0.052	0.007	0.104	0.001	0.069	0.004	0.072	0.003	0.059	0.008
Fe/(Fe+Mn+Mg+Ca)	0.876	0.008	0.650	0.005	0.804	0.003	0.502	0.027	0.733	0.012	0.686	0.000	0.840	0.003	0.762	0.050
Mn/(Fe+Mn+Mg+Ca)	0.002	0.003	0.191	0.007	0.044	0.008	0.353	0.003	0.125	0.008	0.186	0.004	0.014	0.000	0.066	0.002
Mg/(Fe+Mn+Mg+Ca)	0.057	0.003	0.028	0.002	0.071	0.001	0.027	0.005	0.085	0.002	0.051	0.003	0.068	0.003	0.047	0.008
Ca/(Fe+Mn+Mg+Ca)	0.065	0.002	0.131	0.000	0.081	0.009	0.118	0.032	0.057	0.006	0.078	0.002	0.080	0.001	0.124	0.053
<i>Cation proportions on the basis of 8 cations</i>																
Si	2.953	0.015	2.941	0.026	2.967	0.016	2.964	0.016	2.949	0.014	2.963	0.022	2.946	0.014	2.958	0.018
Al	0.047	0.015	0.059	0.026	0.033	0.016	0.036	0.016	0.051	0.014	0.037	0.022	0.054	0.014	0.042	0.018
Sum	3.000	0.000	3.000	0.000	3.000	0.000	3.000	0.000	3.000	0.000	3.000	0.000	3.000	0.000	3.000	0.000
Al	1.932	0.012	1.929	0.034	1.935	0.029	1.930	0.019	1.947	0.003	1.958	0.011	1.930	0.003	1.924	0.015
Cr	0.000	0.001	0.001	0.004	0.000	0.001	0.002	0.004	0.005	0.007	0.003	0.001	0.004	0.001	0.001	0.002
Fe ₃₊	0.114	0.002	0.112	0.077	0.092	0.046	0.093	0.023	0.099	0.023	0.068	0.039	0.117	0.015	0.109	0.022
Ti	0.000	0.000	0.008	0.011	0.003	0.000	0.005	0.001	0.001	0.000	0.004	0.005	0.002	0.001	0.004	0.003
Sum	2.047	0.015	2.051	0.037	2.030	0.016	2.030	0.017	2.051	0.014	2.033	0.026	2.052	0.014	2.038	0.015
Fe ₂₊	2.572	0.012	1.879	0.035	2.369	0.030	1.443	0.092	2.135	0.019	2.013	0.031	2.458	0.006	2.230	0.142
Mn	0.006	0.010	0.585	0.013	0.134	0.022	1.083	0.004	0.382	0.023	0.564	0.012	0.044	0.001	0.203	0.007
Mg	0.176	0.010	0.084	0.007	0.219	0.006	0.084	0.014	0.259	0.008	0.153	0.011	0.201	0.008	0.146	0.024
Ca	0.199	0.007	0.402	0.004	0.248	0.031	0.360	0.101	0.173	0.018	0.238	0.004	0.245	0.002	0.382	0.163
Sum Fe to Ca	2.953	0.015	2.949	0.037	2.970	0.016	2.970	0.017	2.949	0.014	2.967	0.026	2.948	0.014	2.962	0.015
Fe/(Fe+Mg)	0.936	0.004	0.957	0.004	0.915	0.003	0.945	0.007	0.892	0.002	0.929	0.005	0.924	0.003	0.939	0.009
Mg/(Fe+Mg)	0.064	0.004	0.043	0.004	0.085	0.003	0.055	0.007	0.108	0.002	0.071	0.005	0.076	0.003	0.061	0.009
Fe/(Fe+Mn+Mg+Ca)	0.871	0.009	0.637	0.004	0.798	0.006	0.486	0.031	0.724	0.010	0.678	0.005	0.834	0.002	0.753	0.051
Mn/(Fe+Mn+Mg+Ca)	0.002	0.003	0.198	0.002	0.045	0.007	0.365	0.003	0.130	0.007	0.190	0.004	0.015	0.000	0.069	0.002
Mg/(Fe+Mn+Mg+Ca)	0.060	0.003	0.029	0.003	0.074	0.002	0.028	0.005	0.088	0.003	0.052	0.004	0.068	0.002	0.049	0.008
Ca/(Fe+Mn+Mg+Ca)	0.067	0.002	0.136	0.003	0.084	0.011	0.121	0.034	0.059	0.006	0.080	0.001	0.083	0.001	0.129	0.055

Table A5.6 Continued: Representative Garnet Analyses

	91-27a-I Grt+Chl				91-27e-I Grt+Chl+Ctd				93-13b-I Grt+Chl+St+(Rel.Ctd)				90-10d-I Grt+Chl+Ctd			
	Rim		Core		Rim		Core		Rim-Single Pt		Core		Rim-Single Pt		Core	
	n=2	(2σ)	n=4	(2σ)	n=2	(2σ)	n=2	(2σ)	n=1		n=4	(2σ)	n=1		n=4	(2σ)
SiO ₂	36.89	0.56	36.46	0.35	36.56	0.16	36.10	0.32	37.02		36.01	0.31	36.34		36.02	0.31
Al ₂ O ₃	20.98	0.45	20.79	0.33	20.94	0.13	20.69	0.13	21.00		20.94	0.29	20.70		20.47	0.52
Cr ₂ O ₃	0.04	0.07	0.02	0.03	0.04	0.00	0.01	0.03	0.00		0.03	0.08	0.00		0.02	0.04
TiO ₂	0.00	0.01	0.10	0.19	0.00	0.01	0.07	0.21	0.06		0.04	0.09	0.08		0.07	0.10
FeO	32.82	0.20	28.36	0.29	32.75	0.30	27.65	0.06	25.47		20.88	0.26	31.81		23.89	0.22
MnO	3.94	0.17	10.31	0.19	5.29	0.16	10.23	0.11	12.99		18.54	0.22	6.15		14.32	0.34
MgO	1.71	0.09	1.12	0.11	1.38	0.05	1.00	0.07	1.84		1.33	0.08	1.71		1.01	0.14
CaO	3.97	0.18	2.56	0.04	3.32	0.21	3.49	0.04	2.47		2.03	0.24	3.79		3.77	0.20
TOTAL	100.35	1.07	99.72	1.18	100.28	0.33	99.25	0.23	100.86		99.79	0.48	100.58		99.55	1.10
Cation proportions on the basis of 12 oxygens																
Si	2.981	0.007	2.982	0.028	2.971	0.013	2.968	0.015	2.982		2.951	0.024	2.950		2.961	0.011
Al	0.019	0.007	0.018	0.028	0.029	0.013	0.032	0.015	0.018		0.049	0.024	0.050		0.039	0.011
Sum	3.000	0.000	3.000	0.000	3.000	0.000	3.000	0.000	3.000		3.000	0.000	3.000		3.000	0.000
Al	1.979	0.023	1.987	0.016	1.976	0.025	1.974	0.005	1.977		1.973	0.015	1.930		1.944	0.022
Cr	0.002	0.004	0.001	0.002	0.003	0.000	0.001	0.002	0.000		0.002	0.005	0.000		0.001	0.003
Ti	0.000	0.000	0.006	0.012	0.000	0.001	0.004	0.013	0.004		0.003	0.006	0.005		0.004	0.006
Sum	1.981	0.020	1.994	0.009	1.979	0.025	1.979	0.010	1.980		1.977	0.021	1.935		1.949	0.024
Fe	2.218	0.015	1.940	0.015	2.226	0.021	1.901	0.011	1.716		1.431	0.015	2.160		1.642	0.008
Mn	0.270	0.015	0.714	0.010	0.364	0.011	0.713	0.010	0.887		1.287	0.020	0.423		0.997	0.029
Mg	0.206	0.014	0.136	0.013	0.167	0.006	0.123	0.009	0.220		0.162	0.010	0.207		0.123	0.016
Ca	0.344	0.011	0.224	0.001	0.289	0.019	0.307	0.002	0.213		0.178	0.021	0.330		0.332	0.017
Sum Fe to Ca	3.038	0.033	3.015	0.025	3.046	0.044	3.045	0.028	3.037		3.058	0.036	3.119		3.095	0.035
Fe/(Fe+Mg)	0.915	0.005	0.934	0.006	0.930	0.003	0.939	0.004	0.886		0.898	0.005	0.913		0.930	0.009
Mg/(Fe+Mg)	0.085	0.005	0.066	0.006	0.070	0.003	0.061	0.004	0.114		0.102	0.005	0.087		0.070	0.009
Fe/(Fe+Mn+Mg+Ca)	0.730	0.003	0.644	0.003	0.731	0.004	0.625	0.002	0.565		0.468	0.006	0.692		0.531	0.006
Mn/(Fe+Mn+Mg+Ca)	0.089	0.004	0.237	0.002	0.119	0.002	0.234	0.001	0.292		0.421	0.005	0.136		0.322	0.007
Mg/(Fe+Mn+Mg+Ca)	0.068	0.004	0.045	0.004	0.055	0.003	0.040	0.003	0.073		0.053	0.003	0.066		0.040	0.005
Ca/(Fe+Mn+Mg+Ca)	0.113	0.005	0.074	0.001	0.095	0.005	0.101	0.002	0.070		0.058	0.006	0.106		0.107	0.005
Cation proportions on the basis of 8 cations																
Si	2.974	0.012	2.979	0.033	2.962	0.020	2.959	0.022	2.976		2.938	0.029	2.930		2.945	0.012
Al	0.026	0.012	0.021	0.033	0.038	0.020	0.041	0.022	0.024		0.062	0.029	0.070		0.055	0.012
Sum	3.000	0.000	3.000	0.000	3.000	0.000	3.000	0.000	3.000		3.000	0.000	3.000		3.000	0.000
Al	1.967	0.032	1.981	0.023	1.961	0.037	1.959	0.006	1.966		1.951	0.024	1.897		1.917	0.029
Cr	0.002	0.004	0.001	0.002	0.003	0.000	0.001	0.002	0.000		0.002	0.005	0.000		0.001	0.003
Fe ³⁺	0.056	0.040	0.028	0.042	0.075	0.057	0.072	0.056	0.050		0.104	0.051	0.164		0.129	0.038
Ti	0.000	0.000	0.006	0.012	0.000	0.001	0.004	0.013	0.004		0.002	0.006	0.005		0.004	0.006
Sum	2.026	0.012	2.016	0.023	2.038	0.021	2.036	0.035	2.020		2.059	0.028	2.065		2.051	0.017
Fe ²⁺	2.156	0.028	1.910	0.036	2.144	0.042	1.824	0.049	1.662		1.321	0.056	1.982		1.504	0.040
Mn	0.269	0.015	0.714	0.009	0.363	0.010	0.711	0.009	0.885		1.281	0.020	0.420		0.992	0.028
Mg	0.206	0.013	0.136	0.013	0.167	0.006	0.123	0.009	0.220		0.161	0.009	0.205		0.123	0.016
Ca	0.343	0.012	0.224	0.001	0.288	0.018	0.306	0.003	0.213		0.177	0.020	0.328		0.330	0.017
Sum Fe to Ca	2.974	0.012	2.984	0.023	2.962	0.021	2.964	0.035	2.980		2.941	0.028	2.935		2.949	0.017
Fe/(Fe+Mg)	0.913	0.006	0.933	0.006	0.928	0.001	0.937	0.006	0.883		0.891	0.010	0.906		0.925	0.010
Mg/(Fe+Mg)	0.087	0.006	0.067	0.006	0.072	0.001	0.063	0.006	0.117		0.109	0.010	0.094		0.075	0.010
Fe/(Fe+Mn+Mg+Ca)	0.725	0.007	0.640	0.007	0.724	0.009	0.615	0.009	0.558		0.449	0.015	0.675		0.510	0.012
Mn/(Fe+Mn+Mg+Ca)	0.090	0.005	0.239	0.005	0.123	0.004	0.240	0.006	0.297		0.436	0.007	0.143		0.336	0.009
Mg/(Fe+Mn+Mg+Ca)	0.069	0.005	0.046	0.004	0.056	0.002	0.041	0.003	0.074		0.055	0.004	0.070		0.042	0.006
Ca/(Fe+Mn+Mg+Ca)	0.115	0.003	0.075	0.001	0.097	0.007	0.103	0.000	0.071		0.060	0.008	0.112		0.112	0.006

Table A5.6 Continued: Representative Garnet Analyses

	93-16a-II Grt+Chl				93-16b-I Grt+Chl+(Rel.Ctd)				93-15d-I Grt+Chl+Bt+Pl				92-6a-I Grt+Chl			
	Rim		Core		Rim-Single Pt		Core		Rim		Core		Rim-Single Pt		Core	
	n=2	(2σ)	n=4	(2σ)	n=1		n=3	(2σ)	n=2	(2σ)	n=3	(2σ)	n=1		n=3	(2σ)
SiO ₂	37.09	1.56	36.87	0.73	37.17		36.97	0.38	36.51	0.03	36.25	0.07	36.71		35.69	0.31
Al ₂ O ₃	20.96	0.91	20.56	0.58	21.03		20.66	0.28	20.64	0.12	20.38	0.19	20.63		20.31	0.42
Cr ₂ O ₃	0.08	0.06	0.04	0.06	0.05		0.02	0.06	0.14	0.04	0.17	0.07	0.06		0.00	0.00
TiO ₂	0.01	0.03	0.06	0.12	0.05		0.14	0.10	0.12	0.23	0.21	0.25	0.01		0.06	0.02
FeO	34.37	0.11	27.33	0.38	31.27		22.17	0.20	27.79	0.17	23.24	0.02	36.05		27.69	0.43
MnO	2.34	0.22	10.16	0.37	6.71		15.33	0.49	9.11	0.06	13.15	0.27	1.81		11.97	0.44
MgO	1.67	0.11	0.91	0.11	1.67		1.01	0.05	1.72	0.16	1.18	0.11	1.99		0.64	0.08
CaO	3.85	0.21	3.95	0.26	2.98		3.92	0.14	4.40	0.39	5.12	0.15	2.61		2.60	0.04
TOTAL	100.37	2.78	99.89	1.29	100.92		100.22	0.78	100.43	0.95	99.69	0.18	99.87		98.96	0.39
Cation proportions on the basis of 12 oxygens																
Si	2.993	0.024	3.004	0.015	2.990		2.999	0.011	2.959	0.026	2.962	0.005	2.988		2.966	0.012
Al	0.008	0.022	0.001	0.006	0.010		0.003	0.005	0.041	0.026	0.038	0.005	0.012		0.034	0.012
Sum	3.001	0.002	3.005	0.011	3.000		3.002	0.006	3.000	0.000	3.000	0.000	3.000		3.000	0.000
Al	1.986	0.040	1.973	0.028	1.984		1.972	0.026	1.930	0.031	1.925	0.022	1.967		1.955	0.035
Cr	0.005	0.004	0.003	0.004	0.003		0.001	0.004	0.009	0.003	0.011	0.005	0.004		0.000	0.000
Ti	0.001	0.002	0.004	0.008	0.003		0.009	0.006	0.007	0.014	0.013	0.015	0.000		0.004	0.001
Sum	1.992	0.046	1.980	0.025	1.990		1.982	0.020	1.946	0.019	1.948	0.007	1.972		1.959	0.034
Fe	2.320	0.072	1.863	0.035	2.104		1.504	0.019	1.883	0.004	1.588	0.004	2.454		1.925	0.029
Mn	0.160	0.010	0.701	0.033	0.457		1.054	0.029	0.625	0.009	0.910	0.020	0.125		0.842	0.035
Mg	0.201	0.007	0.110	0.013	0.200		0.122	0.006	0.208	0.018	0.144	0.014	0.241		0.079	0.009
Ca	0.333	0.030	0.344	0.020	0.257		0.341	0.010	0.382	0.031	0.448	0.012	0.227		0.231	0.004
Sum Fe to Ca	3.014	0.085	3.019	0.045	3.018		3.020	0.015	3.098	0.035	3.090	0.003	3.048		3.078	0.051
Fe/(Fe+Mg)	0.920	0.005	0.944	0.006	0.913		0.925	0.004	0.901	0.008	0.917	0.007	0.911		0.960	0.005
Mg/(Fe+Mg)	0.080	0.005	0.056	0.006	0.087		0.075	0.004	0.099	0.008	0.083	0.007	0.089		0.040	0.005
Fe/(Fe+Mn+Mg+Ca)	0.770	0.002	0.617	0.010	0.697		0.498	0.009	0.608	0.008	0.514	0.001	0.805		0.625	0.006
Mn/(Fe+Mn+Mg+Ca)	0.053	0.005	0.232	0.008	0.152		0.349	0.008	0.202	0.005	0.295	0.007	0.041		0.274	0.007
Mg/(Fe+Mn+Mg+Ca)	0.067	0.004	0.036	0.004	0.066		0.040	0.002	0.067	0.005	0.047	0.004	0.079		0.026	0.003
Ca/(Fe+Mn+Mg+Ca)	0.110	0.007	0.114	0.007	0.085		0.113	0.003	0.123	0.008	0.145	0.004	0.075		0.075	0.000
Cation proportions on the basis of 8 cations																
Si	2.991	0.038	3.003	0.022	2.987		2.998	0.010	2.942	0.032	2.948	0.006	2.981		2.952	0.015
Al	0.011	0.032	0.003	0.012	0.013		0.004	0.006	0.058	0.032	0.052	0.006	0.019		0.048	0.015
Sum	3.002	0.006	3.006	0.012	3.000		3.001	0.004	3.000	0.000	3.000	0.000	3.000		3.000	0.000
Al	1.981	0.060	1.970	0.035	1.979		1.971	0.024	1.903	0.040	1.901	0.019	1.955		1.933	0.045
Cr	0.005	0.004	0.003	0.004	0.003		0.001	0.004	0.009	0.003	0.011	0.005	0.004		0.000	0.000
Fe ³⁺	0.029	0.083	0.015	0.049	0.025		0.012	0.010	0.132	0.047	0.114	0.014	0.059		0.108	0.051
Ti	0.001	0.002	0.004	0.008	0.003		0.009	0.006	0.007	0.014	0.013	0.015	0.000		0.004	0.001
Sum	2.016	0.018	1.992	0.029	2.010		1.993	0.018	2.050	0.018	2.039	0.018	2.019		2.044	0.015
Fe ²⁺	2.289	0.022	1.847	0.054	2.076		1.491	0.024	1.741	0.054	1.466	0.012	2.389		1.808	0.043
Mn	0.180	0.010	0.701	0.031	0.457		1.053	0.029	0.622	0.010	0.906	0.020	0.125		0.839	0.033
Mg	0.200	0.008	0.110	0.013	0.200		0.122	0.006	0.207	0.017	0.143	0.014	0.241		0.079	0.010
Ca	0.333	0.028	0.344	0.020	0.257		0.341	0.010	0.380	0.030	0.446	0.013	0.227		0.230	0.003
Sum Fe to Ca	2.982	0.013	3.002	0.022	2.990		3.006	0.014	2.950	0.018	2.961	0.018	2.981		2.956	0.015
Fe/(Fe+Mg)	0.919	0.002	0.944	0.006	0.912		0.924	0.004	0.894	0.011	0.911	0.007	0.909		0.958	0.005
Mg/(Fe+Mg)	0.081	0.002	0.056	0.006	0.088		0.076	0.004	0.106	0.011	0.089	0.007	0.091		0.042	0.005
Fe/(Fe+Mn+Mg+Ca)	0.768	0.004	0.615	0.014	0.694		0.496	0.009	0.590	0.015	0.495	0.001	0.801		0.612	0.012
Mn/(Fe+Mn+Mg+Ca)	0.054	0.003	0.234	0.012	0.153		0.350	0.008	0.211	0.002	0.306	0.008	0.042		0.284	0.012
Mg/(Fe+Mn+Mg+Ca)	0.067	0.002	0.037	0.004	0.067		0.041	0.002	0.070	0.006	0.048	0.004	0.081		0.027	0.003
Ca/(Fe+Mn+Mg+Ca)	0.112	0.010	0.115	0.007	0.086		0.113	0.004	0.129	0.011	0.151	0.003	0.076		0.078	0.001

Table A5.6 Continued: Representative Garnet Analyses

	92-6c-III Grt+Ctd+Bt+(Retro Chl)				92-6f1-II Grt+Chl+Ctd+Bt				93-26e-I Grt+Chl+Ctd+Bt+St+Mrgr				93-26g-I Grt+Chl+Bt+St+Mrgr+(Ctd incl)			
	Rim		Core		Rim HlMg		Core		Rim-Start		Core		Rim		Core	
	n=3	(2σ)	n=6	(2σ)	n=2	(2σ)	n=4	(2σ)	n=2	(2σ)	n=4	(2σ)	n=2	(2σ)	n=3	(2σ)
SiO ₂	36.95	0.44	37.04	0.52	36.40	0.29	36.00	0.41	35.82	0.03	36.23	0.18	37.19	2.67	35.97	0.95
Al ₂ O ₃	20.65	0.28	20.84	0.62	20.81	0.45	20.49	0.13	21.08	0.23	21.02	0.38	21.23	1.53	20.15	0.42
Cr ₂ O ₃	0.01	0.03	0.03	0.06	0.05	0.04	0.03	0.03	0.00	0.00	0.01	0.03	0.04	0.01	0.01	0.05
TiO ₂	0.00	0.01	0.05	0.05	0.11	0.06	0.15	0.26	0.02	0.02	0.06	0.05	0.03	0.01	0.18	0.07
FeO	37.94	0.32	36.48	0.48	38.72	0.17	34.08	0.65	32.49	0.68	32.55	0.26	35.99	0.12	26.45	0.55
MnO	1.45	0.14	2.22	0.24	1.61	0.08	4.58	0.15	5.49	0.03	5.17	0.15	1.65	0.03	12.82	0.32
MgO	1.31	0.06	1.02	0.11	1.77	0.12	1.07	0.06	1.43	0.08	1.51	0.06	2.26	0.10	0.56	0.11
CaO	1.95	0.05	2.89	0.14	1.28	0.08	2.76	0.12	2.85	0.17	3.39	0.17	2.70	0.09	2.86	0.07
TOTAL	100.27	0.44	100.57	2.21	100.73	0.81	99.16	0.95	99.19	0.40	99.95	0.45	101.09	4.30	98.99	1.90
Cation proportions on the basis of 12 oxygens																
Si	3.007	0.016	3.003	0.038	2.960	0.004	2.971	0.022	2.945	0.001	2.953	0.015	2.980	0.050	2.983	0.043
Al	0.000	0.000	0.004	0.011	0.040	0.004	0.029	0.022	0.055	0.001	0.047	0.015	0.020	0.050	0.019	0.038
Sum	3.007	0.016	3.007	0.032	3.000	0.000	3.000	0.000	3.000	0.000	3.000	0.000	3.000	0.000	3.002	0.006
Al	1.981	0.016	1.986	0.042	1.955	0.021	1.963	0.027	1.988	0.026	1.972	0.021	1.985	0.085	1.950	0.010
Cr	0.001	0.002	0.002	0.004	0.003	0.003	0.002	0.002	0.000	0.000	0.001	0.002	0.002	0.000	0.001	0.003
Ti	0.000	0.001	0.003	0.003	0.006	0.004	0.009	0.016	0.001	0.001	0.004	0.003	0.002	0.001	0.011	0.004
Sum	1.982	0.015	1.991	0.042	1.964	0.022	1.975	0.027	1.989	0.027	1.977	0.018	1.989	0.085	1.962	0.008
Fe	2.583	0.033	2.473	0.028	2.633	0.012	2.352	0.038	2.234	0.045	2.219	0.021	2.413	0.140	1.834	0.020
Mn	0.100	0.010	0.152	0.016	0.111	0.005	0.320	0.010	0.383	0.002	0.357	0.010	0.112	0.004	0.900	0.021
Mg	0.159	0.007	0.124	0.013	0.214	0.017	0.132	0.008	0.176	0.010	0.184	0.007	0.270	0.003	0.069	0.012
Ca	0.170	0.005	0.251	0.012	0.112	0.008	0.244	0.013	0.251	0.016	0.296	0.014	0.232	0.005	0.254	0.005
Sum Fe to Ca	3.013	0.052	3.000	0.037	3.070	0.032	3.048	0.053	3.044	0.041	3.056	0.026	3.027	0.152	3.057	0.035
Fe/(Fe+Mg)	0.942	0.002	0.952	0.004	0.925	0.005	0.947	0.002	0.927	0.003	0.923	0.003	0.899	0.004	0.964	0.006
Mg/(Fe+Mg)	0.058	0.002	0.048	0.004	0.075	0.005	0.053	0.002	0.073	0.003	0.077	0.003	0.101	0.004	0.036	0.006
Fe/(Fe+Mn+Mg+Ca)	0.857	0.004	0.824	0.003	0.858	0.005	0.772	0.004	0.734	0.005	0.726	0.004	0.797	0.006	0.600	0.001
Mn/(Fe+Mn+Mg+Ca)	0.033	0.003	0.051	0.005	0.036	0.002	0.105	0.002	0.126	0.001	0.117	0.004	0.037	0.001	0.294	0.004
Mg/(Fe+Mn+Mg+Ca)	0.053	0.002	0.041	0.004	0.070	0.005	0.043	0.002	0.058	0.003	0.060	0.002	0.089	0.004	0.022	0.004
Ca/(Fe+Mn+Mg+Ca)	0.057	0.001	0.084	0.004	0.036	0.002	0.080	0.005	0.083	0.006	0.097	0.004	0.077	0.002	0.083	0.003
Cation proportions on the basis of 8 cations																
Si	3.007	0.024	3.003	0.045	2.948	0.000	2.962	0.030	2.933	0.006	2.941	0.017	2.974	0.075	2.975	0.052
Al	0.000	0.002	0.006	0.014	0.052	0.000	0.038	0.030	0.067	0.006	0.059	0.017	0.026	0.074	0.026	0.050
Sum	3.007	0.023	3.009	0.037	3.000	0.000	3.000	0.000	3.000	0.000	3.000	0.000	3.000	0.001	3.001	0.002
Al	1.980	0.022	1.986	0.041	1.933	0.027	1.949	0.040	1.968	0.034	1.952	0.025	1.975	0.126	1.938	0.026
Cr	0.001	0.002	0.002	0.004	0.003	0.003	0.002	0.002	0.000	0.000	0.001	0.002	0.002	0.000	0.001	0.003
Fe ₃₊	0.016	0.028	0.009	0.022	0.103	0.032	0.068	0.079	0.097	0.043	0.098	0.030	0.058	0.164	0.063	0.075
Ti	0.000	0.001	0.003	0.003	0.006	0.004	0.009	0.016	0.001	0.001	0.004	0.003	0.002	0.001	0.011	0.004
Sum	1.997	0.008	1.999	0.043	2.046	0.004	2.028	0.037	2.066	0.007	2.055	0.020	2.037	0.039	2.013	0.052
Fe ₂₊	2.566	0.002	2.465	0.017	2.519	0.023	2.277	0.054	2.128	0.002	2.111	0.028	2.350	0.044	1.766	0.061
Mn	0.100	0.010	0.152	0.016	0.110	0.005	0.319	0.009	0.381	0.001	0.356	0.010	0.112	0.003	0.898	0.018
Mg	0.159	0.007	0.124	0.013	0.213	0.017	0.132	0.007	0.175	0.010	0.183	0.007	0.269	0.001	0.068	0.012
Ca	0.170	0.005	0.251	0.012	0.111	0.008	0.244	0.013	0.250	0.016	0.295	0.014	0.231	0.003	0.253	0.006
Sum Fe to Ca	2.996	0.015	2.992	0.019	2.954	0.004	2.972	0.037	2.934	0.007	2.945	0.020	2.963	0.038	2.986	0.050
Fe/(Fe+Mg)	0.942	0.002	0.952	0.005	0.922	0.006	0.945	0.004	0.924	0.004	0.920	0.004	0.897	0.002	0.963	0.006
Mg/(Fe+Mg)	0.058	0.002	0.048	0.005	0.078	0.006	0.055	0.004	0.076	0.004	0.080	0.004	0.103	0.002	0.037	0.006
Fe/(Fe+Mn+Mg+Ca)	0.857	0.005	0.824	0.004	0.853	0.007	0.766	0.009	0.725	0.001	0.717	0.005	0.793	0.005	0.592	0.011
Mn/(Fe+Mn+Mg+Ca)	0.033	0.003	0.051	0.005	0.037	0.002	0.107	0.004	0.130	0.001	0.121	0.003	0.038	0.001	0.301	0.011
Mg/(Fe+Mn+Mg+Ca)	0.053	0.002	0.041	0.004	0.072	0.006	0.044	0.003	0.060	0.004	0.062	0.003	0.091	0.001	0.023	0.004
Ca/(Fe+Mn+Mg+Ca)	0.057	0.001	0.084	0.004	0.038	0.003	0.082	0.005	0.085	0.005	0.100	0.005	0.078	0.002	0.085	0.001

Table A5.6 Continued: Representative Garnet Analyses

	93-24a-II Grt+Chl+Ctd+Mrg				92-8d-I Grt+Chl+Ctd+Bt+St+Mrg				92-42c-I Grt+Ctd+Bt			93-18a-I Grt+Ctd+Bt			
	Rim		Core		Rim		Core		Rim-Single Pt	Core		Rim-End		Core	
	n=2	(2σ)	n=4	(2σ)	n=2	(2σ)	n=5	(2σ)	n=1	n=2	(2σ)	n=2	(2σ)	n=4	(2σ)
SiO ₂	36.83	0.09	36.37	0.39	36.74	0.04	36.33	0.44	37.18	36.37	0.07	36.96	0.05	37.11	0.40
Al ₂ O ₃	20.86	0.19	20.82	0.25	21.10	0.15	20.81	0.17	21.00	20.37	0.04	20.74	0.07	20.55	0.13
Cr ₂ O ₃	0.04	0.11	0.01	0.04	0.00	0.00	0.03	0.04	0.04	0.01	0.02	0.01	0.01	0.03	0.05
TiO ₂	0.10	0.01	0.05	0.10	0.03	0.04	0.10	0.05	0.32	0.17	0.09	0.01	0.02	0.21	0.18
FeO	31.86	0.85	27.35	0.19	30.50	0.14	26.69	0.50	37.40	31.91	0.28	36.77	0.57	32.50	0.78
MnO	5.36	0.56	10.45	0.13	7.24	0.22	11.20	0.18	1.52	7.13	0.06	4.05	0.03	5.49	0.05
MgO	1.87	0.00	1.43	0.08	1.75	0.10	1.45	0.09	1.60	0.92	0.07	1.41	0.06	0.95	0.20
CaO	3.71	0.19	3.16	0.14	3.65	0.08	3.34	0.48	2.40	3.26	0.15	1.39	0.07	3.90	0.64
TOTAL	100.63	0.49	99.64	0.80	101.02	0.07	99.95	0.82	101.45	100.14	0.39	101.34	0.61	100.73	0.32
Cation proportions on the basis of 12 oxygens															
Si	2.973	0.017	2.971	0.014	2.959	0.002	2.962	0.016	2.984	2.977	0.013	2.989	0.015	3.003	0.016
Al	0.027	0.017	0.029	0.014	0.041	0.002	0.038	0.016	0.016	0.023	0.013	0.011	0.015	0.002	0.007
Sum	3.000	0.000	3.000	0.000	3.000	0.000	3.000	0.000	3.000	3.000	0.000	3.000	0.000	3.004	0.011
Al	1.957	0.006	1.976	0.006	1.962	0.008	1.962	0.015	1.970	1.942	0.014	1.966	0.015	1.958	0.010
Cr	0.003	0.007	0.001	0.003	0.000	0.000	0.002	0.003	0.002	0.001	0.002	0.000	0.001	0.002	0.003
Ti	0.006	0.001	0.003	0.006	0.002	0.002	0.006	0.003	0.019	0.010	0.006	0.000	0.001	0.013	0.011
Sum	1.965	0.012	1.980	0.007	1.964	0.006	1.970	0.012	1.992	1.953	0.006	1.967	0.016	1.973	0.021
Fe	2.150	0.050	1.868	0.020	2.054	0.006	1.820	0.035	2.510	2.184	0.014	2.487	0.030	2.199	0.063
Mn	0.367	0.039	0.723	0.008	0.494	0.016	0.773	0.015	0.103	0.494	0.005	0.278	0.001	0.376	0.003
Mg	0.225	0.000	0.174	0.009	0.210	0.011	0.176	0.012	0.191	0.113	0.008	0.170	0.007	0.114	0.024
Ca	0.320	0.015	0.277	0.010	0.315	0.008	0.291	0.040	0.206	0.286	0.012	0.121	0.006	0.338	0.054
Sum Fe to Ca	3.063	0.026	3.043	0.007	3.073	0.007	3.061	0.021	3.011	3.077	0.013	3.055	0.031	3.027	0.045
Fe/(Fe+Mg)	0.905	0.002	0.915	0.005	0.907	0.004	0.912	0.005	0.929	0.951	0.004	0.936	0.002	0.951	0.010
Mg/(Fe+Mg)	0.095	0.002	0.085	0.005	0.093	0.004	0.088	0.005	0.071	0.049	0.004	0.064	0.002	0.049	0.010
Fe/(Fe+Mn+Mg+Ca)	0.702	0.011	0.614	0.006	0.668	0.003	0.595	0.010	0.834	0.710	0.002	0.814	0.001	0.727	0.013
Mn/(Fe+Mn+Mg+Ca)	0.120	0.014	0.238	0.003	0.161	0.005	0.253	0.006	0.034	0.161	0.002	0.091	0.001	0.124	0.002
Mg/(Fe+Mn+Mg+Ca)	0.073	0.001	0.057	0.003	0.068	0.004	0.058	0.004	0.064	0.037	0.003	0.056	0.002	0.038	0.008
Ca/(Fe+Mn+Mg+Ca)	0.105	0.004	0.091	0.003	0.103	0.002	0.095	0.013	0.068	0.093	0.004	0.039	0.002	0.112	0.018
Cation proportions on the basis of 8 cations															
Si	2.962	0.022	2.963	0.015	2.945	0.002	2.951	0.019	2.983	2.966	0.015	2.981	0.021	3.001	0.022
Al	0.038	0.022	0.037	0.015	0.055	0.002	0.049	0.019	0.017	0.034	0.015	0.019	0.021	0.003	0.014
Sum	3.000	0.000	3.000	0.000	3.000	0.000	3.000	0.000	3.000	3.000	0.000	3.000	0.000	3.005	0.012
Al	1.939	0.014	1.962	0.007	1.939	0.009	1.943	0.020	1.968	1.924	0.018	1.953	0.025	1.955	0.021
Cr	0.003	0.007	0.001	0.003	0.000	0.000	0.002	0.003	0.002	0.001	0.002	0.000	0.001	0.002	0.003
Fe ³⁺	0.084	0.042	0.068	0.006	0.112	0.002	0.093	0.031	0.008	0.090	0.020	0.065	0.047	0.018	0.050
Ti	0.006	0.001	0.003	0.006	0.002	0.002	0.006	0.003	0.019	0.010	0.006	0.000	0.001	0.013	0.011
Sum	2.032	0.021	2.034	0.009	2.053	0.004	2.043	0.017	1.998	2.024	0.009	2.019	0.022	1.988	0.029
Fe ²⁺	2.059	0.005	1.795	0.014	1.933	0.008	1.720	0.037	2.501	2.087	0.008	2.414	0.022	2.180	0.021
Mn	0.365	0.040	0.721	0.008	0.492	0.016	0.770	0.016	0.103	0.492	0.005	0.277	0.000	0.376	0.004
Mg	0.224	0.001	0.174	0.009	0.209	0.011	0.176	0.012	0.191	0.112	0.008	0.170	0.007	0.114	0.024
Ca	0.319	0.014	0.276	0.010	0.314	0.008	0.290	0.040	0.206	0.285	0.012	0.120	0.006	0.338	0.055
Sum Fe to Ca	2.968	0.021	2.966	0.009	2.947	0.004	2.957	0.017	3.002	2.976	0.009	2.981	0.022	3.008	0.019
Fe/(Fe+Mg)	0.902	0.001	0.912	0.005	0.902	0.004	0.907	0.007	0.929	0.949	0.003	0.934	0.003	0.950	0.010
Mg/(Fe+Mg)	0.098	0.001	0.088	0.005	0.098	0.004	0.093	0.007	0.071	0.051	0.003	0.066	0.003	0.050	0.010
Fe/(Fe+Mn+Mg+Ca)	0.694	0.007	0.605	0.006	0.656	0.004	0.582	0.011	0.833	0.701	0.000	0.810	0.002	0.725	0.011
Mn/(Fe+Mn+Mg+Ca)	0.123	0.013	0.243	0.003	0.167	0.005	0.261	0.005	0.034	0.165	0.001	0.093	0.001	0.125	0.002
Mg/(Fe+Mn+Mg+Ca)	0.076	0.000	0.059	0.003	0.071	0.004	0.059	0.004	0.064	0.038	0.003	0.057	0.003	0.038	0.008
Ca/(Fe+Mn+Mg+Ca)	0.108	0.006	0.093	0.003	0.106	0.002	0.098	0.014	0.069	0.096	0.004	0.040	0.002	0.112	0.018

Table A5.6 Continued: Representative Garnet Analyses

	92-41a-I Grt+Ctd+Bt				93-20f-I Grt+Ctd+Bt				92-10a-II Ctd+St+Grt+Bt				90-19a-I Ctd+St+Grt+Bt	
	Rim		Core		Rim-End		Core		Rim		Core		Rim-Single Pt	
	n=2	(2σ)	n=4	(2σ)	n=2	(2σ)	n=5	(2σ)	n=5	(2σ)	n=4	(2σ)	n=1	
SiO ₂	36.55	0.78	36.10	0.37	37.01	0.16	37.26	0.26	36.70	0.35	36.53	0.37	36.58	
Al ₂ O ₃	21.20	0.35	20.76	0.20	20.85	0.22	20.80	0.13	20.92	0.28	20.92	0.23	20.74	
Cr ₂ O ₃	0.00	0.00	0.03	0.05	0.01	0.00	0.05	0.04	0.02	0.06	0.02	0.03	n.d.	
TiO ₂	0.00	0.01	0.04	0.10	0.00	0.00	0.09	0.15	0.04	0.05	0.04	0.05	0.14	
FeO	37.33	0.24	33.88	0.45	39.43	0.14	35.76	0.42	38.24	0.38	35.42	0.21	34.70	
MnO	1.01	0.02	5.36	0.27	0.45	0.11	1.93	0.18	2.17	0.11	3.12	0.21	1.87	
MgO	1.53	0.24	1.11	0.16	1.09	0.01	0.75	0.14	1.26	0.07	1.09	0.14	1.28	
CaO	3.28	0.22	2.50	0.24	2.25	0.02	4.50	0.18	1.59	0.16	2.93	0.18	4.07	
TOTAL	100.90	0.62	99.78	0.76	101.10	0.29	101.13	0.62	100.95	0.74	100.07	0.53	99.38	
Cation proportions on the basis of 12 oxygens														
Si	2.955	0.043	2.963	0.016	2.995	0.018	3.002	0.023	2.978	0.013	2.979	0.015	2.988	
Al	0.045	0.043	0.037	0.016	0.006	0.016	0.003	0.009	0.022	0.013	0.021	0.015	0.012	
Sum	3.000	0.000	3.000	0.000	3.001	0.002	3.005	0.018	3.000	0.000	3.000	0.000	3.000	
Al	1.974	0.004	1.971	0.014	1.983	0.002	1.971	0.012	1.979	0.017	1.990	0.008	1.985	
Cr	0.000	0.000	0.002	0.003	0.000	0.000	0.003	0.003	0.001	0.004	0.001	0.002	n.d.	
Ti	0.000	0.001	0.003	0.006	0.000	0.000	0.005	0.009	0.003	0.003	0.002	0.003	0.009	
Sum	1.974	0.004	1.975	0.007	1.983	0.002	1.980	0.010	1.983	0.017	1.993	0.011	1.993	
Fe	2.524	0.001	2.325	0.022	2.668	0.005	2.409	0.028	2.595	0.029	2.416	0.016	2.370	
Mn	0.069	0.002	0.373	0.018	0.031	0.008	0.132	0.012	0.149	0.007	0.216	0.016	0.129	
Mg	0.184	0.030	0.136	0.020	0.132	0.002	0.090	0.016	0.153	0.008	0.132	0.016	0.156	
Ca	0.284	0.017	0.220	0.021	0.195	0.002	0.389	0.013	0.138	0.015	0.256	0.016	0.356	
Sum Fe to Ca	3.061	0.015	3.055	0.012	3.026	0.009	3.020	0.023	3.035	0.030	3.019	0.016	3.012	
Fe/(Fe+Mg)	0.932	0.010	0.945	0.008	0.953	0.001	0.964	0.007	0.944	0.003	0.948	0.006	0.938	
Mg/(Fe+Mg)	0.068	0.010	0.055	0.008	0.047	0.001	0.036	0.007	0.056	0.003	0.052	0.006	0.062	
Fe/(Fe+Mn+Mg+Ca)	0.825	0.004	0.761	0.008	0.882	0.001	0.798	0.006	0.855	0.002	0.800	0.005	0.787	
Mn/(Fe+Mn+Mg+Ca)	0.023	0.000	0.122	0.006	0.010	0.002	0.044	0.004	0.049	0.002	0.071	0.005	0.043	
Mg/(Fe+Mn+Mg+Ca)	0.060	0.010	0.045	0.007	0.043	0.001	0.030	0.005	0.050	0.003	0.044	0.006	0.052	
Ca/(Fe+Mn+Mg+Ca)	0.093	0.006	0.072	0.007	0.065	0.001	0.129	0.004	0.045	0.005	0.085	0.005	0.118	
Cation proportions on the basis of 8 cations														
Si	2.942	0.050	2.952	0.019	2.991	0.021	3.000	0.028	2.971	0.018	2.974	0.017	2.986	
Al	0.058	0.050	0.048	0.019	0.009	0.021	0.005	0.012	0.029	0.018	0.026	0.017	0.014	
Sum	3.000	0.000	3.000	0.000	3.000	0.000	3.005	0.020	3.000	0.000	3.000	0.000	3.000	
Al	1.952	0.008	1.952	0.017	1.977	0.005	1.969	0.014	1.968	0.025	1.982	0.012	1.981	
Cr	0.000	0.000	0.002	0.003	0.000	0.000	0.003	0.003	0.001	0.004	0.001	0.002	n.d.	
Fe ³⁺	0.106	0.057	0.089	0.024	0.031	0.027	0.017	0.022	0.054	0.042	0.038	0.023	0.015	
Ti	0.000	0.001	0.003	0.006	0.000	0.000	0.005	0.009	0.003	0.003	0.002	0.003	0.009	
Sum	2.058	0.050	2.045	0.018	2.009	0.021	1.994	0.024	2.026	0.019	2.023	0.015	2.005	
Fe ²⁺	2.407	0.063	2.228	0.026	2.634	0.025	2.390	0.018	2.535	0.018	2.374	0.013	2.354	
Mn	0.069	0.001	0.371	0.018	0.031	0.008	0.132	0.012	0.149	0.007	0.215	0.016	0.129	
Mg	0.183	0.029	0.136	0.020	0.131	0.002	0.090	0.016	0.153	0.008	0.132	0.017	0.156	
Ca	0.283	0.018	0.219	0.021	0.195	0.003	0.388	0.013	0.138	0.015	0.255	0.016	0.356	
Sum Fe to Ca	2.942	0.050	2.955	0.018	2.991	0.021	3.001	0.006	2.974	0.019	2.977	0.015	2.995	
Fe/(Fe+Mg)	0.929	0.012	0.943	0.008	0.952	0.000	0.964	0.007	0.943	0.003	0.947	0.006	0.938	
Mg/(Fe+Mg)	0.071	0.012	0.057	0.008	0.048	0.000	0.036	0.007	0.057	0.003	0.053	0.006	0.062	
Fe/(Fe+Mn+Mg+Ca)	0.818	0.008	0.754	0.008	0.881	0.002	0.796	0.006	0.852	0.002	0.797	0.005	0.786	
Mn/(Fe+Mn+Mg+Ca)	0.023	0.001	0.126	0.006	0.010	0.003	0.044	0.004	0.050	0.003	0.072	0.005	0.043	
Mg/(Fe+Mn+Mg+Ca)	0.062	0.011	0.046	0.007	0.044	0.000	0.030	0.005	0.051	0.003	0.044	0.005	0.052	
Ca/(Fe+Mn+Mg+Ca)	0.096	0.004	0.074	0.007	0.065	0.000	0.129	0.005	0.046	0.005	0.086	0.005	0.119	

Table A5.6 Continued: Representative Garnet Analyses

	92-27a-II			92-28a-I			92-9i2-II			92-26b-I					
	Ctd+St+Grt+Bt			Ctd+St+Grt+Bt			Grt+Chl+Bt+Pl+Epid			Grt+Chl+St+Ky+Pl					
	Rim-Single Pt n=1	Core n=2 (2σ)		Rim-End n=2 (2σ)	Core n=3 (2σ)		Rim n=2 (2σ)	Core n=5 (2σ)		Rim-Start n=2 (2σ)	Core n=4 (2σ)				
SiO ₂	36.29	36.74	0.29	36.69	0.21	36.48	0.58	37.10	0.23	37.36	1.04	36.72	0.44	36.52	0.28
Al ₂ O ₃	20.54	20.78	0.02	21.32	0.11	20.80	0.55	21.08	0.07	20.83	0.54	21.01	0.47	20.87	0.41
Cr ₂ O ₃	0.11	0.06	0.05	0.03	0.02	0.02	0.03	0.04	0.05	0.03	0.08	0.02	0.02	0.04	0.08
TiO ₂	0.00	0.10	0.05	0.00	0.00	0.03	0.06	0.07	0.05	0.18	0.09	0.02	0.05	0.07	0.08
FeO	40.27	38.07	0.21	38.06	0.43	37.51	0.70	24.85	0.82	21.05	0.94	21.21	0.55	20.49	0.30
MnO	0.11	0.72	0.24	0.42	0.05	0.87	0.11	11.20	0.12	15.44	0.65	15.03	0.07	16.19	0.18
MgO	1.68	1.11	0.01	1.73	0.02	1.48	0.13	2.52	0.11	2.11	0.18	2.99	0.08	2.71	0.24
CaO	1.27	3.15	0.09	2.96	0.01	3.16	0.34	3.53	0.12	3.17	0.29	2.44	0.25	2.22	0.03
TOTAL	100.26	100.72	0.05	101.21	0.74	100.34	2.07	100.39	0.77	100.17	1.05	99.43	1.14	99.11	0.67
Cation proportions on the basis of 12 oxygens															
Si	2.970	2.981	0.018	2.954	0.002	2.968	0.015	2.979	0.029	3.007	0.083	2.974	0.002	2.974	0.006
Al	0.030	0.019	0.018	0.046	0.002	0.032	0.015	0.021	0.029	0.009	0.013	0.026	0.002	0.026	0.006
Sum	3.000	3.000	0.000	3.000	0.000	3.000	0.000	3.000	0.000	3.016	0.072	3.000	0.000	3.000	0.000
Al	1.950	1.968	0.012	1.977	0.005	1.963	0.020	1.975	0.029	1.967	0.041	1.979	0.018	1.977	0.028
Cr	0.007	0.004	0.003	0.002	0.001	0.001	0.002	0.003	0.003	0.002	0.005	0.001	0.001	0.003	0.005
Ti	0.000	0.006	0.003	0.000	0.000	0.002	0.004	0.004	0.003	0.011	0.005	0.001	0.003	0.004	0.005
Sum	1.957	1.978	0.006	1.979	0.004	1.966	0.023	1.981	0.029	1.979	0.040	1.982	0.014	1.984	0.023
Fe	2.755	2.583	0.010	2.563	0.012	2.552	0.016	1.669	0.049	1.417	0.063	1.437	0.019	1.396	0.026
Mn	0.008	0.049	0.017	0.028	0.003	0.060	0.008	0.762	0.011	1.053	0.045	1.031	0.018	1.116	0.010
Mg	0.205	0.134	0.001	0.208	0.002	0.179	0.012	0.301	0.012	0.253	0.021	0.361	0.005	0.329	0.028
Ca	0.111	0.274	0.008	0.255	0.003	0.276	0.028	0.304	0.009	0.274	0.026	0.212	0.024	0.194	0.004
Sum Fe to Ca	3.079	3.040	0.017	3.054	0.008	3.067	0.034	3.036	0.060	2.998	0.110	3.040	0.018	3.035	0.033
Fe/(Fe+Mg)	0.931	0.951	0.001	0.925	0.000	0.934	0.004	0.847	0.001	0.848	0.013	0.799	0.000	0.809	0.015
Mg/(Fe+Mg)	0.069	0.049	0.001	0.075	0.000	0.066	0.004	0.153	0.001	0.152	0.013	0.201	0.000	0.191	0.015
Fe/(Fe+Mn+Mg+Ca)	0.895	0.850	0.008	0.839	0.002	0.832	0.007	0.550	0.005	0.473	0.005	0.473	0.009	0.460	0.008
Mn/(Fe+Mn+Mg+Ca)	0.002	0.016	0.005	0.009	0.001	0.020	0.003	0.251	0.009	0.351	0.004	0.339	0.004	0.368	0.002
Mg/(Fe+Mn+Mg+Ca)	0.066	0.044	0.000	0.068	0.000	0.058	0.004	0.099	0.002	0.085	0.009	0.119	0.002	0.109	0.009
Ca/(Fe+Mn+Mg+Ca)	0.036	0.090	0.002	0.084	0.001	0.090	0.008	0.100	0.001	0.091	0.008	0.070	0.008	0.064	0.001
Cation proportions on the basis of 8 cations															
Si	2.956	2.974	0.021	2.942	0.004	2.956	0.016	2.973	0.040	3.010	0.107	2.966	0.000	2.967	0.005
Al	0.044	0.026	0.021	0.058	0.004	0.044	0.016	0.027	0.040	0.011	0.015	0.034	0.000	0.033	0.005
Sum	3.000	3.000	0.000	3.000	0.000	3.000	0.000	3.000	0.000	3.021	0.094	3.000	0.000	3.000	0.000
Al	1.928	1.957	0.019	1.956	0.008	1.943	0.027	1.964	0.048	1.967	0.037	1.966	0.020	1.965	0.034
Cr	0.007	0.004	0.003	0.002	0.001	0.001	0.002	0.003	0.003	0.002	0.005	0.001	0.001	0.003	0.005
Fe ³⁺	0.109	0.053	0.031	0.100	0.010	0.097	0.036	0.052	0.092	0.017	0.036	0.065	0.013	0.056	0.029
Ti	0.000	0.006	0.003	0.000	0.000	0.002	0.004	0.004	0.003	0.011	0.005	0.001	0.003	0.004	0.005
Sum	2.044	2.020	0.019	2.058	0.004	2.042	0.013	2.023	0.043	1.996	0.034	2.033	0.003	2.029	0.001
Fe ²⁺	2.634	2.525	0.044	2.452	0.001	2.445	0.036	1.613	0.049	1.402	0.035	1.368	0.033	1.336	0.030
Mn	0.008	0.049	0.017	0.028	0.003	0.060	0.008	0.760	0.014	1.054	0.038	1.028	0.017	1.114	0.009
Mg	0.204	0.134	0.001	0.207	0.001	0.178	0.012	0.301	0.011	0.254	0.022	0.360	0.005	0.328	0.028
Ca	0.111	0.273	0.008	0.254	0.003	0.274	0.027	0.303	0.008	0.274	0.025	0.211	0.024	0.193	0.004
Sum Fe to Ca	2.956	2.980	0.019	2.942	0.004	2.958	0.013	2.977	0.043	2.983	0.064	2.967	0.003	2.971	0.001
Fe/(Fe+Mg)	0.928	0.950	0.001	0.922	0.000	0.932	0.005	0.843	0.009	0.847	0.012	0.792	0.002	0.803	0.017
Mg/(Fe+Mg)	0.072	0.050	0.001	0.078	0.000	0.068	0.005	0.157	0.009	0.153	0.012	0.208	0.002	0.197	0.017
Fe/(Fe+Mn+Mg+Ca)	0.891	0.847	0.010	0.834	0.001	0.827	0.009	0.542	0.009	0.470	0.006	0.461	0.012	0.450	0.010
Mn/(Fe+Mn+Mg+Ca)	0.003	0.016	0.006	0.010	0.001	0.020	0.003	0.255	0.001	0.353	0.008	0.346	0.005	0.375	0.003
Mg/(Fe+Mn+Mg+Ca)	0.069	0.045	0.001	0.070	0.001	0.060	0.004	0.101	0.005	0.085	0.008	0.121	0.002	0.111	0.009
Ca/(Fe+Mn+Mg+Ca)	0.038	0.092	0.003	0.086	0.001	0.093	0.009	0.102	0.004	0.092	0.008	0.071	0.008	0.065	0.001

Table A5.6 Continued: Representative Garnet Analyses

	91-21c2-III			93-10b-II			92-11-I			90-1e-I		
	Grt+Chl+St (Mrg+Ctd incl)			Grt+Chl+St+Bt+Pl+Ky			Grt+Chl+Bt+St+Pl (No Ms)			St+Grt+Bt		
	Rim-Single Pt	Core		Rim-Single Pt	Core		Rim	Core		Rim-End	Core	
	n=1	n=3 (2σ)		n=1	n=4 (2σ)		n=2 (2σ)	n=4 (2σ)		n=2 (2σ)	n=3 (2σ)	
SiO ₂	36.61	36.47 0.27		36.98	36.85 0.28		36.56 0.27	36.66 0.65		36.33 0.01	36.31 0.66	
Al ₂ O ₃	21.36	21.01 0.37		21.21	20.77 0.17		20.61 0.10	20.84 0.20		20.83 0.20	20.65 0.35	
Cr ₂ O ₃	0.02	0.04 0.07		0.00	0.00 0.00		0.06 0.02	0.05 0.10		0.02 0.03	0.03 0.01	
TiO ₂	0.00	0.09 0.04		0.07	0.12 0.11		0.04 0.10	0.08 0.06		0.02 0.05	0.03 0.01	
FeO	32.73	27.82 0.23		24.79	18.11 0.56		34.07 0.40	30.22 0.42		37.42 0.49	36.53 0.80	
MnO	4.47	10.05 0.25		10.92	17.96 0.28		2.61 0.48	7.69 0.28		0.49 0.04	1.04 0.19	
MgO	2.48	1.85 0.07		3.57	1.93 0.19		2.83 0.01	2.10 0.35		2.26 0.18	2.01 0.14	
CaO	3.04	3.12 0.14		2.95	4.53 0.50		2.91 0.16	2.61 0.40		2.62 0.07	3.13 0.11	
TOTAL	100.69	100.44 0.30		100.48	100.26 0.59		99.69 0.65	100.26 0.56		99.97 0.83	99.73 1.58	
Cation proportions on the basis of 12 oxygens												
Si	2.946	2.954 0.004		2.958	2.974 0.010		2.970 0.029	2.971 0.038		2.957 0.021	2.964 0.022	
Al	0.054	0.046 0.004		0.042	0.026 0.010		0.030 0.029	0.029 0.038		0.043 0.021	0.036 0.022	
Sum	3.000	3.000 0.000		3.000	3.000 0.000		3.000 0.000	3.000 0.000		3.000 0.000	3.000 0.000	
Al	1.972	1.960 0.027		1.958	1.950 0.011		1.943 0.024	1.962 0.024		1.956 0.016	1.951 0.009	
Cr	0.001	0.002 0.004		0.000	0.000 0.000		0.004 0.001	0.003 0.006		0.001 0.002	0.002 0.001	
Ti	0.000	0.005 0.002		0.004	0.007 0.006		0.002 0.006	0.005 0.004		0.001 0.003	0.002 0.001	
Sum	1.973	1.968 0.028		1.962	1.957 0.012		1.949 0.017	1.970 0.017		1.958 0.011	1.955 0.009	
Fe	2.203	1.885 0.026		1.658	1.222 0.036		2.315 0.022	2.048 0.027		2.547 0.016	2.494 0.043	
Mn	0.304	0.690 0.020		0.740	1.228 0.018		0.180 0.032	0.528 0.019		0.034 0.003	0.072 0.012	
Mg	0.297	0.223 0.008		0.425	0.232 0.021		0.343 0.002	0.254 0.043		0.274 0.020	0.245 0.020	
Ca	0.262	0.271 0.012		0.253	0.391 0.043		0.253 0.014	0.227 0.035		0.228 0.007	0.273 0.007	
Sum Fe to Ca	3.067	3.069 0.043		3.077	3.073 0.019		3.090 0.038	3.057 0.041		3.083 0.026	3.084 0.024	
Fe/(Fe+Mg)	0.881	0.894 0.003		0.796	0.840 0.012		0.871 0.002	0.890 0.017		0.903 0.006	0.911 0.007	
Mg/(Fe+Mg)	0.119	0.106 0.003		0.204	0.160 0.012		0.129 0.002	0.110 0.017		0.097 0.006	0.089 0.007	
Fe/(Fe+Mn+Mg+Ca)	0.718	0.614 0.001		0.539	0.398 0.011		0.749 0.002	0.670 0.010		0.826 0.002	0.809 0.008	
Mn/(Fe+Mn+Mg+Ca)	0.099	0.225 0.006		0.240	0.399 0.005		0.058 0.010	0.173 0.005		0.011 0.001	0.023 0.004	
Mg/(Fe+Mn+Mg+Ca)	0.097	0.073 0.002		0.138	0.076 0.006		0.111 0.002	0.083 0.014		0.089 0.006	0.079 0.007	
Ca/(Fe+Mn+Mg+Ca)	0.086	0.088 0.004		0.082	0.127 0.014		0.082 0.006	0.074 0.011		0.074 0.003	0.089 0.003	
Cation proportions on the basis of 8 cations												
Si	2.932	2.941 0.010		2.944	2.962 0.012		2.956 0.037	2.961 0.047		2.942 0.027	2.950 0.027	
Al	0.068	0.059 0.010		0.056	0.038 0.012		0.044 0.037	0.039 0.047		0.058 0.027	0.050 0.027	
Sum	3.000	3.000 0.000		3.000	3.000 0.000		3.000 0.000	3.000 0.000		3.000 0.000	3.000 0.000	
Al	1.947	1.938 0.036		1.934	1.931 0.013		1.919 0.037	1.945 0.038		1.931 0.025	1.927 0.018	
Cr	0.001	0.002 0.004		0.000	0.000 0.000		0.004 0.001	0.003 0.006		0.001 0.002	0.002 0.001	
Fe ³⁺	0.120	0.108 0.044		0.114	0.092 0.027		0.117 0.060	0.080 0.076		0.124 0.044	0.118 0.046	
Ti	0.000	0.005 0.002		0.004	0.007 0.006		0.002 0.006	0.005 0.004		0.001 0.003	0.002 0.001	
Sum	2.068	2.054 0.008		2.052	2.030 0.017		2.042 0.031	2.034 0.047		2.057 0.024	2.048 0.027	
Fe ²⁺	2.072	1.768 0.022		1.536	1.126 0.047		2.186 0.044	1.961 0.081		2.410 0.033	2.364 0.010	
Mn	0.303	0.687 0.019		0.736	1.223 0.018		0.179 0.032	0.526 0.019		0.033 0.003	0.071 0.012	
Mg	0.296	0.222 0.008		0.423	0.231 0.021		0.341 0.003	0.253 0.043		0.273 0.020	0.244 0.020	
Ca	0.261	0.270 0.012		0.252	0.390 0.043		0.252 0.015	0.226 0.034		0.227 0.008	0.272 0.007	
Sum Fe to Ca	2.932	2.946 0.008		2.948	2.970 0.017		2.958 0.031	2.966 0.047		2.943 0.024	2.952 0.027	
Fe/(Fe+Mg)	0.875	0.888 0.004		0.784	0.829 0.016		0.865 0.001	0.886 0.019		0.898 0.008	0.906 0.007	
Mg/(Fe+Mg)	0.125	0.112 0.004		0.216	0.171 0.016		0.135 0.001	0.114 0.019		0.102 0.008	0.094 0.007	
Fe/(Fe+Mn+Mg+Ca)	0.707	0.600 0.006		0.521	0.379 0.014		0.739 0.007	0.661 0.017		0.819 0.005	0.801 0.005	
Mn/(Fe+Mn+Mg+Ca)	0.103	0.233 0.007		0.250	0.412 0.007		0.060 0.011	0.177 0.008		0.011 0.001	0.024 0.004	
Mg/(Fe+Mn+Mg+Ca)	0.101	0.075 0.003		0.144	0.078 0.007		0.115 0.000	0.085 0.015		0.093 0.007	0.083 0.007	
Ca/(Fe+Mn+Mg+Ca)	0.089	0.092 0.004		0.085	0.131 0.015		0.085 0.004	0.076 0.012		0.077 0.002	0.092 0.002	

Table A5.6 Continued: Representative Garnet Analyses

	90-4h						91-26a-II				91-26e-II			
	St+Grt+Bt+Pl+(Ctd Incl)						Grt+Chl+St				Grt+Chl+St+Bt			
	Rim-HiMg n=2 (2σ)	Core n=3 (2σ)	Adj St+Ctd Incl n=2 (2σ)				Rim n=2 (2σ)	Core n=8 (2σ)			Rim-Start n=2 (2σ)	Core n=4 (2σ)		
SiO ₂	37.00 0.08	36.22 0.26	36.55 0.53				37.09 0.42	36.94 0.44			36.83 0.37	36.51 0.68		
Al ₂ O ₃	20.79 0.43	20.49 0.23	20.83 0.11				20.70 0.04	20.82 0.32			20.80 0.08	20.78 0.53		
Cr ₂ O ₃	0.00 0.00	0.03 0.07	0.02 0.07				0.03 0.02	0.02 0.03			0.03 0.08	0.02 0.03		
TiO ₂	0.01 0.02	0.06 0.09	0.01 0.04				0.01 0.02	0.09 0.09			0.07 0.05	0.05 0.06		
FeO	34.48 0.46	29.98 0.27	31.29 0.25				26.07 0.00	25.92 0.57			36.22 0.45	35.16 0.20		
MnO	3.25 0.05	7.57 0.09	7.43 0.63				10.69 0.23	10.44 0.23			1.08 0.06	2.56 0.19		
MgO	2.73 0.04	1.87 0.18	1.85 0.02				3.50 0.10	3.34 0.17			2.96 0.03	2.28 0.07		
CaO	2.25 0.11	2.71 0.20	2.17 0.22				2.04 0.12	2.34 0.33			2.18 0.30	2.52 0.15		
TOTAL	100.51 0.95	98.93 0.50	100.15 0.36				100.13 0.71	99.90 0.84			100.16 0.26	99.87 1.15		
Cation proportions on the basis of 12 oxygens														
Si	2.983 0.029	2.978 0.008	2.973 0.023				2.985 0.010	2.978 0.022			2.976 0.015	2.970 0.026		
Al	0.017 0.029	0.022 0.008	0.027 0.023				0.015 0.010	0.022 0.022			0.024 0.015	0.030 0.026		
Sum	3.000 0.000	3.000 0.000	3.000 0.000				3.000 0.000	3.000 0.000			3.000 0.000	3.000 0.000		
Al	1.958 0.002	1.964 0.026	1.970 0.020				1.949 0.002	1.957 0.020			1.957 0.012	1.962 0.022		
Cr	0.000 0.000	0.002 0.005	0.002 0.004				0.002 0.001	0.001 0.002			0.002 0.005	0.001 0.002		
Ti	0.001 0.001	0.003 0.005	0.001 0.002				0.000 0.001	0.005 0.005			0.004 0.003	0.003 0.004		
Sum	1.959 0.001	1.969 0.028	1.973 0.013				1.951 0.000	1.963 0.018			1.963 0.004	1.966 0.022		
Fe	2.325 0.014	2.061 0.023	2.128 0.002				1.755 0.014	1.748 0.035			2.448 0.043	2.392 0.031		
Mn	0.222 0.002	0.527 0.004	0.512 0.047				0.729 0.010	0.713 0.015			0.074 0.004	0.176 0.014		
Mg	0.329 0.008	0.229 0.021	0.225 0.004				0.420 0.009	0.401 0.021			0.356 0.002	0.277 0.005		
Ca	0.194 0.008	0.239 0.016	0.189 0.018				0.176 0.012	0.202 0.028			0.189 0.025	0.220 0.012		
Sum Fe to Ca	3.070 0.016	3.056 0.044	3.054 0.030				3.080 0.006	3.063 0.029			3.066 0.011	3.064 0.034		
Fe/(Fe+Mg)	0.876 0.003	0.900 0.008	0.905 0.002				0.807 0.005	0.813 0.009			0.873 0.003	0.896 0.003		
Mg/(Fe+Mg)	0.124 0.003	0.100 0.008	0.095 0.002				0.193 0.005	0.187 0.009			0.127 0.003	0.104 0.003		
Fe/(Fe+Mn+Mg+Ca)	0.757 0.000	0.674 0.009	0.697 0.008				0.570 0.003	0.570 0.009			0.798 0.011	0.780 0.002		
Mn/(Fe+Mn+Mg+Ca)	0.072 0.000	0.172 0.003	0.168 0.014				0.237 0.004	0.233 0.006			0.024 0.001	0.058 0.004		
Mg/(Fe+Mn+Mg+Ca)	0.107 0.003	0.075 0.006	0.074 0.001				0.136 0.003	0.131 0.006			0.116 0.001	0.090 0.002		
Ca/(Fe+Mn+Mg+Ca)	0.063 0.002	0.078 0.005	0.062 0.007				0.057 0.004	0.066 0.009			0.062 0.008	0.072 0.004		
Cation proportions on the basis of 8 cations														
Si	2.972 0.034	2.969 0.011	2.963 0.029				2.973 0.012	2.968 0.026			2.965 0.018	2.959 0.031		
Al	0.028 0.034	0.031 0.011	0.037 0.029				0.027 0.012	0.032 0.026			0.035 0.018	0.041 0.031		
Sum	3.000 0.000	3.000 0.000	3.000 0.000				3.000 0.000	3.000 0.000			3.000 0.000	3.000 0.000		
Al	1.941 0.011	1.948 0.035	1.954 0.030				1.929 0.002	1.941 0.026			1.939 0.017	1.943 0.029		
Cr	0.000 0.000	0.002 0.005	0.002 0.004				0.002 0.001	0.001 0.002			0.002 0.005	0.001 0.002		
Fe3+	0.086 0.044	0.075 0.050	0.080 0.051				0.094 0.017	0.079 0.042			0.086 0.023	0.091 0.050		
Ti	0.001 0.001	0.003 0.005	0.001 0.002				0.000 0.001	0.005 0.005			0.004 0.003	0.003 0.004		
Sum	2.027 0.033	2.028 0.015	2.036 0.027				2.026 0.013	2.026 0.028			2.031 0.014	2.038 0.033		
Fe2+	2.231 0.034	1.980 0.042	2.042 0.057				1.654 0.005	1.682 0.032			2.353 0.017	2.291 0.031		
Mn	0.221 0.001	0.525 0.004	0.510 0.045				0.726 0.011	0.710 0.015			0.074 0.004	0.176 0.014		
Mg	0.327 0.008	0.228 0.021	0.224 0.003				0.418 0.010	0.400 0.021			0.355 0.002	0.275 0.006		
Ca	0.194 0.008	0.238 0.016	0.188 0.018				0.175 0.011	0.201 0.028			0.188 0.025	0.219 0.013		
Sum Fe to Ca	2.973 0.033	2.972 0.015	2.964 0.027				2.974 0.013	2.974 0.028			2.969 0.014	2.962 0.033		
Fe/(Fe+Mg)	0.872 0.001	0.897 0.010	0.901 0.004				0.798 0.003	0.806 0.010			0.869 0.002	0.893 0.002		
Mg/(Fe+Mg)	0.128 0.001	0.103 0.010	0.099 0.004				0.202 0.003	0.194 0.010			0.131 0.002	0.107 0.002		
Fe/(Fe+Mn+Mg+Ca)	0.750 0.003	0.666 0.013	0.689 0.013				0.556 0.001	0.559 0.008			0.792 0.010	0.774 0.002		
Mn/(Fe+Mn+Mg+Ca)	0.074 0.001	0.177 0.001	0.172 0.017				0.244 0.003	0.239 0.007			0.025 0.001	0.059 0.005		
Mg/(Fe+Mn+Mg+Ca)	0.110 0.002	0.077 0.007	0.076 0.002				0.141 0.003	0.134 0.007			0.119 0.000	0.093 0.002		
Ca/(Fe+Mn+Mg+Ca)	0.065 0.003	0.080 0.005	0.064 0.006				0.059 0.004	0.068 0.009			0.063 0.008	0.074 0.004		

Table A5.6 Continued: Representative Garnet Analyses

	91-24a-I				91-1b2-II				91-1e-I				91-5b-II			
	Grt+St+Chl+Ky				Grt+Chl+St+Bt+Pl				St+Grt+Bt+Ky				St+Grt+Bt+Ky+Pl+Chl			
	Rim		Core		Rim		Core		Rim-Single Pt		Core		Rim-End		Core	
	n=3	(2σ)	n=4	(2σ)	n=2	(2σ)	n=2	(2σ)	n=1		n=4	(2σ)	n=2	(2σ)	n=6	(2σ)
SiO ₂	36.97	0.40	36.95	0.21	37.09	0.20	36.64	0.49	36.76		36.65	0.58	36.88	0.03	36.87	0.38
Al ₂ O ₃	20.91	0.18	20.74	0.29	21.15	0.10	20.46	0.06	20.74		20.86	0.15	20.68	0.16	20.88	0.24
Cr ₂ O ₃	0.05	0.08	0.01	0.03	0.06	0.02	0.04	0.11	0.00		0.02	0.05	0.03	0.08	0.03	0.05
TiO ₂	0.03	0.01	0.07	0.12	0.05	0.04	0.18	0.04	0.00		0.30	0.86	0.06	0.04	0.05	0.11
FeO	25.86	0.45	25.26	0.49	27.17	0.46	24.78	0.72	25.49		25.28	0.98	24.61	0.27	24.80	0.30
MnO	11.24	0.55	11.35	0.31	9.03	0.02	12.03	0.40	11.02		11.27	0.36	11.21	0.35	11.10	0.21
MgO	3.06	0.05	3.14	0.25	3.48	0.03	2.29	0.04	3.76		3.50	0.31	3.77	0.00	3.85	0.29
CaO	1.97	0.11	2.18	0.30	2.14	0.18	3.31	0.19	1.77		1.83	0.24	2.76	0.06	2.47	0.13
TOTAL	100.09	1.11	99.70	1.07	100.16	0.68	99.73	1.90	99.53		99.70	1.44	100.00	0.12	100.06	0.79
Cation proportions on the basis of 12 oxygens																
Si	2.981	0.007	2.987	0.021	2.976	0.002	2.978	0.006	2.974		2.961	0.022	2.968	0.007	2.963	0.029
Al	0.019	0.007	0.013	0.021	0.024	0.002	0.022	0.006	0.026		0.039	0.022	0.032	0.007	0.037	0.029
Sum	3.000	0.000	3.000	0.000	3.000	0.000	3.000	0.000	3.000		3.000	0.000	3.000	0.000	3.000	0.000
Al	1.968	0.026	1.963	0.014	1.976	0.017	1.938	0.030	1.951		1.948	0.022	1.930	0.004	1.941	0.021
Cr	0.003	0.005	0.001	0.002	0.004	0.002	0.002	0.007	0.000		0.001	0.003	0.002	0.005	0.002	0.003
Ti	0.002	0.000	0.004	0.007	0.003	0.002	0.011	0.002	0.000		0.018	0.053	0.004	0.002	0.003	0.007
Sum	1.973	0.029	1.968	0.015	1.983	0.018	1.951	0.025	1.951		1.967	0.045	1.936	0.012	1.947	0.019
Fe	1.744	0.017	1.708	0.025	1.823	0.022	1.684	0.024	1.724		1.708	0.048	1.656	0.015	1.667	0.021
Mn	0.768	0.032	0.777	0.016	0.614	0.004	0.828	0.015	0.755		0.771	0.019	0.764	0.025	0.755	0.013
Mg	0.368	0.002	0.378	0.033	0.416	0.006	0.278	0.009	0.453		0.422	0.033	0.452	0.000	0.461	0.033
Ca	0.170	0.011	0.189	0.025	0.184	0.014	0.288	0.012	0.153		0.159	0.021	0.238	0.006	0.213	0.010
Sum Fe to Ca	3.050	0.040	3.052	0.023	3.036	0.027	3.079	0.042	3.086		3.060	0.086	3.111	0.015	3.097	0.043
Fe/(Fe+Mg)	0.826	0.001	0.819	0.013	0.814	0.004	0.858	0.006	0.792		0.802	0.008	0.786	0.002	0.783	0.012
Mg/(Fe+Mg)	0.174	0.001	0.181	0.013	0.186	0.004	0.142	0.006	0.208		0.198	0.008	0.214	0.002	0.217	0.012
Fe/(Fe+Mn+Mg+Ca)	0.572	0.002	0.560	0.006	0.600	0.002	0.547	0.000	0.559		0.558	0.003	0.532	0.008	0.538	0.009
Mn/(Fe+Mn+Mg+Ca)	0.252	0.007	0.255	0.005	0.202	0.003	0.269	0.001	0.245		0.252	0.006	0.246	0.007	0.244	0.005
Mg/(Fe+Mn+Mg+Ca)	0.121	0.001	0.124	0.011	0.137	0.003	0.090	0.004	0.147		0.138	0.007	0.145	0.001	0.149	0.009
Ca/(Fe+Mn+Mg+Ca)	0.056	0.004	0.062	0.008	0.060	0.004	0.094	0.003	0.050		0.052	0.007	0.077	0.001	0.069	0.003
Cation proportions on the basis of 8 cations																
Si	2.972	0.005	2.980	0.024	2.969	0.001	2.967	0.012	2.960		2.952	0.021	2.951	0.006	2.947	0.038
Al	0.028	0.005	0.020	0.024	0.031	0.001	0.033	0.012	0.040		0.048	0.021	0.049	0.006	0.053	0.038
Sum	3.000	0.000	3.000	0.000	3.000	0.000	3.000	0.000	3.000		3.000	0.000	3.000	0.000	3.000	0.000
Al	1.954	0.033	1.951	0.020	1.965	0.022	1.920	0.040	1.928		1.931	0.031	1.902	0.006	1.915	0.034
Cr	0.003	0.005	0.001	0.002	0.004	0.001	0.002	0.007	0.000		0.001	0.003	0.002	0.005	0.002	0.003
Fe ³⁺	0.067	0.034	0.060	0.031	0.057	0.027	0.089	0.050	0.112		0.081	0.121	0.138	0.010	0.129	0.072
Ti	0.002	0.000	0.004	0.007	0.003	0.002	0.011	0.002	0.000		0.018	0.053	0.004	0.002	0.003	0.007
Sum	2.026	0.006	2.016	0.018	2.028	0.004	2.022	0.014	2.040		2.031	0.051	2.045	0.004	2.049	0.040
Fe ²⁺	1.672	0.019	1.643	0.018	1.762	0.007	1.588	0.029	1.604		1.622	0.084	1.509	0.026	1.529	0.074
Mn	0.768	0.030	0.775	0.015	0.612	0.005	0.825	0.014	0.752		0.769	0.017	0.760	0.024	0.751	0.013
Mg	0.367	0.002	0.377	0.033	0.415	0.006	0.277	0.010	0.451		0.420	0.031	0.449	0.000	0.459	0.032
Ca	0.169	0.011	0.188	0.025	0.183	0.014	0.287	0.012	0.152		0.158	0.021	0.237	0.005	0.212	0.009
Sum Fe to Ca	2.974	0.006	2.984	0.018	2.972	0.004	2.978	0.014	2.960		2.969	0.051	2.955	0.004	2.951	0.040
Fe/(Fe+Mg)	0.820	0.002	0.813	0.012	0.809	0.002	0.852	0.002	0.780		0.794	0.020	0.771	0.003	0.769	0.021
Mg/(Fe+Mg)	0.180	0.002	0.187	0.012	0.191	0.002	0.148	0.002	0.220		0.206	0.020	0.229	0.003	0.231	0.021
Fe/(Fe+Mn+Mg+Ca)	0.562	0.007	0.551	0.005	0.593	0.002	0.533	0.007	0.542		0.546	0.019	0.511	0.009	0.518	0.019
Mn/(Fe+Mn+Mg+Ca)	0.257	0.010	0.260	0.006	0.206	0.001	0.277	0.006	0.254		0.259	0.008	0.257	0.008	0.255	0.005
Mg/(Fe+Mn+Mg+Ca)	0.123	0.001	0.126	0.010	0.140	0.002	0.093	0.003	0.152		0.142	0.013	0.152	0.000	0.155	0.013
Ca/(Fe+Mn+Mg+Ca)	0.057	0.004	0.063	0.008	0.062	0.005	0.096	0.004	0.051		0.053	0.007	0.080	0.002	0.072	0.004

Table A5.6 Continued: Representative Garnet Analyses

	93-39d-III Grt+Bt+Ky+Pl				93-44b-II St+Grt+Bt+Ky+Pl				91-14d-I St+Grt+Bt+Pl				93-45a-I St+Grt+Bt+Pl			
	Rim-Prp Rev.		Core		Rim-Single Pt		Core		Rim-Single Pt		Core		Lo Alm-Start		Core	
	n=2	(2σ)	n=2	(2σ)	n=1		n=3	(2σ)	n=1		n=3	(2σ)	n=2	(2σ)	n=5	(2σ)
SiO ₂	36.99	0.44	36.87	0.03	36.55		36.64	0.34	36.83		36.94	0.74	37.04	0.48	36.50	0.57
Al ₂ O ₃	21.33	0.04	21.20	0.31	21.04		20.95	0.45	21.26		21.03	0.84	21.27	0.43	21.14	0.23
Cr ₂ O ₃	0.00	0.00	0.01	0.02	0.00		0.04	0.05	0.02		0.03	0.05	0.00	0.00	0.04	0.06
TiO ₂	0.03	0.07	0.06	0.00	0.10		0.08	0.06	0.00		0.07	0.19	0.02	0.06	0.01	0.03
FeO	18.08	0.03	16.94	0.07	27.19		24.62	0.48	32.28		32.35	0.10	33.21	0.58	32.75	0.41
MnO	15.28	0.26	15.65	0.07	9.95		11.03	0.34	3.42		4.07	0.21	2.75	0.26	3.17	0.09
MgO	5.29	0.10	5.04	0.05	3.40		3.19	0.16	3.36		3.36	0.12	3.17	0.01	3.17	0.09
CaO	2.63	0.14	3.13	0.29	2.12		3.33	0.07	2.95		2.33	0.06	3.31	0.07	3.00	0.15
TOTAL	99.64	0.01	98.89	0.61	100.34		99.88	0.49	100.13		100.18	1.85	100.77	1.63	99.78	0.89
Cation proportions on the basis of 12 oxygens																
Si	2.950	0.025	2.958	0.019	2.945		2.956	0.017	2.960		2.971	0.011	2.961	0.007	2.950	0.018
Al	0.050	0.025	0.042	0.019	0.055		0.044	0.017	0.040		0.029	0.011	0.039	0.007	0.050	0.018
Sum	3.000	0.000	3.000	0.000	3.000		3.000	0.000	3.000		3.000	0.000	3.000	0.000	3.000	0.000
Al	1.954	0.022	1.962	0.001	1.943		1.948	0.027	1.973		1.964	0.030	1.966	0.003	1.965	0.016
Cr	0.000	0.000	0.000	0.001	0.000		0.003	0.003	0.001		0.002	0.003	0.000	0.000	0.002	0.004
Ti	0.002	0.004	0.004	0.000	0.006		0.005	0.004	0.000		0.004	0.011	0.001	0.003	0.001	0.002
Sum	1.955	0.026	1.966	0.002	1.949		1.955	0.021	1.974		1.970	0.037	1.967	0.000	1.968	0.015
Fe	1.206	0.006	1.136	0.002	1.832		1.661	0.024	2.169		2.176	0.042	2.221	0.006	2.214	0.013
Mn	1.032	0.021	1.063	0.011	0.679		0.754	0.027	0.233		0.277	0.010	0.188	0.015	0.217	0.006
Mg	0.629	0.014	0.602	0.003	0.408		0.384	0.020	0.403		0.403	0.017	0.377	0.005	0.382	0.012
Ca	0.225	0.013	0.269	0.024	0.183		0.288	0.004	0.254		0.201	0.009	0.284	0.010	0.260	0.016
Sum Fe to Ca	3.092	0.054	3.070	0.013	3.102		3.087	0.022	3.059		3.057	0.056	3.068	0.006	3.073	0.026
Fe/(Fe+Mg)	0.657	0.004	0.653	0.001	0.818		0.812	0.008	0.843		0.844	0.005	0.855	0.002	0.853	0.004
Mg/(Fe+Mg)	0.343	0.004	0.347	0.001	0.182		0.188	0.008	0.157		0.156	0.005	0.145	0.002	0.147	0.004
Fe/(Fe+Mn+Mg+Ca)	0.390	0.005	0.370	0.002	0.591		0.538	0.008	0.709		0.712	0.005	0.724	0.000	0.720	0.006
Mn/(Fe+Mn+Mg+Ca)	0.334	0.001	0.346	0.005	0.219		0.244	0.009	0.076		0.091	0.004	0.061	0.005	0.071	0.002
Mg/(Fe+Mn+Mg+Ca)	0.203	0.001	0.196	0.000	0.131		0.124	0.006	0.132		0.132	0.004	0.123	0.002	0.124	0.003
Ca/(Fe+Mn+Mg+Ca)	0.073	0.003	0.087	0.007	0.059		0.093	0.001	0.083		0.066	0.002	0.093	0.003	0.085	0.005
Cation proportions on the basis of 8 cations																
Si	2.932	0.035	2.944	0.023	2.927		2.941	0.017	2.947		2.961	0.008	2.948	0.009	2.935	0.022
Al	0.068	0.035	0.056	0.023	0.073		0.059	0.017	0.053		0.039	0.008	0.052	0.009	0.065	0.022
Sum	3.000	0.000	3.000	0.000	3.000		3.000	0.000	3.000		3.000	0.000	3.000	0.000	3.000	0.000
Al	1.925	0.039	1.940	0.008	1.912		1.922	0.028	1.953		1.947	0.042	1.944	0.000	1.940	0.022
Cr	0.000	0.000	0.000	0.001	0.000		0.002	0.003	0.001		0.002	0.003	0.000	0.000	0.002	0.004
Fe ³⁺	0.140	0.083	0.109	0.032	0.150		0.125	0.011	0.099		0.082	0.057	0.105	0.016	0.121	0.038
Ti	0.002	0.004	0.004	0.000	0.006		0.005	0.004	0.000		0.004	0.011	0.001	0.003	0.001	0.002
Sum	2.066	0.040	2.052	0.023	2.068		2.054	0.020	2.053		2.035	0.009	2.050	0.012	2.064	0.022
Fe ²⁺	1.059	0.081	1.022	0.036	1.670		1.527	0.035	2.061		2.087	0.027	2.106	0.012	2.081	0.043
Mn	1.026	0.018	1.058	0.012	0.675		0.750	0.026	0.232		0.276	0.010	0.186	0.015	0.216	0.006
Mg	0.625	0.012	0.600	0.002	0.405		0.382	0.020	0.401		0.401	0.016	0.376	0.005	0.380	0.012
Ca	0.224	0.012	0.267	0.023	0.182		0.287	0.005	0.253		0.200	0.009	0.283	0.010	0.259	0.015
Sum Fe to Ca	2.934	0.040	2.948	0.023	2.932		2.946	0.020	2.947		2.965	0.009	2.950	0.012	2.936	0.022
Fe/(Fe+Mg)	0.629	0.022	0.630	0.009	0.805		0.800	0.010	0.837		0.839	0.007	0.849	0.001	0.846	0.006
Mg/(Fe+Mg)	0.371	0.022	0.370	0.009	0.195		0.200	0.010	0.163		0.161	0.007	0.151	0.001	0.154	0.006
Fe/(Fe+Mn+Mg+Ca)	0.361	0.023	0.347	0.009	0.570		0.519	0.011	0.699		0.704	0.008	0.714	0.001	0.709	0.010
Mn/(Fe+Mn+Mg+Ca)	0.350	0.011	0.359	0.001	0.230		0.255	0.010	0.079		0.093	0.003	0.063	0.005	0.073	0.002
Mg/(Fe+Mn+Mg+Ca)	0.213	0.007	0.203	0.002	0.138		0.130	0.006	0.136		0.135	0.006	0.127	0.001	0.130	0.005
Ca/(Fe+Mn+Mg+Ca)	0.076	0.005	0.091	0.009	0.082		0.097	0.001	0.086		0.068	0.003	0.096	0.003	0.088	0.006

Table A5.6 Continued: Representative Garnet Analyses

	94-1a-I St+Grt+Bt+Pl				Ardoc 201-V St+Grt+Bt+Sill+Pl+(Rel.Ky)				92-34b-I St+Grt+Bt+Sill+Pl				93-46b-I Grt+Bt+Sill			
	Rim		Core		Rim		Core		Rim-Start		Core		Rim		Core	
	n=3	(2σ)	n=6	(2σ)	n=2	(2σ)	n=4	(2σ)	n=3	(2σ)	n=4	(2σ)	n=4	(2σ)	n=8	(2σ)
SiO ₂	37.08	0.21	36.90	0.37	37.19	0.72	36.90	0.14	36.47	0.50	36.72	0.26	36.11	0.53	36.43	0.51
Al ₂ O ₃	21.07	0.64	20.92	0.38	21.08	0.20	20.72	0.55	21.07	0.18	21.04	0.38	20.85	0.33	20.80	0.38
Cr ₂ O ₃	0.05	0.01	0.02	0.05	0.11	0.05	0.03	0.06	0.03	0.06	0.01	0.05	0.07	0.02	0.02	0.06
TiO ₂	0.02	0.05	0.03	0.09	0.00	0.00	0.02	0.07	0.03	0.08	0.01	0.02	0.00	0.00	0.03	0.13
FeO	34.87	0.54	34.66	0.42	28.60	0.62	28.67	0.28	34.34	0.54	33.95	0.43	40.97	0.22	40.95	0.28
MnO	1.83	0.13	1.93	0.08	9.45	0.23	9.21	0.06	2.93	0.14	3.29	0.21	0.10	0.11	0.12	0.07
MgO	3.14	0.07	3.10	0.11	3.74	0.06	3.80	0.17	2.95	0.12	3.11	0.11	2.25	0.06	2.02	0.15
CaO	2.76	0.16	2.79	0.14	0.52	0.05	0.58	0.02	2.36	0.17	2.36	0.04	0.32	0.09	0.35	0.07
TOTAL	100.81	1.28	100.34	0.88	100.69	0.29	99.92	1.01	100.17	1.04	100.49	0.73	100.67	0.84	100.72	0.50
Cation proportions on the basis of 12 oxygens																
Si	2.969	0.026	2.971	0.022	2.979	0.050	2.981	0.031	2.949	0.016	2.957	0.013	2.944	0.027	2.965	0.023
Al	0.031	0.026	0.029	0.022	0.021	0.050	0.019	0.031	0.051	0.016	0.043	0.013	0.056	0.027	0.035	0.023
Sum	3.000	0.000	3.000	0.000	3.000	0.000	3.000	0.000	3.000	0.000	3.000	0.000	3.000	0.000	3.000	0.000
Al	1.958	0.020	1.955	0.016	1.969	0.026	1.954	0.012	1.958	0.016	1.954	0.014	1.947	0.010	1.960	0.032
Cr	0.003	0.001	0.001	0.003	0.007	0.003	0.002	0.004	0.002	0.004	0.001	0.003	0.004	0.002	0.001	0.004
Ti	0.001	0.003	0.002	0.005	0.000	0.000	0.001	0.004	0.002	0.005	0.001	0.001	0.000	0.000	0.002	0.008
Sum	1.963	0.020	1.958	0.021	1.976	0.029	1.956	0.015	1.962	0.024	1.955	0.015	1.951	0.009	1.963	0.025
Fe	2.336	0.016	2.333	0.023	1.915	0.046	1.937	0.022	2.322	0.017	2.287	0.015	2.793	0.014	2.787	0.034
Mn	0.124	0.008	0.131	0.007	0.641	0.017	0.630	0.005	0.200	0.009	0.225	0.016	0.007	0.007	0.008	0.005
Mg	0.374	0.004	0.372	0.012	0.447	0.008	0.457	0.015	0.355	0.012	0.374	0.013	0.273	0.010	0.245	0.020
Ca	0.237	0.017	0.240	0.013	0.045	0.004	0.050	0.002	0.204	0.015	0.204	0.003	0.028	0.008	0.031	0.006
Sum Fe to Ca	3.071	0.022	3.077	0.038	3.047	0.068	3.074	0.021	3.082	0.030	3.089	0.019	3.101	0.023	3.071	0.042
Fe/(Fe+Mg)	0.862	0.002	0.863	0.003	0.811	0.001	0.809	0.006	0.867	0.003	0.859	0.004	0.911	0.003	0.919	0.006
Mg/(Fe+Mg)	0.138	0.002	0.137	0.003	0.189	0.001	0.191	0.006	0.133	0.003	0.141	0.004	0.089	0.003	0.081	0.006
Fe/(Fe+Mn+Mg+Ca)	0.761	0.002	0.758	0.003	0.628	0.001	0.630	0.004	0.754	0.006	0.740	0.006	0.901	0.004	0.908	0.006
Mn/(Fe+Mn+Mg+Ca)	0.040	0.002	0.043	0.002	0.210	0.001	0.205	0.002	0.065	0.003	0.073	0.005	0.002	0.002	0.003	0.002
Mg/(Fe+Mn+Mg+Ca)	0.122	0.002	0.121	0.003	0.147	0.000	0.149	0.005	0.115	0.003	0.121	0.004	0.088	0.003	0.080	0.006
Ca/(Fe+Mn+Mg+Ca)	0.077	0.005	0.078	0.004	0.015	0.002	0.016	0.000	0.066	0.004	0.066	0.001	0.009	0.003	0.010	0.002
Cation proportions on the basis of 8 cations																
Si	2.957	0.027	2.958	0.028	2.970	0.064	2.969	0.034	2.934	0.014	2.941	0.014	2.925	0.032	2.952	0.029
Al	0.043	0.027	0.042	0.028	0.030	0.064	0.031	0.034	0.066	0.014	0.059	0.014	0.075	0.032	0.048	0.029
Sum	3.000	0.000	3.000	0.000	3.000	0.000	3.000	0.000	3.000	0.000	3.000	0.000	3.000	0.000	3.000	0.000
Al	1.938	0.021	1.934	0.026	1.955	0.050	1.935	0.017	1.931	0.020	1.927	0.016	1.915	0.018	1.939	0.042
Cr	0.003	0.001	0.001	0.003	0.007	0.003	0.002	0.004	0.002	0.004	0.001	0.003	0.004	0.002	0.001	0.004
Fe ³⁺	0.100	0.020	0.104	0.057	0.068	0.117	0.092	0.037	0.130	0.021	0.131	0.021	0.156	0.047	0.104	0.056
Ti	0.001	0.003	0.002	0.005	0.000	0.000	0.001	0.004	0.002	0.005	0.001	0.001	0.000	0.000	0.002	0.008
Sum	2.042	0.024	2.041	0.031	2.030	0.064	2.029	0.030	2.065	0.009	2.059	0.015	2.075	0.032	2.046	0.026
Fe ²⁺	2.226	0.016	2.219	0.041	1.841	0.080	1.838	0.040	2.180	0.015	2.144	0.020	2.618	0.046	2.671	0.045
Mn	0.123	0.008	0.131	0.007	0.639	0.014	0.628	0.006	0.199	0.009	0.223	0.016	0.007	0.007	0.008	0.005
Mg	0.373	0.004	0.370	0.011	0.445	0.006	0.456	0.015	0.353	0.011	0.372	0.013	0.271	0.009	0.244	0.019
Ca	0.236	0.017	0.239	0.012	0.045	0.004	0.050	0.002	0.203	0.014	0.203	0.003	0.028	0.008	0.031	0.006
Sum Fe to Ca	2.958	0.024	2.959	0.031	2.970	0.064	2.971	0.030	2.935	0.009	2.941	0.015	2.925	0.032	2.954	0.026
Fe/(Fe+Mg)	0.857	0.002	0.857	0.005	0.805	0.009	0.801	0.009	0.861	0.004	0.852	0.004	0.906	0.004	0.916	0.007
Mg/(Fe+Mg)	0.143	0.002	0.143	0.005	0.195	0.009	0.199	0.009	0.139	0.004	0.148	0.004	0.094	0.004	0.084	0.007
Fe/(Fe+Mn+Mg+Ca)	0.753	0.001	0.750	0.007	0.620	0.014	0.619	0.007	0.743	0.007	0.729	0.007	0.895	0.006	0.904	0.008
Mn/(Fe+Mn+Mg+Ca)	0.042	0.003	0.044	0.002	0.215	0.009	0.211	0.001	0.068	0.003	0.076	0.005	0.002	0.003	0.003	0.002
Mg/(Fe+Mn+Mg+Ca)	0.126	0.002	0.125	0.005	0.150	0.005	0.153	0.007	0.120	0.004	0.126	0.004	0.093	0.004	0.083	0.007
Ca/(Fe+Mn+Mg+Ca)	0.080	0.005	0.081	0.004	0.015	0.001	0.017	0.001	0.069	0.005	0.069	0.001	0.010	0.003	0.010	0.002

Table A5.6 Continued: Representative Garnet Analyses

	R3 301-II				93-40d-I			
	St+Grt+Bt+Sill+Pl (No Ms)				St+Grt+Bt+Sill			
	Rim		Core		Rim-Start		Core	
	n=2	(2σ)	n=5	(2σ)	n=2	(2σ)	n=5	(2σ)
SiO ₂	36.75	0.37	36.71	0.30	36.80	0.30	36.75	0.29
Al ₂ O ₃	21.30	0.49	20.93	0.38	21.01	0.39	20.97	0.16
Cr ₂ O ₃	0.00	0.01	0.03	0.06	0.00	0.00	0.01	0.03
TiO ₂	0.01	0.04	0.02	0.06	0.01	0.03	0.04	0.04
FeO	34.00	0.23	33.79	0.36	37.72	0.76	38.01	0.59
MnO	3.85	0.07	3.77	0.11	0.12	0.04	0.20	0.07
MgO	3.73	0.16	3.80	0.19	2.58	0.06	2.69	0.17
CaO	1.21	0.24	1.03	0.08	2.50	0.42	2.07	0.24
TOTAL	100.85	0.72	100.09	0.70	100.73	0.11	100.74	0.78
<i>Cation proportions on the basis of 12 oxygens</i>								
Si	2.945	0.002	2.962	0.023	2.965	0.026	2.964	0.015
Al	0.055	0.002	0.038	0.023	0.035	0.026	0.036	0.015
Sum	3.000	0.000	3.000	0.000	3.000	0.000	3.000	0.000
Al	1.958	0.029	1.953	0.029	1.960	0.011	1.956	0.015
Cr	0.000	0.000	0.002	0.004	0.000	0.000	0.001	0.002
Ti	0.001	0.002	0.001	0.004	0.001	0.002	0.002	0.003
Sum	1.958	0.026	1.956	0.024	1.961	0.012	1.959	0.014
Fe	2.279	0.037	2.280	0.018	2.542	0.053	2.563	0.027
Mn	0.261	0.002	0.258	0.006	0.008	0.003	0.013	0.005
Mg	0.446	0.024	0.457	0.023	0.310	0.007	0.323	0.020
Ca	0.103	0.020	0.089	0.007	0.216	0.036	0.179	0.022
Sum Fe to Ca	3.089	0.039	3.085	0.040	3.076	0.007	3.078	0.027
Fe/(Fe+Mg)	0.836	0.005	0.833	0.006	0.891	0.004	0.888	0.006
Mg/(Fe+Mg)	0.164	0.005	0.167	0.006	0.109	0.004	0.112	0.006
Fe/(Fe+Mn+Mg+Ca)	0.738	0.003	0.739	0.005	0.826	0.015	0.833	0.006
Mn/(Fe+Mn+Mg+Ca)	0.085	0.002	0.084	0.002	0.003	0.001	0.004	0.002
Mg/(Fe+Mn+Mg+Ca)	0.144	0.006	0.148	0.006	0.101	0.002	0.105	0.006
Ca/(Fe+Mn+Mg+Ca)	0.033	0.007	0.029	0.002	0.070	0.012	0.058	0.007
<i>Cation proportions on the basis of 8 cations</i>								
Si	2.928	0.006	2.947	0.029	2.952	0.028	2.950	0.019
Al	0.072	0.006	0.053	0.029	0.048	0.028	0.050	0.019
Sum	3.000	0.000	3.000	0.000	3.000	0.000	3.000	0.000
Al	1.928	0.037	1.928	0.038	1.938	0.007	1.933	0.023
Cr	0.000	0.000	0.002	0.004	0.000	0.000	0.001	0.002
Fe ³⁺	0.142	0.038	0.121	0.053	0.109	0.017	0.112	0.040
Ti	0.001	0.002	0.001	0.004	0.001	0.002	0.002	0.003
Sum	2.071	0.004	2.052	0.028	2.048	0.026	2.048	0.018
Fe ²⁺	2.123	0.005	2.148	0.043	2.421	0.071	2.439	0.031
Mn	0.260	0.002	0.257	0.006	0.008	0.003	0.013	0.005
Mg	0.443	0.023	0.455	0.022	0.309	0.007	0.321	0.019
Ca	0.103	0.020	0.089	0.007	0.215	0.036	0.178	0.022
Sum Fe to Ca	2.929	0.004	2.948	0.028	2.952	0.026	2.952	0.018
Fe/(Fe+Mg)	0.827	0.008	0.825	0.009	0.887	0.005	0.884	0.007
Mg/(Fe+Mg)	0.173	0.008	0.175	0.009	0.113	0.005	0.116	0.007
Fe/(Fe+Mn+Mg+Ca)	0.725	0.001	0.728	0.009	0.820	0.017	0.826	0.007
Mn/(Fe+Mn+Mg+Ca)	0.089	0.001	0.087	0.003	0.003	0.001	0.005	0.002
Mg/(Fe+Mn+Mg+Ca)	0.151	0.008	0.154	0.008	0.105	0.003	0.109	0.007
Ca/(Fe+Mn+Mg+Ca)	0.035	0.007	0.030	0.002	0.073	0.013	0.060	0.007

Table A5.6 Continued: Representative Garnet Analyses

	CR-4a-1 St+Grt+Bt+Sill+Pl				CR-8b-1 St+Grt+Bt+Pl				CR-3a-1 Grt+Bt+Pl			
	Rim		Core		Rim-End		Core		Rim		Core	
	n=2	(2σ)	n=5	(2σ)	n=2	(2σ)	n=6	(2σ)	n=2	(2σ)	n=3	(2σ)
SiO ₂	36.54	0.53	36.53	0.44	36.92	0.37	36.63	0.57	36.74	0.09	36.67	0.31
Al ₂ O ₃	20.74	0.45	20.73	0.53	20.83	0.11	20.83	0.27	20.77	0.13	20.79	0.33
Cr ₂ O ₃	0.02	0.01	0.06	0.02	0.03	0.10	0.03	0.06	0.02	0.05	0.00	0.01
TiO ₂	0.04	0.10	0.01	0.03	0.00	0.00	0.05	0.09	0.01	0.00	0.00	0.02
FeO	37.06	0.47	37.28	0.61	33.22	0.04	33.10	0.64	30.23	0.15	28.42	0.28
MnO	1.35	0.05	1.37	0.09	3.52	0.15	3.08	0.16	8.53	0.01	9.98	0.33
MgO	2.71	0.00	2.61	0.23	3.37	0.28	3.27	0.18	3.37	0.10	3.46	0.03
CaO	1.65	0.14	1.39	0.04	2.71	0.03	2.75	0.21	0.54	0.08	0.60	0.04
TOTAL	100.10	1.36	99.97	1.32	100.61	0.78	99.74	1.08	100.20	0.10	99.93	0.89
Cation proportions on the basis of 12 oxygens												
Si	2.968	0.001	2.972	0.017	2.986	0.002	2.984	0.015	2.972	0.005	2.971	0.007
Al	0.032	0.001	0.028	0.017	0.034	0.002	0.036	0.015	0.028	0.005	0.029	0.007
Sum	3.000	0.000	3.000	0.000	3.000	0.000	3.000	0.000	3.000	0.000	3.000	0.000
Al	1.953	0.012	1.959	0.032	1.937	0.006	1.950	0.022	1.952	0.008	1.956	0.008
Cr	0.001	0.000	0.004	0.002	0.002	0.006	0.002	0.004	0.001	0.003	0.000	0.001
Ti	0.002	0.006	0.000	0.002	0.000	0.000	0.003	0.006	0.001	0.000	0.000	0.001
Sum	1.956	0.018	1.963	0.031	1.940	0.000	1.955	0.018	1.954	0.011	1.956	0.009
Fe	2.517	0.006	2.536	0.029	2.231	0.019	2.240	0.035	2.045	0.009	1.925	0.023
Mn	0.093	0.004	0.094	0.007	0.239	0.012	0.211	0.011	0.584	0.000	0.685	0.021
Mg	0.328	0.005	0.317	0.028	0.404	0.029	0.394	0.020	0.406	0.011	0.418	0.005
Ca	0.144	0.014	0.122	0.003	0.233	0.000	0.238	0.020	0.047	0.007	0.052	0.003
Sum Fe to Ca	3.081	0.029	3.069	0.050	3.108	0.001	3.084	0.027	3.082	0.013	3.080	0.014
Fe/(Fe+Mg)	0.885	0.001	0.889	0.009	0.847	0.010	0.850	0.008	0.834	0.003	0.822	0.003
Mg/(Fe+Mg)	0.115	0.001	0.111	0.009	0.153	0.010	0.150	0.008	0.166	0.003	0.178	0.003
Fe/(Fe+Mn+Mg+Ca)	0.817	0.006	0.826	0.008	0.718	0.006	0.726	0.011	0.663	0.000	0.625	0.008
Mn/(Fe+Mn+Mg+Ca)	0.030	0.001	0.031	0.002	0.077	0.004	0.069	0.003	0.190	0.001	0.222	0.006
Mg/(Fe+Mn+Mg+Ca)	0.106	0.001	0.103	0.008	0.130	0.009	0.128	0.006	0.132	0.003	0.136	0.001
Ca/(Fe+Mn+Mg+Ca)	0.047	0.004	0.040	0.001	0.075	0.000	0.077	0.006	0.015	0.002	0.017	0.001
Cation proportions on the basis of 8 cations												
Si	2.954	0.003	2.960	0.023	2.948	0.003	2.950	0.019	2.959	0.004	2.958	0.008
Al	0.046	0.003	0.040	0.023	0.052	0.003	0.050	0.019	0.041	0.004	0.042	0.008
Sum	3.000	0.000	3.000	0.000	3.000	0.000	3.000	0.000	3.000	0.000	3.000	0.000
Al	1.930	0.019	1.939	0.043	1.908	0.005	1.926	0.027	1.930	0.010	1.933	0.011
Cr	0.001	0.000	0.004	0.002	0.002	0.006	0.002	0.004	0.001	0.003	0.000	0.001
Fe ₃₊	0.110	0.034	0.096	0.060	0.141	0.003	0.117	0.036	0.109	0.008	0.108	0.016
Ti	0.002	0.006	0.000	0.002	0.000	0.000	0.003	0.006	0.001	0.000	0.000	0.001
Sum	2.044	0.009	2.040	0.022	2.052	0.003	2.048	0.023	2.041	0.005	2.042	0.008
Fe ₂₊	2.395	0.032	2.430	0.044	2.077	0.015	2.113	0.054	1.927	0.001	1.808	0.033
Mn	0.092	0.004	0.094	0.007	0.238	0.012	0.210	0.011	0.582	0.000	0.682	0.021
Mg	0.326	0.005	0.315	0.028	0.402	0.029	0.392	0.020	0.405	0.011	0.416	0.005
Ca	0.143	0.014	0.121	0.003	0.232	0.000	0.237	0.019	0.046	0.007	0.052	0.003
Sum Fe to Ca	2.956	0.009	2.960	0.022	2.948	0.003	2.952	0.023	2.959	0.005	2.958	0.008
Fe/(Fe+Mg)	0.880	0.003	0.885	0.011	0.838	0.011	0.843	0.009	0.826	0.004	0.813	0.004
Mg/(Fe+Mg)	0.120	0.003	0.115	0.011	0.162	0.011	0.157	0.009	0.174	0.004	0.187	0.004
Fe/(Fe+Mn+Mg+Ca)	0.810	0.008	0.821	0.011	0.704	0.006	0.716	0.013	0.651	0.001	0.611	0.010
Mn/(Fe+Mn+Mg+Ca)	0.031	0.002	0.032	0.002	0.081	0.004	0.071	0.004	0.197	0.000	0.231	0.008
Mg/(Fe+Mn+Mg+Ca)	0.110	0.002	0.107	0.010	0.136	0.010	0.133	0.007	0.137	0.004	0.141	0.002
Ca/(Fe+Mn+Mg+Ca)	0.048	0.005	0.041	0.001	0.079	0.000	0.080	0.007	0.016	0.002	0.018	0.001

Table A5.7: Representative Biotite Analyses

	Madoc-7b2-III		Madoc-2e-V		Queens-1a-I		93-15d-I		92-6c-III		92-6f1-II	
	Grt+Chl+Bt porphyroblasts		Grt+Chl+Bt+St+Cld porph. incl. in Cld		Grt+Chl+Cld+Bt+(St) matrix Bt		Grt+Chl+Bt+Pl small porph.		Grt+Cld+Bt+(Chl) assorted matrix		Grt+Chl+Cld+Bt sm. porph. - core	
	(7,2)	(2σ)	(3,1)	(2σ)	(11,3)	(2σ)	(4,1)	(2σ)	(12,4)	(2σ)	(3,1)	(2σ)
SiO ₂	34.35	0.44	35.32	0.54	34.41	0.57	35.31	0.22	34.48	0.54	34.86	0.07
Al ₂ O ₃	19.68	0.37	19.34	0.21	19.48	0.64	18.68	0.30	19.24	0.49	19.34	0.08
Cr ₂ O ₃	0.04	0.08	0.04	0.08	0.02	0.06	0.25	0.06	0.01	0.03	0.05	0.01
TiO ₂	1.58	0.13	1.48	0.09	1.54	0.11	1.77	0.17	1.74	0.13	1.49	0.11
FeO	23.76	0.34	20.82	0.35	22.92	0.51	20.46	0.13	25.30	0.43	21.96	0.25
MnO	0.02	0.06	0.07	0.09	0.03	0.07	0.13	0.03	0.03	0.04	0.01	0.03
MgO	6.99	0.14	10.01	0.12	7.85	0.27	9.59	0.36	6.51	0.18	8.17	0.21
CaO	0.02	0.03	0.01	0.04	0.01	0.02	0.00	0.01	0.04	0.06	0.02	0.04
Na ₂ O	0.35	0.24	0.27	0.14	0.20	0.23	0.09	0.09	0.28	0.31	0.33	0.33
K ₂ O	9.32	0.12	9.34	0.28	9.60	0.29	9.74	0.12	9.41	0.17	9.81	0.12
BaO	0.07	0.11	n.d.	n.d.	0.36	0.12	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Cl	0.04	0.03	0.08	0.01	0.06	0.03	0.02	0.03	0.06	0.02	0.09	0.04
TOTAL	96.21	0.99	96.78	0.39	96.48	1.00	96.04	0.70	97.10	0.85	96.14	1.07
TOTAL-O=Cl	96.20	0.99	96.76	0.39	96.47	1.01	96.04	0.70	97.08	0.86	96.12	1.07
<i>Cation proportions on the basis of 11 oxygens</i>												
Si	2.650	0.018	2.665	0.026	2.647	0.014	2.689	0.023	2.655	0.020	2.673	0.018
Al	1.350	0.018	1.335	0.026	1.353	0.014	1.311	0.023	1.345	0.020	1.327	0.018
Sum	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000
Al	0.439	0.019	0.384	0.013	0.413	0.049	0.365	0.023	0.401	0.029	0.421	0.028
Cr	0.003	0.005	0.003	0.005	0.001	0.004	0.015	0.003	0.001	0.002	0.003	0.001
Ti	0.091	0.008	0.084	0.004	0.089	0.006	0.102	0.009	0.101	0.007	0.086	0.006
Fe	1.533	0.025	1.313	0.029	1.474	0.045	1.303	0.016	1.629	0.042	1.409	0.004
Mn	0.001	0.004	0.004	0.006	0.002	0.004	0.008	0.002	0.002	0.003	0.001	0.002
Mg	0.804	0.012	1.126	0.020	0.901	0.033	1.089	0.037	0.747	0.023	0.934	0.017
Sum	2.871	0.017	2.914	0.018	2.879	0.032	2.883	0.022	2.881	0.032	2.853	0.005
Ca	0.001	0.002	0.001	0.003	0.001	0.002	0.000	0.001	0.003	0.005	0.002	0.003
Na	0.052	0.036	0.039	0.021	0.030	0.034	0.013	0.013	0.042	0.045	0.049	0.049
K	0.918	0.012	0.899	0.024	0.942	0.026	0.946	0.010	0.924	0.016	0.960	0.011
Ba	0.002	0.003	n.d.	n.d.	0.011	0.004	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sum	0.973	0.037	0.940	0.013	0.984	0.039	0.960	0.020	0.970	0.050	1.011	0.047
Cl	0.006	0.004	0.011	0.001	0.008	0.004	0.002	0.003	0.008	0.003	0.011	0.005
Fe/(Fe+Mg)	0.656	0.005	0.538	0.005	0.621	0.006	0.545	0.009	0.686	0.007	0.601	0.004
Mg/(Fe+Mg)	0.344	0.005	0.462	0.005	0.379	0.006	0.455	0.009	0.314	0.007	0.399	0.004
<i>Cation proportions on the basis of 7 cations</i>												
Si	2.699	0.024	2.698	0.033	2.693	0.025	2.735	0.026	2.701	0.026	2.731	0.018
Al	1.301	0.024	1.302	0.033	1.307	0.025	1.265	0.026	1.299	0.026	1.269	0.018
Sum	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000
Al	0.522	0.025	0.439	0.024	0.490	0.064	0.440	0.036	0.477	0.044	0.516	0.027
Fe ³⁺	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Cr	0.003	0.005	0.003	0.005	0.001	0.004	0.015	0.003	0.001	0.002	0.003	0.001
Ti	0.093	0.008	0.085	0.005	0.090	0.006	0.103	0.009	0.103	0.007	0.088	0.006
Fe ²⁺	1.562	0.023	1.330	0.026	1.500	0.041	1.325	0.015	1.657	0.036	1.439	0.005
Mn	0.001	0.004	0.004	0.006	0.002	0.005	0.008	0.002	0.002	0.003	0.001	0.002
Mg	0.819	0.011	1.139	0.018	0.916	0.030	1.108	0.035	0.760	0.022	0.954	0.017
Sum	3.000	0.000	3.000	0.000	3.000	0.000	3.000	0.000	3.000	0.000	3.000	0.000
Ca	0.001	0.002	0.001	0.003	0.001	0.002	0.000	0.001	0.003	0.005	0.002	0.003
Na	0.053	0.037	0.040	0.021	0.030	0.035	0.013	0.013	0.043	0.046	0.050	0.050
K	0.935	0.014	0.911	0.026	0.959	0.028	0.963	0.013	0.940	0.018	0.980	0.011
Ba	0.004	0.006	n.d.	n.d.	0.022	0.007	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sum	0.994	0.040	0.951	0.012	1.012	0.043	0.976	0.023	0.986	0.055	1.033	0.042
Cl	0.006	0.005	0.011	0.001	0.008	0.005	0.002	0.004	0.008	0.003	0.012	0.005
Fe/(Fe+Mg)	0.656	0.005	0.539	0.005	0.621	0.006	0.545	0.009	0.686	0.396	0.601	0.004
Mg/(Fe+Mg)	0.344	0.005	0.461	0.005	0.379	0.006	0.455	0.009	0.314	0.182	0.399	0.004

Table A5.7 Continued: Representative Biotite Analyses

	93-26e-l		93-26g-l		92-8d-l		92-42c-l		93-18a-l		92-41a-l	
	Grt+Chl+Cld+Bt+St+Mrg tiny xl. nucl. on Cld		Grt+Chl+Bt+St+Mrg sml. porph.-adj. to St		Grt+Chl+Cld+Bt+St+Mrg matrix Bt nucl. on Cld		Grt+Cld+Bt matrix Bt		Grt+Cld+Bt matrix Bt		Grt+Cld+Bt matrix Bt	
	(2,1)	(2σ)	(2,1)	(2σ)	(9,3)	(2σ)	(7,2)	(2σ)	(8,3)	(2σ)	(6,2)	(2σ)
SiO ₂	34.68	0.34	35.06	0.38	35.41	0.38	34.68	0.57	34.53	0.43	34.32	0.19
Al ₂ O ₃	19.04	0.44	18.66	0.54	19.13	0.68	19.61	0.62	19.22	0.94	19.34	0.52
Cr ₂ O ₃	0.03	0.01	0.03	0.07	0.04	0.08	0.01	0.03	0.05	0.08	0.03	0.05
TiO ₂	2.45	0.01	1.56	0.18	1.51	0.15	1.59	0.16	1.66	0.09	1.38	0.07
FeO	22.04	0.57	19.79	0.87	19.68	0.95	23.83	0.40	24.11	0.58	23.76	0.59
MnO	0.10	0.02	0.03	0.06	0.07	0.08	0.03	0.06	0.05	0.04	0.05	0.06
MgO	6.84	0.27	9.69	0.21	9.92	0.48	7.23	0.24	6.82	0.16	7.43	0.31
CaO	0.00	0.00	0.06	0.03	0.02	0.06	0.03	0.05	0.01	0.04	0.02	0.06
Na ₂ O	0.25	0.03	0.37	0.06	0.30	0.26	0.31	0.23	0.21	0.20	0.34	0.32
K ₂ O	9.66	0.31	9.22	0.36	9.46	0.40	9.39	0.40	9.28	0.29	9.54	0.10
BaO	0.03	0.01	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.109	0.135
Cl	0.08	0.01	0.06	0.04	0.40	0.04	0.21	0.05	0.08	0.03	0.07	0.06
TOTAL	95.20	0.27	94.54	0.05	95.94	0.97	96.91	1.02	96.01	0.70	96.37	0.88
TOTAL-O=Cl	95.18	0.27	94.53	0.04	95.85	0.98	96.86	1.03	95.99	0.70	96.35	0.89
<i>Cation proportions on the basis of 11 oxygens</i>												
Si	2.688	0.011	2.699	0.018	2.687	0.019	2.655	0.029	2.672	0.009	2.650	0.014
Al	1.312	0.011	1.301	0.018	1.313	0.019	1.345	0.029	1.328	0.009	1.350	0.014
Sum	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000
Al	0.427	0.042	0.392	0.060	0.398	0.054	0.425	0.030	0.424	0.064	0.410	0.056
Cr	0.002	0.001	0.002	0.004	0.003	0.005	0.001	0.002	0.003	0.005	0.002	0.003
Ti	0.143	0.000	0.091	0.011	0.086	0.009	0.092	0.009	0.096	0.005	0.080	0.004
Fe	1.429	0.045	1.274	0.061	1.249	0.055	1.526	0.036	1.560	0.053	1.535	0.037
Mn	0.007	0.001	0.002	0.004	0.005	0.005	0.002	0.004	0.003	0.003	0.003	0.004
Mg	0.790	0.035	1.112	0.029	1.122	0.048	0.825	0.032	0.786	0.024	0.855	0.034
Sum	2.797	0.037	2.873	0.041	2.862	0.047	2.871	0.047	2.873	0.023	2.885	0.025
Ca	0.000	0.000	0.005	0.003	0.002	0.005	0.003	0.004	0.001	0.004	0.001	0.005
Na	0.038	0.005	0.056	0.009	0.044	0.038	0.046	0.035	0.032	0.031	0.050	0.048
K	0.955	0.025	0.906	0.032	0.915	0.043	0.917	0.037	0.916	0.033	0.939	0.010
Ba	0.001	0.000	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.003	0.004
Sum	0.994	0.021	0.967	0.006	0.961	0.036	0.948	0.056	0.950	0.037	0.994	0.056
Cl	0.010	0.001	0.008	0.005	0.052	0.005	0.027	0.006	0.011	0.004	0.009	0.008
Fe/(Fe+Mg)	0.644	0.003	0.534	0.005	0.527	0.007	0.649	0.004	0.665	0.005	0.642	0.004
Mg/(Fe+Mg)	0.356	0.003	0.466	0.005	0.473	0.007	0.351	0.004	0.335	0.005	0.358	0.004
<i>Cation proportions on the basis of 7 cations</i>												
Si	2.768	0.027	2.749	0.035	2.741	0.019	2.705	0.047	2.721	0.014	2.694	0.023
Al	1.232	0.027	1.251	0.035	1.259	0.019	1.295	0.047	1.279	0.014	1.306	0.023
Sum	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000
Al	0.559	0.068	0.474	0.088	0.486	0.080	0.509	0.054	0.506	0.076	0.484	0.068
Fe ³⁺	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Cr	0.002	0.001	0.002	0.004	0.003	0.005	0.001	0.002	0.003	0.005	0.002	0.003
Ti	0.147	0.001	0.092	0.011	0.088	0.009	0.093	0.009	0.098	0.006	0.081	0.004
Fe ²⁺	1.471	0.038	1.298	0.054	1.274	0.049	1.555	0.028	1.589	0.050	1.560	0.033
Mn	0.007	0.001	0.002	0.004	0.005	0.005	0.002	0.004	0.003	0.003	0.003	0.004
Mg	0.814	0.032	1.132	0.023	1.144	0.043	0.841	0.027	0.801	0.022	0.869	0.033
Sum	3.000	0.000	3.000	0.000	3.000	0.000	3.000	0.000	3.000	0.000	3.000	0.000
Ca	0.000	0.000	0.005	0.003	0.002	0.005	0.003	0.004	0.001	0.004	0.001	0.005
Na	0.039	0.005	0.057	0.009	0.045	0.039	0.046	0.036	0.033	0.031	0.051	0.049
K	0.984	0.031	0.923	0.038	0.934	0.049	0.934	0.043	0.933	0.034	0.955	0.009
Ba	0.002	0.001	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.007	0.008
Sum	1.024	0.028	0.985	0.006	0.980	0.037	0.949	0.063	0.967	0.039	1.014	0.059
Cl	0.011	0.002	0.008	0.005	0.053	0.005	0.027	0.006	0.011	0.004	0.009	0.008
Fe/(Fe+Mg)	0.644	0.003	0.534	0.005	0.527	0.007	0.649	0.004	0.665	0.005	0.642	0.004
Mg/(Fe+Mg)	0.356	0.003	0.466	0.005	0.473	0.007	0.351	0.004	0.335	0.005	0.358	0.004

Table A5.7 Continued: Representative Biotite Analyses

	93-20f-I		92-10a-II		90-19a-I		92-27a-II		92-28a-I		92-9i2-II	
	Grt+Cld+Bt		Cld+St+Grt+Bt		Cld+St+Grt+Bt+Pl		Cld+St+Grt+Bt		Cld+St+Grt+Bt		Grt+Chl+Bt+Pl+Epid	
	Hi Mg-matrix Bt		matrix Bt		small porph.		small porph.		small Bt porphs.		matrix Bt	
	(2,1)	(2σ)	(4,1)	(2σ)	(3,1)	(2σ)	(3,1)	(2σ)	(7,2)	(2σ)	(3,1)	(2σ)
SiO ₂	34.03	0.37	33.12	0.51	34.43	0.21	34.09	0.18	34.55	0.54	36.40	0.20
Al ₂ O ₃	20.28	0.53	19.67	0.37	19.88	0.46	18.76	0.55	19.52	0.25	18.75	0.33
Cr ₂ O ₃	0.02	0.06	0.06	0.11	0.01	0.05	0.04	0.07	0.05	0.06	0.03	0.10
TiO ₂	1.69	0.01	1.56	0.10	1.48	0.03	1.48	0.09	1.54	0.15	1.44	0.11
FeO	25.57	0.01	24.64	0.12	24.33	0.64	24.16	0.66	23.16	0.47	16.94	0.34
MnO	0.00	0.01	0.01	0.03	0.04	0.05	0.03	0.10	0.01	0.03	0.09	0.08
MgO	5.26	0.20	5.64	0.28	6.47	0.14	7.29	0.26	7.69	0.30	12.24	0.15
CaO	0.00	0.00	0.07	0.09	0.00	0.00	0.02	0.05	0.01	0.02	0.00	0.00
Na ₂ O	0.23	0.01	0.15	0.26	0.24	0.21	0.07	0.07	0.23	0.36	0.16	0.20
K ₂ O	9.41	0.14	9.21	0.12	9.05	0.12	9.79	0.10	9.63	0.14	9.58	0.10
BaO	n.d.	n.d.	0.082	0.190	n.d.	n.d.	0.141	0.086	0.199	0.117	n.d.	n.d.
Cl	0.26	0.00	0.63	0.04	0.31	0.15	0.06	0.02	0.03	0.03	0.01	0.02
TOTAL	96.76	0.49	94.86	0.77	96.24	1.37	95.95	0.64	96.62	1.24	95.66	1.22
TOTAL-O=Cl	96.70	0.49	94.71	0.76	96.17	1.36	95.93	0.64	96.61	1.23	95.65	1.23
Cation proportions on the basis of 11 oxygens												
Si	2.633	0.006	2.619	0.027	2.657	0.018	2.656	0.030	2.652	0.021	2.725	0.023
Al	1.367	0.006	1.381	0.027	1.343	0.018	1.344	0.030	1.348	0.021	1.275	0.023
Sum	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000
Al	0.483	0.039	0.452	0.010	0.465	0.011	0.379	0.031	0.418	0.024	0.380	0.017
Cr	0.001	0.003	0.004	0.007	0.001	0.003	0.002	0.004	0.003	0.003	0.002	0.006
Ti	0.098	0.001	0.093	0.006	0.086	0.003	0.087	0.005	0.089	0.008	0.081	0.005
Fe	1.655	0.014	1.629	0.013	1.570	0.028	1.574	0.042	1.487	0.018	1.061	0.010
Mn	0.000	0.001	0.001	0.002	0.003	0.003	0.002	0.006	0.000	0.002	0.006	0.005
Mg	0.607	0.028	0.665	0.034	0.744	0.009	0.847	0.025	0.880	0.030	1.366	0.014
Sum	2.844	0.009	2.843	0.029	2.869	0.017	2.892	0.023	2.877	0.034	2.896	0.003
Ca	0.000	0.000	0.006	0.007	0.000	0.000	0.002	0.004	0.001	0.002	0.000	0.000
Na	0.035	0.001	0.024	0.040	0.036	0.032	0.011	0.011	0.034	0.054	0.023	0.029
K	0.929	0.021	0.929	0.004	0.891	0.006	0.974	0.015	0.943	0.012	0.915	0.001
Ba	n.d.	n.d.	0.003	0.006	n.d.	n.d.	0.004	0.003	0.006	0.004	n.d.	n.d.
Sum	0.964	0.020	0.961	0.048	0.927	0.027	0.991	0.018	0.984	0.062	0.923	0.029
Cl	0.034	0.000	0.085	0.005	0.041	0.020	0.008	0.003	0.004	0.004	0.001	0.002
Fe/(Fe+Mg)	0.732	0.007	0.710	0.010	0.678	0.005	0.650	0.010	0.628	0.006	0.437	0.004
Mg/(Fe+Mg)	0.268	0.007	0.290	0.010	0.322	0.005	0.350	0.010	0.372	0.006	0.563	0.004
Cation proportions on the basis of 7 cations												
Si	2.693	0.010	2.679	0.033	2.708	0.025	2.698	0.039	2.699	0.026	2.767	0.023
Al	1.307	0.010	1.321	0.033	1.292	0.025	1.302	0.039	1.301	0.026	1.233	0.023
Sum	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000
Al	0.585	0.046	0.554	0.022	0.550	0.020	0.448	0.040	0.497	0.036	0.446	0.018
Fe ³⁺	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Cr	0.001	0.003	0.004	0.007	0.001	0.003	0.002	0.004	0.003	0.004	0.002	0.006
Ti	0.100	0.001	0.095	0.006	0.087	0.003	0.088	0.005	0.091	0.008	0.082	0.005
Fe ²⁺	1.692	0.012	1.667	0.012	1.600	0.025	1.599	0.042	1.513	0.014	1.077	0.010
Mn	0.000	0.001	0.001	0.002	0.003	0.003	0.002	0.006	0.000	0.002	0.006	0.005
Mg	0.621	0.028	0.680	0.032	0.758	0.009	0.860	0.023	0.895	0.027	1.387	0.014
Sum	3.000	0.000	3.000	0.000	3.000	0.000	3.000	0.000	3.000	0.000	3.000	0.000
Ca	0.000	0.000	0.006	0.008	0.000	0.000	0.002	0.004	0.001	0.002	0.000	0.000
Na	0.035	0.001	0.024	0.041	0.037	0.032	0.011	0.011	0.035	0.055	0.024	0.029
K	0.950	0.021	0.950	0.006	0.908	0.005	0.989	0.018	0.960	0.016	0.929	0.001
Ba	n.d.	n.d.	0.005	0.012	n.d.	n.d.	0.009	0.005	0.012	0.007	n.d.	n.d.
Sum	0.986	0.019	0.985	0.055	0.945	0.029	1.011	0.023	1.008	0.069	0.924	0.029
Cl	0.035	0.000	0.087	0.005	0.042	0.020	0.009	0.003	0.004	0.004	0.001	0.002
Fe/(Fe+Mg)	0.732	0.007	0.710	0.010	0.678	0.005	0.650	0.010	0.628	0.006	0.437	0.004
Mg/(Fe+Mg)	0.268	0.007	0.290	0.010	0.322	0.005	0.350	0.010	0.372	0.006	0.563	0.004

Table A5.7 Continued: Representative Biotite Analyses

	93-10b-II		92-11-I		90-1e-I		90-4h-I		91-26e-II		91-1b2-II	
	Grt+Chl+St+Bt+Pl+Ky matrix Bt		Grt+Chl+Bt+St+Pl matrix Bt		St+Grt+Bt matrix Bt		St+Grt+Bt+Pl+(Cld) matrix Bt		Grt+Chl+St+Bt matrix Bt in Qtz		Grt+Chl+St+Bt+Pl matrix Bt	
	(7,2)	(2σ)	(11,3)	(2σ)	(2,1)	(2σ)	(3,1)	(2σ)	(3,1)	(2σ)	(3,1)	(2σ)
SiO ₂	36.56	0.65	35.49	0.58	35.61	0.16	35.72	0.17	35.97	0.38	36.27	0.95
Al ₂ O ₃	19.19	0.81	19.30	0.82	19.83	0.14	19.66	0.17	18.89	0.34	18.85	0.35
Cr ₂ O ₃	0.06	0.04	0.05	0.07	0.01	0.01	0.00	0.00	0.02	0.08	0.04	0.07
TiO ₂	1.44	0.10	1.69	0.13	1.70	0.01	1.37	0.05	1.30	0.03	1.27	0.18
FeO	14.37	1.13	18.94	0.77	20.28	0.27	18.09	0.27	17.57	0.34	14.43	0.96
MnO	0.21	0.09	0.03	0.06	0.01	0.01	0.02	0.04	0.05	0.09	0.10	0.05
MgO	13.51	0.67	10.35	0.28	9.21	0.15	11.05	0.16	11.87	0.11	14.98	0.91
CaO	0.01	0.01	0.01	0.03	0.00	0.00	0.01	0.02	0.00	0.00	0.01	0.02
Na ₂ O	0.18	0.25	0.28	0.37	0.04	0.09	0.30	0.20	0.13	0.11	0.19	0.23
K ₂ O	9.73	0.46	9.74	0.33	9.68	0.48	9.55	0.15	9.61	0.17	8.64	1.23
BaO	0.05	0.10	0.071	0.144	0.00	0.00	0.114	0.219	0.043	0.079	0.050	0.136
Cl	0.02	0.05	0.03	0.04	0.03	0.01	0.02	0.00	0.01	0.01	0.02	0.03
TOTAL	95.33	0.90	95.99	1.13	96.38	0.72	95.90	0.08	95.45	0.41	94.84	0.18
TOTAL-O=Cl	95.32	0.91	95.98	1.13	96.37	0.72	95.90	0.08	95.45	0.41	94.84	0.18
<i>Cation proportions on the basis of 11 oxygens</i>												
Si	2.716	0.027	2.682	0.033	2.687	0.018	2.695	0.013	2.710	0.014	2.695	0.071
Al	1.284	0.027	1.318	0.033	1.313	0.018	1.315	0.013	1.290	0.014	1.305	0.071
Sum	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000
Al	0.397	0.074	0.401	0.046	0.451	0.034	0.427	0.008	0.386	0.028	0.345	0.063
Cr	0.004	0.002	0.003	0.004	0.000	0.001	0.000	0.000	0.001	0.005	0.002	0.004
Ti	0.081	0.006	0.096	0.008	0.096	0.001	0.078	0.003	0.074	0.002	0.071	0.010
Fe	0.893	0.072	1.197	0.055	1.280	0.014	1.137	0.018	1.107	0.028	0.897	0.058
Mn	0.013	0.005	0.002	0.004	0.000	0.001	0.001	0.002	0.003	0.005	0.006	0.003
Mg	1.496	0.083	1.166	0.032	1.036	0.015	1.238	0.017	1.333	0.020	1.660	0.098
Sum	2.884	0.078	2.866	0.043	2.864	0.003	2.881	0.030	2.904	0.017	2.981	0.109
Ca	0.001	0.001	0.000	0.003	0.000	0.000	0.001	0.002	0.000	0.000	0.000	0.002
Na	0.025	0.036	0.041	0.054	0.006	0.013	0.044	0.029	0.019	0.016	0.027	0.033
K	0.923	0.036	0.939	0.029	0.932	0.044	0.916	0.013	0.923	0.012	0.819	0.118
Ba	0.002	0.003	0.002	0.004	0.000	0.000	0.003	0.006	0.001	0.002	0.001	0.004
Sum	0.950	0.073	0.983	0.061	0.938	0.057	0.964	0.044	0.944	0.015	0.848	0.106
Cl	0.003	0.006	0.004	0.005	0.003	0.001	0.003	0.000	0.001	0.001	0.002	0.004
Fe/(Fe+Mg)	0.374	0.014	0.507	0.010	0.553	0.001	0.479	0.003	0.454	0.003	0.351	0.002
Mg/(Fe+Mg)	0.626	0.014	0.493	0.010	0.447	0.001	0.521	0.003	0.546	0.003	0.649	0.002
<i>Cation proportions on the basis of 7 cations</i>												
Si	2.762	0.056	2.735	0.043	2.741	0.017	2.732	0.025	2.747	0.019	2.703	0.112
Al	1.238	0.056	1.265	0.043	1.259	0.017	1.268	0.025	1.253	0.019	1.297	0.112
Sum	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000
Al	0.471	0.122	0.488	0.065	0.540	0.032	0.503	0.026	0.447	0.040	0.358	0.130
Fe ³⁺	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Cr	0.004	0.002	0.003	0.004	0.000	0.001	0.000	0.000	0.001	0.005	0.002	0.004
Ti	0.082	0.006	0.098	0.008	0.098	0.000	0.079	0.003	0.075	0.002	0.071	0.009
Fe ²⁺	0.908	0.066	1.220	0.050	1.305	0.015	1.157	0.014	1.122	0.026	0.899	0.045
Mn	0.014	0.006	0.002	0.004	0.000	0.001	0.001	0.002	0.003	0.006	0.006	0.003
Mg	1.521	0.069	1.189	0.028	1.056	0.016	1.259	0.012	1.351	0.017	1.664	0.072
Sum	3.000	0.000	3.000	0.000	3.000	0.000	3.000	0.000	3.000	0.000	3.000	0.000
Ca	0.001	0.001	0.001	0.003	0.000	0.000	0.001	0.002	0.000	0.000	0.000	0.002
Na	0.026	0.036	0.042	0.055	0.006	0.013	0.045	0.029	0.020	0.016	0.027	0.033
K	0.938	0.047	0.958	0.035	0.950	0.046	0.932	0.017	0.936	0.014	0.821	0.131
Ba	0.003	0.006	0.004	0.009	0.000	0.000	0.007	0.013	0.003	0.005	0.003	0.008
Sum	0.968	0.088	1.004	0.066	0.956	0.059	0.985	0.052	0.958	0.016	0.852	0.120
Cl	0.003	0.006	0.004	0.005	0.003	0.001	0.003	0.000	0.001	0.001	0.002	0.004
Fe/(Fe+Mg)	0.374	0.014	0.507	0.010	0.553	0.001	0.479	0.003	0.454	0.003	0.351	0.002
Mg/(Fe+Mg)	0.626	0.014	0.493	0.010	0.447	0.001	0.521	0.003	0.546	0.003	0.649	0.002

Table A5.7 Continued: Representative Biotite Analyses

	91-1e-I		91-5b-II		93-39d-III		93-44b-II		91-14d-I		93-45a-I	
	St+Grt+Bt+Ky matrix Bt		St+Grt+Bt+Ky+Pl+Chl med. porphs.		Grt+Bt+Ky+Pl matrix Bt		St+Grt+Bt+Ky+Pl matrix Bt		St+Grt+Bt+Pl Bt porphs.		St+Grt+Bt+Pl med. Bt porph.	
	(4,1)	(2σ)	(4,1)	(2σ)	(15,3)	(2σ)	(8,2)	(2σ)	(7,2)	(2σ)	(3,1)	(2σ)
SiO ₂	37.06	0.89	37.39	0.48	37.87	0.53	36.48	0.45	36.26	0.48	35.84	0.44
Al ₂ O ₃	18.32	0.39	19.40	0.32	18.19	0.37	19.39	0.56	19.33	0.51	19.22	0.70
Cr ₂ O ₃	0.04	0.09	0.01	0.03	0.01	0.03	0.04	0.04	0.07	0.06	0.04	0.09
TiO ₂	1.19	0.30	1.13	0.08	1.05	0.08	1.68	0.30	1.48	0.15	1.63	0.22
FeO	12.42	0.23	12.58	0.25	10.79	0.23	16.11	0.31	17.49	0.34	18.02	0.80
MnO	0.08	0.12	0.15	0.09	0.27	0.10	0.18	0.08	0.04	0.08	0.02	0.08
MgO	15.21	0.59	15.08	0.14	16.90	0.38	12.25	0.28	11.71	0.32	11.21	0.28
CaO	0.02	0.05	0.02	0.05	0.00	0.01	0.00	0.00	0.01	0.02	0.00	0.00
Na ₂ O	0.25	0.27	0.46	0.61	0.44	0.34	0.39	0.22	0.40	0.18	0.22	0.10
K ₂ O	9.14	0.60	9.28	0.14	9.36	0.39	9.58	0.14	9.26	0.16	9.31	0.15
BaO	0.08	0.18	0.036	0.140	0.26	0.11	0.177	0.283	0.054	0.146	0.054	0.187
Cl	0.00	0.01	0.00	0.00	0.07	0.05	0.01	0.01	0.01	0.01	0.01	0.03
TOTAL	93.81	1.16	95.52	1.03	95.21	1.11	96.27	0.87	96.11	0.84	95.57	2.20
TOTAL-O=Cl	93.81	1.16	95.52	1.03	95.20	1.11	95.53	0.87	96.11	0.84	95.57	2.20
Cation proportions on the basis of 11 oxygens												
Si	2.762	0.037	2.737	0.025	2.768	0.025	2.707	0.028	2.705	0.018	2.698	0.028
Al	1.238	0.037	1.263	0.025	1.232	0.025	1.293	0.028	1.295	0.018	1.302	0.028
Sum	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000
Al	0.371	0.028	0.410	0.019	0.335	0.018	0.402	0.031	0.404	0.036	0.403	0.019
Cr	0.002	0.005	0.000	0.002	0.001	0.002	0.003	0.003	0.004	0.003	0.003	0.006
Ti	0.067	0.017	0.062	0.004	0.058	0.004	0.093	0.017	0.083	0.008	0.092	0.010
Fe	0.774	0.023	0.770	0.014	0.660	0.016	1.000	0.024	1.091	0.023	1.134	0.025
Mn	0.005	0.007	0.009	0.006	0.017	0.006	0.011	0.005	0.003	0.005	0.001	0.005
Mg	1.689	0.062	1.645	0.009	1.842	0.044	1.355	0.018	1.303	0.035	1.257	0.024
Sum	2.909	0.035	2.896	0.029	2.911	0.039	2.864	0.011	2.888	0.020	2.891	0.018
Ca	0.002	0.004	0.002	0.004	0.000	0.000	0.000	0.000	0.001	0.002	0.000	0.000
Na	0.036	0.039	0.065	0.087	0.062	0.048	0.055	0.031	0.057	0.026	0.032	0.014
K	0.869	0.049	0.866	0.009	0.873	0.032	0.906	0.020	0.882	0.021	0.894	0.015
Ba	0.002	0.005	0.001	0.004	0.008	0.003	0.005	0.008	0.002	0.004	0.002	0.006
Sum	0.909	0.048	0.934	0.082	0.942	0.056	0.967	0.039	0.941	0.033	0.928	0.012
Cl	0.001	0.001	0.000	0.000	0.009	0.006	0.001	0.002	0.001	0.002	0.001	0.004
Fe/(Fe+Mg)	0.314	0.011	0.319	0.003	0.264	0.004	0.425	0.008	0.456	0.005	0.474	0.009
Mg/(Fe+Mg)	0.686	0.011	0.681	0.003	0.736	0.004	0.575	0.008	0.544	0.005	0.526	0.009
Cation proportions on the basis of 7 cations												
Si	2.799	0.052	2.778	0.021	2.804	0.037	2.760	0.029	2.749	0.020	2.741	0.035
Al	1.201	0.052	1.222	0.021	1.196	0.037	1.240	0.029	1.251	0.020	1.259	0.035
Sum	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000
Al	0.429	0.040	0.476	0.016	0.391	0.040	0.489	0.030	0.476	0.048	0.473	0.029
Fe ³⁺	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Cr	0.003	0.005	0.000	0.002	0.001	0.002	0.003	0.003	0.004	0.003	0.003	0.006
Ti	0.068	0.018	0.063	0.004	0.058	0.004	0.095	0.017	0.084	0.008	0.094	0.010
Fe ²⁺	0.785	0.022	0.781	0.011	0.668	0.013	1.020	0.025	1.109	0.020	1.152	0.022
Mn	0.005	0.008	0.009	0.006	0.017	0.006	0.012	0.005	0.003	0.005	0.001	0.005
Mg	1.711	0.058	1.670	0.002	1.865	0.034	1.382	0.018	1.323	0.032	1.277	0.025
Sum	3.000	0.000	3.000	0.000	3.000	0.000	3.000	0.000	3.000	0.000	3.000	0.000
Ca	0.002	0.004	0.002	0.004	0.000	0.000	0.000	0.000	0.001	0.002	0.000	0.000
Na	0.036	0.039	0.066	0.088	0.063	0.049	0.057	0.032	0.058	0.026	0.033	0.014
K	0.880	0.054	0.880	0.006	0.884	0.036	0.924	0.021	0.896	0.022	0.908	0.018
Ba	0.005	0.010	0.002	0.008	0.015	0.006	0.011	0.017	0.003	0.009	0.003	0.011
Sum	0.923	0.051	0.949	0.086	0.962	0.061	0.991	0.046	0.958	0.037	0.944	0.020
Cl	0.001	0.001	0.000	0.000	0.009	0.007	0.001	0.002	0.001	0.002	0.002	0.004
Fe/(Fe+Mg)	0.314	0.011	0.319	0.003	0.264	0.004	0.425	0.008	0.456	0.005	0.474	0.009
Mg/(Fe+Mg)	0.686	0.011	0.681	0.003	0.736	0.004	0.575	0.008	0.544	0.005	0.526	0.009

Table A5.7 Continued: Representative Biotite Analyses

	94-1a-I		Ardoc 201-V		92-34b-I		93-46b-I	
	St+Grt+Bt+Pl matrix Bt		St+Grt+Bt+Sill+Pl+(Ky) matrix Bt		St+Grt+Bt+Sill+Pl matrix Bt		Grt+Bt+Sill matrix Bt	
	(6,2)	(2σ)	(3,1)	(2σ)	(8,2)	(2σ)	(12,3)	(2σ)
SiO ₂	35.29	0.51	35.65	0.42	35.27	0.25	33.96	0.48
Al ₂ O ₃	19.22	0.29	18.59	0.26	19.38	0.49	19.53	0.63
Cr ₂ O ₃	0.02	0.08	0.02	0.07	0.06	0.09	0.03	0.07
TiO ₂	1.47	0.13	1.58	0.23	2.24	0.33	3.14	0.55
FeO	18.96	0.38	17.44	0.35	19.78	0.55	23.65	0.44
MnO	0.02	0.05	0.14	0.06	0.06	0.07	0.01	0.03
MgO	10.65	0.24	12.21	0.15	9.25	0.20	5.91	0.17
CaO	0.00	0.02	0.00	0.00	0.01	0.04	0.00	0.01
Na ₂ O	0.27	0.48	0.36	0.19	0.15	0.27	0.20	0.37
K ₂ O	9.26	0.42	9.27	0.40	9.93	0.08	9.47	0.19
BaO	0.12	0.19	0.071	0.246	0.12	0.22	0.158	0.178
Cl	0.04	0.03	0.01	0.03	0.03	0.03	0.01	0.02
TOTAL	95.32	0.62	95.35	1.06	96.27	0.78	96.08	1.02
TOTAL-O=Cl	95.31	0.62	95.35	1.06	96.26	0.76	96.08	1.02
<i>Cation proportions on the basis of 11 oxygens</i>								
Si	2.681	0.034	2.690	0.001	2.673	0.028	2.629	0.017
Al	1.319	0.034	1.310	0.001	1.327	0.028	1.371	0.017
Sum	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000
Al	0.402	0.023	0.343	0.004	0.403	0.031	0.410	0.048
Cr	0.001	0.005	0.001	0.004	0.004	0.005	0.002	0.004
Ti	0.084	0.007	0.090	0.012	0.128	0.018	0.183	0.031
Fe	1.204	0.027	1.100	0.033	1.252	0.032	1.531	0.027
Mn	0.001	0.003	0.009	0.004	0.004	0.005	0.001	0.002
Mg	1.206	0.027	1.374	0.019	1.045	0.023	0.682	0.021
Sum	2.899	0.035	2.918	0.034	2.835	0.017	2.809	0.024
Ca	0.000	0.001	0.000	0.000	0.001	0.003	0.000	0.001
Na	0.040	0.071	0.053	0.027	0.022	0.040	0.030	0.056
K	0.898	0.037	0.892	0.032	0.960	0.012	0.935	0.018
Ba	0.004	0.006	0.002	0.007	0.004	0.007	0.005	0.005
Sum	0.942	0.073	0.947	0.049	0.986	0.038	0.970	0.049
Cl	0.005	0.004	0.001	0.004	0.004	0.004	0.001	0.003
Fe/(Fe+Mg)	0.500	0.004	0.445	0.008	0.545	0.008	0.692	0.007
Mg/(Fe+Mg)	0.500	0.004	0.555	0.008	0.455	0.008	0.308	0.007
<i>Cation proportions on the basis of 7 cations</i>								
Si	2.721	0.041	2.722	0.013	2.737	0.028	2.702	0.025
Al	1.279	0.041	1.278	0.013	1.263	0.028	1.298	0.025
Sum	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000
Al	0.467	0.038	0.395	0.025	0.510	0.038	0.534	0.045
Fe ₃₊	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Cr	0.001	0.005	0.001	0.004	0.004	0.006	0.002	0.004
Ti	0.085	0.007	0.091	0.013	0.131	0.019	0.188	0.033
Fe ₂₊	1.222	0.021	1.114	0.030	1.282	0.031	1.574	0.025
Mn	0.001	0.003	0.009	0.004	0.004	0.005	0.001	0.002
Mg	1.223	0.022	1.390	0.015	1.070	0.022	0.702	0.022
Sum	3.000	0.000	3.000	0.000	3.000	0.000	3.000	0.000
Ca	0.000	0.001	0.000	0.000	0.001	0.003	0.000	0.001
Na	0.041	0.073	0.054	0.027	0.022	0.041	0.031	0.057
K	0.911	0.041	0.903	0.036	0.983	0.013	0.961	0.019
Ba	0.007	0.011	0.004	0.015	0.007	0.014	0.010	0.011
Sum	0.959	0.077	0.961	0.057	1.013	0.039	1.003	0.053
Cl	0.005	0.004	0.001	0.004	0.005	0.004	0.001	0.003
Fe/(Fe+Mg)	0.500	0.004	0.445	0.008	0.545	0.008	0.692	0.007
Mg/(Fe+Mg)	0.500	0.004	0.555	0.008	0.455	0.008	0.308	0.007

Table A5.7 Continued: Representative Biotite Analyses

	R3 301-II		93-40d-I		CR-8b-I		CR-4a-1		CR-3a-1	
	St+Grt+Bt+Sill+Pl matrix in Qtz & Sill		St+Grt+Bt+Sill matrix Bt in Qtz		St+Grt+Bt+Pl matrix Bt		St+Grt+Bt+Sill+Pl matrix Bt		Grt+Bt+Pl matrix Bt	
	(3,1)	(2σ)	(4,1)	(2σ)	(3,1)	(2σ)	(3,1)	(2σ)	(6,2)	(2σ)
SiO ₂	35.74	0.37	34.73	0.25	35.99	0.28	34.88	0.47	35.61	0.25
Al ₂ O ₃	20.08	0.19	19.61	0.33	19.47	0.06	20.03	0.51	19.46	0.90
Cr ₂ O ₃	0.08	0.02	0.06	0.11	0.02	0.06	0.04	0.06	0.03	0.06
TiO ₂	1.59	0.12	2.30	0.11	1.91	0.09	2.02	0.11	2.32	0.31
FeO	18.83	0.10	21.53	0.27	17.84	0.51	21.46	0.25	18.49	0.55
MnO	0.06	0.06	0.01	0.02	0.04	0.08	0.00	0.00	0.13	0.05
MgO	10.09	0.40	8.00	0.16	11.07	0.31	7.89	0.13	10.32	0.28
CaO	0.01	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Na ₂ O	0.57	0.33	0.09	0.12	0.42	0.25	0.34	0.15	0.33	0.26
K ₂ O	9.38	0.09	9.77	0.04	9.62	0.17	9.68	0.03	9.78	0.26
BaO	0.28	0.08	0.130	0.279	0.10	0.13	0.047	0.164	0.050	0.070
Cl	0.01	0.02	0.03	0.04	0.00	0.01	0.02	0.06	0.01	0.02
TOTAL	96.72	0.70	96.25	0.40	96.48	1.50	96.40	0.96	96.52	0.84
TOTAL-O=Cl	96.72	0.70	96.24	0.40	96.48	1.49	96.39	0.97	96.52	0.84
Cation proportions on the basis of 11 oxygens										
Si	2.675	0.031	2.654	0.020	2.687	0.023	2.655	0.031	2.670	0.027
Al	1.325	0.031	1.346	0.020	1.313	0.023	1.345	0.031	1.330	0.027
Sum	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000
Al	0.446	0.041	0.419	0.018	0.400	0.033	0.452	0.007	0.390	0.042
Cr	0.005	0.001	0.004	0.006	0.001	0.004	0.002	0.004	0.002	0.003
Ti	0.089	0.007	0.132	0.006	0.107	0.006	0.115	0.005	0.131	0.016
Fe	1.179	0.008	1.375	0.018	1.114	0.021	1.367	0.001	1.160	0.045
Mn	0.004	0.004	0.000	0.001	0.003	0.005	0.000	0.000	0.009	0.003
Mg	1.126	0.041	0.911	0.017	1.232	0.022	0.895	0.006	1.154	0.043
Sum	2.849	0.010	2.842	0.011	2.857	0.016	2.832	0.011	2.845	0.036
Ca	0.001	0.002	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Na	0.083	0.047	0.013	0.018	0.060	0.035	0.050	0.022	0.048	0.038
K	0.896	0.007	0.952	0.003	0.916	0.007	0.940	0.011	0.936	0.018
Ba	0.008	0.002	0.004	0.008	0.003	0.004	0.001	0.005	0.001	0.002
Sum	0.988	0.049	0.969	0.024	0.980	0.044	0.992	0.020	0.985	0.036
Cl	0.001	0.002	0.003	0.005	0.000	0.001	0.002	0.008	0.001	0.002
Fe/(Fe+Mg)	0.511	0.009	0.602	0.006	0.475	0.001	0.604	0.001	0.501	0.002
Mg/(Fe+Mg)	0.489	0.009	0.398	0.006	0.525	0.001	0.396	0.001	0.499	0.002
Cation proportions on the basis of 7 cations										
Si	2.734	0.035	2.715	0.024	2.743	0.029	2.721	0.034	2.731	0.023
Al	1.266	0.035	1.285	0.024	1.257	0.029	1.279	0.034	1.269	0.023
Sum	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000
Al	0.545	0.048	0.522	0.018	0.492	0.041	0.562	0.009	0.490	0.065
Fe ³⁺	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Cr	0.005	0.001	0.004	0.007	0.001	0.004	0.002	0.004	0.002	0.003
Ti	0.091	0.007	0.135	0.007	0.110	0.006	0.118	0.005	0.134	0.017
Fe ²⁺	1.205	0.008	1.407	0.018	1.137	0.020	1.400	0.001	1.186	0.040
Mn	0.004	0.004	0.000	0.001	0.003	0.005	0.000	0.000	0.009	0.003
Mg	1.151	0.040	0.932	0.017	1.257	0.021	0.917	0.005	1.180	0.038
Sum	3.000	0.000	3.000	0.000	3.000	0.000	3.000	0.000	3.000	0.000
Ca	0.001	0.002	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Na	0.085	0.048	0.013	0.019	0.062	0.036	0.051	0.022	0.049	0.039
K	0.916	0.006	0.974	0.003	0.935	0.009	0.963	0.013	0.957	0.021
Ba	0.017	0.005	0.008	0.017	0.006	0.008	0.003	0.010	0.003	0.004
Sum	1.018	0.046	0.995	0.030	1.003	0.048	1.017	0.020	1.009	0.041
Cl	0.001	0.002	0.003	0.005	0.000	0.001	0.002	0.008	0.001	0.002
Fe/(Fe+Mg)	0.511	0.009	0.602	0.006	0.475	0.001	0.604	0.001	0.501	0.002
Mg/(Fe+Mg)	0.489	0.009	0.398	0.006	0.525	0.001	0.396	0.001	0.499	0.002

Table A5.8: Representative Staurolite Analyses

	Madoc-4a-I		Madoc-2e-V		Queens-1a-I		93-13b-I				93-26e-I	
	Ctd+Ky+Chl+St		Grt+Chl+Bt+St+Ctd		Grt+Chl+Ctd+Bt+(St)		Grt+Chl+St+(Ctd)				Grt+Chl+Ctd+Bt+St+Mgr	
	sml. porph.	repl. Ctd	sml. porph.		tiny Xls. repl. Ctd		small poik.		small poik.		sml. Xls. nucl. in Ctd.	
	(3,1)	(2σ)	(4,1)	(2σ)	(3,1)	(2σ)	(5,1)	(2σ)	(4,1)	(2σ)	(7,2)	(2σ)
SiO ₂	28.12	0.28	27.05	0.38	25.81	0.79	27.22	0.37	27.01	0.39	27.00	0.56
Al ₂ O ₃	54.94	0.27	53.19	0.42	53.85	1.65	53.85	0.64	54.00	0.48	54.40	0.62
Cr ₂ O ₃	0.05	0.08	0.03	0.06	0.00	0.00	0.03	0.06	0.04	0.06	0.04	0.07
TiO ₂	0.45	0.02	0.45	0.06	0.13	0.04	0.42	0.09	0.40	0.08	0.34	0.18
FeO (total)	12.91	0.29	14.45	0.36	11.00	0.31	9.50	0.38	8.90	0.26	8.33	0.21
MnO	0.73	0.06	0.31	0.04	0.04	0.06	0.63	0.05	0.64	0.05	0.18	0.07
MgO	1.86	0.03	1.48	0.17	0.93	0.15	1.30	0.06	1.32	0.11	1.07	0.09
ZnO	0.39	0.10	0.42	0.05	5.49	0.35	4.40	0.10	5.06	0.07	6.11	0.19
TOTAL	99.44	0.78	97.40	0.79	97.25	1.27	97.34	1.26	97.37	0.62	97.47	1.11
<i>Cation proportions on the basis of 46 oxygens and 3.5% Fe₂O₃</i>												
Si	7.672	0.024	7.601	0.071	7.343	0.255	7.636	0.077	7.584	0.109	7.575	0.086
Al (IV)	0.328	0.024	0.399	0.071	0.657	0.255	0.364	0.077	0.416	0.109	0.425	0.086
Sum T(1)	8.000	0.000	8.000	0.000	8.000	0.000	8.000	0.000	8.000	0.000	8.000	0.000
Al (VI)	17.343	0.051	17.213	0.039	17.399	0.185	17.441	0.038	17.454	0.013	17.563	0.044
Cr	0.010	0.018	0.008	0.014	0.000	0.000	0.007	0.013	0.010	0.013	0.008	0.017
Fe ³⁺	0.069	0.001	0.079	0.002	0.061	0.002	0.052	0.002	0.049	0.001	0.046	0.001
Ti	0.093	0.003	0.096	0.012	0.028	0.009	0.088	0.020	0.085	0.017	0.072	0.038
Mg	0.303	0.006	0.247	0.028	0.158	0.025	0.218	0.012	0.220	0.019	0.180	0.014
Fe (2+)	0.207	0.004	0.238	0.006	0.184	0.005	0.156	0.005	0.147	0.004	0.137	0.003
Sum M	18.024	0.031	17.882	0.041	17.829	0.146	17.963	0.044	17.965	0.027	18.005	0.030
Fe (2+)	2.635	0.054	3.038	0.076	2.342	0.070	1.994	0.058	1.871	0.048	1.748	0.037
Mn	0.169	0.014	0.075	0.010	0.009	0.014	0.149	0.011	0.152	0.011	0.043	0.016
Mg	0.455	0.009	0.371	0.042	0.237	0.037	0.327	0.017	0.331	0.028	0.270	0.021
Zn	0.078	0.020	0.088	0.011	1.154	0.061	0.911	0.012	1.048	0.018	1.266	0.045
Sum T(2)	3.337	0.056	3.572	0.025	3.741	0.117	3.381	0.057	3.401	0.049	3.326	0.053
Fe/(Fe+Mn+Mg+Zn)	0.739	0.003	0.808	0.021	0.619	0.009	0.573	0.010	0.535	0.007	0.517	0.006
Mg/(Fe+Mn+Mg+Zn)	0.197	0.002	0.152	0.017	0.097	0.012	0.145	0.009	0.146	0.010	0.123	0.010
Mn/(Fe+Mn+Mg+Zn)	0.044	0.003	0.018	0.002	0.002	0.003	0.040	0.003	0.040	0.003	0.012	0.005
Zn/(Fe+Mn+Mg+Zn)	0.020	0.006	0.022	0.003	0.283	0.015	0.243	0.003	0.278	0.009	0.348	0.010
<i>Cation proportions on the basis of 46 oxygens with Total Iron as FeO</i>												
Si	7.500	0.000	7.500	0.000	7.343	0.255	7.500	0.000	7.500	0.000	7.500	0.001
Al (IV)	0.000	0.000	0.000	0.000	0.157	0.255	0.000	0.000	0.000	0.000	0.000	0.001
Sum T(1)	7.500	0.000	7.500	0.000	7.500	0.000	7.500	0.000	7.500	0.000	7.500	0.000
Si	0.172	0.024	0.101	0.071	0.000	0.000	0.136	0.077	0.084	0.109	0.076	0.085
Al (VI)	17.670	0.055	17.613	0.107	17.899	0.185	17.806	0.092	17.870	0.102	17.987	0.114
Cr	0.010	0.018	0.008	0.014	0.000	0.000	0.007	0.013	0.010	0.013	0.008	0.017
Ti	0.093	0.003	0.096	0.012	0.028	0.009	0.088	0.020	0.085	0.017	0.072	0.038
Sum M	17.945	0.041	17.817	0.036	17.927	0.178	18.036	0.041	18.049	0.028	18.143	0.020
Fe ²⁺	2.945	0.061	3.395	0.085	2.617	0.078	2.228	0.065	2.090	0.053	1.953	0.041
Mn	0.169	0.014	0.075	0.010	0.009	0.014	0.149	0.011	0.152	0.011	0.043	0.016
Mg	0.758	0.014	0.618	0.070	0.395	0.062	0.545	0.029	0.551	0.047	0.449	0.035
Zn	0.078	0.020	0.088	0.011	1.154	0.061	0.911	0.012	1.048	0.018	1.266	0.045
Sum T(2)	3.949	0.067	4.176	0.028	4.174	0.148	3.834	0.055	3.842	0.071	3.712	0.057
Fe/(Fe+Mn+Mg+Zn)	0.746	0.003	0.813	0.021	0.627	0.009	0.581	0.009	0.544	0.006	0.526	0.006
Mg/(Fe+Mn+Mg+Zn)	0.192	0.002	0.148	0.016	0.095	0.012	0.142	0.009	0.143	0.010	0.121	0.009
Mn/(Fe+Mn+Mg+Zn)	0.043	0.003	0.018	0.002	0.002	0.003	0.039	0.002	0.039	0.003	0.011	0.004
Zn/(Fe+Mn+Mg+Zn)	0.020	0.005	0.021	0.003	0.276	0.015	0.238	0.003	0.273	0.009	0.341	0.010

Table A5.8 Continued: Representative Staurolite Analyses

	93-26g-I		92-8d-I		92-10a-II		90-19a-I		92-27a-II		92-28a-I	
	Grt+Chl+Bt+St+Mrg xenoblastic porph.		Grt+Chl+Ctd+Bt+St+Mrg sml. St nucl. in Ctd.		Ctd+St+Grt+Bt St nucl. in Ctd.		Ctd+St+Grt+Bt+Pl small porphs.		Ctd+St+Grt+Bt St poik. repl. Ctd		Ctd+St+Grt+Bt small xl. repl. Ctd	
	(4,1)	(2 σ)	(6,1)	(2 σ)	(4,2)	(2 σ)	(4,2)	(2 σ)	(4,1)	(2 σ)	(3,1)	(2 σ)
SiO ₂	26.90	0.63	26.79	0.19	26.96	0.58	27.16	1.05	27.32	0.24	26.47	0.24
Al ₂ O ₃	53.86	0.92	54.45	0.62	54.42	1.00	53.62	1.28	54.54	0.33	55.14	0.71
Cr ₂ O ₃	0.04	0.04	0.04	0.07	0.02	0.09	0.06	0.10	0.04	0.05	0.03	0.06
TiO ₂	0.47	0.12	0.34	0.04	0.38	0.14	0.41	0.12	0.44	0.12	0.35	0.04
FeO (total)	8.36	0.16	9.88	0.31	13.13	0.14	14.09	1.46	13.21	0.26	12.79	0.08
MnO	0.07	0.10	0.24	0.06	0.08	0.06	0.17	0.10	0.01	0.03	0.02	0.03
MgO	1.00	0.11	1.30	0.08	0.79	0.06	0.90	0.18	1.16	0.08	0.98	0.02
ZnO	6.57	0.18	5.56	0.25	1.80	0.15	1.13	0.10	0.58	0.26	0.70	0.09
TOTAL	97.27	1.47	98.62	1.08	97.59	0.85	97.53	1.37	97.30	0.28	96.48	0.96
<i>Cation proportions on the basis of 46 oxygens and 3.5% Fe₂O₃</i>												
Si	7.583	0.056	7.473	0.071	7.548	0.163	7.623	0.185	7.618	0.045	7.441	0.048
Al (IV)	0.417	0.056	0.527	0.071	0.452	0.163	0.377	0.185	0.382	0.045	0.559	0.048
Sum T(1)	8.000	0.000	8.000	0.000	8.000	0.000	8.000	0.000	8.000	0.000	8.000	0.000
Al (VI)	17.480	0.070	17.371	0.062	17.507	0.086	17.360	0.262	17.541	0.081	17.703	0.020
Cr	0.009	0.008	0.010	0.015	0.005	0.020	0.013	0.022	0.008	0.011	0.007	0.012
Fe ³⁺	0.046	0.001	0.054	0.001	0.072	0.001	0.077	0.009	0.072	0.002	0.070	0.000
Ti	0.099	0.024	0.072	0.009	0.081	0.030	0.086	0.026	0.092	0.026	0.074	0.008
Mg	0.168	0.018	0.217	0.013	0.132	0.010	0.151	0.032	0.192	0.013	0.165	0.002
Fe (2+)	0.138	0.004	0.162	0.004	0.216	0.003	0.232	0.027	0.216	0.005	0.211	0.001
Sum M	17.941	0.061	17.885	0.057	18.012	0.048	17.918	0.188	18.121	0.040	18.230	0.025
Fe (2+)	1.765	0.056	2.063	0.049	2.751	0.040	2.960	0.344	2.756	0.064	2.689	0.014
Mn	0.016	0.024	0.058	0.015	0.020	0.014	0.040	0.024	0.003	0.007	0.006	0.008
Mg	0.252	0.027	0.325	0.019	0.198	0.014	0.226	0.047	0.288	0.020	0.247	0.003
Zn	1.367	0.038	1.144	0.048	0.373	0.032	0.234	0.022	0.119	0.054	0.145	0.019
Sum T(2)	3.400	0.111	3.590	0.094	3.341	0.050	3.459	0.386	3.167	0.073	3.086	0.035
Fe/(Fe+Mn+Mg+Zn)	0.513	0.009	0.561	0.004	0.804	0.006	0.831	0.006	0.831	0.023	0.838	0.005
Mg/(Fe+Mn+Mg+Zn)	0.114	0.011	0.137	0.008	0.089	0.007	0.098	0.010	0.134	0.008	0.119	0.002
Mn/(Fe+Mn+Mg+Zn)	0.004	0.006	0.015	0.004	0.005	0.004	0.010	0.007	0.001	0.002	0.002	0.002
Zn/(Fe+Mn+Mg+Zn)	0.369	0.004	0.288	0.008	0.101	0.008	0.061	0.002	0.033	0.015	0.042	0.005
<i>Cation proportions on the basis of 46 oxygens with Total Iron as FeO</i>												
Si	7.500	0.000	7.470	0.064	7.482	0.072	7.500	0.000	7.500	0.000	7.441	0.048
Al (IV)	0.000	0.000	0.030	0.064	0.018	0.072	0.000	0.000	0.000	0.000	0.059	0.048
Sum T(1)	7.500	0.000	7.500	0.000	7.500	0.000	7.500	0.000	7.500	0.000	7.500	0.000
Si	0.083	0.056	0.003	0.013	0.066	0.092	0.123	0.185	0.118	0.045	0.000	0.000
Al (VI)	17.897	0.081	17.868	0.067	17.941	0.175	17.736	0.140	17.922	0.038	18.203	0.020
Cr	0.009	0.008	0.010	0.015	0.005	0.020	0.013	0.022	0.008	0.011	0.007	0.012
Ti	0.099	0.024	0.072	0.009	0.081	0.030	0.086	0.026	0.092	0.026	0.074	0.008
Sum M	18.089	0.075	17.952	0.060	18.093	0.050	17.958	0.253	18.141	0.048	18.284	0.025
Fe ²⁺	1.972	0.062	2.305	0.055	3.074	0.044	3.308	0.384	3.080	0.072	3.005	0.015
Mn	0.016	0.024	0.058	0.015	0.020	0.014	0.040	0.024	0.003	0.007	0.006	0.008
Mg	0.421	0.046	0.542	0.032	0.330	0.024	0.377	0.079	0.480	0.033	0.411	0.004
Zn	1.367	0.038	1.144	0.048	0.373	0.032	0.234	0.022	0.119	0.054	0.145	0.019
Sum T(2)	3.776	0.125	4.049	0.102	3.796	0.054	3.958	0.457	3.683	0.082	3.567	0.035
Fe/(Fe+Mn+Mg+Zn)	0.522	0.009	0.569	0.004	0.810	0.006	0.836	0.006	0.836	0.023	0.843	0.004
Mg/(Fe+Mn+Mg+Zn)	0.111	0.011	0.134	0.008	0.087	0.006	0.095	0.010	0.130	0.008	0.115	0.002
Mn/(Fe+Mn+Mg+Zn)	0.004	0.006	0.014	0.004	0.005	0.004	0.010	0.007	0.001	0.002	0.002	0.002
Zn/(Fe+Mn+Mg+Zn)	0.362	0.004	0.283	0.008	0.098	0.008	0.059	0.002	0.032	0.014	0.041	0.005

Table A5.8 Continued: Representative Staurolite Analyses

	92-26b-I		91-21c2-III		93-10b-II		92-11-I		90-1e-I	
	Grt+Chl+St+Ky+Pl med. poik.		Grt+Chl+St (Mrg+Cld) med. porph.		Grt+Chl+St+Bt+Pl+Ky small porph.		Grt+Chl+Bt+St+Pl small porph.		St+Grt+Bt matrix St	
	(3,1)	(2σ)	(2,1)	(2σ)	(2,1)	(2σ)	(3,1)	(2σ)	(3,1)	(2σ)
SiO ₂	28.43	2.83	26.74	0.66	26.48	0.10	26.89	0.62	26.93	0.18
Al ₂ O ₃	53.88	2.32	54.06	0.91	53.99	0.46	53.26	0.72	53.76	0.56
Cr ₂ O ₃	0.04	0.06	0.02	0.05	0.07	0.13	0.07	0.01	0.02	0.02
TiO ₂	0.30	0.12	0.45	0.12	0.43	0.11	0.49	0.04	0.45	0.11
FeO (total)	10.33	0.64	14.00	0.51	9.04	0.01	12.47	0.54	14.28	0.04
MnO	0.77	0.28	0.21	0.02	0.46	0.08	0.14	0.07	0.02	0.07
MgO	2.18	0.15	1.69	0.03	1.95	0.02	1.62	0.15	1.42	0.10
ZnO	2.54	0.11	0.35	0.11	3.83	0.14	2.00	0.28	0.37	0.07
TOTAL	98.48	0.88	97.51	0.78	96.24	0.64	96.95	0.97	97.25	0.76
<i>Cation proportions on the basis of 46 oxygens and 3.5% Fe₂O₃</i>										
Si	7.830	0.756	7.481	0.221	7.482	0.066	7.579	0.208	7.556	0.017
Al (IV)	0.257	0.459	0.519	0.221	0.518	0.066	0.421	0.208	0.444	0.017
Sum T(1)	8.087	0.302	8.000	0.000	8.000	0.000	8.000	0.000	8.000	0.000
Al (VI)	17.229	0.344	17.308	0.011	17.459	0.004	17.272	0.058	17.333	0.035
Cr	0.010	0.013	0.004	0.012	0.015	0.030	0.016	0.001	0.004	0.004
Fe ³⁺	0.056	0.004	0.076	0.002	0.050	0.000	0.069	0.003	0.078	0.001
Ti	0.062	0.026	0.094	0.025	0.091	0.023	0.103	0.009	0.095	0.023
Mg	0.358	0.024	0.283	0.004	0.329	0.002	0.273	0.024	0.238	0.015
Fe (2+)	0.167	0.011	0.230	0.007	0.150	0.001	0.206	0.008	0.235	0.002
Sum M	17.881	0.391	17.995	0.016	18.094	0.004	17.939	0.036	17.984	0.028
Fe (2+)	2.129	0.137	2.931	0.093	1.911	0.007	2.631	0.101	2.997	0.021
Mn	0.180	0.066	0.049	0.004	0.109	0.019	0.033	0.016	0.005	0.016
Mg	0.537	0.036	0.424	0.006	0.493	0.003	0.409	0.036	0.357	0.022
Zn	0.517	0.025	0.072	0.023	0.798	0.025	0.417	0.057	0.076	0.015
Sum T(2)	3.364	0.257	3.476	0.080	3.311	0.040	3.490	0.165	3.435	0.024
Fe/(Fe+Mn+Mg+Zn)	0.590	0.010	0.793	0.007	0.544	0.008	0.715	0.012	0.827	0.003
Mg/(Fe+Mn+Mg+Zn)	0.230	0.007	0.177	0.002	0.217	0.001	0.172	0.013	0.152	0.010
Mn/(Fe+Mn+Mg+Zn)	0.046	0.014	0.012	0.001	0.029	0.005	0.008	0.004	0.001	0.004
Zn/(Fe+Mn+Mg+Zn)	0.133	0.004	0.018	0.006	0.211	0.004	0.105	0.011	0.019	0.004
<i>Cation proportions on the basis of 46 oxygens with Total Iron as FeO</i>										
Si	7.500	0.000	7.452	0.137	7.479	0.059	7.493	0.025	7.500	0.000
Al (IV)	0.000	0.000	0.048	0.137	0.021	0.059	0.007	0.025	0.000	0.000
Sum T(1)	7.500	0.000	7.500	0.000	7.500	0.000	7.500	0.000	7.500	0.000
Si	0.330	0.756	0.030	0.084	0.003	0.007	0.086	0.188	0.056	0.017
Al (VI)	17.487	0.799	17.778	0.073	17.957	0.003	17.686	0.141	17.777	0.039
Cr	0.010	0.013	0.004	0.012	0.015	0.030	0.016	0.001	0.004	0.004
Ti	0.062	0.026	0.094	0.025	0.091	0.023	0.103	0.009	0.095	0.023
Sum M	17.888	0.057	17.906	0.002	18.066	0.002	17.891	0.062	17.932	0.017
Fe ²⁺	2.380	0.154	3.275	0.104	2.136	0.008	2.940	0.113	3.350	0.024
Mn	0.180	0.066	0.049	0.004	0.109	0.019	0.033	0.016	0.005	0.016
Mg	0.895	0.060	0.707	0.009	0.822	0.005	0.682	0.060	0.595	0.037
Zn	0.517	0.025	0.072	0.023	0.798	0.025	0.417	0.057	0.076	0.015
Sum T(2)	3.972	0.295	4.103	0.095	3.864	0.041	4.071	0.188	4.026	0.013
Fe/(Fe+Mn+Mg+Zn)	0.599	0.010	0.798	0.007	0.553	0.008	0.722	0.012	0.832	0.003
Mg/(Fe+Mn+Mg+Zn)	0.225	0.007	0.172	0.002	0.213	0.001	0.167	0.013	0.148	0.010
Mn/(Fe+Mn+Mg+Zn)	0.045	0.014	0.012	0.001	0.028	0.005	0.008	0.004	0.001	0.004
Zn/(Fe+Mn+Mg+Zn)	0.130	0.004	0.017	0.006	0.207	0.004	0.102	0.010	0.019	0.004

Table A5.8 Continued: Representative Staurolite Analyses

	90-4h				91-26a-II		91-26e-II		91-24a-I		91-1b2-II	
	St+Grt+Bt+Pl+(Ctd)				Grt+Chl+St		Grt+Chl+St+Bt		Grt+St+Chl+Ky		Grt+Chl+St+Bt+Pl	
	med. porph.		incl. in Grt		med. porph.		med. idio. porph.		med. porph.		matrix St	
	(6,2)	(2σ)	(3,1)	(2σ)	(3,1)	(2σ)	(3,1)	(2σ)	(3,1)	(2σ)	(3,1)	(2σ)
SiO ₂	27.80	0.76	26.80	1.07	27.43	0.20	27.06	0.41	26.69	0.60	27.33	0.59
Al ₂ O ₃	53.30	1.19	53.80	1.75	53.90	1.09	53.46	0.54	53.74	0.08	54.00	1.30
Cr ₂ O ₃	0.08	0.10	0.06	0.05	0.04	0.04	0.01	0.04	0.03	0.03	0.05	0.02
TiO ₂	0.53	0.06	0.47	0.13	0.64	0.38	0.53	0.14	0.43	0.07	0.53	0.07
FeO (total)	14.85	1.24	15.05	0.16	12.79	0.06	14.46	0.24	12.66	0.06	12.92	0.27
MnO	0.22	0.10	0.52	0.09	0.68	0.12	0.05	0.04	0.71	0.09	0.64	0.07
MgO	1.84	0.16	1.62	0.01	2.31	0.09	1.83	0.06	2.30	0.02	2.47	0.04
ZnO	0.32	0.08	0.20	0.09	0.22	0.11	0.19	0.18	0.59	0.10	0.30	0.09
TOTAL	98.94	0.99	98.51	1.37	98.01	1.27	97.60	0.90	97.15	0.56	98.23	1.60
<i>Cation proportions on the basis of 46 oxygens and 3.5% Fe₂O₃</i>												
Si	7.691	0.131	7.468	0.313	7.600	0.083	7.569	0.064	7.481	0.117	7.563	0.044
Al (IV)	0.309	0.131	0.532	0.313	0.400	0.083	0.431	0.064	0.519	0.117	0.437	0.044
Sum T(1)	8.000	0.000	8.000	0.000	8.000	0.000	8.000	0.000	8.000	0.000	8.000	0.000
Al (VI)	17.066	0.247	17.138	0.108	17.200	0.089	17.193	0.081	17.233	0.010	17.176	0.102
Cr	0.018	0.021	0.013	0.012	0.009	0.009	0.002	0.008	0.006	0.006	0.010	0.005
Fe ³⁺	0.080	0.007	0.082	0.002	0.069	0.001	0.079	0.001	0.069	0.001	0.070	0.003
Ti	0.110	0.012	0.098	0.026	0.133	0.079	0.112	0.030	0.090	0.016	0.110	0.017
Mg	0.303	0.030	0.269	0.002	0.381	0.016	0.305	0.013	0.385	0.002	0.407	0.007
Fe (2+)	0.241	0.022	0.246	0.006	0.208	0.004	0.237	0.003	0.208	0.002	0.210	0.008
Sum M	17.818	0.199	17.846	0.123	18.000	0.048	17.929	0.062	17.992	0.020	17.983	0.068
Fe (2+)	3.074	0.281	3.138	0.080	2.653	0.046	3.027	0.041	2.656	0.025	2.677	0.106
Mn	0.052	0.023	0.123	0.022	0.159	0.027	0.012	0.010	0.168	0.021	0.149	0.019
Mg	0.454	0.045	0.403	0.004	0.572	0.024	0.458	0.019	0.577	0.003	0.611	0.010
Zn	0.065	0.015	0.042	0.018	0.045	0.023	0.040	0.036	0.122	0.020	0.060	0.017
Sum T(2)	3.645	0.334	3.706	0.085	3.429	0.059	3.537	0.059	3.524	0.032	3.497	0.109
Fe/(Fe+Mn+Mg+Zn)	0.791	0.003	0.802	0.005	0.712	0.006	0.800	0.002	0.696	0.001	0.702	0.007
Mg/(Fe+Mn+Mg+Zn)	0.181	0.006	0.159	0.002	0.237	0.006	0.187	0.007	0.234	0.002	0.248	0.005
Mn/(Fe+Mn+Mg+Zn)	0.012	0.005	0.029	0.005	0.040	0.008	0.003	0.002	0.041	0.005	0.036	0.004
Zn/(Fe+Mn+Mg+Zn)	0.016	0.005	0.010	0.005	0.011	0.006	0.010	0.009	0.030	0.005	0.015	0.005
<i>Cation proportions on the basis of 46 oxygens with Total Iron as FeO</i>												
Si	7.500	0.000	7.430	0.242	7.500	0.000	7.500	0.000	7.469	0.089	7.500	0.000
Al (IV)	0.000	0.000	0.070	0.242	0.000	0.000	0.000	0.000	0.031	0.089	0.000	0.000
Sum T(1)	7.500	0.000	7.500	0.000	7.500	0.000	7.500	0.000	7.500	0.000	7.500	0.000
Si	0.191	0.131	0.038	0.087	0.100	0.083	0.069	0.064	0.011	0.040	0.063	0.044
Al (VI)	17.375	0.270	17.601	0.194	17.600	0.160	17.624	0.135	17.722	0.043	17.613	0.099
Cr	0.018	0.021	0.013	0.012	0.009	0.009	0.002	0.008	0.006	0.006	0.010	0.005
Ti	0.110	0.012	0.098	0.026	0.133	0.079	0.112	0.030	0.090	0.016	0.110	0.017
Sum M	17.694	0.254	17.749	0.131	17.841	0.055	17.807	0.069	17.829	0.020	17.796	0.082
Fe ²⁺	3.436	0.315	3.507	0.090	2.965	0.051	3.382	0.045	2.969	0.028	2.991	0.118
Mn	0.052	0.023	0.123	0.022	0.159	0.027	0.012	0.010	0.168	0.021	0.149	0.019
Mg	0.757	0.075	0.672	0.006	0.953	0.040	0.764	0.032	0.962	0.005	1.019	0.017
Zn	0.065	0.015	0.042	0.018	0.045	0.023	0.040	0.036	0.122	0.020	0.060	0.017
Sum T(2)	4.309	0.395	4.343	0.097	4.122	0.079	4.198	0.067	4.221	0.036	4.220	0.127
Fe/(Fe+Mn+Mg+Zn)	0.797	0.003	0.807	0.005	0.719	0.006	0.806	0.002	0.703	0.001	0.709	0.007
Mg/(Fe+Mn+Mg+Zn)	0.176	0.005	0.155	0.002	0.231	0.006	0.182	0.007	0.228	0.002	0.241	0.005
Mn/(Fe+Mn+Mg+Zn)	0.012	0.005	0.028	0.005	0.039	0.007	0.003	0.002	0.040	0.005	0.035	0.004
Zn/(Fe+Mn+Mg+Zn)	0.015	0.005	0.010	0.004	0.011	0.005	0.010	0.009	0.029	0.005	0.014	0.004

Table A5.8 Continued: Representative Staurolite Analyses

	91-1e-I		91-5b-II		93-44b-II		91-14d-I		93-45a-I		94-1a-I	
	St+Grt+Bt+Ky matrix St		St+Grt+Bt+Ky+Pl+Chl lrg. poik. adj. Qtz		St+Grt+Bt+Ky+Pl scattered xenoblasts		St+Grt+Bt+Pl lrg. poikiloblast		St+Grt+Bt+Pl lrg. poikiloblast		St+Grt+Bt+Pl matrix St	
	(2,1)	(2σ)	(4,1)	(2σ)	(4,1)	(2σ)	(8,1)	(2σ)	(8,1)	(2σ)	(4,1)	(2σ)
SiO ₂	27.03	0.08	26.74	0.46	26.68	0.38	26.93	0.39	26.75	0.52	26.76	0.50
Al ₂ O ₃	52.84	0.10	53.03	0.72	53.55	0.52	52.99	0.46	52.80	1.04	53.58	0.28
Cr ₂ O ₃	0.05	0.08	0.03	0.04	0.05	0.04	0.05	0.06	0.04	0.04	0.02	0.04
TiO ₂	0.50	0.14	0.37	0.11	0.52	0.04	0.58	0.07	0.61	0.10	0.55	0.06
FeO (total)	12.48	0.09	12.70	0.11	13.07	0.36	14.51	0.13	14.60	0.40	14.29	0.14
MnO	0.51	0.05	0.77	0.04	0.81	0.07	0.19	0.08	0.16	0.08	0.09	0.06
MgO	2.40	0.12	2.93	0.05	2.39	0.31	2.24	0.18	2.12	0.20	1.89	0.17
ZnO	0.69	0.06	0.30	0.16	0.65	0.16	0.18	0.15	0.12	0.12	0.14	0.07
TOTAL	96.50	0.16	96.87	0.99	97.72	0.26	97.67	0.57	97.21	1.48	97.32	0.34
<i>Cation proportions on the basis of 46 oxygens and 3.5% Fe₂O₃</i>												
Si	7.616	0.030	7.514	0.102	7.461	0.106	7.542	0.105	7.530	0.090	7.504	0.117
Al (IV)	0.384	0.030	0.486	0.102	0.539	0.106	0.458	0.105	0.470	0.090	0.496	0.117
Sum T(1)	8.000	0.000	8.000	0.000	8.000	0.000	8.000	0.000	8.000	0.000	8.000	0.000
Al (VI)	17.166	0.014	17.080	0.055	17.107	0.065	17.036	0.039	17.048	0.094	17.213	0.044
Cr	0.010	0.018	0.007	0.009	0.010	0.010	0.011	0.013	0.009	0.010	0.004	0.009
Fe ³⁺	0.069	0.000	0.070	0.000	0.071	0.002	0.079	0.001	0.080	0.003	0.078	0.001
Ti	0.106	0.029	0.077	0.024	0.109	0.008	0.122	0.015	0.130	0.022	0.115	0.013
Mg	0.403	0.020	0.491	0.013	0.398	0.051	0.373	0.029	0.356	0.031	0.316	0.027
Fe (2+)	0.206	0.001	0.209	0.001	0.214	0.006	0.239	0.002	0.241	0.009	0.235	0.003
Sum M	17.960	0.004	17.934	0.047	17.909	0.035	17.859	0.026	17.863	0.084	17.962	0.025
Fe (2+)	2.632	0.016	2.671	0.011	2.735	0.074	3.042	0.031	3.076	0.110	2.998	0.032
Mn	0.123	0.011	0.184	0.008	0.192	0.016	0.046	0.019	0.039	0.020	0.021	0.015
Mg	0.604	0.030	0.737	0.019	0.597	0.076	0.560	0.044	0.533	0.047	0.474	0.041
Zn	0.144	0.012	0.062	0.033	0.135	0.032	0.038	0.031	0.026	0.024	0.030	0.015
Sum T(2)	3.503	0.046	3.654	0.016	3.658	0.031	3.685	0.049	3.674	0.117	3.523	0.026
Fe/(Fe+Mn+Mg+Zn)	0.690	0.007	0.661	0.001	0.691	0.022	0.763	0.014	0.777	0.018	0.793	0.011
Mg/(Fe+Mn+Mg+Zn)	0.245	0.008	0.282	0.007	0.233	0.027	0.217	0.014	0.208	0.018	0.194	0.015
Mn/(Fe+Mn+Mg+Zn)	0.030	0.002	0.042	0.002	0.045	0.004	0.011	0.004	0.009	0.005	0.005	0.004
Zn/(Fe+Mn+Mg+Zn)	0.035	0.003	0.014	0.008	0.032	0.008	0.009	0.007	0.006	0.006	0.007	0.004
<i>Cation proportions on the basis of 46 oxygens with Total Iron as FeO</i>												
Si	7.500	0.000	7.486	0.037	7.454	0.084	7.492	0.035	7.493	0.031	7.482	0.064
Al (IV)	0.000	0.000	0.014	0.037	0.046	0.084	0.008	0.035	0.007	0.031	0.018	0.064
Sum T(1)	7.500	0.000	7.500	0.000	7.500	0.000	7.500	0.000	7.500	0.000	7.500	0.000
Si	0.116	0.030	0.028	0.069	0.007	0.028	0.050	0.078	0.037	0.070	0.022	0.075
Al (VI)	17.550	0.016	17.551	0.124	17.600	0.089	17.485	0.089	17.511	0.127	17.692	0.099
Cr	0.010	0.018	0.007	0.009	0.010	0.010	0.011	0.013	0.009	0.010	0.004	0.009
Ti	0.106	0.029	0.077	0.024	0.109	0.008	0.122	0.015	0.130	0.022	0.115	0.013
Sum M	17.783	0.025	17.664	0.045	17.726	0.071	17.668	0.033	17.686	0.091	17.833	0.050
Fe ²⁺	2.941	0.018	2.985	0.012	3.056	0.082	3.399	0.035	3.437	0.123	3.350	0.036
Mn	0.123	0.011	0.184	0.008	0.192	0.016	0.046	0.019	0.039	0.020	0.021	0.015
Mg	1.007	0.050	1.228	0.032	0.994	0.127	0.933	0.074	0.889	0.078	0.791	0.068
Zn	0.144	0.012	0.062	0.033	0.135	0.032	0.038	0.031	0.026	0.024	0.030	0.015
Sum T(2)	4.215	0.068	4.459	0.012	4.377	0.056	4.416	0.072	4.391	0.133	4.192	0.043
Fe/(Fe+Mn+Mg+Zn)	0.698	0.007	0.669	0.001	0.698	0.022	0.770	0.014	0.783	0.018	0.799	0.011
Mg/(Fe+Mn+Mg+Zn)	0.239	0.008	0.275	0.007	0.227	0.027	0.211	0.014	0.202	0.017	0.189	0.015
Mn/(Fe+Mn+Mg+Zn)	0.029	0.002	0.041	0.002	0.044	0.004	0.010	0.004	0.009	0.005	0.005	0.004
Zn/(Fe+Mn+Mg+Zn)	0.034	0.003	0.014	0.007	0.031	0.008	0.009	0.007	0.006	0.005	0.007	0.004

Table A5.8 Continued: Representative Staurolite Analyses

	Ardoc 201-V		92-34b-I		R3 301-II		93-40d-I		CR-8b-I		CR-4a-I	
	St+Grt+Bt+Sill+Pl+(Ky)		St+Grt+Bt+Sill+Pl		St+Grt+Bt+Sill+Pl		St+Grt+Bt+Sill		St+Grt+Bt+Pl		St+Grt+Bt+Sill+Pl	
	matrix St		matrix St		relict incl. in Plag		med. poikiloblast		lrg. poik. - core		matrix St	
	(6,2)	(2σ)	(4,1)	(2σ)	(4,1)	(2σ)	(4,1)	(2σ)	(3,1)	(2σ)	(3,1)	(2σ)
SiO ₂	26.75	0.18	26.22	0.51	26.29	0.37	26.53	0.58	26.85	0.30	26.56	0.67
Al ₂ O ₃	53.79	0.62	53.84	0.72	52.87	0.50	53.77	0.49	53.15	0.51	54.34	0.33
Cr ₂ O ₃	0.15	0.09	0.08	0.09	0.06	0.13	0.03	0.08	0.03	0.02	0.09	0.09
TiO ₂	0.55	0.08	0.48	0.09	0.58	0.09	0.61	0.09	0.58	0.10	0.49	0.13
FeO (total)	13.66	0.28	13.56	0.31	14.21	0.27	15.09	0.52	14.99	0.10	13.79	0.26
MnO	0.51	0.13	0.14	0.05	0.22	0.06	0.01	0.03	0.25	0.07	0.04	0.07
MgO	2.27	0.25	1.59	0.20	1.86	0.13	1.47	0.14	2.20	0.15	1.31	0.14
ZnO	0.21	0.06	0.96	0.14	0.99	0.10	0.18	0.12	0.13	0.17	1.20	0.11
TOTAL	97.89	0.60	96.89	0.99	97.07	1.10	97.68	1.15	98.19	0.84	97.83	0.74
<i>Cation proportions on the basis of 46 oxygens and 3.5% Fe₂O₃</i>												
Si	7.458	0.039	7.401	0.088	7.439	0.034	7.440	0.106	7.500	0.019	7.430	0.126
Al (IV)	0.542	0.039	0.599	0.088	0.561	0.034	0.560	0.106	0.500	0.019	0.570	0.126
Sum T(1)	8.000	0.000	8.000	0.000	8.000	0.000	8.000	0.000	8.000	0.000	8.000	0.000
Al (VI)	17.132	0.067	17.308	0.063	17.071	0.035	17.213	0.077	16.994	0.052	17.345	0.045
Cr	0.034	0.019	0.018	0.019	0.013	0.028	0.007	0.017	0.008	0.004	0.021	0.019
Fe ³⁺	0.074	0.002	0.075	0.003	0.078	0.001	0.083	0.003	0.082	0.001	0.075	0.002
Ti	0.115	0.018	0.103	0.019	0.124	0.021	0.128	0.020	0.123	0.020	0.103	0.029
Mg	0.377	0.041	0.268	0.032	0.314	0.021	0.246	0.024	0.366	0.029	0.218	0.025
Fe (2+)	0.224	0.006	0.225	0.008	0.236	0.004	0.248	0.009	0.246	0.003	0.226	0.006
Sum M	17.955	0.058	17.996	0.034	17.837	0.033	17.924	0.050	17.818	0.022	17.989	0.015
Fe (2+)	2.850	0.078	2.865	0.098	3.008	0.051	3.167	0.109	3.133	0.039	2.886	0.076
Mn	0.121	0.032	0.034	0.012	0.052	0.013	0.003	0.006	0.058	0.017	0.010	0.017
Mg	0.565	0.061	0.401	0.048	0.471	0.032	0.369	0.036	0.550	0.043	0.328	0.038
Zn	0.044	0.012	0.200	0.026	0.206	0.020	0.038	0.025	0.027	0.035	0.248	0.022
Sum T(2)	3.581	0.072	3.500	0.081	3.738	0.064	3.577	0.125	3.768	0.045	3.472	0.101
Fe/(Fe+Mn+Mg+Zn)	0.735	0.021	0.774	0.020	0.757	0.011	0.839	0.011	0.771	0.011	0.795	0.007
Mg/(Fe+Mn+Mg+Zn)	0.225	0.022	0.168	0.017	0.183	0.010	0.151	0.010	0.209	0.013	0.139	0.012
Mn/(Fe+Mn+Mg+Zn)	0.029	0.008	0.009	0.003	0.012	0.003	0.001	0.002	0.013	0.004	0.003	0.004
Zn/(Fe+Mn+Mg+Zn)	0.010	0.003	0.050	0.008	0.048	0.005	0.009	0.006	0.006	0.008	0.063	0.006
<i>Cation proportions on the basis of 46 oxygens with Total Iron as FeO</i>												
Si	7.458	0.039	7.401	0.088	7.439	0.034	7.440	0.106	7.496	0.007	7.430	0.126
Al (IV)	0.042	0.039	0.099	0.088	0.061	0.034	0.060	0.106	0.004	0.007	0.070	0.126
Sum T(1)	7.500	0.000	7.500	0.000	7.500	0.000	7.500	0.000	7.500	0.000	7.500	0.000
Si	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.004	0.012	0.000	0.000
Al (VI)	17.632	0.067	17.808	0.063	17.571	0.035	17.713	0.077	17.490	0.044	17.845	0.045
Cr	0.034	0.019	0.018	0.019	0.013	0.028	0.007	0.017	0.008	0.004	0.021	0.019
Ti	0.115	0.018	0.103	0.019	0.124	0.021	0.128	0.020	0.123	0.020	0.103	0.029
Sum M	17.781	0.072	17.929	0.061	17.709	0.048	17.847	0.077	17.624	0.045	17.969	0.047
Fe ²⁺	3.185	0.087	3.201	0.109	3.362	0.057	3.539	0.122	3.501	0.044	3.225	0.085
Mn	0.121	0.032	0.034	0.012	0.052	0.013	0.003	0.006	0.058	0.017	0.010	0.017
Mg	0.942	0.102	0.669	0.081	0.785	0.054	0.616	0.060	0.916	0.071	0.546	0.063
Zn	0.044	0.012	0.200	0.026	0.206	0.020	0.038	0.025	0.027	0.035	0.248	0.022
Sum T(2)	4.293	0.093	4.104	0.109	4.406	0.081	4.195	0.157	4.503	0.075	4.029	0.134
Fe/(Fe+Mn+Mg+Zn)	0.742	0.021	0.780	0.020	0.763	0.011	0.844	0.011	0.778	0.011	0.800	0.007
Mg/(Fe+Mn+Mg+Zn)	0.220	0.021	0.163	0.017	0.178	0.010	0.147	0.010	0.203	0.013	0.136	0.011
Mn/(Fe+Mn+Mg+Zn)	0.028	0.007	0.008	0.003	0.012	0.003	0.001	0.002	0.013	0.004	0.002	0.004
Zn/(Fe+Mn+Mg+Zn)	0.010	0.003	0.049	0.007	0.047	0.004	0.009	0.006	0.006	0.008	0.062	0.006

Table A5.9: Representative Muscovite Analyses

	Madoc-4a-I		Madoc-7b2-III		Madoc-5e-II		Madoc-2e-V		91-27a-I		91-27e-I	
	Ctd+Ky+Chl+St		Grt+Chl+Bt		Grt+Chl+Ctd		Grt+Chl+Bt+St+Ctd		Grt+Chl		Grt+Chl+Ctd	
	lrg. laths repl. porph.		lrg. xl in Ms-rich area		matrix Ms		fin-gr. matrix Ms		avg. mix. Ms		matrix, pl. fol.	
	(6,2)	(2σ)	(4,1)	(2σ)	(3,1)	(2σ)	(3,1)	(2σ)	(6,2)	(2σ)	(7,3)	(2σ)
SiO ₂	45.82	0.38	44.91	0.34	45.68	0.51	45.71	0.14	45.72	0.85	45.26	0.92
Al ₂ O ₃	37.64	0.45	37.20	0.37	36.74	0.57	36.54	0.55	37.41	0.81	36.84	1.45
Cr ₂ O ₃	0.01	0.05	0.03	0.05	0.03	0.05	0.01	0.02	0.03	0.07	0.04	0.05
TiO ₂	0.28	0.07	0.23	0.07	0.23	0.21	0.29	0.10	0.22	0.15	0.52	1.14
FeO	2.22	0.43	1.63	0.05	2.50	0.12	2.44	0.09	2.29	0.15	2.33	0.84
MnO	0.03	0.08	0.03	0.07	0.01	0.03	0.03	0.06	0.01	0.03	0.03	0.06
MgO	0.41	0.07	0.41	0.09	0.59	0.04	0.64	0.29	0.52	0.13	0.47	0.23
CaO	0.05	0.05	0.02	0.04	0.01	0.02	0.03	0.05	0.03	0.08	0.01	0.03
Na ₂ O	1.69	0.17	0.93	0.11	1.07	0.33	1.06	0.13	1.34	0.19	1.10	0.11
K ₂ O	8.88	0.21	10.36	0.20	10.19	0.10	9.40	0.11	9.49	0.09	9.69	0.28
BaO	0.11	0.16	0.19	0.09	0.16	0.24	0.27	0.06	0.16	0.10	0.15	0.17
TOTAL	97.14	0.63	95.93	0.62	97.20	1.34	96.42	0.72	97.23	1.49	96.44	0.90
<i>Cation proportions on the basis of 11 oxygens</i>												
Si	2.991	0.013	2.984	0.027	3.004	0.011	3.017	0.016	2.992	0.016	2.991	0.043
Al	1.009	0.013	1.016	0.027	0.996	0.011	0.983	0.016	1.008	0.016	1.009	0.043
Sum	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000
Al	1.887	0.021	1.897	0.012	1.851	0.015	1.860	0.016	1.877	0.027	1.860	0.101
Cr	0.001	0.002	0.001	0.002	0.002	0.003	0.001	0.001	0.002	0.003	0.002	0.003
Ti	0.014	0.003	0.011	0.003	0.011	0.010	0.014	0.005	0.011	0.007	0.026	0.057
Fe	0.121	0.024	0.091	0.003	0.138	0.008	0.135	0.005	0.125	0.007	0.129	0.047
Mn	0.002	0.004	0.002	0.004	0.001	0.002	0.002	0.003	0.000	0.002	0.002	0.004
Mg	0.040	0.007	0.040	0.009	0.058	0.004	0.062	0.029	0.051	0.012	0.046	0.023
Sum	2.064	0.015	2.042	0.003	2.060	0.006	2.074	0.011	2.066	0.010	2.064	0.014
Ca	0.003	0.003	0.002	0.003	0.000	0.001	0.002	0.004	0.002	0.006	0.001	0.002
Na	0.214	0.021	0.120	0.014	0.136	0.040	0.136	0.016	0.170	0.023	0.141	0.015
K	0.739	0.016	0.878	0.016	0.855	0.006	0.792	0.014	0.792	0.012	0.817	0.018
Ba	0.003	0.004	0.005	0.002	0.004	0.006	0.007	0.002	0.004	0.002	0.004	0.004
Sum	0.960	0.021	1.004	0.027	0.995	0.029	0.936	0.009	0.969	0.023	0.962	0.021
K/(K+Na+Ca)	0.773	0.019	0.879	0.011	0.863	0.035	0.852	0.015	0.821	0.022	0.852	0.015
Na/(K+Na+Ca)	0.224	0.020	0.120	0.011	0.137	0.036	0.146	0.017	0.176	0.021	0.147	0.014
Ca/(K+Na+Ca)	0.003	0.004	0.002	0.003	0.000	0.001	0.002	0.004	0.002	0.006	0.001	0.002
<i>Cation proportions on the basis of 6 cations</i>												
Si	2.959	0.017	2.963	0.028	2.974	0.008	2.981	0.019	2.959	0.018	2.959	0.047
Al	1.041	0.017	1.037	0.028	1.026	0.008	1.019	0.019	1.041	0.018	1.041	0.047
Sum	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000
Al	1.825	0.024	1.856	0.013	1.793	0.010	1.789	0.025	1.813	0.019	1.798	0.109
Fe ³⁺	0.120	0.023	0.090	0.003	0.136	0.008	0.133	0.006	0.124	0.007	0.127	0.046
Cr	0.001	0.002	0.001	0.002	0.002	0.003	0.001	0.001	0.002	0.003	0.002	0.003
Ti	0.013	0.003	0.011	0.003	0.011	0.010	0.014	0.005	0.011	0.007	0.026	0.056
Fe ²⁺	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Mn	0.002	0.004	0.002	0.004	0.001	0.002	0.002	0.003	0.000	0.002	0.002	0.003
Mg	0.040	0.007	0.040	0.009	0.057	0.004	0.062	0.028	0.050	0.012	0.046	0.022
Sum	2.000	0.000	2.000	0.000	2.000	0.000	2.000	0.000	2.000	0.000	2.000	0.000
Ca	0.003	0.003	0.002	0.003	0.000	0.001	0.002	0.003	0.002	0.006	0.001	0.002
Na	0.212	0.021	0.119	0.014	0.134	0.040	0.134	0.016	0.168	0.023	0.140	0.015
K	0.732	0.016	0.872	0.016	0.846	0.005	0.782	0.015	0.784	0.012	0.808	0.020
Ba	0.003	0.004	0.005	0.002	0.004	0.006	0.007	0.002	0.004	0.002	0.004	0.004
Sum	0.949	0.023	0.997	0.026	0.985	0.030	0.925	0.008	0.958	0.024	0.952	0.022
K/(K+Na+Ca)	0.773	0.019	0.879	0.011	0.863	0.035	0.852	0.015	0.821	0.022	0.852	0.015
Na/(K+Na+Ca)	0.224	0.020	0.120	0.011	0.137	0.036	0.146	0.017	0.176	0.021	0.147	0.014
Ca/(K+Na+Ca)	0.003	0.004	0.002	0.003	0.000	0.001	0.002	0.004	0.002	0.006	0.001	0.002

Table A5.9 Continued: Representative Muscovite Analyses

	93-13b-I		93-15d-I		93-16a-II		93-16b-I		92-6f1-II		93-26a-I	
	Grt+Chl+St+(Cld) Ms in Cld pseudo.		Grt+Chl+Bt+Pl fn-gr. mtr. Ms		Grt+Chl matrix Ms		Grt+Chl+(Relict Cld) Grt incl. with Paragonite		Grt+Chl+Cld+Bt matrix, pl. fol.		Grt+Chl+Cld+Bt+St+Mgr matrix Ms	
	(5,2)	(2σ)	(8,3)	(2σ)	(3,2)	(2σ)	(2,1)	(2σ)	(3,1)	(2σ)	(8,3)	(2σ)
SiO ₂	45.27	0.79	45.24	0.92	45.11	0.07	44.97	0.39	45.15	0.10	45.12	0.83
Al ₂ O ₃	37.50	0.83	35.43	0.98	36.13	0.37	37.99	0.57	36.53	0.26	36.10	0.77
Cr ₂ O ₃	0.02	0.04	0.25	0.08	0.04	0.05	0.07	0.13	0.02	0.07	0.03	0.07
TiO ₂	0.25	0.11	0.37	0.10	0.21	0.06	0.36	0.16	0.32	0.10	0.21	0.15
FeO	2.12	0.22	2.73	0.37	2.32	0.12	1.78	0.02	2.11	0.27	2.63	0.61
MnO	0.02	0.07	0.02	0.05	0.01	0.02	0.21	0.04	0.04	0.08	0.01	0.02
MgO	0.36	0.09	0.82	0.31	0.57	0.07	0.29	0.01	0.52	0.05	0.64	0.20
CaO	0.01	0.04	0.01	0.04	0.02	0.05	0.03	0.08	0.07	0.04	0.02	0.07
Na ₂ O	1.68	0.08	0.72	0.09	1.09	0.09	1.82	0.07	0.66	0.07	0.79	0.14
K ₂ O	8.82	0.13	10.69	0.22	9.64	0.06	8.80	0.06	10.36	0.17	10.21	0.23
BaO	0.18	0.16	0.36	0.28	0.11	0.10	0.06	0.16	0.29	0.17	0.43	0.14
TOTAL	96.23	1.87	96.64	1.00	95.22	0.55	96.38	1.29	96.07	0.22	96.20	1.42
<i>Cation proportions on the basis of 11 oxygens</i>												
Si	2.984	0.012	3.013	0.051	3.017	0.011	2.958	0.009	3.003	0.004	3.007	0.030
Al	1.016	0.012	0.987	0.051	0.983	0.011	1.042	0.009	0.997	0.004	0.993	0.030
Sum	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000
Al	1.897	0.014	1.794	0.031	1.864	0.005	1.902	0.001	1.866	0.014	1.842	0.024
Cr	0.001	0.002	0.013	0.004	0.002	0.003	0.004	0.007	0.001	0.004	0.002	0.004
Ti	0.012	0.005	0.019	0.005	0.010	0.003	0.018	0.008	0.016	0.005	0.011	0.008
Fe	0.117	0.010	0.152	0.021	0.130	0.006	0.098	0.000	0.117	0.015	0.146	0.034
Mn	0.001	0.004	0.001	0.003	0.000	0.001	0.012	0.002	0.002	0.004	0.001	0.001
Mg	0.036	0.009	0.081	0.031	0.056	0.007	0.029	0.001	0.051	0.005	0.064	0.020
Sum	2.063	0.013	2.060	0.024	2.063	0.012	2.062	0.002	2.054	0.003	2.066	0.024
Ca	0.001	0.003	0.001	0.003	0.001	0.004	0.002	0.006	0.005	0.003	0.002	0.005
Na	0.214	0.011	0.093	0.011	0.141	0.012	0.232	0.006	0.085	0.009	0.102	0.018
K	0.742	0.011	0.908	0.026	0.822	0.010	0.738	0.004	0.879	0.017	0.868	0.011
Ba	0.005	0.004	0.009	0.007	0.003	0.003	0.001	0.004	0.007	0.005	0.011	0.004
Sum	0.962	0.019	1.011	0.026	0.967	0.010	0.974	0.012	0.977	0.010	0.983	0.023
K/(K+Na+Ca)	0.775	0.006	0.907	0.012	0.852	0.010	0.760	0.010	0.907	0.013	0.893	0.018
Na/(K+Na+Ca)	0.224	0.008	0.092	0.010	0.147	0.012	0.238	0.004	0.088	0.010	0.105	0.017
Ca/(K+Na+Ca)	0.001	0.003	0.001	0.003	0.001	0.004	0.002	0.006	0.005	0.003	0.002	0.005
<i>Cation proportions on the basis of 6 cations</i>												
Si	2.953	0.017	2.983	0.057	2.985	0.015	2.928	0.008	2.976	0.003	2.975	0.036
Al	1.047	0.017	1.017	0.057	1.015	0.015	1.072	0.008	1.024	0.003	1.025	0.036
Sum	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000
Al	1.835	0.013	1.736	0.043	1.803	0.013	1.842	0.003	1.814	0.013	1.779	0.034
Fe ³⁺	0.116	0.010	0.150	0.020	0.128	0.006	0.097	0.000	0.116	0.015	0.145	0.034
Cr	0.001	0.002	0.013	0.004	0.002	0.003	0.004	0.007	0.001	0.004	0.002	0.004
Ti	0.012	0.005	0.019	0.005	0.010	0.003	0.018	0.008	0.016	0.005	0.011	0.008
Fe ²⁺	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Mn	0.001	0.004	0.001	0.003	0.000	0.001	0.012	0.002	0.002	0.004	0.001	0.001
Mg	0.035	0.008	0.080	0.030	0.056	0.007	0.028	0.001	0.051	0.005	0.063	0.019
Sum	2.000	0.000	2.000	0.000	2.000	0.000	2.000	0.000	2.000	0.000	2.000	0.000
Ca	0.001	0.003	0.001	0.003	0.001	0.004	0.002	0.006	0.005	0.003	0.002	0.005
Na	0.212	0.011	0.092	0.011	0.140	0.012	0.229	0.006	0.085	0.009	0.101	0.017
K	0.734	0.012	0.899	0.027	0.814	0.011	0.731	0.003	0.871	0.016	0.859	0.013
Ba	0.005	0.004	0.009	0.007	0.003	0.003	0.001	0.004	0.007	0.004	0.011	0.004
Sum	0.952	0.021	1.001	0.028	0.957	0.012	0.964	0.012	0.968	0.010	0.973	0.025
K/(K+Na+Ca)	0.775	0.006	0.907	0.012	0.852	0.010	0.760	0.010	0.907	0.013	0.893	0.018
Na/(K+Na+Ca)	0.224	0.008	0.092	0.010	0.147	0.012	0.238	0.004	0.088	0.010	0.105	0.017
Ca/(K+Na+Ca)	0.001	0.003	0.001	0.003	0.001	0.004	0.002	0.006	0.005	0.003	0.002	0.005

Table A5.9 Continued: Representative Muscovite Analyses

	93-26g-I		93-24a-II		92-8d-I		92-42c-I		93-18a-I		92-41a-I	
	Grt+Chl+Bt+St+Mrg matrix Ms		Grt+Chl+Cld+Mrg matrix, pll. fol.		Grt+Chl+Cld+Bt+St+Mrg matrix Ms		Best Ms1b matrix Ms		Ms1a+ConMs2a matrix, pll. fol.		Grt+Cld+Bt matrix Ms	
	(9,3)	(2σ)	(3,1)	(2σ)	(6,2)	(2σ)	(3,1)	(2σ)	(5,2)	(2σ)	(11,4)	(2σ)
SiO ₂	45.47	0.48	46.09	0.41	45.43	0.73	45.08	0.24	44.96	0.88	45.33	1.16
Al ₂ O ₃	35.66	0.44	35.76	1.08	36.79	0.80	36.92	0.41	35.77	0.35	37.38	0.93
Cr ₂ O ₃	0.04	0.07	0.06	0.10	0.04	0.08	0.01	0.04	0.02	0.05	0.04	0.07
TiO ₂	0.28	0.13	0.28	0.08	0.23	0.10	0.17	0.03	0.25	0.17	0.21	0.12
FeO	2.22	0.18	2.29	0.05	2.24	0.13	1.63	0.21	1.95	0.21	1.78	0.24
MnO	0.01	0.04	0.01	0.05	0.00	0.02	0.01	0.02	0.03	0.06	0.01	0.04
MgO	0.77	0.18	0.55	0.17	0.58	0.20	0.63	0.11	0.60	0.22	0.55	0.17
CaO	0.03	0.05	0.08	0.05	0.02	0.04	0.02	0.03	0.01	0.02	0.01	0.04
Na ₂ O	0.80	0.09	0.84	0.06	0.88	0.08	0.70	0.08	0.55	0.05	0.76	0.13
K ₂ O	10.14	0.13	9.54	0.10	10.14	0.27	10.48	0.18	10.29	0.24	10.51	0.34
BaO	0.54	0.23	n.d.	n.d.	0.29	0.15	0.56	0.13	0.35	0.16	0.34	0.19
TOTAL	95.94	1.09	95.52	1.18	96.62	1.42	96.21	0.44	94.77	1.00	96.93	1.29
<i>Cation proportions on the basis of 11 oxygens</i>												
Si	3.032	0.020	3.061	0.034	3.002	0.020	2.994	0.025	3.028	0.027	2.985	0.061
Al	0.968	0.020	0.939	0.034	0.998	0.020	1.006	0.025	0.972	0.027	1.015	0.061
Sum	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000
Al	1.836	0.014	1.860	0.022	1.867	0.022	1.885	0.011	1.867	0.027	1.887	0.018
Cr	0.002	0.004	0.003	0.005	0.002	0.004	0.001	0.002	0.001	0.003	0.002	0.004
Ti	0.014	0.006	0.014	0.004	0.011	0.005	0.008	0.001	0.012	0.009	0.011	0.006
Fe	0.124	0.010	0.127	0.003	0.124	0.008	0.091	0.012	0.110	0.013	0.098	0.013
Mn	0.001	0.002	0.001	0.003	0.000	0.001	0.000	0.001	0.002	0.003	0.000	0.002
Mg	0.076	0.017	0.055	0.017	0.057	0.019	0.062	0.011	0.060	0.022	0.054	0.017
Sum	2.052	0.013	2.060	0.008	2.061	0.008	2.047	0.011	2.052	0.013	2.052	0.018
Ca	0.002	0.003	0.006	0.003	0.001	0.003	0.001	0.002	0.001	0.002	0.001	0.002
Na	0.103	0.011	0.108	0.006	0.112	0.009	0.090	0.010	0.072	0.007	0.097	0.017
K	0.863	0.009	0.809	0.013	0.854	0.014	0.888	0.013	0.884	0.018	0.883	0.031
Ba	0.014	0.006	n.d.	n.d.	0.007	0.004	0.014	0.003	0.009	0.004	0.009	0.005
Sum	0.982	0.013	0.922	0.013	0.975	0.017	0.994	0.012	0.966	0.024	0.990	0.041
K/(K+Na+Ca)	0.891	0.012	0.877	0.004	0.883	0.009	0.907	0.010	0.924	0.005	0.900	0.013
Na/(K+Na+Ca)	0.107	0.010	0.117	0.007	0.116	0.008	0.092	0.010	0.075	0.006	0.099	0.014
Ca/(K+Na+Ca)	0.002	0.003	0.006	0.004	0.001	0.003	0.001	0.002	0.001	0.002	0.001	0.003
<i>Cation proportions on the basis of 6 cations</i>												
Si	3.007	0.025	3.031	0.038	2.971	0.023	2.971	0.029	3.002	0.032	2.959	0.068
Al	0.993	0.025	0.969	0.038	1.029	0.023	1.029	0.029	0.998	0.032	1.041	0.068
Sum	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000
Al	1.786	0.025	1.802	0.014	1.808	0.018	1.839	0.020	1.817	0.030	1.836	0.028
Fe ³⁺	0.123	0.009	0.125	0.006	0.123	0.008	0.090	0.011	0.109	0.012	0.096	0.018
Cr	0.002	0.004	0.003	0.005	0.002	0.004	0.001	0.002	0.001	0.003	0.002	0.004
Ti	0.014	0.006	0.014	0.004	0.011	0.005	0.008	0.001	0.012	0.009	0.010	0.006
Fe ²⁺	0.000	0.000	0.001	0.004	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.009
Mn	0.001	0.002	0.001	0.003	0.000	0.001	0.000	0.001	0.002	0.003	0.000	0.002
Mg	0.075	0.017	0.054	0.017	0.056	0.018	0.062	0.011	0.059	0.022	0.054	0.017
Sum	2.000	0.000	2.000	0.000	2.000	0.000	2.000	0.000	2.000	0.000	2.000	0.000
Ca	0.002	0.003	0.006	0.003	0.001	0.003	0.001	0.002	0.001	0.002	0.001	0.002
Na	0.103	0.011	0.107	0.006	0.111	0.009	0.089	0.010	0.071	0.007	0.096	0.016
K	0.855	0.009	0.801	0.014	0.846	0.015	0.881	0.013	0.877	0.018	0.875	0.030
Ba	0.014	0.006	n.d.	n.d.	0.007	0.004	0.014	0.003	0.009	0.004	0.009	0.005
Sum	0.974	0.013	0.913	0.013	0.965	0.017	0.986	0.010	0.958	0.024	0.981	0.040
K/(K+Na+Ca)	0.891	0.012	0.877	0.004	0.883	0.009	0.907	0.010	0.924	0.005	0.900	0.013
Na/(K+Na+Ca)	0.107	0.010	0.117	0.007	0.116	0.008	0.092	0.010	0.075	0.006	0.099	0.014
Ca/(K+Na+Ca)	0.002	0.003	0.006	0.004	0.001	0.003	0.001	0.002	0.001	0.002	0.001	0.003

Table A5.9 Continued: Representative Muscovite Analyses

	92-41d-I		93-20f-I		92-10a-II		90-19a-I		92-27a-II		92-28a-I	
	Chl+Cld+Mrg matrix, pll. fol.		Grt+Cld+Bt matrix, pll. fol.		Cld+St+Grt+Bt matrix Ms		Cld+St+Grt+Bt matrix Ms		Cld+St+Grt+Bt matrix, pll. fol.		Cld+St+Grt+Bt fn. mtrx, adj. Grt	
	(6,2)	(2σ)	(5,2)	(2σ)	(7,2)	(2σ)	(6,2)	(2σ)	(3,1)	(2σ)	(3,1)	(2σ)
SiO ₂	45.11	0.72	44.73	0.38	45.59	0.53	46.31	1.13	44.94	0.13	44.91	0.64
Al ₂ O ₃	36.36	0.66	36.88	0.34	37.28	0.84	36.56	0.40	36.78	0.19	36.59	1.08
Cr ₂ O ₃	0.04	0.04	0.05	0.05	0.04	0.07	0.03	0.07	0.02	0.04	0.00	0.01
TiO ₂	0.17	0.11	0.21	0.06	0.18	0.09	0.06	0.14	0.26	0.05	0.24	0.03
FeO	2.18	0.40	1.74	0.36	1.54	0.36	1.47	0.15	1.87	0.07	2.01	0.26
MnO	0.01	0.03	0.02	0.07	0.02	0.07	0.03	0.05	0.03	0.06	0.01	0.03
MgO	0.58	0.19	0.46	0.14	0.45	0.06	0.17	0.23	0.47	0.07	0.51	0.09
CaO	0.02	0.05	0.01	0.02	0.01	0.02	0.01	0.03	0.02	0.04	0.01	0.03
Na ₂ O	0.92	0.05	0.85	0.08	1.06	0.08	0.84	0.57	0.80	0.06	0.87	0.02
K ₂ O	10.05	0.20	9.96	0.12	9.79	0.19	9.90	0.12	10.24	0.10	10.04	0.13
BaO	0.37	0.26	0.40	0.27	0.23	0.20	0.33	0.29	0.51	0.02	0.44	0.16
TOTAL	95.81	1.38	95.29	0.27	96.18	1.23	95.68	1.23	95.95	0.44	95.64	1.47
Cation proportions on the basis of 11 oxygens												
Si	3.008	0.016	2.991	0.021	3.007	0.033	3.070	0.036	2.994	0.007	2.999	0.012
Al	0.992	0.016	1.009	0.021	0.993	0.033	0.930	0.036	1.006	0.007	1.001	0.012
Sum	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000
Al	1.865	0.039	1.897	0.021	1.906	0.014	1.927	0.026	1.881	0.005	1.878	0.022
Cr	0.002	0.002	0.002	0.003	0.002	0.003	0.001	0.004	0.001	0.002	0.000	0.001
Ti	0.009	0.005	0.010	0.003	0.009	0.004	0.003	0.007	0.013	0.003	0.012	0.002
Fe	0.121	0.021	0.097	0.021	0.085	0.020	0.081	0.009	0.104	0.003	0.112	0.015
Mn	0.001	0.002	0.001	0.004	0.001	0.004	0.002	0.003	0.002	0.004	0.001	0.002
Mg	0.058	0.019	0.046	0.014	0.044	0.005	0.017	0.023	0.047	0.007	0.050	0.010
Sum	2.056	0.005	2.054	0.014	2.047	0.012	2.031	0.011	2.048	0.008	2.053	0.009
Ca	0.001	0.003	0.000	0.002	0.000	0.002	0.001	0.002	0.001	0.003	0.001	0.002
Na	0.119	0.007	0.110	0.011	0.135	0.009	0.078	0.001	0.103	0.007	0.113	0.004
K	0.855	0.017	0.849	0.012	0.824	0.012	0.837	0.010	0.870	0.011	0.855	0.009
Ba	0.010	0.007	0.010	0.007	0.006	0.005	0.008	0.008	0.013	0.001	0.011	0.004
Sum	0.985	0.022	0.970	0.015	0.965	0.020	0.925	0.010	0.988	0.010	0.980	0.019
K/(K+Na+Ca)	0.877	0.005	0.885	0.009	0.859	0.006	0.914	0.003	0.893	0.004	0.883	0.004
Na/(K+Na+Ca)	0.122	0.007	0.114	0.010	0.141	0.007	0.086	0.001	0.106	0.008	0.117	0.002
Ca/(K+Na+Ca)	0.001	0.003	0.000	0.002	0.000	0.002	0.001	0.002	0.001	0.003	0.001	0.002
Cation proportions on the basis of 6 cations												
Si	2.980	0.018	2.964	0.025	2.984	0.035	3.055	0.041	2.970	0.011	2.972	0.015
Al	1.020	0.018	1.036	0.025	1.016	0.035	0.945	0.041	1.030	0.011	1.028	0.015
Sum	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000
Al	1.812	0.036	1.844	0.033	1.860	0.020	1.897	0.029	1.835	0.013	1.826	0.019
Fe ³⁺	0.120	0.021	0.096	0.020	0.084	0.020	0.041	0.046	0.103	0.003	0.111	0.015
Cr	0.002	0.002	0.002	0.003	0.002	0.003	0.001	0.003	0.001	0.002	0.000	0.001
Ti	0.008	0.005	0.010	0.003	0.009	0.004	0.003	0.007	0.013	0.002	0.012	0.002
Fe ²⁺	0.000	0.000	0.000	0.000	0.000	0.000	0.040	0.042	0.000	0.000	0.000	0.000
Mn	0.001	0.002	0.001	0.004	0.001	0.004	0.001	0.003	0.002	0.003	0.001	0.002
Mg	0.057	0.019	0.046	0.014	0.043	0.005	0.017	0.023	0.046	0.007	0.050	0.010
Sum	2.000	0.000	2.000	0.000	2.000	0.000	2.000	0.000	2.000	0.000	2.000	0.000
Ca	0.001	0.003	0.000	0.002	0.000	0.002	0.001	0.002	0.001	0.003	0.001	0.002
Na	0.118	0.006	0.109	0.010	0.134	0.009	0.078	0.001	0.102	0.007	0.112	0.004
K	0.847	0.017	0.842	0.013	0.817	0.013	0.833	0.009	0.863	0.012	0.848	0.010
Ba	0.010	0.007	0.010	0.007	0.006	0.005	0.008	0.008	0.013	0.001	0.011	0.004
Sum	0.976	0.022	0.961	0.015	0.958	0.021	0.920	0.009	0.980	0.010	0.972	0.020
K/(K+Na+Ca)	0.877	0.005	0.885	0.009	0.859	0.006	0.914	0.003	0.893	0.004	0.883	0.004
Na/(K+Na+Ca)	0.122	0.007	0.114	0.010	0.141	0.007	0.086	0.001	0.106	0.008	0.117	0.002
Ca/(K+Na+Ca)	0.001	0.003	0.000	0.002	0.000	0.002	0.001	0.002	0.001	0.003	0.001	0.002

Table A5.9 Continued: Representative Muscovite Analyses

	92-912-II		92-26b-I		91-21c2-III		93-10b-II		90-1e-I		90-4h	
	Grt+Chl+Bt+Pl+Ep matrix Ms		Grt+Chl+St+Ky+Pl matrix Ms		Grt+Chl+St (Mrg+Ctd) matrix Ms		Grt+Chl+St+Bt+Pl+Ky matrix Ms		St+Grt+Bt matrix Ms		St+Grt+Bt+Pl+(Ctd) matrix Ms	
	(3,1)	(2σ)	(3,1)	(2σ)	(7,3)	(2σ)	(7,3)	(2σ)	(6,2)	(2σ)	(8,2)	(2σ)
SiO ₂	45.25	0.38	44.93	0.45	45.03	0.67	45.23	1.66	45.80	0.49	46.19	0.46
Al ₂ O ₃	35.91	0.43	36.10	0.82	36.65	0.51	35.97	1.30	36.87	0.74	36.12	0.39
Cr ₂ O ₃	0.07	0.04	0.02	0.07	0.03	0.07	0.04	0.06	0.02	0.07	0.08	0.09
TiO ₂	0.45	0.06	0.22	0.07	0.30	0.11	0.39	0.07	0.28	0.14	0.11	0.14
FeO	2.60	0.10	2.48	0.06	2.24	0.29	2.79	0.72	2.28	0.09	2.27	0.23
MnO	0.01	0.03	0.01	0.01	0.01	0.03	0.01	0.02	0.02	0.04	0.06	0.09
MgO	0.84	0.04	0.69	0.08	0.47	0.13	1.08	0.82	0.57	0.21	0.39	0.08
CaO	0.02	0.03	0.00	0.01	0.04	0.06	0.01	0.03	0.00	0.00	0.10	0.06
Na ₂ O	0.97	0.12	1.92	0.21	1.40	0.12	0.73	0.14	0.84	0.18	1.81	0.21
K ₂ O	10.09	0.13	8.80	0.07	9.45	0.23	10.24	0.57	10.38	0.21	8.55	0.14
BaO	0.20	0.10	0.20	0.08	0.18	0.16	0.24	0.22	0.14	0.23	0.36	0.39
TOTAL	96.40	0.91	95.36	1.25	95.79	1.53	96.73	2.35	97.19	0.88	96.03	1.25
<i>Cation proportions on the basis of 11 oxygens</i>												
Si	3.005	0.011	3.001	0.013	2.995	0.018	2.997	0.044	3.008	0.029	3.074	0.008
Al	0.995	0.011	0.999	0.013	1.005	0.018	1.003	0.044	0.992	0.029	0.926	0.008
Sum	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000
Al	1.815	0.011	1.843	0.020	1.867	0.015	1.807	0.059	1.862	0.024	1.906	0.012
Cr	0.004	0.002	0.001	0.003	0.002	0.004	0.002	0.003	0.001	0.003	0.004	0.005
Ti	0.022	0.003	0.011	0.004	0.015	0.005	0.020	0.004	0.014	0.007	0.008	0.007
Fe	0.144	0.005	0.138	0.005	0.124	0.015	0.155	0.044	0.125	0.004	0.126	0.012
Mn	0.000	0.001	0.000	0.001	0.001	0.001	0.001	0.001	0.001	0.002	0.003	0.005
Mg	0.083	0.004	0.068	0.008	0.047	0.013	0.107	0.084	0.056	0.020	0.038	0.008
Sum	2.069	0.006	2.062	0.007	2.055	0.008	2.090	0.070	2.059	0.017	2.084	0.011
Ca	0.002	0.002	0.000	0.000	0.003	0.004	0.000	0.002	0.000	0.000	0.007	0.005
Na	0.124	0.016	0.248	0.025	0.180	0.015	0.094	0.018	0.107	0.023	0.079	0.001
K	0.855	0.015	0.750	0.006	0.801	0.014	0.866	0.034	0.869	0.019	0.726	0.013
Ba	0.005	0.003	0.005	0.002	0.005	0.004	0.006	0.006	0.003	0.006	0.009	0.010
Sum	0.986	0.019	1.003	0.025	0.989	0.019	0.967	0.046	0.980	0.032	0.821	0.014
K/(K+Na+Ca)	0.872	0.013	0.751	0.019	0.814	0.012	0.901	0.014	0.890	0.021	0.894	0.006
Na/(K+Na+Ca)	0.127	0.015	0.249	0.019	0.183	0.013	0.098	0.015	0.110	0.021	0.097	0.001
Ca/(K+Na+Ca)	0.002	0.002	0.000	0.000	0.003	0.004	0.001	0.002	0.000	0.000	0.009	0.006
<i>Cation proportions on the basis of 6 cations</i>												
Si	2.971	0.011	2.970	0.010	2.967	0.020	2.953	0.075	2.979	0.036	3.031	0.013
Al	1.029	0.011	1.030	0.010	1.033	0.020	1.047	0.075	1.021	0.036	0.969	0.013
Sum	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000
Al	1.749	0.011	1.783	0.020	1.814	0.019	1.721	0.121	1.805	0.018	1.825	0.016
Fe ³⁺	0.143	0.004	0.137	0.005	0.123	0.015	0.152	0.041	0.124	0.004	0.122	0.017
Cr	0.004	0.002	0.001	0.003	0.002	0.004	0.002	0.003	0.001	0.003	0.004	0.005
Ti	0.022	0.003	0.011	0.004	0.015	0.005	0.019	0.004	0.014	0.007	0.005	0.007
Fe ²⁺	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.002	0.009
Mn	0.000	0.001	0.000	0.001	0.001	0.001	0.001	0.001	0.001	0.002	0.003	0.005
Mg	0.082	0.004	0.068	0.008	0.046	0.013	0.105	0.081	0.055	0.020	0.038	0.008
Sum	2.000	0.000	2.000	0.000	2.000	0.000	2.000	0.000	2.000	0.000	2.000	0.000
Ca	0.002	0.002	0.000	0.000	0.003	0.004	0.000	0.002	0.000	0.000	0.007	0.005
Na	0.123	0.015	0.246	0.025	0.178	0.015	0.093	0.018	0.106	0.023	0.078	0.001
K	0.845	0.016	0.742	0.006	0.794	0.014	0.853	0.042	0.861	0.021	0.716	0.014
Ba	0.005	0.003	0.005	0.002	0.005	0.004	0.006	0.006	0.003	0.006	0.009	0.010
Sum	0.975	0.019	0.993	0.026	0.980	0.019	0.953	0.055	0.970	0.034	0.810	0.014
K/(K+Na+Ca)	0.872	0.013	0.751	0.019	0.814	0.012	0.901	0.014	0.890	0.021	0.894	0.006
Na/(K+Na+Ca)	0.127	0.015	0.249	0.019	0.183	0.013	0.098	0.015	0.110	0.021	0.097	0.001
Ca/(K+Na+Ca)	0.002	0.002	0.000	0.000	0.003	0.004	0.001	0.002	0.000	0.000	0.009	0.006

Table A5.9 Continued: Representative Muscovite Analyses

	91-26a-II		91-26e-II		91-24a-I		91-1b2-II		91-1e-I		91-5b-II	
	Grt+Chl+St matrix Ms		Grt+Chl+St+Bt late porph. cuts fol.		Grt+St+Chl+Ky matrix Ms		Grt+Chl+St+Bt+Pl matrix Ms		St+Grt+Bt+Ky matrix Ms		St+Grt+Bt+Ky+Pl+Chl very fin. matrix laths	
	(6,2)	(2σ)	(2,1)	(2σ)	(5,2)	(2σ)	(3,1)	(2σ)	(5,3)	(2σ)	(3,1)	(2σ)
SiO ₂	45.83	0.71	46.00	0.68	45.75	1.02	45.34	0.09	45.08	0.27	45.43	0.76
Al ₂ O ₃	37.04	0.49	36.06	0.09	37.66	0.93	37.46	0.29	36.77	0.65	36.51	0.26
Cr ₂ O ₃	0.03	0.06	0.04	0.06	0.01	0.03	0.04	0.02	0.02	0.07	0.04	0.05
TiO ₂	0.33	0.07	0.16	0.10	0.29	0.05	0.37	0.04	0.41	0.09	0.25	0.05
FeO	2.12	0.27	1.52	0.13	2.15	0.54	2.03	0.14	2.03	0.36	2.40	0.09
MnO	0.04	0.10	0.02	0.05	0.01	0.02	0.00	0.01	0.02	0.05	0.02	0.08
MgO	0.58	0.12	0.44	0.45	0.52	0.16	0.56	0.16	0.53	0.18	0.71	0.17
CaO	0.02	0.03	0.03	0.08	0.00	0.00	0.00	0.00	0.04	0.06	0.00	0.00
Na ₂ O	2.27	0.14	1.49	0.07	2.26	0.28	1.54	0.11	2.02	0.10	1.63	0.06
K ₂ O	8.47	0.21	9.24	0.34	8.47	0.22	8.77	0.26	8.37	0.22	9.39	0.17
BaO	0.18	0.19	0.12	0.03	0.14	0.16	0.19	0.06	0.17	0.17	0.23	0.19
TOTAL	96.90	1.11	97.11	1.29	97.25	1.72	96.32	0.34	95.46	0.94	96.62	0.73
<i>Cation proportions on the basis of 11 oxygens</i>												
Si	3.000	0.018	2.996	0.009	2.982	0.019	2.982	0.009	2.992	0.025	3.000	0.025
Al	1.000	0.018	1.004	0.009	1.018	0.019	1.018	0.009	1.008	0.025	1.000	0.025
Sum	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000
Al	1.858	0.011	1.917	0.031	1.875	0.032	1.887	0.019	1.869	0.028	1.841	0.010
Cr	0.002	0.003	0.002	0.003	0.000	0.001	0.002	0.001	0.001	0.004	0.002	0.002
Ti	0.016	0.004	0.008	0.005	0.014	0.002	0.018	0.002	0.020	0.004	0.013	0.002
Fe	0.116	0.015	0.083	0.008	0.117	0.031	0.112	0.008	0.112	0.020	0.133	0.005
Mn	0.002	0.005	0.001	0.003	0.000	0.001	0.000	0.001	0.001	0.003	0.001	0.005
Mg	0.057	0.012	0.043	0.043	0.050	0.016	0.055	0.016	0.053	0.018	0.070	0.018
Sum	2.050	0.014	2.053	0.004	2.058	0.009	2.075	0.010	2.057	0.018	2.060	0.014
Ca	0.001	0.002	0.002	0.006	0.000	0.000	0.000	0.000	0.003	0.004	0.000	0.000
Na	0.288	0.017	0.188	0.011	0.286	0.036	0.196	0.014	0.260	0.012	0.208	0.006
K	0.708	0.014	0.768	0.019	0.705	0.021	0.736	0.021	0.709	0.014	0.791	0.007
Ba	0.005	0.005	0.003	0.001	0.004	0.004	0.005	0.002	0.004	0.005	0.006	0.005
Sum	1.002	0.025	0.960	0.014	0.994	0.031	0.938	0.036	0.976	0.020	1.005	0.008
K/(K+Na+Ca)	0.710	0.014	0.802	0.009	0.711	0.029	0.789	0.007	0.730	0.007	0.792	0.004
Na/(K+Na+Ca)	0.289	0.012	0.196	0.015	0.289	0.029	0.211	0.007	0.267	0.011	0.208	0.004
Ca/(K+Na+Ca)	0.001	0.002	0.002	0.006	0.000	0.000	0.000	0.000	0.003	0.004	0.000	0.000
<i>Cation proportions on the basis of 6 cations</i>												
Si	2.975	0.023	2.970	0.007	2.954	0.021	2.946	0.004	2.964	0.031	2.970	0.031
Al	1.025	0.023	1.030	0.007	1.046	0.021	1.054	0.004	1.036	0.031	1.030	0.031
Sum	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000
Al	1.809	0.017	1.865	0.035	1.819	0.033	1.815	0.020	1.814	0.041	1.783	0.017
Fe ³⁺	0.115	0.015	0.082	0.008	0.116	0.030	0.111	0.008	0.111	0.020	0.131	0.005
Cr	0.002	0.003	0.002	0.003	0.000	0.001	0.002	0.001	0.001	0.004	0.002	0.002
Ti	0.016	0.004	0.008	0.005	0.014	0.002	0.018	0.002	0.020	0.004	0.012	0.002
Fe ²⁺	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Mn	0.002	0.005	0.001	0.003	0.000	0.001	0.000	0.001	0.001	0.003	0.001	0.005
Mg	0.056	0.012	0.042	0.043	0.050	0.015	0.055	0.016	0.052	0.018	0.069	0.017
Sum	2.000	0.000	2.000	0.000	2.000	0.000	2.000	0.000	2.000	0.000	2.000	0.000
Ca	0.001	0.002	0.002	0.006	0.000	0.000	0.000	0.000	0.003	0.004	0.000	0.000
Na	0.286	0.017	0.186	0.011	0.283	0.036	0.194	0.014	0.257	0.012	0.206	0.007
K	0.702	0.014	0.761	0.018	0.698	0.021	0.727	0.022	0.702	0.014	0.783	0.009
Ba	0.005	0.005	0.003	0.001	0.004	0.004	0.005	0.002	0.004	0.004	0.006	0.005
Sum	0.993	0.027	0.952	0.013	0.985	0.031	0.926	0.037	0.967	0.021	0.995	0.010
K/(K+Na+Ca)	0.710	0.014	0.802	0.009	0.711	0.029	0.789	0.007	0.730	0.007	0.792	0.004
Na/(K+Na+Ca)	0.289	0.012	0.196	0.015	0.289	0.029	0.211	0.007	0.267	0.011	0.208	0.004
Ca/(K+Na+Ca)	0.001	0.002	0.002	0.006	0.000	0.000	0.000	0.000	0.003	0.004	0.000	0.000

Table A5.9 Continued: Representative Muscovite Analyses

	93-44b-II		91-14d-I		93-45a-I		94-1a-I		Ardoc 201-V		92-34b-I	
	St+Grt+Bt+Ky+Pl matrix Ms		St+Grt+Bt+Pl matrix near Grt		St+Grt+Bt+Pl mtr. & late porph.		St+Grt+Bt+Pl crs. matrix Ms		St+Grt+Bt+Sill+Pl+(Ky) matrix Ms		St+Grt+Bt+Sill+Pl matrix Ms	
	(8,3)	(2σ)	(3,1)	(2σ)	(16,4)	(2σ)	(9,3)	(2σ)	(6,3)	(2σ)	(3,1)	(2σ)
SiO ₂	45.45	0.66	46.05	0.72	45.21	0.75	45.08	0.53	45.43	0.42	45.22	0.55
Al ₂ O ₃	36.16	0.54	37.38	0.44	36.81	0.94	36.31	0.93	37.16	0.72	35.22	0.51
Cr ₂ O ₃	0.03	0.06	0.05	0.10	0.04	0.06	0.05	0.07	0.01	0.05	0.02	0.07
TiO ₂	0.48	0.13	0.37	0.12	0.47	0.19	0.47	0.17	0.46	0.23	0.77	0.05
FeO	2.85	0.28	1.84	0.08	1.86	0.63	2.49	0.12	2.36	0.26	2.98	0.17
MnO	0.01	0.04	0.03	0.07	0.01	0.05	0.00	0.02	0.00	0.00	0.03	0.06
MgO	0.83	0.16	0.60	0.22	0.67	0.18	0.62	0.19	0.61	0.16	0.78	0.14
CaO	0.00	0.01	0.01	0.03	0.01	0.02	0.00	0.00	0.00	0.00	0.01	0.04
Na ₂ O	0.98	0.13	1.42	0.06	1.00	0.29	0.94	0.07	2.03	0.21	0.66	0.05
K ₂ O	10.13	0.11	9.45	0.06	9.90	0.27	10.03	0.11	8.54	0.18	10.54	0.08
BaO	0.43	0.21	0.18	0.34	0.13	0.19	0.23	0.24	0.30	0.21	0.22	0.11
TOTAL	97.35	1.13	97.37	1.08	96.11	1.43	96.22	1.26	96.90	1.29	96.46	0.94
Cation proportions on the basis of 11 oxygens												
Si	2.998	0.028	3.002	0.019	2.993	0.022	2.996	0.021	2.980	0.030	3.014	0.014
Al	1.002	0.028	0.998	0.019	1.007	0.022	1.004	0.021	1.020	0.030	0.986	0.014
Sum	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000
Al	1.808	0.016	1.874	0.019	1.865	0.032	1.840	0.025	1.854	0.034	1.781	0.019
Cr	0.001	0.003	0.003	0.005	0.002	0.003	0.002	0.004	0.001	0.003	0.001	0.004
Ti	0.024	0.007	0.018	0.006	0.023	0.009	0.023	0.009	0.023	0.012	0.039	0.003
Fe	0.157	0.015	0.100	0.004	0.103	0.036	0.138	0.007	0.129	0.013	0.166	0.008
Mn	0.001	0.002	0.001	0.004	0.001	0.003	0.000	0.001	0.000	0.000	0.002	0.003
Mg	0.081	0.016	0.058	0.021	0.066	0.018	0.061	0.019	0.060	0.016	0.078	0.015
Sum	2.072	0.017	2.054	0.005	2.060	0.029	2.065	0.013	2.066	0.007	2.066	0.007
Ca	0.000	0.001	0.001	0.002	0.000	0.002	0.000	0.000	0.000	0.000	0.001	0.003
Na	0.126	0.017	0.180	0.009	0.129	0.037	0.121	0.008	0.258	0.026	0.085	0.006
K	0.853	0.008	0.786	0.005	0.836	0.025	0.851	0.012	0.715	0.012	0.896	0.015
Ba	0.011	0.005	0.005	0.009	0.003	0.005	0.006	0.006	0.008	0.005	0.006	0.003
Sum	0.990	0.024	0.971	0.010	0.968	0.048	0.978	0.010	0.981	0.033	0.988	0.019
K/(K+Na+Ca)	0.871	0.015	0.814	0.009	0.866	0.034	0.876	0.008	0.735	0.018	0.912	0.008
Na/(K+Na+Ca)	0.129	0.015	0.186	0.007	0.133	0.033	0.124	0.008	0.265	0.018	0.087	0.005
Ca/(K+Na+Ca)	0.000	0.001	0.001	0.002	0.000	0.002	0.000	0.000	0.000	0.000	0.001	0.003
Cation proportions on the basis of 6 cations												
Si	2.962	0.034	2.975	0.019	2.963	0.031	2.964	0.026	2.948	0.032	2.981	0.017
Al	1.038	0.034	1.025	0.019	1.037	0.031	1.036	0.026	1.052	0.032	1.019	0.017
Sum	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000
Al	1.739	0.028	1.821	0.016	1.807	0.050	1.777	0.022	1.790	0.036	1.718	0.012
Fe ³⁺	0.155	0.014	0.100	0.004	0.102	0.035	0.137	0.007	0.128	0.013	0.164	0.008
Cr	0.001	0.003	0.003	0.005	0.002	0.003	0.002	0.004	0.001	0.003	0.001	0.004
Ti	0.023	0.007	0.018	0.006	0.023	0.009	0.023	0.009	0.022	0.012	0.038	0.003
Fe ²⁺	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Mn	0.001	0.002	0.001	0.004	0.001	0.003	0.000	0.001	0.000	0.000	0.002	0.003
Mg	0.080	0.015	0.057	0.020	0.065	0.017	0.060	0.018	0.059	0.016	0.077	0.015
Sum	2.000	0.000	2.000	0.000	2.000	0.000	2.000	0.000	2.000	0.000	2.000	0.000
Ca	0.000	0.001	0.001	0.002	0.000	0.002	0.000	0.000	0.000	0.000	0.001	0.003
Na	0.124	0.017	0.178	0.009	0.127	0.037	0.120	0.008	0.255	0.026	0.084	0.006
K	0.842	0.009	0.779	0.006	0.828	0.028	0.841	0.013	0.707	0.012	0.886	0.015
Ba	0.011	0.005	0.004	0.009	0.003	0.005	0.006	0.006	0.008	0.005	0.006	0.003
Sum	0.978	0.025	0.962	0.011	0.959	0.051	0.967	0.011	0.970	0.033	0.977	0.019
K/(K+Na+Ca)	0.871	0.015	0.814	0.009	0.866	0.034	0.876	0.008	0.735	0.018	0.912	0.008
Na/(K+Na+Ca)	0.129	0.015	0.186	0.007	0.133	0.033	0.124	0.008	0.265	0.018	0.087	0.005
Ca/(K+Na+Ca)	0.000	0.001	0.001	0.002	0.000	0.002	0.000	0.000	0.000	0.000	0.001	0.003

Table A5.9 Continued: Representative Muscovite Analyses

	93-46b-I		93-40d-I		CR-8b-I		CR-4a-1		CR-3a-1	
	Grt+Bt+Sill		St+Grt+Bt+Sill		St+Grt+Bt+Pl		St+Grt+Bt+Sill+Pl		Grt+Bt+Pl	
	matrix Ms		mtrx. Ms near Grt		matrix Ms		matrix Ms		matrix Ms	
	(9,3)	(2σ)	(3,1)	(2σ)	(3,2)	(2σ)	(5,2)	(2σ)	(3,1)	(2σ)
SiO ₂	44.67	0.71	45.13	0.33	45.31	0.82	45.27	0.55	45.21	0.66
Al ₂ O ₃	37.14	0.74	37.00	0.12	35.83	0.42	36.42	0.18	36.24	0.63
Cr ₂ O ₃	0.04	0.07	0.03	0.05	0.02	0.03	0.01	0.03	0.05	0.03
TiO ₂	0.82	0.13	0.61	0.09	0.64	0.10	0.79	0.10	0.65	0.04
FeO	1.72	0.20	1.71	0.02	2.83	0.30	2.64	0.22	2.96	0.12
MnO	0.02	0.06	0.00	0.00	0.04	0.07	0.01	0.04	0.01	0.02
MgO	0.42	0.11	0.82	0.12	0.72	0.04	0.58	0.16	0.79	0.16
CaO	0.00	0.01	0.00	0.00	0.01	0.04	0.00	0.00	0.00	0.00
Na ₂ O	1.00	0.23	0.54	0.06	0.93	0.07	1.16	0.12	1.32	0.12
K ₂ O	10.21	0.16	10.92	0.01	10.06	0.11	9.90	0.17	9.74	0.20
BaO	0.27	0.17	0.16	0.21	0.31	0.07	0.24	0.15	0.13	0.15
TOTAL	96.30	1.66	96.72	0.47	96.71	0.58	97.04	0.93	97.10	1.71
<i>Cation proportions on the basis of 11 oxygens</i>										
Si	2.961	0.011	2.981	0.008	3.005	0.035	2.986	0.017	2.983	0.021
Al	1.039	0.011	1.019	0.008	0.995	0.035	1.014	0.017	1.017	0.021
Sum	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000
Al	1.863	0.016	1.862	0.005	1.805	0.020	1.818	0.021	1.801	0.020
Cr	0.002	0.003	0.001	0.002	0.001	0.002	0.001	0.002	0.002	0.002
Ti	0.041	0.007	0.030	0.005	0.032	0.005	0.039	0.005	0.032	0.002
Fe	0.095	0.011	0.095	0.001	0.157	0.016	0.146	0.012	0.163	0.005
Mn	0.001	0.003	0.000	0.000	0.002	0.004	0.001	0.002	0.000	0.001
Mg	0.041	0.011	0.061	0.012	0.071	0.003	0.057	0.016	0.078	0.015
Sum	2.043	0.015	2.049	0.003	2.069	0.003	2.061	0.011	2.077	0.002
Ca	0.000	0.001	0.000	0.000	0.001	0.003	0.000	0.000	0.000	0.000
Na	0.128	0.029	0.069	0.008	0.119	0.010	0.149	0.015	0.169	0.013
K	0.863	0.012	0.920	0.004	0.851	0.014	0.833	0.012	0.820	0.006
Ba	0.007	0.004	0.004	0.005	0.008	0.002	0.006	0.004	0.003	0.004
Sum	0.998	0.034	0.993	0.006	0.979	0.025	0.988	0.019	0.992	0.018
K/(K+Na+Ca)	0.871	0.025	0.931	0.007	0.877	0.008	0.849	0.012	0.829	0.011
Na/(K+Na+Ca)	0.129	0.025	0.069	0.007	0.123	0.007	0.151	0.012	0.171	0.011
Ca/(K+Na+Ca)	0.000	0.001	0.000	0.000	0.001	0.003	0.000	0.000	0.000	0.000
<i>Cation proportions on the basis of 6 cations</i>										
Si	2.940	0.017	2.957	0.007	2.971	0.033	2.956	0.021	2.945	0.021
Al	1.060	0.017	1.043	0.007	1.029	0.033	1.044	0.021	1.055	0.021
Sum	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000
Al	1.821	0.015	1.814	0.008	1.739	0.022	1.759	0.025	1.727	0.019
Fe ³⁺	0.095	0.011	0.094	0.001	0.155	0.016	0.144	0.011	0.161	0.005
Cr	0.002	0.003	0.001	0.002	0.001	0.002	0.001	0.002	0.002	0.002
Ti	0.040	0.007	0.030	0.004	0.031	0.005	0.039	0.005	0.032	0.002
Fe ²⁺	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Mn	0.001	0.003	0.000	0.000	0.002	0.004	0.001	0.002	0.000	0.001
Mg	0.041	0.011	0.060	0.012	0.071	0.003	0.056	0.015	0.077	0.014
Sum	2.000	0.000	2.000	0.000	2.000	0.000	2.000	0.000	2.000	0.000
Ca	0.000	0.001	0.000	0.000	0.001	0.003	0.000	0.000	0.000	0.000
Na	0.127	0.029	0.068	0.008	0.118	0.010	0.147	0.015	0.167	0.013
K	0.857	0.014	0.913	0.004	0.842	0.015	0.825	0.012	0.809	0.006
Ba	0.007	0.004	0.004	0.005	0.008	0.002	0.006	0.004	0.003	0.004
Sum	0.991	0.036	0.985	0.007	0.968	0.025	0.978	0.019	0.980	0.018
K/(K+Na+Ca)	0.871	0.025	0.931	0.007	0.877	0.008	0.849	0.012	0.829	0.011
Na/(K+Na+Ca)	0.129	0.025	0.069	0.007	0.123	0.007	0.151	0.012	0.171	0.011
Ca/(K+Na+Ca)	0.000	0.001	0.000	0.000	0.001	0.003	0.000	0.000	0.000	0.000

Table A5.10: Representative Margarite Analyses

	93-16b-I		93-26e-I		93-26g-I		93-24a-II		92-8d-I		92-41d-I	
	Grt+Chl+(Relict Ctd)		Grt+Chl+Ctd+Bt+St+Mrg		Grt+Chl+Bt+St+Mrg		Grt+Chl+Ctd+Mrg		Grt+Chl+Ctd+Bt+St+Mrg		Chl+Ctd+Mrg	
	incl. in Grt		med-gr. Xl. cuts fol.		matrix, pli. fol.		med-gr. Xl. cuts fol.		matrix Xl.		med-gr. Xl. cuts fol.	
	(2,1)	(2σ)	(5,2)	(2σ)	(4,1)	(2σ)	(2,1)	(2σ)	(3,1)	(2σ)	(4,2)	(2σ)
SiO ₂	31.47	0.45	30.91	0.95	31.34	0.46	31.99	0.88	31.30	0.28	30.68	1.17
Al ₂ O ₃	51.12	0.50	50.73	2.42	50.82	0.57	50.13	0.55	50.38	1.06	49.91	1.95
Cr ₂ O ₃	0.05	0.06	0.03	0.07	0.02	0.03	0.04	0.10	0.03	0.10	0.02	0.04
TiO ₂	0.09	0.10	0.08	0.10	0.09	0.10	0.06	0.03	0.07	0.12	0.03	0.07
FeO	1.20	0.02	0.73	0.09	0.67	0.08	0.58	0.02	0.88	0.14	1.03	0.28
MnO	0.21	0.08	0.01	0.05	0.01	0.02	0.00	0.00	0.02	0.02	0.02	0.06
MgO	0.24	0.17	0.19	0.16	0.20	0.11	0.11	0.00	0.20	0.08	0.25	0.18
CaO	11.14	0.15	12.12	0.39	11.50	0.43	10.97	0.39	11.13	0.13	11.54	0.40
Na ₂ O	1.78	0.14	0.96	0.08	1.00	0.09	1.27	0.06	1.41	0.16	1.33	0.22
K ₂ O	0.00	0.00	0.15	0.06	0.33	0.11	0.34	0.07	0.14	0.04	0.13	0.16
BaO	0.04	0.11	0.02	0.10	0.07	0.10	n.d.	n.d.	0.03	0.11	0.07	0.13
TOTAL	97.34	0.24	95.94	1.62	96.06	0.76	95.48	0.20	95.61	0.65	95.00	1.07
<i>Cation proportions on the basis of 11 oxygens</i>												
Si	2.052	0.031	2.041	0.091	2.063	0.032	2.112	0.056	2.071	0.031	2.049	0.096
Al	1.948	0.031	1.959	0.091	1.937	0.032	1.888	0.056	1.929	0.031	1.951	0.096
Sum	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000
Al	1.980	0.003	1.988	0.037	2.006	0.013	2.014	0.009	1.999	0.022	1.979	0.030
Cr	0.002	0.003	0.002	0.004	0.001	0.001	0.002	0.005	0.002	0.005	0.001	0.002
Ti	0.004	0.005	0.004	0.005	0.005	0.005	0.003	0.002	0.004	0.006	0.001	0.003
Fe	0.065	0.001	0.040	0.005	0.037	0.005	0.032	0.001	0.049	0.008	0.057	0.015
Mn	0.012	0.005	0.001	0.003	0.000	0.001	0.000	0.000	0.001	0.001	0.001	0.003
Mg	0.024	0.016	0.019	0.016	0.020	0.010	0.011	0.000	0.020	0.008	0.024	0.018
Sum	2.087	0.014	2.054	0.023	2.069	0.008	2.061	0.001	2.074	0.013	2.064	0.041
Ca	0.778	0.010	0.857	0.020	0.811	0.028	0.776	0.028	0.789	0.004	0.826	0.022
Na	0.225	0.017	0.123	0.010	0.128	0.010	0.163	0.007	0.181	0.022	0.172	0.029
K	0.000	0.000	0.013	0.005	0.028	0.010	0.028	0.006	0.012	0.004	0.011	0.013
Ba	0.001	0.003	0.001	0.003	0.002	0.003	0.000	0.000	0.001	0.003	0.002	0.003
Sum	1.004	0.005	0.994	0.025	0.969	0.024	0.968	0.030	0.983	0.026	1.011	0.043
K/(K+Na+Ca)	0.000	0.000	0.013	0.005	0.029	0.010	0.029	0.007	0.012	0.004	0.011	0.013
Na/(K+Na+Ca)	0.225	0.016	0.124	0.008	0.132	0.009	0.168	0.002	0.184	0.018	0.171	0.021
Ca/(K+Na+Ca)	0.775	0.016	0.863	0.008	0.839	0.009	0.802	0.005	0.804	0.022	0.818	0.025
<i>Cation proportions on the basis of 6 cations</i>												
Si	2.022	0.036	2.023	0.097	2.040	0.030	2.091	0.055	2.046	0.035	2.028	0.105
Al	1.978	0.036	1.977	0.097	1.960	0.030	1.909	0.055	1.954	0.035	1.972	0.105
Sum	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000	4.000	0.000
Al	1.894	0.010	1.935	0.020	1.938	0.006	1.953	0.008	1.926	0.013	1.915	0.034
Fe ³⁺	0.064	0.001	0.040	0.005	0.037	0.005	0.032	0.001	0.048	0.008	0.057	0.015
Cr	0.002	0.003	0.002	0.004	0.001	0.001	0.002	0.005	0.002	0.005	0.001	0.002
Ti	0.004	0.005	0.004	0.005	0.004	0.005	0.003	0.002	0.004	0.006	0.001	0.003
Fe ²⁺	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Mn	0.011	0.005	0.001	0.003	0.000	0.001	0.000	0.000	0.001	0.001	0.001	0.003
Mg	0.023	0.016	0.019	0.016	0.020	0.010	0.010	0.000	0.019	0.008	0.024	0.018
Sum	2.000	0.000	2.000	0.000	2.000	0.000	2.000	0.000	2.000	0.000	2.000	0.000
Ca	0.767	0.008	0.850	0.020	0.802	0.028	0.769	0.028	0.780	0.004	0.817	0.023
Na	0.222	0.018	0.122	0.010	0.127	0.010	0.161	0.007	0.178	0.022	0.170	0.029
K	0.000	0.000	0.012	0.005	0.027	0.009	0.028	0.006	0.012	0.004	0.011	0.013
Ba	0.001	0.003	0.001	0.003	0.002	0.003	0.000	0.000	0.001	0.003	0.002	0.003
Sum	0.990	0.007	0.985	0.025	0.958	0.024	0.958	0.029	0.971	0.027	1.001	0.047
K/(K+Na+Ca)	0.000	0.000	0.013	0.005	0.029	0.010	0.029	0.007	0.012	0.004	0.011	0.013
Na/(K+Na+Ca)	0.225	0.016	0.124	0.008	0.132	0.009	0.168	0.002	0.184	0.018	0.171	0.021
Ca/(K+Na+Ca)	0.775	0.016	0.863	0.008	0.839	0.009	0.802	0.005	0.804	0.022	0.818	0.025

Table A5.10 Continued: Representative Margarite Analyses

91-21c2-III				
Grt+Chl+St (Mrg+Ctd)				
	incl. in Grt		incl. in Grt with Ctd	
	(2,1)	(2σ)	(2,1)	(2σ)
SiO ₂	30.16	0.38	30.46	0.45
Al ₂ O ₃	50.86	0.34	50.13	0.08
Cr ₂ O ₃	0.04	0.03	0.05	0.00
TiO ₂	0.08	0.08	0.10	0.06
FeO	1.23	0.13	1.19	0.03
MnO	0.07	0.04	0.10	0.04
MgO	0.23	0.06	0.24	0.04
CaO	11.13	0.01	10.62	0.55
Na ₂ O	1.55	0.08	1.77	0.18
K ₂ O	0.02	0.04	0.06	0.03
BaO	0.03	0.07	0.02	0.04
TOTAL	95.37	0.74	94.72	0.27
Cation proportions on the basis of 11 oxygens				
Si	2.007	0.008	2.039	0.028
Al	1.993	0.008	1.961	0.028
Sum	4.000	0.000	4.000	0.000
Al	1.997	0.001	1.995	0.018
Cr	0.002	0.001	0.003	0.000
Ti	0.004	0.004	0.005	0.003
Fe	0.068	0.007	0.067	0.002
Mn	0.004	0.002	0.005	0.002
Mg	0.023	0.006	0.023	0.004
Sum	2.098	0.005	2.098	0.026
Ca	0.793	0.008	0.761	0.040
Na	0.200	0.013	0.229	0.024
K	0.001	0.004	0.005	0.002
Ba	0.001	0.002	0.000	0.001
Sum	0.995	0.019	0.996	0.063
K/(K+Na+Ca)	0.001	0.004	0.005	0.003
Na/(K+Na+Ca)	0.201	0.009	0.230	0.010
Ca/(K+Na+Ca)	0.798	0.006	0.765	0.007
Cation proportions on the basis of 6 cations				
Si	1.975	0.007	2.007	0.019
Al	2.025	0.007	1.993	0.019
Sum	4.000	0.000	4.000	0.000
Al	1.901	0.004	1.899	0.007
Fe ³⁺	0.067	0.006	0.066	0.002
Cr	0.002	0.001	0.003	0.000
Ti	0.004	0.004	0.005	0.003
Fe ²⁺	0.000	0.000	0.000	0.000
Mn	0.004	0.002	0.005	0.002
Mg	0.022	0.006	0.023	0.004
Sum	2.000	0.000	2.000	0.000
Ca	0.781	0.008	0.749	0.043
Na	0.197	0.013	0.225	0.025
K	0.001	0.004	0.005	0.002
Ba	0.001	0.002	0.000	0.001
Sum	0.979	0.019	0.980	0.066
K/(K+Na+Ca)	0.001	0.004	0.005	0.003
Na/(K+Na+Ca)	0.201	0.009	0.230	0.010
Ca/(K+Na+Ca)	0.798	0.006	0.765	0.007

Table A5.11 Continued: Representative Plagioclase Analyses

	92-26b-I						93-10b-II						92-11-I						90-4h-I						91-1b2-II					
	Grt+Chl+St+Ky+Pl			Grt+Chl+St+Bl+Pl+Ky			Grt+Chl+Bl+St+Pl (No Ms)			St+Grt+Bl+Pl+Hr (Cld incl)			Grt+Chl+Bl+St+Pl (No Ms)			St+Grt+Bl+Pl+Hr (Cld incl)			Grt+Chl+Bl+St+Pl (No Ms)			St+Grt+Bl+Pl+Hr (Cld incl)			Grt+Chl+Bl+St+Pl (No Ms)			St+Grt+Bl+Pl+Hr (Cld incl)		
	high An	low An	core	high An	low An	core	high An	low An	core	high An	low An	core	high An	low An	core	high An	low An	core	high An	low An	core	high An	low An	core	high An	low An	core	high An	low An	core
SiO ₂	60.27	61.79	61.90	60.27	61.79	61.90	60.27	61.79	61.90	60.27	61.79	61.90	60.27	61.79	61.90	60.27	61.79	61.90	60.27	61.79	61.90	60.27	61.79	61.90	60.27	61.79	61.90	60.27	61.79	61.90
Al ₂ O ₃	25.46	23.53	23.50	25.46	23.53	23.50	25.46	23.53	23.50	25.46	23.53	23.50	25.46	23.53	23.50	25.46	23.53	23.50	25.46	23.53	23.50	25.46	23.53	23.50	25.46	23.53	23.50	25.46	23.53	23.50
Cr ₂ O ₃	0.00	0.01	0.03	0.00	0.01	0.03	0.00	0.01	0.03	0.00	0.01	0.03	0.00	0.01	0.03	0.00	0.01	0.03	0.00	0.01	0.03	0.00	0.01	0.03	0.00	0.01	0.03	0.00	0.01	0.03
TiO ₂	0.00	0.01	0.01	0.00	0.01	0.01	0.00	0.01	0.01	0.00	0.01	0.01	0.00	0.01	0.01	0.00	0.01	0.01	0.00	0.01	0.01	0.00	0.01	0.01	0.00	0.01	0.01	0.00	0.01	0.01
Fe ₂ O ₃	0.22	0.25	0.23	0.04	0.07	0.11	0.13	0.07	0.11	0.13	0.07	0.11	0.13	0.07	0.11	0.13	0.07	0.11	0.13	0.07	0.11	0.13	0.07	0.11	0.13	0.07	0.11	0.13	0.07	0.11
MnO	0.05	0.01	0.01	0.00	0.01	0.00	0.06	0.01	0.00	0.06	0.01	0.00	0.06	0.01	0.00	0.06	0.01	0.00	0.06	0.01	0.00	0.06	0.01	0.00	0.06	0.01	0.00	0.06	0.01	0.00
MgO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CaO	6.64	4.99	5.00	0.04	14.01	6.74	6.81	0.19	18.23	14.13	13.62	0.88	5.64	3.50	4.16	0.16	5.60	3.84	4.18	0.19	5.60	3.84	4.18	0.19	5.60	3.84	4.18	0.19	5.60	3.84
Na ₂ O	7.61	8.90	8.81	0.25	3.74	8.07	8.04	0.10	1.15	4.26	4.04	0.39	7.66	9.45	8.49	0.49	8.40	9.44	9.27	0.32	8.40	9.44	9.27	0.32	8.40	9.44	9.27	0.32	8.40	9.44
K ₂ O	0.01	0.06	0.07	0.01	0.04	0.08	0.07	0.02	0.01	0.00	0.02	0.04	0.08	0.03	0.05	0.06	0.06	0.09	0.05	0.03	0.06	0.09	0.05	0.03	0.06	0.09	0.05	0.03	0.06	0.09
BaO	0.05	0.03	0.05	0.06	0.00	0.00	0.01	0.01	0.06	0.00	0.02	0.06	0.06	0.00	0.02	0.06	0.06	0.00	0.02	0.06	0.06	0.00	0.02	0.06	0.06	0.00	0.02	0.06	0.06	0.00
TOTAL	100.32	99.57	98.60	0.08	99.65	99.67	99.77	0.29	100.11	100.07	99.85	0.40	98.42	100.26	99.33	0.03	99.64	100.12	98.98	1.03	99.64	100.12	98.98	1.03	99.64	100.12	98.98	1.03	99.64	100.12

		Cation proportions on the basis of 8 oxygens	
Si	2.673	2.754	2.757
Al	0.327	0.246	0.243
Sum	3.000	3.000	3.000
Al	1.004	0.990	0.991
Cr	0.000	0.000	0.001
Ti	0.000	0.000	0.000
Fe ³⁺	0.000	0.008	0.008
Sum	1.004	0.999	1.000
Fe ³⁺	0.007	0.000	0.000
Mn	0.002	0.000	0.000
Mg	0.000	0.000	0.000
Ca	0.315	0.298	0.299
Na	0.655	0.769	0.761
K	0.001	0.003	0.004
Ba	0.001	0.001	0.001
Sum	0.981	1.011	1.004
Anorthite	0.325	0.236	0.238
Albite	0.674	0.761	0.758
Orthoclase	0.001	0.003	0.004

Table A5.11 Continued: Representative Plagioclase Analyses

	91-14d-I										93-45a-I									
	91-14d-I					93-44b-II					93-39d-III					91-5b-II				
	high An	low An	rim	core	utilized	high An	low An	rim	core	utilized	high An	low An	rim	core	utilized	high An	low An	rim	core	utilized
SiO ₂	58.91	61.69	61.68	0.04	0.04	57.38	58.34	58.51	0.94	0.94	57.38	58.34	58.51	0.94	0.94	58.91	61.69	61.68	0.04	0.04
Al ₂ O ₃	25.98	23.72	23.84	0.34	0.34	26.92	25.77	25.81	0.42	0.42	26.92	25.77	25.81	0.42	0.42	25.98	23.72	23.84	0.34	0.34
Cr ₂ O ₃	0.00	0.04	0.02	0.06	0.06	0.07	0.00	0.01	0.05	0.05	0.07	0.00	0.01	0.05	0.05	0.00	0.04	0.02	0.06	0.06
TiO ₂	0.00	0.00	0.05	0.13	0.13	0.00	0.00	0.01	0.03	0.03	0.00	0.00	0.01	0.03	0.03	0.00	0.00	0.05	0.13	0.13
Fe ₂ O ₃	0.19	0.18	0.19	0.03	0.03	0.16	0.08	0.10	0.06	0.06	0.16	0.08	0.10	0.06	0.06	0.19	0.18	0.19	0.03	0.03
MnO	0.03	0.00	0.00	0.00	0.00	0.04	0.00	0.02	0.07	0.07	0.04	0.00	0.02	0.07	0.07	0.03	0.00	0.00	0.00	0.00
MgO	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.01	0.01	0.02	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.00
CaO	7.63	5.04	5.21	0.47	0.47	8.74	7.69	7.75	0.13	0.13	8.74	7.69	7.75	0.13	0.13	7.63	5.04	5.21	0.47	0.47
Na ₂ O	7.28	8.83	8.79	0.12	0.12	6.39	7.37	7.44	0.16	0.16	6.39	7.37	7.44	0.16	0.16	7.28	8.83	8.79	0.12	0.12
K ₂ O	0.04	0.16	0.12	0.11	0.11	0.05	0.02	0.02	0.04	0.04	0.05	0.02	0.02	0.04	0.04	0.04	0.16	0.12	0.11	0.11
BaO	0.05	0.04	0.02	0.06	0.06	0.13	0.09	0.05	0.09	0.09	0.13	0.09	0.05	0.09	0.09	0.05	0.04	0.02	0.06	0.06
TOTAL	100.11	99.71	99.91	0.57	0.57	99.90	99.35	99.74	0.67	0.67	99.90	99.35	99.74	0.67	0.67	100.11	99.71	99.91	0.57	0.57
Cation proportions on the basis of 8 oxygens																				
Si	2.629	2.747	2.741	0.017	0.017	2.574	2.626	2.624	0.029	0.029	2.574	2.626	2.624	0.029	0.029	2.629	2.747	2.741	0.017	0.017
Al	0.371	0.253	0.259	0.017	0.017	0.426	0.374	0.376	0.029	0.029	0.426	0.374	0.376	0.029	0.029	0.371	0.253	0.259	0.017	0.017
Sum	3.000	3.000	3.000	0.000	0.000	3.000	3.000	3.000	0.000	0.000	3.000	3.000	3.000	0.000	0.000	3.000	3.000	3.000	0.000	0.000
Al	0.995	0.992	0.990	0.005	0.005	0.998	0.992	0.989	0.007	0.007	0.998	0.992	0.989	0.007	0.007	0.995	0.992	0.990	0.005	0.005
Cr	0.000	0.002	0.001	0.002	0.002	0.002	0.000	0.000	0.002	0.002	0.002	0.000	0.000	0.002	0.002	0.000	0.002	0.001	0.002	0.002
Ti	0.000	0.000	0.002	0.004	0.004	0.000	0.000	0.000	0.001	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.002	0.004	0.004
Fe ₃₊	0.006	0.006	0.006	0.001	0.001	0.000	0.003	0.003	0.002	0.002	0.000	0.003	0.003	0.002	0.002	0.006	0.006	0.006	0.001	0.001
Sum	1.002	1.000	0.999	0.002	0.002	1.000	0.995	0.993	0.004	0.004	1.000	0.995	0.993	0.004	0.004	1.002	1.000	0.999	0.002	0.002
Fe ₃₊	0.000	0.000	0.000	0.000	0.000	0.005	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Mn	0.001	0.000	0.000	0.000	0.000	0.002	0.000	0.001	0.003	0.003	0.002	0.000	0.001	0.003	0.003	0.001	0.000	0.000	0.000	0.000
Mg	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.001	0.001	0.001	0.000	0.000	0.001	0.001	0.000	0.000	0.000	0.000	0.000
Ca	0.365	0.240	0.248	0.021	0.021	0.420	0.371	0.373	0.006	0.006	0.420	0.371	0.373	0.006	0.006	0.365	0.240	0.248	0.021	0.021
Na	0.630	0.762	0.757	0.014	0.014	0.556	0.643	0.647	0.013	0.013	0.556	0.643	0.647	0.013	0.013	0.630	0.762	0.757	0.014	0.014
K	0.002	0.009	0.007	0.007	0.007	0.003	0.001	0.001	0.002	0.002	0.003	0.001	0.001	0.002	0.002	0.002	0.009	0.007	0.007	0.007
Ba	0.001	0.001	0.000	0.001	0.001	0.002	0.001	0.001	0.002	0.002	0.002	0.001	0.001	0.002	0.002	0.001	0.001	0.000	0.001	0.001
Sum	0.999	1.012	1.012	0.001	0.001	0.999	1.017	1.023	0.023	0.023	0.999	1.017	1.023	0.023	0.023	0.999	1.012	1.012	0.001	0.001
Anorthite	0.366	0.238	0.245	0.021	0.021	0.429	0.365	0.365	0.002	0.002	0.429	0.365	0.365	0.002	0.002	0.366	0.238	0.245	0.021	0.021
Albite	0.632	0.753	0.748	0.014	0.014	0.568	0.633	0.634	0.001	0.001	0.568	0.633	0.634	0.001	0.001	0.632	0.753	0.748	0.014	0.014
Orthoclase	0.002	0.009	0.007	0.006	0.006	0.003	0.001	0.001	0.002	0.002	0.003	0.001	0.001	0.002	0.002	0.002	0.009	0.007	0.006	0.006

Table A5.11 Continued: Representative Plagioclase Analyses

	94-1a-I				Ardoc 201-V				92-34b-I				R3-301-II			
	St+Grt+Bt+Pl				St+Grt+Bt+Sill+Pl+K (Rel. Ky)				St+Grt+Bt+Sill+Pl				St+Grt+Bt+Sill+Pl (No Ms)			
	high An	low An	core	utilized	high An	low An	core	utilized	high An	low An	core	utilized	high An	low An	core	utilized
SiO ₂	57.76	57.36	57.27	57.27	65.63	66.19	65.63	65.63	58.09	59.64	59.81	59.81	63.08	63.72	63.11	63.11
Al ₂ O ₃	26.62	26.03	26.53	26.53	21.20	20.94	21.20	21.20	26.37	25.37	25.43	25.43	22.92	22.49	23.04	23.04
Cr ₂ O ₃	0.00	0.00	0.05	0.05	0.01	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.04	0.01	0.04
TiO ₂	0.05	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.03	0.02	0.00	0.01	0.03
Fe ₂ O ₃	0.06	0.13	0.18	0.18	0.03	0.09	0.03	0.03	0.12	0.14	0.12	0.06	0.00	0.08	0.05	0.14
MnO	0.01	0.00	0.00	0.00	0.00	0.03	0.00	0.00	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MgO	0.00	0.00	0.00	0.00	0.11	0.04	0.11	0.11	0.06	0.10	0.07	0.11	0.00	0.00	0.00	0.00
CaO	8.53	8.58	8.54	8.54	1.80	1.54	1.80	1.80	8.44	7.50	7.48	7.48	4.12	3.34	4.19	4.21
Na ₂ O	6.42	6.99	6.98	6.98	10.44	10.42	10.44	10.44	7.05	7.63	7.56	7.56	9.35	9.65	9.54	9.53
K ₂ O	0.09	0.08	0.02	0.02	0.04	0.04	0.04	0.04	0.03	0.05	0.06	0.03	0.07	0.09	0.07	0.02
BaO	0.01	0.00	0.00	0.00	0.05	0.09	0.05	0.05	0.00	0.06	0.03	0.09	0.08	0.04	0.08	0.02
TOTAL	99.54	99.22	99.57	99.57	99.31	99.39	99.31	99.31	100.17	100.49	100.57	100.57	99.64	99.46	100.11	1.34
Cation proportions on the basis of 8 oxygens																
Si	2.594	2.593	2.579	2.579	2.900	2.919	2.900	2.900	2.597	2.652	2.655	2.655	2.799	2.827	2.791	0.022
Al	0.406	0.407	0.421	0.421	0.100	0.081	0.100	0.100	0.403	0.348	0.345	0.345	0.201	0.173	0.209	0.022
Sum	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	0.000
Al	1.003	0.980	0.987	0.987	1.004	1.007	1.004	1.004	0.987	0.981	0.985	0.985	0.998	1.003	0.993	0.015
Cr	0.000	0.000	0.002	0.002	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.001
Ti	0.002	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.001
Fe ₃₊	0.000	0.004	0.006	0.006	0.000	0.000	0.000	0.000	0.004	0.005	0.004	0.002	0.000	0.000	0.002	0.005
Sum	1.004	0.986	0.995	0.995	1.005	1.008	1.005	1.005	0.991	0.986	0.990	0.990	0.999	1.004	0.995	0.010
Fe ₃₊	0.002	0.000	0.000	0.000	0.001	0.003	0.001	0.001	0.000	0.000	0.000	0.000	0.000	0.003	0.000	0.000
Mn	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Mg	0.000	0.000	0.000	0.000	0.007	0.003	0.007	0.007	0.004	0.007	0.000	0.01	0.000	0.000	0.000	0.000
Ca	0.410	0.416	0.412	0.412	0.085	0.073	0.085	0.085	0.404	0.357	0.356	0.005	0.196	0.159	0.199	0.008
Na	0.559	0.613	0.609	0.609	0.894	0.891	0.894	0.894	0.611	0.657	0.651	0.018	0.805	0.830	0.818	0.038
K	0.005	0.005	0.001	0.001	0.002	0.002	0.002	0.002	0.002	0.003	0.003	0.002	0.004	0.005	0.004	0.001
Ba	0.000	0.000	0.000	0.000	0.001	0.002	0.001	0.001	0.000	0.001	0.000	0.000	0.001	0.001	0.001	0.000
Sum	0.976	1.033	1.023	1.023	0.991	0.974	0.991	0.991	1.021	1.026	1.015	0.030	1.006	0.997	1.022	0.047
Anorthite	0.421	0.402	0.403	0.403	0.087	0.076	0.087	0.087	0.398	0.351	0.352	0.003	0.195	0.160	0.195	0.001
Albite	0.573	0.593	0.596	0.596	0.911	0.922	0.911	0.911	0.601	0.646	0.644	0.004	0.801	0.835	0.801	0.000
Orthoclase	0.005	0.005	0.001	0.001	0.003	0.003	0.003	0.003	0.002	0.003	0.003	0.002	0.004	0.005	0.004	0.001

Table A5.11 Continued: Representative Plagioclase Analyses

	CR-8b-1				CR-4a-1				CR-3a-1			
	St+Grt+Bt+Pl				St+Grt+Bt+Sill+Pl				Grt+Bt+Pl			
	high An core	low An Mtx. Pl Adj. to Bt	Utilized		high An rim	low An rim	Porph.-fict rim (3.2)	K-Spar (All) (6.2)	high An rim	low An rim-Bt	Avg. Matrix Pl (4.2)	(2σ)
SiO ₂	55.47	60.16	60.16	62.39	65.69	62.58	0.34	64.87	65.68	65.88	65.37	0.70
Al ₂ O ₃	28.16	24.81	24.81	23.54	21.88	23.42	0.23	18.31	21.50	20.55	21.37	0.39
Cr ₂ O ₃	0.00	0.05	0.05	0.00	0.08	0.03	0.09	0.02	0.03	0.04	0.02	0.04
TiO ₂	0.00	0.05	0.05	0.02	0.02	0.01	0.03	0.03	0.00	0.00	0.00	0.02
Fe ₂ O ₃	0.07	0.25	0.25	0.23	0.23	0.17	0.21	0.14	0.06	0.16	0.05	0.04
MnO	0.03	0.00	0.00	0.02	0.06	0.01	0.02	0.01	0.02	0.02	0.03	0.05
MgO	0.00	0.00	0.00	0.07	0.01	0.02	0.08	0.06	0.01	0.00	0.06	0.18
CaO	10.04	6.54	6.54	4.72	2.90	4.62	0.16	0.01	2.24	1.66	2.23	0.04
Na ₂ O	5.80	7.95	7.95	8.93	10.68	8.98	0.15	0.06	10.55	10.92	10.68	0.32
K ₂ O	0.03	0.06	0.06	0.09	0.02	0.08	0.04	17.32	0.07	0.02	0.06	0.01
BaO	0.00	0.00	0.00	0.00	0.00	0.03	0.10	0.02	0.04	0.10	0.04	0.06
TOTAL	99.60	99.87	99.87	100.01	101.55	99.94	0.18	100.86	100.20	99.36	99.91	0.99
Cation proportions on the basis of 8 oxygens												
Si	2.504	2.683	2.683	2.764	2.857	2.773	0.016	2.990	2.884	2.916	2.881	0.005
Al	0.496	0.317	0.317	0.236	0.143	0.227	0.016	0.010	0.116	0.084	0.119	0.005
Sum	3.000	3.000	3.000	3.000	3.000	3.000	0.000	3.000	3.000	3.000	3.000	0.000
Al	1.002	0.988	0.988	0.993	0.978	0.996	0.010	0.985	0.997	0.988	0.991	0.008
Cr	0.000	0.002	0.002	0.000	0.003	0.001	0.003	0.001	0.001	0.001	0.001	0.001
Ti	0.000	0.002	0.002	0.001	0.001	0.000	0.001	0.001	0.000	0.000	0.000	0.001
Fe ₃₊	0.000	0.008	0.008	0.008	0.008	0.005	0.009	0.005	0.002	0.005	0.002	0.001
Sum	1.002	0.999	0.999	1.002	0.989	1.002	0.001	0.991	1.000	0.994	0.994	0.009
Fe ₃₊	0.002	0.000	0.000	0.000	0.000	0.000	0.002	0.000	0.000	0.000	0.000	0.000
Mn	0.001	0.000	0.000	0.001	0.002	0.000	0.001	0.000	0.001	0.001	0.001	0.002
Mg	0.000	0.000	0.000	0.004	0.000	0.001	0.005	0.004	0.000	0.000	0.004	0.012
Ca	0.486	0.313	0.313	0.224	0.135	0.219	0.008	0.000	0.105	0.079	0.105	0.002
Na	0.507	0.688	0.688	0.767	0.901	0.772	0.012	0.005	0.899	0.937	0.913	0.031
K	0.002	0.003	0.003	0.005	0.001	0.004	0.002	1.019	0.004	0.001	0.004	0.000
Ba	0.000	0.000	0.000	0.000	0.000	0.001	0.002	0.000	0.001	0.002	0.001	0.001
Sum	0.998	1.004	1.004	1.001	1.039	0.998	0.008	1.029	1.009	1.019	1.027	0.028
Anorthite	0.488	0.311	0.311	0.225	0.130	0.220	0.008	0.000	0.105	0.078	0.103	0.002
Albite	0.510	0.685	0.685	0.770	0.869	0.775	0.009	0.005	0.892	0.921	0.893	0.002
Orthoclase	0.002	0.003	0.003	0.005	0.001	0.004	0.002	0.994	0.004	0.001	0.004	0.000

Table A5.12: Representative Aluminosilicate Analyses

	Madoc-4a-I		92-26b-I		93-10b-II		91-24a-I		91-1e-I		91-5b-II		93-39d-III		93-44b-II	
	Cld+Ky+Chl+St		Grt+Chl+St+Ky+Pl		Grt+Chl+St+Bt+Pl+Ky		Grt+St+Chl+Ky		St+Grt+Bt+Ky		St+Grt+Bt+Ky+Pl+Chl		Grt+Bt+Ky+Pl		St+Grt+Bt+Ky+Pl	
	Kyanite		Kyanite		Kyanite		Kyanite		Kyanite		Kyanite		Kyanite		Kyanite	
	porph.		porph.		porph.		porph.		porph.		crs-gr. polk.		crs-gr. porph.		crs-gr. polk.	
	(3,1)	(2σ)	(6,2)	(2σ)	(6,2)	(2σ)	(6,2)	(2σ)	(4,1)	(2σ)	(4,1)	(2σ)	(6,2)	(2σ)	(7,2)	(2σ)
SiO ₂	36.32	0.12	35.90	0.50	35.63	0.48	36.12	0.42	35.76	0.51	36.00	0.74	35.53	0.59	35.88	0.26
Al ₂ O ₃	62.23	0.33	63.74	0.66	63.36	0.29	64.01	1.16	62.98	0.84	63.39	0.44	63.30	0.84	63.59	0.71
Cr ₂ O ₃	0.05	0.02	0.01	0.04	0.06	0.06	0.02	0.06	0.03	0.06	0.02	0.04	0.02	0.08	0.02	0.05
TiO ₂	0.01	0.02	0.02	0.04	0.01	0.02	0.02	0.04	0.01	0.02	0.03	0.04	0.02	0.02	0.01	0.04
Fe ₂ O ₃	0.88	0.14	0.93	0.23	0.87	0.14	0.75	0.07	1.11	0.21	0.96	0.06	1.20	0.39	0.99	0.18
MgO	n.d.	n.d.	0.10	0.23	n.d.	n.d.	0.00	0.00	n.d.	n.d.	0.04	0.14	n.d.	n.d.	0.11	0.17
TOTAL	99.49	0.28	100.70	1.11	99.94	0.40	100.91	1.64	99.88	1.33	100.44	1.20	100.07	0.83	100.61	0.78
Cation proportions on the basis of 5 oxygens																
Si	0.988	0.002	0.966	0.005	0.966	0.009	0.969	0.006	0.971	0.003	0.971	0.009	0.964	0.010	0.967	0.010
Al	0.012	0.002	0.034	0.005	0.034	0.009	0.031	0.006	0.029	0.003	0.029	0.009	0.036	0.010	0.033	0.010
Sum	1.000	0.000	1.000	0.000	1.000	0.000	1.000	0.000	1.000	0.000	1.000	0.000	1.000	0.000	1.000	0.000
Al	1.985	0.003	1.989	0.006	1.992	0.003	1.994	0.002	1.986	0.004	1.988	0.005	1.987	0.010	1.987	0.004
Cr	0.001	0.000	0.000	0.001	0.001	0.001	0.000	0.001	0.001	0.001	0.001	0.001	0.000	0.002	0.000	0.001
Ti	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.001	0.000	0.000	0.001	0.001	0.000	0.000	0.000	0.001
Fe ₃₊	0.018	0.003	0.019	0.005	0.018	0.003	0.015	0.001	0.023	0.004	0.020	0.001	0.024	0.008	0.020	0.004
Mg	n.d.	n.d.	0.004	0.009	n.d.	n.d.	0.000	0.000	n.d.	n.d.	0.002	0.006	n.d.	n.d.	0.004	0.007
Sum	2.004	0.001	2.012	0.003	2.011	0.003	2.010	0.002	2.010	0.001	2.010	0.004	2.012	0.003	2.012	0.006

Table A5.12 Continued: Representative Aluminosilicate Analyses

	Ardoc 201-V		92-34b-I		93-46b-I		R3 301-II		93-40d-I		CR-4a-I	
	St+Grt+Bt+Sill+Pl+P (relict Ky)	Kyanite	St+Grt+Bt+Sill+Pl	Sillimanite	Grt+Bt+Sill	Sillimanite	St+Grt+Bt+Sill+Pl	Sillimanite	St+Grt+Bt+Sill	Sillimanite	St+Grt+Bt+Sill+Pl	Sillimanite
	fibrolite	relict Ky porph.	fibrolite	fibrolite	fibrolite+crs. Sill	fibrolite	fibrolite	fibrolite	fibrolite	fibrolite	fibrolite	fibrolite
	(7,2)	(4,1)	(5,1)	(2 σ)	(7,3)	(2 σ)	(6,2)	(2 σ)	(6,2)	(2 σ)	(5,2)	(2 σ)
SiO ₂	35.68	35.90	35.57	0.67	35.62	0.67	35.83	0.79	35.82	0.40	35.90	0.36
Al ₂ O ₃	63.98	64.22	64.63	0.66	63.68	0.78	63.70	0.17	64.01	0.35	63.55	0.58
Cr ₂ O ₃	0.03	0.05	0.03	0.05	0.02	0.04	0.03	0.06	0.04	0.10	0.03	0.05
TiO ₂	0.01	0.03	0.02	0.06	0.01	0.02	0.01	0.02	0.02	0.04	0.03	0.05
Fe ₂ O ₃	0.61	0.10	0.57	0.07	0.48	0.21	0.64	0.10	0.35	0.12	0.61	0.16
MgO	0.09	0.12	0.08	0.06	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
TOTAL	100.40	101.13	100.91	1.20	99.80	1.48	100.21	0.97	100.24	0.76	100.11	0.88
Cation proportions on the basis of 5 oxygens												
Si	0.963	0.007	0.955	0.007	0.966	0.008	0.968	0.012	0.967	0.006	0.971	0.003
Al	0.037	0.007	0.045	0.007	0.034	0.008	0.032	0.012	0.033	0.006	0.029	0.003
Sum	1.000	0.000	1.000	0.000	1.000	0.000	1.000	0.000	1.000	0.000	1.000	0.000
Al	1.997	0.003	1.991	0.005	2.001	0.007	1.997	0.005	2.003	0.005	1.996	0.005
Cr	0.001	0.002	0.001	0.001	0.000	0.001	0.001	0.001	0.001	0.002	0.001	0.001
Ti	0.000	0.001	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.001	0.001	0.001
Fe ₃₊	0.012	0.002	0.017	0.003	0.010	0.004	0.013	0.002	0.007	0.002	0.012	0.003
Mg	0.003	0.005	0.003	0.007	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sum	2.014	0.004	2.016	0.003	2.011	0.003	2.011	0.004	2.011	0.002	2.010	0.001

Table A5.13: Representative Ilmenite Analyses

	91-27a-I		91-27e-I		93-26e-I		93-24a-II		92-41a-I	
	Grt+Chl		Grt+Chl+Cld		Grt+Chl+Cld+Bt+St+Mrg		Grt+Chl+Cld+Mrg		Grt+Cld+Bt	
	avg. matrix ilm		avg. matrix ilm		matrix ilm		matrix ilm		avg. matrix ilm	
	(6,2)	(2 σ)	(6,2)	(2 σ)	(6,2)	(2 σ)	(2,1)	(2 σ)	(6,2)	(2 σ)
SiO ₂	0.27	0.08	0.22	0.17	0.40	0.16	0.98	0.02	0.33	0.05
Al ₂ O ₃	0.04	0.07	0.06	0.09	0.05	0.12	0.33	0.01	0.10	0.12
Cr ₂ O ₃	0.03	0.05	0.05	0.02	0.03	0.04	0.01	0.03	0.03	0.05
V ₂ O ₃	0.04	0.13	0.06	0.19	0.08	0.11	0.28	0.38	0.18	0.19
TiO ₂	49.89	0.97	49.30	0.47	50.64	0.18	48.90	0.31	51.07	0.69
ZnO	0.01	0.05	0.01	0.06	0.09	0.15	0.06	0.18	0.08	0.19
CuO	0.02	0.07	0.05	0.11	0.02	0.06	n.d.	n.d.	0.04	0.10
NiO	0.03	0.10	0.04	0.07	0.02	0.08	n.d.	n.d.	0.03	0.06
CoO	0.00	0.01	0.00	0.00	0.03	0.09	n.d.	n.d.	0.00	0.00
FeO (Total)	46.27	0.70	47.74	0.61	45.87	0.19	47.75	0.22	47.29	0.47
FeO (Calc)	42.90	1.00	42.95	0.47	44.55	0.26	43.60	0.02	45.55	0.59
Fe ₂ O ₃ (Calc)	3.74	1.79	5.33	1.00	1.47	0.24	4.61	0.27	1.93	0.54
MnO	1.81	0.04	1.43	0.09	1.20	0.16	1.33	0.11	0.50	0.13
MgO	0.06	0.12	0.04	0.09	0.05	0.11	0.07	0.14	0.06	0.11
CaO	0.24	0.03	0.03	0.04	0.02	0.07	0.02	0.06	0.01	0.02
TOTAL (All FeO)	98.70	0.71	99.03	0.59	98.51	0.20	99.73	0.19	99.71	0.81
TOTAL (Fe ²⁺ , Fe ³⁺)	99.08	0.72	99.57	0.67	98.66	0.21	100.20	0.21	99.90	0.79
Cation proportions on the basis of 2 Cations, 3 Oxygens										
Zn	0.000	0.001	0.000	0.001	0.002	0.003	0.001	0.003	0.001	0.004
Cu	0.000	0.001	0.001	0.002	0.000	0.001	n.d.	n.d.	0.001	0.002
Ni	0.001	0.002	0.001	0.001	0.000	0.002	n.d.	n.d.	0.001	0.001
Co	0.000	0.000	0.000	0.000	0.001	0.002	n.d.	n.d.	0.000	0.000
Fe ²⁺	0.914	0.021	0.912	0.014	0.952	0.005	0.916	0.001	0.962	0.006
Mn	0.039	0.001	0.031	0.002	0.026	0.004	0.028	0.002	0.011	0.003
Mg	0.002	0.004	0.002	0.003	0.002	0.004	0.003	0.005	0.002	0.004
Ca	0.006	0.001	0.001	0.001	0.001	0.002	0.001	0.001	0.000	0.000
Sum	0.963	0.018	0.947	0.010	0.984	0.004	0.949	0.007	0.978	0.007
Si	0.007	0.002	0.006	0.004	0.010	0.004	0.025	0.000	0.008	0.001
Al	0.001	0.002	0.002	0.003	0.001	0.004	0.010	0.000	0.003	0.003
Fe ³⁺	0.072	0.034	0.102	0.019	0.028	0.005	0.087	0.005	0.037	0.010
Cr	0.001	0.001	0.001	0.000	0.001	0.001	0.000	0.001	0.001	0.001
V	0.001	0.003	0.001	0.004	0.002	0.002	0.006	0.008	0.004	0.004
Ti	0.956	0.018	0.942	0.011	0.974	0.006	0.924	0.006	0.970	0.008
Sum	1.037	0.018	1.053	0.010	1.016	0.004	1.051	0.007	1.022	0.007

Table A5.14: Representative Rutile Analyses

	91-27e-1	93-15d-1	93-16a-II	93-24a-II	92-42c-I	92-912-II
	Grt+Chl+Cld avg. matrix Rut	Grt+Chl+Bl+Pl matrix near Grt	Grt+Chl avg. matrix Rut	Grt+Chl+Cld+Mg incl. in ilm	Grt+Chl+Bl avg. matrix Rut	Grt+Chl+Bl+Pl+Ep incl. in Grt
SiO ₂	(6,2) (2σ) 0.39 0.16	(3,1) (2σ) 0.22 0.18	(6,2) (2σ) 1.06 0.42	(2,1) (2σ) 1.07 0.02	(6,2) (2σ) 0.93 0.11	(3,1) (2σ) 0.28 0.13
Al ₂ O ₃	0.10 0.10	0.04 0.07	0.25 0.09	0.32 0.18	0.31 0.13	0.08 0.05
Cr ₂ O ₃	0.00 0.01	0.41 0.22	0.07 0.10	0.00 0.00	0.01 0.05	0.07 0.07
V ₂ O ₃	0.20 0.21	0.00 0.00	0.01 0.07	0.70 0.63	0.11 0.26	0.05 0.10
TiO ₂	97.43 0.74	99.78 0.53	95.11 5.32	92.36 0.48	98.20 0.62	97.44 0.65
ZnO	0.02 0.05	0.02 0.04	0.03 0.12	0.09 0.20	0.07 0.12	0.03 0.10
CuO	0.01 0.05	0.03 0.05	0.01 0.06	n.d.	0.02 0.06	0.04 0.06
NiO	0.03 0.06	0.01 0.05	0.02 0.06	n.d.	0.00 0.00	0.00 0.02
CoO	0.05 0.07	0.00 0.00	0.05 0.09	n.d.	0.06 0.12	0.00 0.01
FeO (Total)	0.68 0.47	0.25 0.19	2.51 2.97	5.25 0.62	0.70 0.33	1.15 0.21
FeO (Calc)	0.00 0.00	0.00 0.00	0.00 0.00	0.00 0.00	0.00 0.00	0.00 0.00
Fe ₂ O ₃ (Calc)	0.75 0.53	0.28 0.21	2.79 3.30	5.84 0.69	0.78 0.37	1.28 0.24
MnO	0.02 0.03	0.00 0.00	0.04 0.06	0.03 0.01	0.02 0.07	0.30 0.08
MgO	0.03 0.12	0.01 0.02	0.06 0.08	0.04 0.11	0.06 0.13	0.07 0.15
CaO	0.05 0.04	0.52 0.03	0.09 0.10	0.06 0.02	0.02 0.04	0.13 0.04
TOTAL (All FeO)	99.01 0.47	101.29 1.05	99.31 1.90	99.91 0.72	100.51 0.13	99.65 0.78
TOTAL (Fe ²⁺ , Fe ³⁺)	99.08 0.45	101.31 1.06	99.59 1.57	100.50 0.65	100.59 0.12	99.78 0.79
Cation proportions on the basis of 1 Cation, 2 Oxygens						
Zn	0.000 0.001	0.000 0.000	0.000 0.001	0.001 0.002	0.001 0.001	0.000 0.001
Cu	0.000 0.000	0.000 0.000	0.000 0.001	n.d.	0.000 0.001	0.000 0.001
Ni	0.000 0.001	0.000 0.001	0.000 0.001	n.d.	0.000 0.000	0.000 0.000
Co	0.001 0.001	0.000 0.000	0.001 0.001	n.d.	0.001 0.001	0.000 0.000
Fe ²⁺	0.000 0.000	0.000 0.000	0.000 0.000	0.000 0.000	0.000 0.000	0.000 0.000
Mn	0.000 0.000	0.000 0.000	0.000 0.001	0.000 0.000	0.000 0.001	0.003 0.001
Mg	0.001 0.002	0.000 0.000	0.001 0.002	0.001 0.002	0.001 0.003	0.001 0.003
Ca	0.001 0.001	0.007 0.000	0.001 0.001	0.001 0.000	0.000 0.001	0.002 0.001
Si	0.005 0.002	0.003 0.002	0.014 0.006	0.014 0.000	0.012 0.001	0.004 0.002
Al	0.002 0.002	0.001 0.001	0.004 0.001	0.005 0.003	0.005 0.002	0.001 0.001
Fe ³⁺	0.008 0.005	0.003 0.002	0.028 0.033	0.058 0.007	0.008 0.004	0.013 0.002
Cr	0.000 0.000	0.004 0.002	0.001 0.001	0.000 0.000	0.000 0.001	0.001 0.001
V	0.002 0.002	0.000 0.000	0.000 0.001	0.007 0.007	0.001 0.003	0.001 0.001
Ti	0.981 0.007	0.982 0.006	0.949 0.041	0.913 0.001	0.971 0.007	0.973 0.001
Sum	1.000 0.000	1.000 0.000	1.000 0.000	1.000 0.000	1.000 0.000	1.000 0.000