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**Sm-Nd and Sr Isotopic Studies
of Scheelite From Some
Superior Province Gold Deposits**

by

Carolyn D. Anglin, B.Sc. (Hons), M.Sc.

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

Ottawa-Carleton Geoscience Centre

and

Department of Earth Sciences

Carleton University

Ottawa, Ontario

April 26, 1992

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**Sm-Nd and Sr Isotopic Studies
of Scheelite From Some
Superior Province Gold Deposits**
submitted by Carolyn D. Anglin, M.Sc., B.Sc. (Hons).
in partial fulfilment of the requirements
for the degree of Doctor of Philosophy

Chairman, Department of
Earth Sciences

Thesis Supervisor

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April 26, 1992

ABSTRACT

Sm-Nd data on scheelites from gold-bearing veins in the Val d'Or and Timmins areas yield very good linear arrays that correspond to isochron ages of 2611 Ma and 2425 Ma respectively. The Val d'Or age is in very good agreement with U-Pb dating of titanites and rutiles from gold deposits in the Val d'Or area. The Timmins date is considered by some to be controversial; however, there is evidence from other isotopic systems that some of the gold mineralization in the Timmins camp may be late "Archean" in age. The Sm-Nd isotopic data indicate that gold mineralization in the southern Superior Province did not occur contemporaneously in all areas, but that different areas may have been mineralized at different times during the Archean.

The initial Nd ratios of the Val d'Or and Timmins scheelites indicate that the rare earth elements (REEs) in the gold-bearing fluids were derived from a source with a depleted mantle-like isotopic signature. The Sm-Nd isotopic data support the hypothesis that depleted mantle may have been the source of some of the constituents of the gold-mineralizing fluids. Mantle degassing of CO₂ may have provided an effective transport medium for REEs and gold to higher crustal levels.

Strontium initial ratios of scheelites from Superior Province gold deposits indicate derivation of Sr from a source that is more evolved than contemporaneous upper mantle. There is a small but consistent shift in the ⁸⁷Sr/⁸⁶Sr ratios of the scheelites from lower average values in the southern Superior Province deposits, to slightly higher average values from deposits in the Wabigoon and Shebandowan subprovinces. The provincially in Sr isotopic signature of the hydrothermal fluids may reflect the "average" wallrock that interacted with the fluids in the lower crust. Basement and cratonization ages of the Superior Province increase from southeast to northwest, consistent with the apparent shift in Sr isotope ratios.

The Nd and Sr isotopic data provide evidence that gold mineralizing fluids may have been derived from a depleted mantle source that has interacted with the lower crust on its way to higher crustal levels. In addition, the Sm-Nd isotopic method proved to be a valuable geochronological tool for dating hydrothermal gold mineralization. This method should prove very useful for dating a variety of types of hydrothermal mineralization.

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Chapter 1 - INTRODUCTION

Archean gold deposits account for 60% of world gold production and almost 1/3 of this production is from Archean lode gold deposits. The Superior Province of the Canadian Shield is the world's largest lode gold producer and has yielded in excess of 170 million ounces of gold (Roberts, 1987) (Fig. 2.1). However, gold deposits are becoming increasingly more difficult to find. Gold production is one of the most important components of the economies of many northern Canadian communities, thus, any improvement or refinement of genetic models and exploration guidelines for gold deposits may have important beneficial effects on these economies. An important constraint on theories of the genesis of gold deposits that is lacking in most proposed models is that of the age of the gold deposits themselves. Field relationships and structural mapping have determined the relative timing of events but, without absolute age constraints, identification of the importance of the structural relationships of certain rock types or structural features to the mineralization has had to rely on inference and interpretation.

The aim of this study is to examine the Sm-Nd isotopic, Rb-Sr isotopic, and trace element characteristics of scheelite, a common gangue mineral in mesothermal Archean lode gold deposits, in order to evaluate the feasibility of dating the scheelites, and to identify the possible source(s) for the mineralizing fluids. Scheelite is a common vein mineral in many lode gold deposits in the Superior Province of the Canadian Shield, and it forms an integral part of the hydrothermal mineral assemblage

in these veins. In gold deposits where the paragenetic sequence of the vein minerals has been established, scheelite precipitation commonly predates gold precipitation in the veins. Thus dating the time of mineralization of scheelite will provide an age of vein mineral precipitation, and a maximum age constraint on the introduction of gold into the vein.

Unravelling some of the complexities of the geochronology of Archean gold mineralizing systems, and identifying the possible source(s) of the mineralizing fluids, will aid in developing genetic models and exploration guidelines for these deposits, and may provide important constraints on our understanding of crustal development and evolution during the Archean.

1.1 Genetic Models of Archean Mesothermal Gold Deposits

Discussions of the genesis of mesothermal gold deposits have generated considerable controversy. The plethora of models presently proposed for the origin of these deposits can be found in the introduction to and contents of the volume "The Geology of Gold Deposits: The Perspective in 1988" edited by Keays and Skinner (1989). These models include:

- 1) granulitization in the lower crust during the last stages of cratonization of mobile belts (Colvine, 1989; Card et al., 1989; Fyon et al., 1989),
- 2) transportation of gold by metamorphic fluids generated by mantle and crustal outgassing (Groves et al., 1989),
- 3) fractional crystallization of felsic magmas emplaced into the upper crust

(Burrows and Spooner, 1989), and

4) circulation of meteoric water in deeply penetrating fracture systems (Nesbitt and Muehlenbachs, 1989).

Other models that have been proposed include a syngenetic origin similar to that envisioned for volcanogenic massive sulphides (Hutchinson, 1976), gold-enriched lamprophyric magmas as the source and mode of transport of gold (Rock et al., 1989), and fluids released from metamorphic aureoles surrounding large granitic batholiths (Boyle, 1961).

Fluid inclusion and light stable isotope studies have not unequivocally defined a source for the hydrothermal fluids associated with gold mineralization other than to suggest that seawater is an unlikely source, and magmatic or metamorphic fluids may be involved (Roberts, 1987). In a comprehensive summary of the geochemical data available from mesothermal gold deposits Kerrich (1989) concludes that

"The systematically low salinity and moderate CO_2 contents, and variability of calculated δD , $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, and $\delta^{34}\text{S}$ values, and Sr and Pb isotopic compositions of the gold carrying hydrothermal fluids, are consistent with metamorphic dehydration under amphibolite facies conditions, or equilibration of externally derived fluids with metamorphic rocks under conditions of low water/rock ratios, in lithologically complex tectonic melange source regions or their subducted equivalents. Such characteristics are not consistent with purely magmatic or granulitization processes, although contributions from alternative fluid sources cannot be ruled out."

Currently, two models appear to dominate the debate concerning the origin of the lode gold mineralization: (1) the magmatic model, which proposes that the close spatial association between gold mineralization and felsic intrusive rocks observed in many gold camps is indicative of a magmatic derivation of the mineralizing fluid

and/or gold (Burrows and Spooner, 1986; Burrows and Spooner, 1989; Cameron and Hattori, 1987; Hattori, 1987; Wood et al., 1986); and (2) the metamorphic-replacement model (Groves and Phillips, 1987), which calls upon structural focusing of auriferous fluid from an unknown source which may include metamorphic dewatering of underlying greenstones (Kerrick and Fyfe, 1981) or derivation of fluids during granulite formation in the lower crust (Cameron, 1988; Colvine et al., 1988). Both models are based on essentially the same geological, structural and geochemical observations.

All of the genetic models proposed in Keays and Skinner (1989) are restricted by a lack of knowledge of the absolute timing of the mineralization event(s). Stratigraphic and structural relationships, and geochronological studies of host rocks, reveal the relative timing of events but generally do not precisely constrain mineralization. And, as noted above, the fluid inclusion and light stable isotope data are equivocal.

Clearly, precise dating of the mineralizing event(s) and the magmatic/metamorphic/granulitization events in the Archean crust associated with gold mineralization, and determination of the isotopic characteristics of the source area(s), are required to better define the genetic models.

1.2 Dating of Gold Deposits

Archean lode gold deposits have traditionally been difficult to date by conventional radiometric techniques, due to the paucity of hydrothermal minerals in

these deposits that are suitable for radiogenic isotopic analysis and geochronological interpretation. Lode gold deposits are dominantly composed of quartz with carbonate, neither of which are presently useful for geochronological studies. Previously, $^{40}\text{Ar}/^{39}\text{Ar}$ techniques have been applied to alteration micas in a few cases (Masliwec et al., 1985; McMaster et al., 1987; Watson and Kerrich, 1984), and recently to vein micas (Hanes et al., 1989), and a pyrite Pb-Pb secondary isochron was obtained on gold-related alteration pyrite in the Geraldton area (Anglin, 1987).

The discovery of some hydrothermal minerals, associated with the auriferous mineralization, that are suitable for U-Pb dating, and improvements in chemical and mechanical separation techniques, have recently resulted in some precise dating of mineralization in the Val d'Or camp in the Abitibi greenstone belt of the Superior Province (Corfu and Muir, 1989; Wong et al., 1989; Zweng and Mortensen, 1989; Jemielita et al., 1990). The U-Pb technique, and in some cases the $^{40}\text{Ar}/^{39}\text{Ar}$ technique, provide relatively precise age determinations of the hydrothermal event(s). However, neither of these techniques give information on the possible source(s) of the gold-bearing fluids, and hydrothermal minerals suitable for U-Pb analysis are relatively rare, or do not occur, in most Superior Province lode gold deposits.

Scheelite is a common gangue mineral in many Superior Province lode gold vein systems including those in the Val D'Or, Timmins, Shebandowan, Pickle Crow, Beardmore and Geraldton areas. Following a suggestion by Fryer and Taylor (1984), and Ludden et al. (1984), that the Sm-Nd system might be useful for dating hydrothermal mineralization, Anglin et al. (1987) demonstrated that scheelite contains

significant quantities of both Sr and the REE and suggested that scheelite, "a common constituent of gold-bearing veins, may be a suitable mineral for U/Pb, Sm/Nd and or Sr isotopic analysis" in order to directly determine the age of Archean gold deposits.

To follow up on the recommendation that scheelite may be useful for geochronological examination of gold deposits, an initial study was made on a few scheelite samples from the Timmins camp, and several other Superior Province gold deposits, to determine the feasibility of Sm-Nd and Rb-Sr isotopic analyses of scheelites (Bell et al., 1989). This study illustrated the possible value of Sm-Nd isotopic analysis as a dating technique for scheelite (and by inference, for other hydrothermal minerals which incorporate the rare earth elements (REE)). In addition, information on the source of the fluids which precipitated the scheelites may be obtained from the $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ initial ratios.

The results of the Bell et al. (1989) study gave a preliminary indication that gold mineralization in the Timmins area of the Superior Province may be significantly younger than the host rocks into which the veins were emplaced, and that both a depleted mantle-like source, and a more evolved reservoir such as continental crust may have contributed, respectively, the Nd and Sr to the gold mineralizing fluids (Bell et al., 1989). However, the Timmins area is geologically very complex, the scheelite samples analysed were not well located or documented, and some other independent sources of data on the timing of gold mineralization in the Timmins area provided conflicting evidence to the Sm-Nd isochron age obtained by Bell et al. (1989). Therefore, a more constrained test of the Sm-Nd isotopic systematics of scheelite from

auriferous veins is required to further evaluate the results of the Bell et al. (1989) study.

1.3 Study Approach

The main aims of this study are:

- 1) to analyse scheelite samples (+/- carbonate and tourmaline), from geologically well-constrained auriferous veins in the Val d'Or area, for Sm-Nd and Rb-Sr isotopic signatures to evaluate these systems in terms of providing information on the timing of hydrothermal activity,
- 2) to analyse additional scheelite samples from the Timmins area to complement data presented in Bell et al. (1989),
- 3) to use initial Sr and Nd isotopic ratios and trace element signatures of hydrothermal minerals to constrain the nature and possible source(s) of the mineralizing fluids, and
- 4) to use the resulting information to constrain the setting of these deposits in terms of Archean crustal development.

Information from this study may, in addition, identify criteria (timing and/or isotopic and trace element signatures): 1) that allow mineralized shear/alteration systems to be distinguished from barren ones, and 2) that add to the understanding of the development of the Archean crust.

This thesis presents an overview of the trace element and isotopic characteristics of scheelite from several gold mining districts in the Superior Province,

as well as a test of the validity of the Sm-Nd isotopic method to dating of these deposits. Initial chapters present the general geology and petrography of the deposits/districts studied (Chapter 2), followed by the trace element data from the vein scheelites (Chapter 3). The Rb-Sr isotopic analyses of scheelites, from all deposits studied, are presented in Chapter 4 and the Sm-Nd isotopic analyses in Chapter 5.

Chapter 2 - GEOLOGY OF DEPOSITS

2.1 INTRODUCTION

2.1.1 General Description of Archean Gold Deposits

Hodgson and MacGeehan (1982), Roberts (1987), Colvine et al. (1988), Keays and Skinner (1989), Card et al. (1989), and Robert (1990) have reviewed the characteristics of Archean lode gold deposits and their genetic models. The following section summarizes the salient points of their reviews.

Archean lode gold deposits are hosted in a wide range of lithological types and structural settings. The ore generally consists of veins and altered wallrock. The veins are dominantly composed of quartz with lesser amounts (in generally decreasing order) of carbonate, albite, tourmaline, sericite, chlorite, pyrite and scheelite. Pyrite and other opaque minerals usually comprise less than 5% of the vein material. Pyrite is ubiquitous in these deposits, and pyrrhotite and arsenopyrite are present in many (Roberts, 1987).

The deposits occur almost exclusively within the deformed and metamorphosed volcanic-intrusive-sedimentary rock sequences of greenstone belts (Roberts, 1987, Colvine et al., 1988). Most authors point out that the deposits are regionally distributed along large crustal-scale faults or structural "breaks" (Hodgson and MacGeehan, 1982), although they tend to be more closely associated with smaller-scale splays and subsidiary faults (Robert, 1990). Most gold deposits are hosted

within these "breaks" in steeply-dipping planar shear zones that are generally subparallel to the stratigraphy, and this structural control appears to be more important than a stratigraphic or lithological association.

The deformation zones that host gold deposits may be several kilometres wide and over 100 kilometres long (Roberts, 1987) and are clearly regional-scale geological features (i.e. the Porcupine-Destor fault (PD), and the Kirkland Lake-Cadillac fault (KLC) also known as the Cadillac-Malartic break, the Kirkland Lake-Larder Lake break or the Cadillac break) (Fig. 2.1). Although the mineralized veins occur within all rock types in the greenstone belts (Robert, 1990), a strong spatial association is observed between gold mineralization and small intrusions of felsic rocks, such as diorite, granodiorite and monzonite (Hodgson and MacGeehan, 1982; Robert, 1990).

It is generally accepted by most researchers that the gold-bearing quartz veins were emplaced into their host lithologies relatively late in the evolution of the greenstone belts. In most gold camps the veins crosscut folded, faulted and metamorphosed supracrustals, and in most cases the spatially-associated felsic intrusions have been deformed prior to introduction of the veins. In a few cases, a close temporal association has been documented between felsic intrusions and gold mineralization (for example, Red Lake (Andrews and Corfu, 1986)), but in general gold mineralization appears to be younger than the felsic magmatism locally observed. These observations suggest that the introduction of gold into the host greenstone belts occurred during, or following, the main phase of deformation or orogeny of the greenstone belt (Robert, 1990).

Figure 2.1. Generalized geology map of the Superior Province showing distribution of greenstone belts (shaded), large scale faults (heavy dashed lines) and gold deposits (small black dots). The important greenstone belts of the Superior Province are labelled. Abbreviations: B = Beardmore; G = Geraldton; GLTZ = Great Lakes Tectonic Zone; IL = Ivanhoe Lake Fault; KLC = Kirkland Lake-Cadillac fault; LH = Lake Head; PC = Pickle Crow; PD = Porcupine-Destor fault; Q = Quietico fault; SL = Sydney lake fault; SR = Seine River fault; T = Timmins; V = Val d'Or. (modified after Card et al., 1989).

For most Archean gold camps, however, it remains an unanswered question as to what the absolute time separation is between metamorphism, deformation, felsic intrusion and gold mineralization. The general lack of hydrothermal minerals suitable for geochronological studies (with the exception of the recent work on titanite and rutile in the Val d'Or area (Zweng, 1991; Jemielita et al., 1990) has provided the impetus for this investigation into the Sm-Nd and Rb-Sr isotopic characteristics of common gangue minerals, concentrating in this case on scheelite, from gold-bearing quartz veins.

Scheelite (CaWO_4) is a common gangue mineral in many of the large lode gold deposits in the Superior Province and appears to have elevated trace element abundances, particularly Sr and the REE (Anglin et al., 1987) which make it suitable for studying the chemical characteristics of the hydrothermal mineralizing fluid.

2.1.2 Sample Locations

Scheelite samples for this study were obtained from mineralized vein systems in, the Val d'Or gold mining camp in the southeastern Abitibi subprovince, the Timmins-Porcupine camp in the southwestern Abitibi, the Geraldton-Beardmore area of the eastern Wabigoon subprovince and one sample each from the Lake Head gold occurrence near Thunder Bay in the Shebandowan Subprovince and the Pickle Crow gold deposit in the Uchi subprovince (Fig. 2.1).

Scheelite and other vein minerals were sampled by the author from underground workings at the Sigma, Pascalis and Siscoe Extension mines in the Val

d'Or area. Additional samples from these deposits were provided by F. Robert (Geological Survey of Canada) and D. Burrows (Inco Research, Sudbury).

The majority of the other samples used in this study were obtained from the collections of the Geological Survey of Canada (GSC), or donated by other geologists. Most of the samples from the Timmins area are from the GSC collections. Several additional Timmins samples were provided by D. Burrows, the Queen's University Economic Geology collections, and one Hollinger mine sample was donated by R. Shegelski, Esso Minerals. Two samples from the Dome mine were provided by D. Rogers, former mine geologist, and one by R. Thorpe, GSC geologist. The Preston East mine sample was collected by the author from the mine tailings dump. Geraldton and Beardmore area samples were obtained from the GSC collections and by the author from mine tailing dumps. The Lake Head and Pickle Crow samples were obtained from the GSC collections.

Most of the scheelite samples from the GSC collection were collected by Dr. Eardley-Wilmott in the period from 1925 to 1945 and in most cases, sample location sketches and descriptions are available.

It is important to note that all of these samples have been collected from veins that were mined for gold, with the exception of those samples that were collected from mine tailings dumps where their exact relationship to gold-bearing veins is unknown, however, they were obviously associated with gold mineralization. A listing of sample locations and descriptions of all of the samples analyzed in this study is given in Appendix 1.

2.1.3 Study Approach

Bell et al. (1989) evaluated the feasibility of Rb-Sr and Sm-Nd dating of scheelites using a small suite of samples from Timmins, plus one sample from each of the Little Long Lac and Lake Head mines. This initial study showed that scheelites can be dated by the Sm-Nd method, and because scheelite contains very little Rb and abundant Sr, it is a useful indicator of Sr initial ratios. In addition, this study indicated a young age for the gold deposits in the Timmins area (relative to 'conventional wisdom' and other dating that had been done in the area). However, as the Timmins area is geologically complex, and there is no unequivocal minimum constraint on the age of mineralization, the Sm-Nd age remains controversial.

In this study, the Val d'Or area of the Abitibi Province was chosen as a more constrained test of the scheelite Sm-Nd age dating method for the hydrothermal gold mineralizing event. The Val d'Or area was chosen for this study for several reasons:

1. the geology of the deposits sampled is well known following the work of Robert at the Sigma mine (Robert et al., 1983; Robert and Brown, 1984; 1986a and b; Robert and Kelly, 1987) and A. Tessier at the Pascalis mine (Tessier, 1990);
2. the structural setting of the Val d'Or gold deposits appears to be less complex (in large part due to the detailed structural work of F. Robert) than many of the other large gold deposits in the Superior Province; and
3. several of the deposits were accessible for study and sampling in 1988.

Subsequent to the initiation of this study the Val d'Or area has been the subject of precise U-Pb dating of hydrothermal minerals in veins and altered wallrock (Zweng and Mortensen, 1989; Wong et al., 1989; Jemielita et al., 1989, 1990; Zweng, 1991). The results of these studies provide an invaluable comparison with the results of the Rb-Sr and Sm-Nd analyses for evaluating the reliability of these methods for geochronological work on hydrothermal systems.

2.2 GEOLOGY OF THE DEPOSITS SAMPLED

All of the samples used in this study come from gold-bearing quartz vein systems located in the Superior Province of the Canadian Shield. In the sections below, a brief description of the greenstone belts which host the deposits studied (including geochronological constraints on the gold mineralizing event where data is available), and a brief description of the deposit will be given for each deposit sampled. In addition, Table 2.1 summarizes the host lithologies present in each deposit sampled. Deposits sampled in the Abitibi Subprovince include the Sigma, Pascalis, and Siscoe Extension mines in the Val d'Or area and the Hollinger, McIntyre, Coniaurum, Dome and Preston East Dome mines in the Timmins area. Deposits sampled in the Geraldton-Beardmore belt of the Wabigoon Subprovince include the Hard Rock, Little Long Lac, and Leitch mines. The Lake Head mine is situated in the Shebandowan Subprovince and the Pickle Crow mine in the Uchi Subprovince (Fig. 2.1).

Table 2.1. Summary of the Geology of Superior Province Gold Deposits Sampled For Scheelite.

GREENSTONE BELT	Extrusive Rocks			Sediments		Intrusive Rocks		
Deposit	Ultra-mafic	Mafic	Intermediate to Felsic	Clastic	Chemical	Mafic	Intermediate to Felsic	Refs.
EASTERN ABITIBI								
Sigma	○	■	○	○	○	□	■	1,2
Pascalis	○	□	○	○	○	■	■	3,4
Siscoe Extension	○	□	○	○	○	□	■	5
WESTERN ABITIBI								
Hollinger	○	■	●	○	○	○	■	6,7
McIntyre	○	■	○	○	○	○	■	6,8
Coniaurum	○	■	○	○	○	○	■	9,10
Dome	□	■	●	■	□	○	■	11,12,13
Preston E. Dome	●	□	●	●	●	●	■	14
EASTERN WABIGOON								
Hard Rock	○	●	○	■	■	●	■	15,16
Little Long Lac	○	●	○	■	●	●	●	17,18
Leitch	○	●	○	■	■	●	●	19
SHEBANDOWAN								
Lake Head	○	●	■	○	○	○	○	20
UCHI								
Pickle Crow	○	□	○	●	■	●	■	21

Legend

- = important host to ore
 □ = minor host to ore
 ● = found in mine area but does not host ore
 ○ = not found in mine area

References

1 - Robert et al. (1983); 2 - Robert and Brown (1984, 1986a,b); 3 - Tessier (1990); 4 - Ames (1948); 5 - A. Duquette, pers. comm. (1988); 6 - Wood et al. (1986); 7 - Jones (1948); 8 - Furse (1948); 9 - Carter (1948); 10 - Piroshko and Hodgson (1988); 11 - Holmes (1948); 12 - Rogers (1982); 13 - Colvine et al. (1984); 14 - Hawley and Hart (1948); 15 - Horwood and Pye (1955); 16 - Matheson and Douglas (1948); 17 - Bruce (1935, 1937); 18 - Pye (1952); 19 - McKay et al. (1948); 20 - Macdonald (1941); 21 - Corking (1948).

2.2.1 Geology of the Abitibi Subprovince

Both the Val d'Or and the Timmins gold mining camps are located in the southern part of the Abitibi subprovince. Timmins is located on the western extension of the Porcupine-Destor fault in the southwestern part of the subprovince and Val d'Or is located on the eastern extension of the Kirkland Lake-Cadillac fault in the southeastern part of the subprovince (Fig. 2.1).

The Abitibi Subprovince is an east-west trending greenstone belt located in the southeastern part of the Superior Province of the Canadian Shield (Fig. 2.1). This belt is one of the largest continuous units of the Superior Province, extending over 700 km along strike and up to 200 km wide (Dimroth et al., 1982). The Abitibi belt is characterized by a series of E-W trending, elongate, mafic-to-felsic volcanic complexes flanked by sedimentary belts. Volcanic cycles generally grade upwards from basal ultramafic (komatiitic) units to tholeiitic, calc-alkaline basalt to rhyolite sequences at the top. Many of the volcanic complexes contain synvolcanic tonalite-trondhjemite plutons and are cut by later mafic, intermediate and felsic dyke swarms. The Pontiac (greywackes) and the Timiskaming (greywackes and conglomerates) Groups are in part stratigraphically equivalent to the upper volcanic cycles of the belt, and formed as sedimentary aprons to the developing volcanic chain to the north (Dimroth et al., 1983a). Metamorphic facies in the Abitibi belt range from prehnite-pumpellyite to amphibolite grade (Dimroth, 1982).

The Abitibi Belt is characterized by a pattern of generally east-trending isoclinal folds with subvertical axial planes. The predominant structural trend in the

belt is east-west and is the result of laterally continuous E-W trending fault zones and isoclinal folds (Tessier, 1990). The regional fabric is planar, vertical and also strikes E-W. The regional schistosity also trends east and parallels the axial planes of the east-trending F2 folds.

Major E-W trending faults, often referred to as breaks, are important structural features of the southern part of the Abitibi belt (Fig. 2.1). The southernmost fault, the Kirkland Lake - Cadillac fault (or break) (KLC) defines the southern limit of the Abitibi belt in Quebec and extends for more than 300 km from Matachewan in the west to the Grenville Front in the east (Tessier, 1990). The KLC break is marked by a rusty weathering carbonatized and chloritized zone, 30-200m wide. North of the KLC break is the Porcupine - Destor (PD) fault (or break) that extends for at least 150 km from Timmins to Duparquet. The PD fault is also marked by a carbonatized and chloritized zone, and has a strongly developed schistosity (Dimroth et al., 1983a).

These major faults are narrow zones of intense deformation, often showing anastomosed patterns, characterized by carbonate alteration zones and intense tectonic layering (Dimroth et al., 1982; Hodgson and Hamilton, 1989). These two faults are typical of those observed in other Archean gold camps, and the structural style associated with them is best explained by transpressive tectonic regimes (Poulsen and Robert, 1988). Numerous structurally controlled gold-quartz vein deposits occur in smaller branches of these major breaks (Tessier, 1990).

2.2.2 Geology of the Val d'Or Area

The geology of the Val d'Or area has been summarized by Robert et al. (1983), Robert and Brown (1984, 1986a,b), Poulsen and Robert (1988) and Tessier (1990). Only those features relevant to this study will be discussed here.

The Val D'Or area is underlain mainly by a southward younging sequence of ultramafic, mafic and felsic volcanic rocks interbedded with minor sedimentary rocks. This sequence is in contact with a thick clastic sedimentary sequence to the south (Fig. 2.2). All volcanic and sedimentary rocks are metamorphosed to the greenschist facies (Tessier, 1990).

Two main types of intrusive rocks are present in the Val D'Or area:

1) Syn-volcanic and early syn-tectonic intrusions including gabbro and diorite sills and plugs such as the Sigma porphyritic diorite (Robert et al., 1983) and quartz-diorite plutons such as the Bourlamaque Batholith (Latulippe, 1976). The Bourlamaque Batholith is the largest intrusion in the area and is host to numerous gold deposits including the Pascalis and Perron deposits (Fig. 2.2). These early intrusive bodies are well foliated, metamorphosed, and cross-cut by E-W shear zones. They show a broad spatial association with gold mineralization (Tessier, 1990).

2) Late syn- to post-tectonic intrusions including feldspar porphyry dykes which are unfoliated but metamorphosed and deformed by the E-W shear zones (Robert et al., 1983). In addition, there are a few later diorite dykes that cut the feldspar porphyry dykes. A few narrow, undeformed, cross-cutting diabase dykes represent the youngest intrusive event in the area (Robert et al., 1983).

Figure 2.2. Simplified geology of the Val d'Or area showing the main Cadillac break (Cadillac Tectonic Zone) and significant quartz-vein gold deposits (modified after Robert (1989)).

Two generations of faults are observed in the Val D'Or area, an early set of dominantly E-W faults, and a later conjugate set of faults trending NE-SW and NW-SE. The early E-W trending faults dip subvertically to the north, and are high angle reverse faults characterized by a component of approximately northerly-directed shortening with subsequent dextral transcurrent shear (Poulsen and Robert, 1988). These faults are high strain zones ranging up to tens of metres wide and typically contain carbonate alteration, quartz stockworks, and small-scale folds.

Gold mineralization is generally associated with the early E-W generation of faults (Tessier, 1990). Most of the gold deposits and occurrences in the area occur within 10 km of the major E-W fault in the area, the Cadillac break, and most are located to the north of it (Tessier, 1990). Gold-quartz vein deposits of the Val d'Or area typically consist of simple to complex quartz-carbonate-pyrite veins in reverse shear zones and extensional fractures (Robert, 1990). Gold mineralization is interpreted as having been introduced relatively late during or after the main phase of deformation, as the veins crosscut all rock units in the area except for the very late diabase dykes and faults (Robert et al., 1983; Tessier, 1990).

Recently, a detailed geochronological framework has been established by several groups of researchers for the Val d'Or area, and for the mineralization at the Sigma and Camflo mines. The results of these studies are summarized in Table 2.2. Essentially these data suggest that volcanism and subvolcanic magmatism ended around 2700 Ma, later magmatism took place between 2695 and 2680 Ma, and metamorphism peaked around 2680 Ma. In addition to the data referenced in Table

Table 2.2 Geochronology of the Val d'Or Area

Lithology/Event	Min	Age (Ma)	Reference
Columbiere Rhyolite	z	2705 +/- 1	1.
Sigma porphyritic diorite	z	2703 +/- 3	1.
Bourlamaque Batholith	z	2699 +/- 1	1.
Sigma feldspar porphyry dykes	z	2694 +/- 2	1.
Metamorphic Mg-hornblende	h	2693 +/- 10	2.
Metamorphic Fe-hornblende	h	2672 +/- 16	2.
Metamorphic rutile in Columbiere rhyolite	r	2680 +/- 2	1.
Camflo quartz syenite	t	2680 +/- 4	3.
	z	2685 +/- 9	4.
Hydrothermal alteration, Camflo Mine	r,t	2625 +/- 7	3.
	t	2625 +/- 7	4.
Hydrothermal alteration, Sigma Mine	r	2592 +/- 2	1.
Muscovite in vein, Sigma	m	2579 +/- 3	2.
Pyrite Pb secondary isochron, Pascalis	p	2454 +/- 20	5.

Minerals:

z	= U-Pb zircon
t	= U-Pb titanite
r	= U-Pb rutile
m	= $^{40}\text{Ar}/^{39}\text{Ar}$ muscovite
h	= $^{40}\text{Ar}/^{39}\text{Ar}$ hornblende
p	= pyrite Pb isotope analyses

(errors are quoted at the 2 sigma level)

References:

1. Wong et al., 1989; 2. Hanes et al., 1989; 3. Jemielita et al., 1990;
4. Zweng, 1991; Zweng and Mortensen, 1989; 5. Anglin, 1989

2.2, Mortensen (1987) has dated volcanic and plutonic rocks using U-Pb on zircons in the Noranda-Lac Abitibi area and obtained similar ages for volcanism and associated magmatism around 2700 Ma, and an older age of magmatism of 2730 Ma. Three late to post tectonic plutons gave ages ranging from 2694 to 2689 Ma.

U-Pb ages on hydrothermal titanites and rutiles from the Camflo and Sigma gold deposits (Table 2.2) indicate that the mineralization event appears to be significantly younger than the latest period of magmatic activity. At the Camflo mine the mineralization age is 55 to 60 Ma later, and at Sigma 90 to 100 Ma later, than the youngest magmatic activity indicated at each mine.

In contrast to these data, recent ion-microprobe U-Pb analyses of zircons found in the veins in several deposits in the Val d'Or area yield ages very similar to the ages of the respective host intrusions to the veins (Claoue-Long et al., 1990) and are interpreted as representing the time of gold mineralization. Claoue-Long et al. (1990) interpret these zircons to be hydrothermal on the basis of limited textural evidence (Robert, 1990). They argue that younger ages obtained for vein and alteration minerals using other methods are reflecting resetting of isotopic systems or renewed hydrothermal mineral growth. Their model, however, does not explain the rutile and titanite U-Pb dating results, nor is it compatible with observations made by Robert and Brown (1986a) that the youngest intrusive rocks had been regionally metamorphosed prior to emplacement of the veins, therefore making it difficult to relate the mineralizing fluids to the magmatic rocks observed in the mine. In addition, the textural and optical characteristics of the zircons analysed by Claoue-Long et al.

(1990) are very similar to magmatic zircons in the Bourlamaque batholith (D. Davis, pers. comm, 1990). The zircons in the veins would seem more likely to be wallrock zircons entrained in the veins, and much more resistant to alteration than their surrounding wallrock.

2.2.3 Descriptions of Deposits Sampled in the Val d'Or area

2.2.3.1 Sigma Mine

The following description of the geology and petrography of the Sigma mine is based on work by Robert and Brown (1984, 1986a and 1986b), Robert et al. (1983), and Ludden et al. (1984).

The Sigma deposit consists of gold-bearing quartz vein systems that are superimposed on regionally deformed metavolcanic rocks which were intruded by an irregular porphyritic diorite body, and feldspar porphyry dykes. The feldspar porphyry dykes are unaffected by the regional deformation and crosscut the volcanic rocks and the porphyritic diorite body but are themselves crosscut by the veins. All of these rock types have been regionally metamorphosed to greenschist facies.

The Sigma mine veins are composed mainly of quartz and tourmaline, with minor carbonate, pyrite, chlorite, scheelite and free gold. The veins cut all rock types in the area, and the alteration associated with the gold mineralization is superimposed on the regional greenschist metamorphic mineralogy (Ludden et al., 1984; Robert and Brown, 1986a).

Two main types of veins are found in the mine, subvertical and subhorizontal (the latter are also referred to as "flats" or tension) veins. The subvertical veins are hosted in steeply-dipping shear zones, and occupy openings created during progressive shearing movements. The minerals in the subvertical veins exhibit a fibrous habit.

The subhorizontal (tension or "flat") veins occupy extensional fractures, and internal vein-filling textures indicate that they formed by one or more episodes of subhorizontal fracture opening and subsequent open-space filling. Minerals in the "flat" veins are commonly sub to euhedral (Robert and Brown, 1986a). In the veins, minerals display textures that indicate free crystal growth into open space (Robert and Brown, 1986b). Typically, scheelite, calcite and tourmaline form continuous coatings of millimetre to centimetre-sized crystals pointing toward the centre of the ribbons of vein material, on either or both walls of the ribbons, the central zone of which is occupied chiefly by quartz (Robert and Brown, 1986b).

Structural observations indicate that the two types of vein systems formed contemporaneously and are co-genetic. The quartz veins are undeformed except for some small displacements along shear zones and late faults (Robert and Brown, 1986a). However, the vein minerals do show evidence of deformation, including subgrains and fractures, suggesting that the veins were emplaced in a dynamic tectonic environment (Robert and Brown, 1986a).

Most "flat" veins at the Sigma mine contain gold, which typically occurs as the native metal in fractures within other vein minerals (mostly quartz, scheelite, tourmaline and pyrite) thus appearing to be hosted in deformational features produced

in vein minerals after filling of the veins (Robert and Brown, 1986b). A minor amount of gold also forms small globular inclusions in pyrite.

Scheelite is moderately abundant in the quartz veins at the Sigma mine, and typically occurs as well-developed coarse-grained crystals ranging in size from 1 to 20 cm. Quartz, tourmaline needles, and pyrite cubes typically surround or are attached to scheelite crystals. Scheelite is commonly fractured and veined by quartz, calcite, and more locally by gold. In many cases, textures indicate that the scheelite was fractured prior to or during quartz deposition. Scheelite crystals also show evidence of deformation, annealing, and various degrees of recrystallization (Robert and Brown, 1986b).

A general vein paragenesis has been outlined by Robert and Brown (1986b) for the vein filling at the Sigma mine (Fig. 2.3). The precipitation of calcium-bearing minerals (carbonates, scheelite, apatite and epidote) on the ribbon walls was followed by deposition of tourmaline and then pyrite. Most quartz deposition occurred after these minerals had precipitated and infilled the individual veins or ribbons. Veins and vein minerals were then subjected to a post-filling deformation, after which gold, tellurides, calcite and other minerals were deposited in late fractures, around crystal aggregates and in recrystallized zones in vein minerals (Robert and Brown, 1986b). Thus, the gold introduction is paragenetically late in the veins.

Most of the samples collected by the author for this study were obtained from "flat" veins. Scheelites were generally euhedral, coarse crystals. A typical example of a tension vein is the 1708 stope flat vein sampled by the author (Figures 2.4 and 2.5).

Figure 2.3. Schematic paragenetic diagram for the tension ("flat") veins in the Sigma mine. Line thickness represents the relative quantities of the mineral deposited. The dotted lines represent uncertainties (after Robert and Brown, 1986b).

Figure 2.4. Plan section of the 1708 W stope, 16 level, Sigma mine, showing sample locations for samples S-01 to S-11. North is to the top of the diagram.

Figure 2.5a. Sketch of a section of the southeast wall of the 1708 W flat vein, looking east, showing the locations of sample S-01 to S-07. The abundance of tourmaline in the central part of the vein is greater where the vein cuts the C-porphry (C- π). Tourmaline abundance decreases toward the south termination of the vein. Pyrite cubes appear in all wall rocks; however they are found at greater distances from the vein margins in the volcanics (lavas) than in the C- π or G-dyke. (Diagram modified from a sketch by F. Robert, pers. comm., 1988).

Figure 2.5b. Photograph of a hand sample S-01 showing a vein in the G-dyke at the contact with the volcanics. The orange scheelite crystal is in contact with a carbonate-quartz layer at the bottom of the vein margin.

This vein cross-cuts mafic volcanics, porphyritic diorite (C-porphyry), and feldspar porphyry dykes (G-dykes). Sketches of slabbed surfaces of several of the samples from this deposit illustrate the characteristic open-space filling texture observed in these veins (Figure 2.6).

2.2.3.2 Pascalis Mine

This deposit was exploited by three mines, the Perron mine to the northwest, the Beaufor mine to the southwest and the Pascalis Nord mine to the east (Tessier, 1990). The samples in this study were all obtained from the Pascalis mine region of the deposit. Gold-bearing quartz veins are hosted in shear fractures (similar to the subvertical shear veins at the Sigma mine) and extension fractures (sub-horizontal or "flat" veins) which cross-cut the Bourlamaque batholith near its eastern contact with surrounding mafic metavolcanic rocks (Figures 2.2 and 2.7). Veins pinch out where they enter the volcanic rocks. The Bourlamaque batholith has yielded a U-Pb zircon date of 2699 ± 1 Ma, and it has been suggested that it represents a subvolcanic intrusion associated with the volcanic rocks in the area (Wong et al., 1989).

In addition to the quartz-diorite batholith, mafic dykes, mafic volcanic rocks, and minor aplitic felsic dykes, are exposed underground as hosts to the veins in the Pascalis mine (in decreasing order of importance as hosts to ore). The felsic dykes are volumetrically minor and probably represent late stage differentiates of the batholith. The mafic dykes exposed in the mine are the youngest rock type cross-cut by the veins. They occupy the same fracture system as the subvertical quartz veins, but

Sketch of slab, sample S-10

Sketch of slab, sample S-06

Figure 2.6. Sketches of slabbed hand samples taken from the 1708 W flat vein, 16 level of the Sigma mine, illustrating the 'open-space filling' textures of this 'flat' or tension vein, indicating formation in an extensional environment. Samples S-01, S-06 and S-10 are illustrated. Sample S-06 does not contain scheelite.

Figure 2.7. Plan of Niveau (level) 825, Pascalis mine. North is at the top of the map. (modified after Tessier, pers. comm., 1988).

predate the veins and are typically very altered and deformed (Tessier, 1990) (Fig. 2.7). A more detailed discussion of the rock types in this deposit is given in Tessier (1990).

The vein mineralogy, textures and paragenesis are very similar to those described above for the Sigma deposit. Quartz and tourmaline are the most abundant vein minerals, but their relative proportions are highly variable. Carbonates are also relatively common. Other minor minerals, in approximate decreasing order of abundance include, chlorite, pyrite, scheelite, sericite, chalcopyrite, pyrrhotite, rare visible gold and very rare tellurides (Tessier, 1990).

Scheelite is a common mineral of the gold-bearing veins, but it does not occur in every vein. It is pinkish-orange to buff coloured and usually occurs as crystals attached to tourmaline-altered vein walls, or growing on tourmaline planes within the veins. Euhedral crystals and large crystal sizes are only encountered in extension veins. Locally, anhedral scheelite grains occur "floating" in the central part of veins, surrounded by quartz (Tessier, 1990).

Scheelite from both types of gold-bearing veins (shear and "flat" veins) at the Pascalis mine were sampled by the author. Samples P-01 to P-25 and P-35 were taken from a subhorizontal extension or "flat" vein on the 825 level of the Pascalis mine (see Figures 2.7 to 2.11). The open space filling texture of this flat extension vein, exposed in the 888N crosscut (XC), is typical of this type of vein (Figures 2.10 and 2.12). A similar "flat" vein was also sampled in the 637E drift (P-30, -31 and -32) (Figure 2.13).

Figure 2.8. Slope map of XC 888N Niveau (level) 825, Pascalis mine (modified after Tessier, pers. comm., 1988), showing locations of the more detailed sketches presented in Figures 2.9, 2.10 and 2.11 and sample locations. Small s's = location of schellies in vein. Small x's = sample locations.

PASCALIS N. MINE
XC 888N - E. WALL
AREA 1
1:40

(samples P-01 to P-10)

Detail of sample P-01

Sketch of samples 06, 07, 09 and 10

Figure 2.9. Sketch of the East Wall of XC 888N, Area 1, Pascalis mine, showing cross section characteristics of the vein, alteration and a mafic dyke. Samples P-01 to P-10. X = sample location and the numbers refer to the sample numbers P-01, P-02 etc. Note the subhedral crystal of schreeite growing on a tourmaline plane oriented parallel to the vein wall (P-06), indicating multiple openings of this vein (Tessier, 1990). Tourmaline in this vein is often found as delicate rosettes of fine grained black fibres coating the vein walls or other vein minerals, or replaces wallrock fragments within the veins.

Figure 2.10. Sketch of the east wall of XC 888N, Area 2, Pascalis mine, showing locations for samples P-12 to P-17. Open circles mark the sample locations, numbers (P-12, P-13 etc.) refer to the sample. Note the euhedral crystal of schellite (P-16) and large sub- to euhedral crystals of pyrite, in this part of the vein (see also figure caption 2.9).

Figure 2.11. Sketch of the north wall of 88N raise, 888N XC, Pascalis mine. Open circles and dashed lines outline sample locations. Numbers refer to the samples (P-20, P-21 etc). C = carbonate, S = scheelite, Tm = tourmaline, py = pyrite, G = quartz diorite.

Figure 2.12. Photo of the east wall of XC 888N, Area 2, Pascalis mine (see also Fig. 2.10), showing a euhedral scheelite crystal projecting upward from the lower vein margin, just to the left of the film box-top included for scale. The scheelite is bounded on the left side by large pyrite crystals, and on the right by a mass of fine-grained black tourmaline.

Figure 2.13. Plan of Niveau (level) 625 of the Pascalis mine. North is at the top of the map (modified after Tessier pers comm, 1988). X indicates sample locations for samples P-27 to P-32 and P-37 to P-38 (see also fig. 2.7).

Several samples of scheelite were also taken from shear veins exposed in stopes 637S (P-27, -28 and -29) and 631E (P-37) (Figure 2.13). The scheelite in these veins is commonly anhedral. Samples 86-036, -037 and 87-055, donated by F. Robert, are also samples of the "32-type", or shear, vein which constituted most of the ore at the Pascalis deposit (Tessier, 1990).

2.2.3.3 Siscoe Extension Mine

The geological setting of the Siscoe Extension mine is similar to that of the Sigma mine. The Siscoe Extension mine is hosted in mafic volcanics and intrusive diorite which have been crosscut by aplites, mafic dykes and quartz-feldspar porphyry dykes. In this mine the mafic dykes cross-cut the diorite/volcanics, but their relationship to the quartz-feldspar porphyry dykes is unknown. These lithologies are all cross-cut by quartz veins. The veins consist of south-dipping veins (oblique veins with some shear component), flat veins, and late tourmaline veins which crosscut the other veins. The first two types of veins are similar to those observed in the Sigma and Pascalis mines.

The quartz-feldspar porphyry is the dominant host rock for all veins. It appears to be one large body, but with multiple "tongues" and irregular contacts. The scheelite sample from this deposit (SE-1) was taken from the east wall of drill station B on level 725, approximately 60 metres west of the shaft. The vein exposed at this location is a south-dipping (shear-type) vein (Figure 2.14). The scheelite forms light brownish-orange patches surrounded by white quartz. The quartz is cut by many fine-

Figure 2.14. Photo of south-dipping oblique (shear) vein in east wall of drill station B on level 725 of the Siscoe Extension mine. Scheelite forms light-brownish-orange irregular patches in the quartz. Rare well formed euhedral crystals surfaces are observed in scheelite in this vein. However, the scheelite is commonly anhedral and appears to have been sheared and fractured. (Notebook for scale.)

grained veinlets/irregular seams of chlorite-pyrite-carbonate in the quartz. A few small, well-formed, crystal outlines were observed in the scheelite, but for the most part the scheelite is anhedral and appears to have been sheared and fractured. The vein contains abundant scheelite and a large (approximately 10 kg) sample of the scheelite-bearing quartz was taken from this location.

2.2.4 Geology of the Timmins Area

In the Timmins area the volcanic rocks were divided into the Deloro Group and the overlying Tisdale Group on the basis of lithogeochemistry and age (Nunes and Pyke, 1980; Pyke, 1982). The volcanic cycle in each group commences with ultramafic flows which are overlain by tholeiitic and calc alkaline sequences. The Porcupine Group, a sequence of interlayered metasediments and felsic volcanics, is similar in age to the Tisdale Group. Unconformably overlying these sequences are Timiskaming-type metasediments. The sequence was intruded by granitic rocks and later diabase dykes (Matachewan and Keweenawan) that crosscut all Archean lithologies (Fig. 2.15).

The rocks in the Timmins area have been extensively folded. The dominant fold structure in the area is the Porcupine syncline, which is situated north of the Porcupine-Destor fault and encompasses the main gold camp (Fig. 2.15). This eastward-plunging syncline, formed by an original north-trending series of folds, was subsequently refolded about an E-W axis (Pyke, 1982).

Figure 2.15. Geological map of a portion of the Timmins gold camp. The solid squares indicate gold deposits and the dashed lines represent faults. Diagram modified after Colvine (1989).

The most prominent structure in the Timmins area, however, is the Porcupine-Destor (PD) fault, a major east-west oriented deformation zone which extends from the Kapuskasing structure in the west to the Noranda area in the east, where it passes into the Cadillac break (Figs. 2.1 and 2.15). The PD fault zone is typical of the regionally extensive, linear tectonic zones of altered and deformed rocks termed "breaks" (Hodgson and MacGeehan, 1982; Roberts, 1987) that commonly show a spatial relationship with gold mining camps.

Gold mineralization in the Timmins area is hosted in quartz-rich veins and sulphidized wallrocks, dominantly in mafic metavolcanics and felsic porphyritic intrusions. Carbonatization and sulphidization are common alteration features associated with the mineralization. Gold introduction occurred relatively late in the geological development of the Archean rocks in the Timmins area. Mafic volcanism was followed by felsic volcanism, sedimentation, folding, faulting, and intrusion of the porphyries. The rocks were then re-folded and sheared prior to alteration and mineralization (Colvine et al., 1984).

Dating of the host lithologies for the gold mineralization in the Timmins area places maximum age constraints on the time of mineralization (Marmont and Corfu, 1989). A summary of the geochronological data available on the Timmins area is presented in Table 2.3. Marmont and Corfu (1989) conclude that in the Timmins area volcanism ceased around 2700 Ma and they grouped the felsic intrusive rocks into three chronological categories:

1. Synvolcanic, dioritic intrusions (ages circa 2700Ma).

Lithology/Event	Min	Age (Ma)	Reference
Deloro Group dacite tuff	z	2727 +/- 1.5	1.
Tisdale Group dacite tuff	z	2703 +/- 1.5	1.
Krist Fragmental, Tisdale	z	2698 +/- 4	1.
synvolcanic dioritic intrusions east of Timmins	z	2705 +/- ?	1.
post-volcanic granodioritic intrusions, five determinations made of Timmins porphyries	z	2691 to 2688	1.
monzonite intrusion east of Timmins	z	2678 +/- 2	1.
post-volcanic, post-porphyry monzonitic (and lamprophyric?) intrusions = albitite dyke, predate gold mineralization	z	2673 +/- 6	1.
Davidson-Tisdale muscovite	m	2615 +/- 2	2.
Hollinger muscovite	m	2570 +/- ?	3.
alteration fuchsite, Hollinger	f	2617 to 2573	4.
alteration fuchsite, Dome	f	2633 to 2560	4.
alteration fuchsite, Dome; integrated total gas ages	f	2570 to 2480	4.
disturbance in fuchsite age spectra	f	2450 +/- ?	5.
metasomatised shear zone, Hollinger	w	2410 +/- ?	6.
secondary Pb isochron, Matachewan	g	2406 +/- ?	7.
Hearst dyke (correlative with Matachewan dykes?)	z	2454 +/- 2	8.

Minerals:

z	= U-Pb zircon
m	= $^{40}\text{Ar}/^{39}\text{Ar}$ muscovite
f	= $^{40}\text{Ar}/^{39}\text{Ar}$ fuchsite
w	= whole rock Rb-Sr isochron
g	= galena Pb isotope secondary isochron

References:

1. Marmont and Corfu, 1989; 2. Hanes et al., 1987; 3. Kerrich et al., 1984; 4. Masliwec et al., 1985; 5. McMaster et al., 1987; 6. Kerrich et al., 1987; 7. Sinclair, 1982; 8. Heaman, 1988

2. Post-volcanic, granodioritic intrusions. These intrusive bodies cut deformed supracrustal rocks and, in the Timmins mines, consist of a suite of mineralized quartz porphyries localized along the Destor-Porcupine break and related structures (Marmont and Corfu, 1989). These porphyries cluster in age from 2691 to 2688 Ma.

3. Post-volcanic, post-porphyry, monzonitic (lamprophyric?) intrusions. Marmont and Corfu (1989) state that in the McIntyre and Hollinger mines, at depths greater than 2000 feet, the porphyries are cross-cut by highly altered "albitite" dykes considered by Burrows and Spooner (1986) to be lamprophyres. One of these dykes yielded an age of $2673 \pm 6/-2$ Ma. These dykes provide a maximum age for the introduction of gold in the Timmins area.

The gold mineralization in the Timmins area is cut by Matachewan-type diabase dykes. Gates and Hurley (1973) obtained a Rb-Sr age of 2633 ± 93 Ma for the Matachewan dyke swarm. Fahrig (1987), however, pointed out that this isochron was not very precise and he correlated the Matachewan swarm with the early Huronian Thessalon and Copper Cliff volcanism which has been dated at 2450 Ma (Krogh et al., 1984). A diabase dyke from the Hearst swarm, west of the Kapuskasing structure, has recently yielded a U-Pb age of 2454 ± 2 Ma (Heaman, 1988), and is thought to be correlative with the Matachewan dykes (Ernst and Halls, 1984).

Attempts to date the time of gold emplacement in the Timmins area by techniques other than U-Pb on zircons (primarily $^{40}\text{Ar}/^{39}\text{Ar}$, see Table 2.3) have yielded younger ages than that of the "albitite" dyke reported by Marmont and Corfu (1989).

2.2.5 Description of Deposits Sampled in the Timmins Area

2.2.5.1 Hollinger-McIntyre-Coniaurum Mines

The Hollinger, McIntyre and Coniaurum mines form part of the second largest known Archean gold vein/shear zone deposit in the world (Wood et al., 1986) (Fig. 2.15). This mineralized zone, consisting of the Hollinger-McIntyre-Coniaurum-Vipond-Moneta-Crown vein system, extends over approximately 5 km of strike length, reaches a maximum of 2 km in width, and has been mined to a depth of 2.4 km at the McIntyre mine (Wood et al., 1986). The Hollinger-McIntyre-Coniaurum ore zones cross-cut a series of deformed and metamorphosed Fe- and Mg- tholeiitic basalts and carbonaceous interflow sediments of the Tisdale Group, highly strained and altered quartz-feldspar porphyries, and minor albitite dykes. The albitite dykes cross-cut the porphyries and appear to be less deformed than other lithologies in the mines (Wood et al., 1986).

The principal type of gold mineralization in the Hollinger and McIntyre deposits consists of cross-cutting, quartz-dominated veins and stringers with well-developed, spatially associated pyrite-ankeritic carbonate-sericite alteration envelopes. This main stage of vein development postdates an earlier series of tourmaline-bearing and scheelite-rich veins, containing little gold (Wood et al., 1986). Jones (1948) states that there is evidence for several periods of quartz deposition in the veins at the Hollinger mine, although it is very difficult to differentiate the sequence of events in vein formation, and "... different observers cannot entirely agree upon the sequence of

mineralization."

Several workers have investigated the relationship between scheelite and gold mineralization in the Hollinger mine (representative of the three mines). On the basis of two representative scheelite-mineralized stopes in the Hollinger mine, Wood (1983) concluded that scheelite associated with the Millerton porphyry occurs in two forms, one an early phase of scheelite-rich veins, and a later phase that appears to be co-genetic with the quartz of the main vein filling (Fig. 2.16). The relationship between scheelite veins and porphyry intrusions at the Hollinger mine was examined by Allen and Folinsbee (1944) who suggested that a close relationship exists between scheelite-mineralized veins and porphyry bodies. They also observed that gold mineralization crosscuts earlier scheelite-bearing veins. Although Allen and Folinsbee (1948) state that "In most parts of the Canadian Shield the presence of scheelite in quartz veins is an indicator of conditions favouring the formation of gold lodes.", the relationship between the gold and the scheelite is not clear-cut except that scheelite precedes gold in the vein paragenesis.

2.2.5.2 Dome Mine

The Dome mine is located approximately 1 km north of the Destor-Porcupine Fault on the south limb of the Porcupine syncline (Fig. 2.15). The geology of the mine has been described by Holmes (1948) and Rogers (1982) and summarized by Colvine et al. (1984). The host lithologies for ore in the Dome mine are highly variable, and include tholeiitic pillowed basalts, rhyolitic pyroclastics and flows, slates,

Figure 2.16. Schematic mineral paragenesis diagram for the Hollinger mine, Timmins for veins (upper diagram), and wallrock (lower diagram). After Wood et al. (1986).

conglomerates, cherts, ankeritic sediments, and quartz porphyries. The ore shoots consist of foliation-parallel and -oblique quartz-carbonate-tourmaline and quartz-carbonate-green muscovite veins and the ore zones consist of stockworks of these veins and range from irregular to concordant tabular bodies (Colvine et al., 1984). Scheelite is found in minor quantities in the mine, predominantly in association with the porphyry ore (D. Rogers, pers. comm. 1986).

2.2.5.3 Preston East Dome Mine

The Preston East Dome mine geology is located immediately south of the Dome mines property. Most of the mineralization is hosted in quartz porphyry intrusions, although minor mineralization occurs in the surrounding volcanics. The ore is predominantly hosted in fractures, although a minor component consists of replacement of schistose wallrocks (Hawley and Hart, 1948). The scheelite samples from this deposit were obtained by the author from mine dump material. Their exact location and setting, therefore, is unknown although it is likely that they are from veins hosted within the deformed porphyry.

2.2.6 Geology of the Geraldton-Beardmore Area, Wabigoon Subprovince

The Wabigoon Subprovince is a typical granite-greenstone terrain of Archean age, that consists of a supracrustal assemblage of predominantly volcanic rocks and lesser amounts of sedimentary rocks. The sequence was intruded by plutons that vary in composition from granite, to syenite and gabbro (Card, 1983; Blackburn et al.,

1985). Metamorphic grade is characteristically low-greenschist facies throughout most of the belt, with grade increasing abruptly to amphibolitic grade at the margins of plutonic bodies.

The Geraldton-Beardmore belt forms the southern margin of the Wabigoon belt where the strike of the supracrustal units is predominantly east-west and the volcanic rocks are predominantly mafic in composition. The rocks in this belt are distributed in lens-shaped elongate panels which alternate between domains dominated by mafic volcanics and those dominated by clastic sedimentary rocks (Anglin, 1987).

Numerous east-west striking faults are identified throughout the area, commonly marking the contacts between sedimentary rock- and volcanic rock-dominated terrains. Kehlenbeck (1986) has identified the entire Beardmore-Geraldton belt as a complex folded terrain.

The gold deposits in the Geraldton area (the Hard Rock and Little Long Lac mines were sampled for this study) are hosted in an elliptical zone of intense deformation to the north of a major dextral shear zone (Pye, 1952; Horwood and Pye, 1955; Anglin, 1987). Dating in the Geraldton area includes a 2691 Ma zircon age on a quartz feldspar porphyry intrusion that hosts gold mineralization, and a 2540 Ma Pb isotope secondary isochron on alteration pyrite overgrowing the porphyry (Anglin, 1987).

The Leitch mine in the Beardmore area is located along the apparent western extension of a strike slip fault (the Watson Lake Fault) in a sedimentary rock-dominated terrane (Anglin, 1987).

2.2.6.1 Hard Rock Mine

The Hard Rock mine is hosted in a sequence of clastic and chemical sedimentary rocks that include greywacke, conglomerate and oxide (magnetite-chert) iron formation, that were intruded by a large mass of albite porphyry. The gold mineralization at the Hard Rock mine is most closely associated with the intrusive porphyry and the iron formation. Mineralization is hosted either along contacts, or within fractured, more competent rocks such as the porphyry and iron formation. The two scheelite samples analyzed from the Hard Rock deposit are unlocated (one from the Queen's University collections, the other obtained by the author from the mine dump in 1985). On the basis of the mineralogy of the veins and wallrock fragments, these samples probably came from veins within the porphyry.

2.2.6.2 Little Long Lac Mine

The orebodies at the Little Long Lac mine consisted of narrow, continuous, closely-spaced, parallel quartz veins occupying shear planes in folded and fractured quartz greywacke. The veins pinched out where they entered finer-grained slate layers stratigraphically above and below the coarser quartz greywacke. The veins occupy fractures that parallel the axial plane of the folds in the quartz greywacke (Bruce 1935, 1937). The scheelite-bearing sample from this deposit was obtained from the ore stockpile by Eardley-Wilmott in 1942.

2.2.6.3 Leitch Mine

The gold mineralization at the Leitch mine is hosted in a series of folded and sheared iron formation and greywacke. The iron formation consists of interstratified beds of jasper, hematite, slates, schists and greywacke (McKay et al., 1948). Material found on the mine dump reveals that the quartz in the veins is ribboned with dark streaks of chlorite-sulphide-telluride-gold-bearing schist. McKay et al. (1948) state that "... the darker and more numerous these streaks, the higher is the grade of the ore.". The samples for this study were obtained from the ore pile in 1942 by Eardley-Wilmott, and from the dump in 1985 by the author. In both of these samples scheelite occurs as small irregular 0.5 to 1 cm size anhedral blebs along the dark chlorite-rich laminae. Both samples contain visible gold that occurs along fractures within the scheelite and other gangue minerals.

2.2.7 Geology of the Lake Head Gold Mine, Shebandowan Subprovince

The Lake Head Gold mine is located northwest of Thunder Bay in the Shebandowan Belt. The gold mineralization is hosted in quartz veins in shear zones and fractures in felsic tuffs and agglomerates (Macdonald, 1941). The scheelite sample analyzed in this study was collected by Eardley-Wilmott, in October 1942, from section A of the Number 2 vein. Macdonald (1941) describes this vein as occupying a sheared zone in chloritic and agglomeratic tuff. He also reports that the vein contains visible gold, and consists of quartz with ankerite and irregular pyrite.

2.2.8 Geology of the Pickle Crow Mine, Uchi Subprovince

The rocks in the vicinity of the Pickle Crow mine include mafic volcanics with minor interbedded sediments, iron formation, a diorite intrusive and a sericitic quartz porphyry (Corking, 1948). The mineralization is hosted in two quartz veins, the Howell vein and the No. 2 vein. The Howell vein is hosted in a shear zone where it cuts across a layer of siliceous iron formation from mafic volcanics on one side and back into mafic volcanics on the other. The No. 2 vein is hosted entirely within a mass of sericitic quartz porphyry (Corking, 1948). The sample used in this study was collected by Eardley-Wilmott in 1943 and is unlocated.

Chapter 3 - TRACE ELEMENT ANALYSES OF SCHEELITE

3.1 INTRODUCTION

Trace element, including rare earth element (REE), studies of hydrothermal minerals can yield much useful information about the mineralizing solutions from which they were precipitated. It may therefore may be possible to identify the source of the fluids (and, by inference, the gold) and the evolution of the mineralizing fluid(s). Trace element (including REE) analyses of scheelite from Archean lode gold deposits were determined to see if scheelite could be used for isotopic studies (Anglin et al., 1987). These data indicated that the abundances of Sr and the REE in scheelite were sufficient for isotopic analyses. In addition, these data indicated that there were differences in the trace element, particularly REE, distributions in scheelites from different deposits and regions. A preliminary database of trace element contents of scheelites has been developed from Superior Province gold mining camps, namely Val d'Or and Timmins in the Abitibi Subprovince, and several smaller deposits in the Wabigoon, Shebandowan and Uchi subprovinces, to further examine the variations in the trace element contents of scheelites from lode gold deposits.

To date, a collection of more than 70 samples of scheelite has been acquired from active or past-producing gold mines, or gold prospects within known mining camps. Forty-four samples have been analyzed by instrumental neutron activation (INAA) for their trace element, including REE, contents. All samples in this study come from vein systems that were mined for gold, including several samples that

contain visible native gold. The scheelite neutron activation analyses presented here (number of samples analysed indicated in parentheses) include;

- (a) Val d'Or area: Sigma mine (9), Pascalis mine (15)
- (b) Timmins area: Hollinger mine (6), McIntyre mine (1), Coniaurum mine (1), Dome mine (3), and Preston East Dome mine (1),
- (c) Geraldton-Beardmore area: Leitch mine (2), Hard Rock mine (3), Little Long Lac mine (1)
- (d) Lake Head Gold mine (1), and
- (e) Pickle Crow mine (1).

In addition, many of these samples have also been analysed by electron microprobe for strontium contents, and by isotope dilution for Rb, Sr, Sm and Nd (see below and Chapters 4 and 5).

Scheelite is a common gangue mineral in many Archean lode gold deposits, and paragenetic relationships between scheelite and gold have been documented at the Sigma mine (Robert and Brown, 1986b) and at the Hollinger and McIntyre mines (Wood, 1983; Wood et al., 1986; Allen and Folinsbee, 1944). In all of these deposits, and also in polished thin sections of samples studied by the author from the Geraldton-Beardmore area, the scheelite predates, or is contemporaneous with, gold deposition in the veins. Gold is commonly hosted in fractures within scheelite grains at the Sigma and Hollinger mines (Robert and Brown, 1986b; Wood et al., 1986), and Allen and Folinsbee (1944) noted a spatial relationship between scheelite in the veins and high gold values at the Hollinger mine. Scheelite is an integral part of the hydrothermal

vein assemblage and does not represent a remobilized phase from the wallrocks, or a later alteration phase superimposed on the vein mineralogy.

3.1.1 Trace Element Abundances in Hydrothermal Minerals

Morgan and Wandless (1980) concluded from their study of the REE distribution in some hydrothermal minerals that "... although complex formation may have an influence on the absolute values of partition coefficients, the relative REE pattern in a simple hydrothermal mineral is governed largely by the ionic radius of the major cation," i.e. the REE closest in ionic radius to the size of the major substitutional sites are preferentially incorporated in the crystal structure. Minerals with large major ions such as Ca^{2+} (1.08 Å) favour replacement by the largest (lightest) REE ions (Morgan and Wandless, 1980).

Fryer and Taylor's (1987) study of the REE distributions in uraninites from a variety of hydrothermal mineral deposits showed that these minerals exhibit wide variations in REE abundances and patterns. As the variations in patterns and abundances of the REE were recorded by one mineral phase, and assuming that the crystallographic site for substitution of the REE remained the same, Fryer and Taylor (1987) suggested that the composition of the hydrothermal fluid from which the uraninites were deposited may be an important control on the REE distributions in the uraninites. This implies that the REE patterns in these hydrothermal uraninites may be reflecting the REE patterns in the fluids, and may not be governed solely by the crystallographic controls on the substitution site.

Previous studies of the REE content of scheelite (Cottrant, 1981; Guion, 1984; Guion et al., 1985; Raimbault, 1985; Richard et al., 1981; Guiliani et al., 1987; Yuxue et al., 1990) indicate that scheelites from different mineral deposit types have distinct variations in REE patterns that may characterize specific mineralizing environments, including oxidation states. Most notably, scheelites from different hydrothermal deposit types exhibit different Eu anomalies, some positive, some neutral, and some negative.

3.2 MINERAL CHEMISTRY OF SCHEELITE

The two basic structural types of the $R^{+2}WO_4$ tungstates, are scheelite and wolframite. Generally small cations such as Mg, Zn, Ni, Fe and Mn form tungstates of the wolframite-type structure, whereas large cations such as Ca, Sr, Pb and Ba form the scheelite-type tungstates. The scheelite-type structure has tetragonal symmetry, the divalent cation occupies an 8-coordinated position and the tungsten ion has a distinct 4-coordinated position (Morell, 1978).

Baumer et al.'s (1980) experimental study of scheelite-ferberite transformations under hydrothermal conditions showed that scheelite stability is enhanced in hydrothermal fluids by the presence of an increased Ca/Fe ratio and CO_3^{2-} or Na^+ concentration in the hydrothermal fluid. Scheelite is found in "rather carbonate and calcium rich, basic..." environments, while wolframite is found in "rather carbonate poor, more acidic and F rich..." settings (Baumer et al., 1980).

Cottrant (1981) established that the REE in scheelite are hosted in the Ca^{2+} site and suggested that scheelites show a slight preference for LREE over HREE, as predicted from the similarity in ionic radius of the LREE and Ca^{2+} . Because the scheelite/fluid partition coefficients appear to be very high for the REE, the scheelite REE patterns may therefore reflect that of the fluid from which they were precipitated.

3.3 SAMPLE LOCATIONS

Gold mineralized areas sampled for scheelite include the Val d'Or gold mining camp in eastern Abitibi subprovince, the Timmins-Porcupine camp in western Abitibi, the Geraldton-Beardmore area of the eastern Wabigoon subprovince and one sample each from the Lake Head gold occurrence near Thunder Bay in the Shebandowan subprovince and the Pickle Crow gold deposit in the Uchi subprovince.

Samples were obtained from underground sampling by the author at Sigma, Pascalis and Siscoe Extension mines in Val d'Or. Some Val d'Or scheelites were provided by F. Robert of the Geological Survey of Canada (GSC) and D. Burrows (Inco Research, Sudbury).

Timmins samples were obtained from the collections of the GSC, several samples were provided by D. Burrows, and several from the Queen's University Economic Geology collections. Also two samples from the Dome mine were provided by D. Rogers, former mine geologist, and one by R. Thorpe (GSC). The Preston East Dome mine sample was collected by the author from the mine dump.

Beardmore-Geraldton samples were obtained from the GSC collections and from investigation of the mine dumps with a UV lamp. The Lake Head and Pickle Crow samples were obtained from the GSC collections.

3.3.1 Relationship of Scheelite and Gold

Scheelite is a common gangue mineral in Archean lode gold deposits (Boyle, 1979). Many large gold mines in the Superior Province produced some scheelite concentrates during the 1940's. Scheelite is a common indicator mineral for gold in lode quartz veins, however, the relationship between scheelite and gold is not clearly understood. Allen and Folinsbee (1944) noted a close relationship between scheelite and the felsic porphyries cross-cut by gold-bearing veins at the Hollinger mine. Wood (1983) states that miners "... note an empirical relationship of higher ore grades where scheelite occurs" at the Hollinger mine.

While the exact relationship between scheelite and gold is not well understood, it should be noted that scheelite is a hydrothermal vein gangue mineral in all of the deposits sampled. Although many of the samples do not contain visible gold in the same hand sample, all were collected from veins that were mined for gold (possible exceptions include those samples for which precise locations are unavailable).

Paragenetic studies on the vein mineralogy, including studies at Sigma (Robert and Brown 1986b), Pascalis (Tessier, 1990) and Hollinger (Wood et al., 1986), and observations on the samples collected for this study, indicate that scheelite is a relatively early hydrothermal phase in the veins and appears to consistently pre-date

gold mineralization in the vein-filling sequence. As noted above, the scheelites in all cases appear to be an integral part of the hydrothermal vein filling event and therefore are assumed to be closely related to the fluid(s) responsible for the gold mineralization.

3.4. ANALYTICAL METHODS

3.4.1 Sample Preparation

Samples were crushed in a small steel jaw crusher, followed by an agate cone crusher or agate mortar and pestle, and sieved, using copper or nylon mesh sieves, into two fractions, -100+200 and -200 mesh. The coarser fraction was purified by superpanning (and in a few cases heavy liquid techniques) followed by washing with acetone. A Frantz magnetic separator was used for further purification. Sample purity was checked using a binocular microscope. A few of the samples (notably, 85-014, 85-015, 85-016, 85-017, 85-022) contained sulphides (pyrite and arsenopyrite), and the two Leitch samples contained tellurides (85-001 and 85-015), up to a maximum of approximately 2% by volume (based on a visual estimate using a binocular microscope). The sulphides could not be removed as they have the same specific gravity and magnetic susceptibility as scheelite.

3.4.2 Neutron Activation Analyses

The scheelites were analyzed by instrumental neutron activation (INAA), in the laboratories of Nuclear Activation Services (NAS), and X-Ray Assay Labs. (XRAL), in Hamilton, Ontario, for a selection of trace elements including the REE. Analytical techniques are given in Appendix 2.

The presence of appreciable quantities of tungsten in scheelite presents a problem in neutron activation analysis (Appendix 2). The two REEs most likely to be affected by the interference caused by the tungsten activity are La and Sm. Yb may also be affected. Other trace elements for which the W may cause significant interference include Na, Mo, Au, and U. In addition, the presence of considerable background radiative activity due to the abundance of tungsten in these samples raises the detection limits for many of the other trace elements. For these reasons, the data are treated only as qualitative indicators of relative REE and other trace element abundances.

Uranium and thorium also produce interferences with the REE determinations during neutron activation analysis. It is difficult to assess how much of a problem this is with the scheelites analysed in this study because reported U and Th abundances show poor analytical reproducibility, or are reported as below detection limits (many analyses reported as "less than" some value).

Estimates of the reproducibility of the neutron activation data are presented in Appendix 2.

3.4.3 Isotope Dilution Analyses

Rb, Sr, Sm, and Nd concentrations were also determined by isotope dilution analysis (see Chapter 4 for Rb and Sr, and Chapter 5 for Sm and Nd, isotopic analyses of scheelite). The analytical methods and estimates of the reproducibility of the analyses are presented in Appendix 3.

3.4.4 Electron Microprobe Analyses

Neutron activation analyses of scheelites indicate very high abundances of Sr in some of the scheelites. Electron microprobe (EMP) analyses of the Sr content of scheelites were performed by G. LeCheminant (Mineralogy Division, Geological Survey of Canada), to determine if the EMP could reliably analyse for Sr in scheelite, and if so, to determine if there was any zonation of Sr concentration in the scheelite grains. Polished thin sections of massive vein scheelites from several Archean Au deposits were analyzed using the CAMECA routine TRACE. Strontianite was used as a standard. A scheelite, which had been analyzed by INAA as containing 100 ppm Sr was used as a "blank" or zero point. For each sample ten random spots were analyzed over the largest area of massive scheelite in the slides. In addition, a few analyses of the Sr content of carbonates were performed by J. Stirling, (Mineralogy Division, Geological Survey of Canada). Polished thin sections of several Sigma mine vein samples containing carbonate in the vein and in altered wallrock were analysed for a preliminary estimate of Sr content.

3.4.5 Comment on the Comparison Between the Different Analytical Techniques

A comparison of the results by the different analytical methods is given in Appendix 4. In summary, there is a fairly good linear correlation between Sm analyses by isotope dilution and by neutron activation analyses, however the INAA consistently underestimates Sm concentration compared with the isotope dilution analyses. The correlation between Nd analysis by isotope dilution and by INAA is not as good as for Sm. The INAA method also underestimates the Nd concentration. For the most part the INAA analyses appear to underestimate Sr concentrations, particularly in the high Sr (greater than 5000 ppm Sr) samples.

The range of and mean values obtained by EMP analysis, for individual samples, show a wide range in measured Sr concentrations in the high Sr content scheelites, but a good overall agreement between the average EMP data and the INAA and isotope dilution analyses in most of the samples with average Sr less than 6000 ppm. In the higher Sr content scheelites (greater than 6000 ppm), the EMP average analysis is consistently higher than the isotope dilution and NA data.

3.5 RESULTS

Forty-four scheelite samples were analysed by neutron activation analysis for 8 rare earth elements (REEs) (La, Ce, Nd, Cm, Eu, Tb, Yb, Lu) and 22 other trace elements (As, Au, Ba, Br, Co, Cr, Cs, Fe, Hf, Mo, Na, Ni, Rb, Sb, Sc, Se, Sr, Ta, Th, U, W, and Zn). The samples analysed include; 24 Val d'Or scheelites (3 repeat

analyses), 8 Timmins (Hollinger-McIntyre-Coniaurum) samples (2 repeats); 4 other Timmins samples (3 Dome and one Preston East Dome, 2 samples repeated, one 6 times), 6 Wabigoon subprovince samples, one Shebandowan belt sample (Lake Head), and one Uchi Belt sample (Pickle Crow) (6 of these latter samples repeated). Sixty-two INAA analyses are reported.

Trace elements not reported in the tables below include Br, Cs, Hf, Rb, Se, and Ta because they were consistently reported below the detection limit. Data for Na were also omitted because of poor reproducibility and abundances commonly reported below the detection limit (probably due to the W interference). W, consistently reported as greater than 60,000 ppm, was not included in the tables.

3.6 DISCUSSION

The data indicate that scheelite typically contains several tens of ppm of REE (sum of REE analysed (excluding La - see below) range from less than 10 to greater than 400 ppm). (Note that in the tables many values are reported as "less than" the value listed. These "less than" values represent the elevated detection limits of the analyses due to the tungsten activity. In the plots of these data, the "less than" values are assigned a value equal to half their reported "less than" value.) Most scheelites analysed also contain greater than 100 ppm Sr and several samples contain greater than 10000 ppm. Rubidium is essentially absent in all specimens.

The quality of the data for the other trace elements, as indicated by repeat analyses (see Appendix 2), is poor for all elements reported except Ni, Sc, and Th.

Ni values are reported consistently for all repeat samples except Dome (86-033). Sc and Th show good agreement between most repeated analyses, but the values are very low. Because of the apparently poor quality of the INAA data for most of the trace elements, the discussion of the trace element data is brief and qualitative only.

3.6.1 Trace Elements Other than Sr and REE

The trace element data for elements other than the REE are presented in Tables 3.1, 3.2, 3.3 and 3.4.

3.6.1.1 Au, As, Co, Fe, and Sb

Gold (Au): Thirty-one out of 62 scheelite analyses reported Au above detection limits. (Note the variable detection limits due to the tungsten background. Gold values were not determined in analytical batch F due to the tungsten interference). The reported values range from 18 to 1,000,000 ppb. The high gold values probably represent inclusions of gold in the scheelite.

Arsenic (As): Only 10 of the 62 analyses are above detection levels. In most of these cases, relatively high Fe analyses are also reported.

Cobalt (Co): Thirty-six of the scheelites analysed have Co values above detection limits. However, duplicates are generally not in good agreement. The maximum value reported is 18 ppm in sample 85-014 (good agreement between duplicate samples) and 17 ppm in sample 85-016 (poor agreement between duplicates). Fifty-three of the analyses are reported as 2 ppm or less (including those reported as below detection limits).

Table 3.1 Trace Element Neutron Activation Analyses of Val d'Or Scheelites

LOCATION	SAMPLE	As	Au(ppb)	Ba	Co	Cr	Fe%	Ni	Mo	Sb	Sc	Sr	Zn	Th	U
SIGMA	D 85-009	<12	<33	<200	5.3	2.3	<0.005	250	<13	<0.7	0.06	<100	<10	<0.2	<3.4
SIGMA	D 85-010	<20	1	1800	0.2	2.4	0.023	250	<2	17.0	2.25	200	100	<0.2	1
SIGMA	C 85-011	<67	<83	<80	<0.3	1.6	0.026	220	41	12	0.05	200	<10	<0.2	25.2
SIGMA	B 85-011	<100	<150	<500	<0.5	1.5	0.046	200	150	23.0	0.06	200	55	<0.5	<0.5
SIGMA	C 85-012	<61	<97	<70	0.4	<1.5	<0.017	400	<2	16	0.06	300	<10	<0.2	38.0
SIGMA	B 85-012	<100	<150	<1000	<0.5	1.5	0.010	330	80	2.7	0.05	100	70	<0.2	0.2
SIGMA	B 85-013	<100	29000	<1000	<0.5	1.8	0.013	120	100	11.0	0.14	200	33	<0.3	0.1
SIGMA	C 85-014	130	6700	<110	18.0	3.0	1.420	190	<2	<1.8	0.58	<100	180	<0.2	27.7
SIGMA	B 85-014	100	1800	<500	18.0	3.8	1.010	220	10	17.0	0.31	200	140	<0.2	0.1
SIGMA	D 87-049	<25	31000	<70	0.5	4.4	0.043	310	<15	<3.0	2.05	200	<10	<0.2	1
SIGMA	D 87-050	83	2700	<100	2.4	3.6	0.769	230	<38	12.0	0.83	200	<10	<0.2	1
SIGMA	D 87-051	390	20	<80	<0.1	5.7	0.020	80	<2	0.7	0.05	300	<10	<0.3	1
PASCALIS	D 86-036	<16	1	<130	0.2	3.3	0.034	180	<2	8.6	1.61	500	50	<0.2	<0.1
PASCALIS	D 86-037	<16	<100	2300	0.1	3.4	<0.015	120	<2	5.9	1.66	700	50	<0.2	1
PASCALIS	F P-06	1	820	<500	7.0	<20	0.428	110	1	3.7	<0.03	<100	1	<0.5	1
PASCALIS	F P-09	1	<100	<500	<0.5	<20	0.076	120	1	6	<0.03	<100	1	<0.5	1
PASCALIS	F P-15	1	<100	<500	<0.5	<20	0.036	130	1	4	<0.03	<100	1	<0.5	1
PASCALIS	F P-16	1	<100	<500	<0.5	<20	0.029	70	1	4.3	<0.03	<100	1	<0.5	1
PASCALIS	F P-19	1	<100	<500	<0.5	<20	<0.020	160	1	3.6	<0.03	<100	1	<0.5	1
PASCALIS	F P-20	1	<100	<500	<0.5	<20	<0.020	200	1	3.4	<0.03	<100	1	<0.5	1
PASCALIS	F P-21	1	<100	<500	<0.5	<20	0.039	140	1	2.1	<0.03	<100	1	<0.5	1
PASCALIS	F P-27	1	1300	<500	<0.5	<20	0.341	170	1	2.8	<0.03	<100	1	<0.5	1
PASCALIS	F P-28	1	14000	<500	<0.5	<20	0.132	190	1	2.9	<0.03	<100	1	<0.5	1
PASCALIS	F P-29	1	<100	<500	<0.5	<20	<0.030	190	1	4.1	<0.03	<100	1	<0.5	1
PASCALIS	F P-30	1	<100	<500	<0.5	<20	<0.020	230	1	2.8	<0.03	<100	1	<0.5	1
PASCALIS	F P-32	1	<100	<500	<0.5	<20	<0.020	120	1	1.6	<0.03	<100	1	<0.5	1
PASCALIS	F P-37	1	<100	<500	<0.5	<20	0.043	200	1	2.8	<0.03	<100	1	<0.5	1

FOOTNOTES (for Tables 3.1 to 3.4 and 3.8 to 3.12):

Letters in the second column refer to INAA analytical batch: A = XRAL26275, B = NAS3687, C = NAS8229, D = NAS10547, E = NAS11999, F = XRAL11156.

< sign indicates values reported as "less than" the value indicated (elevated detection limits due to tungsten interferences).

1 indicates value not determined due to interferences.

All values are in ppm except where noted (ie. gold values are reported in ppb).

Table 3.2 Trace Element Neutron Activation Analyses of Hollinger-McIntyre-Coniaurum scheelites.

LOCATION	SAMPLE	As	Au (ppb)	Ba	Co	Cr	Fe%	Ni	Mo	Sb	Sc	Sr	Zn	Th	U
Coniaurum	A 85-022	<48	1600	910	1.7	<12.0	5.200	540	54	4.9	<0.05	900	140	20.0	24.7
Hollinger	B 85-018	<100	8900	<500	0.6	4.4	0.045	300	100	2.4	0.03	1100	20	<0.5	0.7
Hollinger	D 87-048	<30	<30	1200	0.4	3.4	<0.026	360	<2	11.0	1.60	1100	<10	0.5	1
McIntyre	B 85-019	<100	<50	<500	<0.5	<2.0	0.350	520	100	5.1	0.30	<100	20	<0.2	0.1
McIntyre	C 85-019	<63	180	90	0.3	1.9	0.061	490	<23	30.0	0.29	100	<10	0.4	35.4
Hollinger	E 87-059	1	300	900	<0.5	<10.0	0.130	200	1	6.0	<0.10	<1000	<20	<0.5	<1
Hollinger	E 88-040H	<20	400	<200	1.6	<10.0	<0.050	300	70	7.0	0.10	2000	<20	<0.5	<1
Hollinger	E 86-039	1	300	1000	0.9	30.0	<0.050	300	180	8.0	<0.10	<1000	<20	<0.5	<1
Hollinger	E 86-040	<20	300	700	<0.5	10.0	<0.050	300	<20	6.0	0.10	2000	<20	0.7	<1
Hollinger	E 86-042	<20	300	600	0.8	<10.0	<0.050	300	<20	6.0	<0.10	<1000	<20	<0.5	<1

Table 3.3 Trace Element Neutron Activation Analyses of the Dome and Preston East Dome Mine Scheelites

LOCATION	SAMPLE	As	Au(ppb)	Ba	Co	Cr	Fe%	Ni	Mo	Sb	Sc	Sr	Zn	Th	U
DOME	C 85-017	<60	230	<180	5.8	10.0	0.901	150	<17	9.6	0.04	1200	180	0.3	44.6
DOME	B 85-017	<100	<150	<500	1.1	<1.0	0.120	170	100	3.5	0.04	1300	<30	0.5	6.5
DOME	D 86-033-1	<77	1	380	0.2	1.3	0.022	80	<3	8.7	2.40	400	<10	0.2	1
DOME	D 86-033-2	110	1	650	0.2	3.0	<0.005	250	<2	12.0	17.50	900	<10	0.6	<0.1
DOME	D 86-033-3	<38	1	<160	<0.2	3.7	0.066	260	<2	21.0	2.20	1000	<10	0.6	1
DOME	D 87-033-4	330	18	<70	0.4	3.0	0.019	60	<2	0.5	0.10	1000	1300	0.5	<1.4
DOME	F 86-033-5	1	<100	<500	<0.5	<20.0	0.059	280	1	7.4	<0.03	<100	1	<0.5	1
DOME	F 86-033-6	1	<100	<500	<0.5	<20.0	<0.020	300	1	3.0	<0.03	<100	1	<0.5	1
DOME	B 85-003	<100	640000	<1000	0.7	2.1	0.037	270	<50	23.0	0.04	700	<50	0.5	1.6
DOME	C 85-003	<61	520000	<100	0.7	3.0	0.059	240	<31	13.0	0.04	800	<20	0.5	66.4
Preston E.D.	D 86-035-2	1	1	<160	0.2	2.9	0.724	280	<2	22.0	1.90	1100	150	0.3	1

Table 3.4 Trace Element Neutron Activation Analyses of Wabigoon Subprovince and Pickle Crow Mine Scheelites.

LOCATION	SAMPLE	As	Au(ppb)	Sa	Co	Cr	Fe%	Ni	Mo	Sb	Sc	Sr	Zn	Th	U
Hard Rock	C 85-002	<78	<120	<100	0.3	3.3	0.035	150	<17	12	0.04	5100	<10	0.3	<4.3
Hard Rock	B 85-002	100	700	<1000	<0.5	3.0	0.037	120	<50	4.1	0.03	5700	<10	0.4	2.0
Hard Rock	D 86-032-1	<80	1	710	0.2	3.3	0.016	130	<2	18.0	15.00	5300	20	0.3	9.0
Hard Rock	D 86-032-2	<80	1	<50	0.6	2.3	0.213	120	<2	9.5	0.00	4400	<10	0.2	1
Little LL	A 85-021	<35	<50	<260	0.4	25.0	0.020	<60	46	<1.2	<0.05	10000	<8	3.2	<5.0
Little LL	C 85-021	<60	200	<40	0.2	0.6	0.038	<50	<2	2.4	0.06	25000	<10	0.3	44.6
Leitch	B 85-001	<100	1.0*10 ⁹	<500	<0.5	<4.0	0.037	<70	<50	2500.0	0.10	6200	110	<0.4	6.3
Leitch	C 85-001	<92	910000	370	<0.7	3.0	0.056	80	<22	1900.0	0.11	4700	110	1.0	1
Leitch	C 85-015	860	94000	<60	2.3	9.6	1.050	50	<2	17	0.63	5100	30	1.0	46.3
Leitch	B 85-015	100	650	<500	0.3	2.0	0.080	<50	100	8.2	0.23	5300	33	1.1	7.6
Lake Head	C 85-020	<60	110	20	0.2	0.7	0.041	<50	<13	1.1	0.14	8000	<10	0.2	<2.6
Lake Head	A 85-020	<45	650	<400	0.2	29.0	3.500	<60	18	<1.2	0.12	10000	<8	<2.0	10.0
Pickle C.	A 85-016	<43	10000	890	0.4	30.0	.200	<70	31	<1.2	0.17	<100	<10	<2.2	<6.0
Pickle C.	C 85-016	170	13000	<80	17	1.7	4.370	70	<17	4.5	0.09	2200	<30	0.2	41.7

Iron (Fe): Forty-seven of the analyses are reported above detection limit. Most of the duplicate samples show good general agreement. Elevated Fe contents can be correlated, in most cases, with high sulphide contents. It is difficult to determine whether inconsistencies between duplicate analyses are due to analytical problems or sample inhomogeneity.

Antimony (Sb): Fifty-six Sb analyses are reported above detection limits. Extremely high values relative to other samples are reported for duplicates of sample 85-001 from the Leitch mine in Beardmore (2500, 1900 ppm). This sample also contains the highest Au analyses of all scheelites analysed (910,000 and 1,000,000 ppb). These extreme Sb values are probably due to tellurides, commonly associated with gold mineralization at the Leitch mine.

Comment on Au, As, Co, Fe and Sb in scheelite:

Gold mineralization is commonly associated with tellurides at the Leitch mine (J. Mason, pers. comm. 1982), and is commonly associated with tellur-bismuth at Sigma (Robert et al., 1983). Tellurides are also reported from the Pascalis mine but are extremely rare (Tessier, 1990). Tellurides were identified in samples 85-001 and -015 from the Leitch mine.

Scheelite separates with significant pyrite content include 85-001, -003, -014, -015, -016, -017, -022, and 86-032. Minor pyrite may also be present in samples 86-039, 87-049, -050, P-06, -09, -27, -28 and -29. In almost all of the samples with significant pyrite content, Fe values are relatively high. In many of these cases the high Fe values are also associated with relatively high Au, Co and Sb and, in some

cases, As abundances. For example, Au, Fe, and Sb (+/-As) seem to be positively correlated in samples 85-014, 85-015, 87-050, 85-001 and 85-003. Sample 85-022 also has high As, Au Fe and Sb, but As is reported below detection limit. Repeat analyses of 85-017 are poor for Co, Fe and Au. There appears, however, to be a consistent positive correlation between the levels of these three elements and Cr as well, suggesting some sample inhomogeneity perhaps related to included phases within the scheelite, likely sulphides. A similar relationship is seen in sample 85-015.

3.6.1.2 Ni, Mo, Sc, Zn, Th, U and Ba

Nickel (Ni): Fifty-five samples had Ni contents above detection limit (which is reported as varying from 50 to 100 ppm, due to variable effects of the W interference). Average Ni contents range from 365 ppm in Hollinger-McIntyre-Coniaurum samples (n=10), 210 ppm in Dome samples (n=11), 190 ppm in Val d'Or scheelites (n=27), and 103 in scheelites from the other subprovinces (n=7, 7 samples below detection limits). The Ni values do not seem to show any correlation with Fe, Co or As abundances.

These variable Ni values could reflect the presence of ultramafic rocks, which are relatively common in the Timmins area, and the absence of them in the immediate areas around the deposits in the Val d'Or, Geraldton and other areas. It is uncertain from these data if the Ni is residing in included phases or in a crystallographic site within the scheelite. The good agreement, however, between replicates suggest that the Ni may be incorporated within the crystallographic structure of the scheelite, rather

than included in other mineral phases.

Molybdenum (Mo): Only 15 analyses are reported that indicate Mo above the detection level. Mo is one of the trace elements most likely to suffer interference from W activation during NA analysis. These data are therefore considered unreliable and will not be dealt with further.

Scandium (Sc): Although Sc analyses show good reproducibility, the majority of Sc analyses are less than 1 ppm.

Zinc (Zn): The Zn analyses are also generally low and reproducibility is poor.

Thorium (Th): The Th analyses agree well between duplicates, however the values are (with one exception) very low. Thirty-eight samples were reported as below detection limits.

Uranium (U): The U analyses exhibit a few high values, but duplicate analyses are not in good agreement. There appears to be an analytical bias in that the analytical batch "C" were reported with significantly higher values than the duplicate result from batch "B" 8 out of 9 times, and greater than batch "A" 2 out of 3 times. These data are considered unreliable.

Barium (Ba): Only 15 of 62 analyses yielded values above detection limits. Reported detection limits vary from 40 to 1000 ppm (due to the W interference). In spite of this very limited data set, a broad generalization can be made. The Val d'Or samples show the highest Ba content (n=2) followed by the Hollinger-McIntyre-Coniaurum samples (n=7) while Dome and other scheelites contain slightly lower Ba (n=2 and 4 respectively). There may be a correlation with wallrocks (Val d'Or is

more related to sediments than the other deposits), however, the number of analyses reported above detection limits is small and these data are therefore not considered further.

3.6.2 Strontium in Scheelites

Strontium concentrations in scheelites were determined by INAA (40 out of 62 analyses reported Sr above detection limits. See Tables 3.1, 3.2, 3.3, and 3.4), electron microprobe (EMP) analyses of 18 polished thin sections (Table 3.5), and isotope dilution (ID) analyses of 31 samples (Table 3.6, also see Tables 4.1 and 4.2 in Chapter 4). A summary of all Sr analytical results is presented in Table 3.6. The maximum, minimum, and average Sr contents for scheelites from each mine sampled are plotted in Figure 3.1, and EMP results are plotted in Figure 3.2.

Electron microprobe analyses indicate that there is a significant variation in Sr contents within individual samples (on the scale of a polished thin section). The mean of the EMP Sr analyses are in good agreement with INAA and ID results, however, the values are variable, with the greatest variation observed in those scheelites that contain the most Sr. No visible zonation was detected under the optical microscope or with backscattered electron images of these scheelite samples, and the variation within the scheelite grains appears to be random (G. LeCheminant, pers. comm. 1987).

Figure 3.1 shows that the range of Sr contents in scheelites from individual deposits is more restricted than the total Sr range for all scheelites analysed from Superior Province gold deposits. There appear to be significant differences in Sr

Table 3.5 Electron Microprobe Analyses of Sr in Scheelite.

LOC.	SAMPLE NO.	RANGE: MIN	MAX	MEAN	INAA	ID
S	85012	0	690	101	100	320
S	85011	0	380	177	200	
S	85014	0	720	294	200	
P	86037	170	1240	584		
P	86036	60	1220	756		678
C	85022	0	1470	775	9000 [†]	643
D	86033	0	1050	567		
D	85003	390	1640	1027	700	
PE	86035	0	2000	652		1355
PE	86035B	720	1550	1174		1355
PE	86035A	220	2420	1250		1355
HR	86032	5170	7530	6130		
HR	85002	5280	10050	7070	5700	
HR	86032	6390	8710	7730		
L	85015	5310	7390	5509	5300	
LH	85001	6960	14350	9650	6200	
LL	85021	6970	28010	18014	10000 [*]	11260

Abbreviations:

S = Sigma mine, Val d'Or

P = Pascalis mine, Val d'Or

PE = Preston East Dome mine, Timmins

D = Dome mine, Timmins

C = Coniaurum mine, Timmins

L = Leitch mine, Beardmore

LL = Little Long Lac mine, Geraldton

HR = Hard Rock mine, Geraldton

ID = Isotope Dilution

INAA = Instrumental Neutron Activation Analyses

Notes: Electron microprobe analyses consist of ten random spots analysed over the largest possible area of scheelite in each polished thin section.

[†]INAA value for sample number 85022 was reported as 9000. This is likely a reporting error and a value of 900 seems much more consistent with the other analytical results, and the tendency for INAA to underestimate Sr abundances in scheelite. A value of 900 ppm is used in all other plots and tables.

Table 3.6 Summary of Strontium Analyses by INAA, ID, and EMP.

LOC.	Sample	INAA	ID	EMP	Avg. Sr	n	LOC.	Sample	INAA	ID	EMP	Avg. Sr	n
S	D 85-009	<100	338				C	A 85-022	900	643	775		
S	D 85-010	200					C	85-022a				773	3
S	C 85-011	200		177			H	B 85-018	1100	1260			
S	B 85-011	200					H	E 86-039	<1000	1248			
S	C 85-012	300	320	101			H	E 86-040	2000				
S	B 85-012	100					H	E 88-040H	2000	1523			
S	B 85-013	200					H	E 86-042	<1000	1571			
S	C 85-014	<100		294			H	D 87-048	1100				
S	B 85-014	200					H	E 87-059	<1000				
S	D 87-049	200	313				H	EW-167		1278			
S	87-049H		316				H	EW-168					
S	D 87-050	200					H	EW-169			1215	12	
S	D 87-051	300	350				M	B 85-019	<100	121			
S	S-01		231				M	C 85-019	100				
S	S-03						M	88-060w			90	3	
S	S-04		221				D	C 85-017	1200				
S	S-05		244				D	B 85-017	1300				
S	S-08		238				D	D 86-033-1	400		567		
S	S-09		253				D	D 86-033-2	900				
S	S-10		214				D	D 86-033-3	1000				
S	S-11		210		223	27	D	D 86-033-4	1000				
P	D 86-036	500	678	756			D	F 86-033-5					
P	D 86-037	700		584			D	F 86-033-6					
P	87-055		661				D	Av. 033	825	1129			
P	F P-06		546				D	B 85-003	700		1027		
P	F P-09						D	C 85-003	800			911	11
P	F P-15						PED	D 86-035-2	1100		1174		
P	F P-16		560					86-035-1		1355	1250	1220	4
P	F P-19						HR	C 85-002	5100		7070		
P	F P-20		555				HR	B 85-002	5700				
P	P-20a		563				HR	D 86-032-1	5300		7730		
P	F P-21						HR	D 86-032-2	4400		6130	5919	7
P	F P-27						L	B 85-001	6200		9650		
P	F P-28						L	C 85-001	4700				
P	F P-29						L	C 85-015	5100		5509		
P	F P-30		676				L	B 85-015	5300			6077	6
P	F P-32		667				LLL	A 85-021	10000	11260	18014		
P	F P-37		698		626	13	LLL	C 85-021	25000			16069	4
SE	SE-1		1856				LH	C 85-020	6000	6862			
	SE-1(A)				1856	1	LH	A 85-020	10000			7621	3
							PC	A 85-016	<100				
							PC	C 85-016	2200			1125	2

Notes: Where INAA values are reported as < 'detection limit', the average is calculated on the basis of assigning one half of the 'detection limit' value.

Letters in the second column refer to INAA analytical batch number (see footnotes to Table 3.1).

Figure 3.1. A) Average Sr abundance in scheelites by all methods (Table 3.6). Note, the average EMP value for each sample analysed was used in calculating the overall average for each deposit. The areas from which the samples were obtained are identified by different shadings. Abbreviations: S = Sigma, P = Pascalis, SE = Siscoe Extension, H = Hollinger, M= McIntyre, D = Dome, PED = Preston East Dome, HR = Hard Rock, LLL = Little Long Lac, L = Leich, LH = Lake Head, PC = Pickle Crow. Number of values used in calculating the averages are given in brackets below the locality identifiers; B) Maximum, minimum and mean values of data in (A).

Figure 3.2. Electron microprobe analyses of Sr abundance in scheelites (maximum, minimum and mean values). Seventeen polished thin sections of scheelite from nine different deposits in the Superior Province were analysed. One large grain/crystal of scheelite was analysed in each polished section and ten spot analyses were done per grain. The results are also presented in Table 3.5. The average Sr content by INAA and by ID are plotted for comparison.

contents of scheelites between deposits in the Abitibi greenstone belt (Timmins and Val d'Or) versus those in the Wabigoon and Shebandowan subprovinces (Figure 3.1, and 3.2)

In the Val d'Or area, the variation in content of strontium within scheelite samples from a single deposit is relatively restricted. At Sigma the scheelite Sr contents range from <100 to 338 ppm (n=27), with an average value of 223 ppm (all methods). Similarly, the Pascalis mine samples also have a relatively restricted range of Sr contents, with Sr values ranging from 500 to 756 ppm, with an average value of 626 ppm (n=13). The single samples from the Siscoe Extension mine contains 1856 ppm Sr (ID).

In the Timmins area, the Hollinger-McIntyre-Coniaurum samples have Sr contents of <100 to 2000 ppm. The average Sr value reported for these deposits, by all methods, is 950 ppm (n=18). The McIntyre sample (one sample analysed twice by INAA and once by ID) has distinctly lower Sr contents than the Hollinger samples and the one Coniaurum sample. The Hollinger samples alone have average Sr of 1215 ppm (n=12). Scheelite samples from the other deposits in the Timmins area, the Dome and Preston East Dome mines, have Sr contents ranging from 400 to 1355 ppm and contain an average of 994 ppm Sr (n=15, all methods).

The Wabigoon and Shebandowan subprovince (Geraldton-Beardmore and Lake Head areas, respectively) scheelites have higher Sr contents than the scheelites from the Abitibi subprovince. The average Sr contents of these scheelites by individual

deposits are: Hard Rock = 5919 ppm (n=7); Leitch = 6077 ppm (n=6); Little Long Lac = 16069 ppm (n=4); Lake Head = 7621 ppm (n=3). The Pickle Crow sample was analysed for Sr by INAA only, however, duplicate analyses are not in good agreement (reported values are 2200 and <100 ppm).

3.6.2.1 Significance of Sr Content and Variations in Scheelite

The Sr^{2+} ion is equivalent in charge to the Ca^{2+} , but has a slightly larger ionic radius than calcium, prefers 8-fold coordination positions, and thus is readily accepted into the Ca^{2+} position in scheelite. As scheelite is an integral part of the hydrothermal mineral suite in the gold-bearing veins, the Sr content of the scheelites is interpreted to reflect that of the fluid from which the scheelite precipitated.

The Sr content of the fluid may be influenced by many factors including:

- a) the Sr content the fluid derived in the original "source" area,
- b) Sr contributed to the fluid from the breakdown of wallrock minerals during alteration (particularly plagioclase altering to sericite+epidote+carbonate, a typical alteration reaction observed in wallrocks to gold-bearing veins), and
- c) partition coefficients between fluid and minerals (scheelite and other co-precipitating phases in the veins, for example, carbonate, albite, tourmaline and apatite, etc.).

The Sr content of the scheelites may also be influenced by Sr partition coefficients between scheelite and other co-precipitating phases, and by the abundance of other elements in the fluid (eg. Ca^{2+} , REEs $^{3+}$) that may be competing with the Sr

for the 8-fold co-ordination position in the scheelite.

A large variation (several orders of magnitude) is observed in the Sr content of scheelites from gold mineralization in different areas of the Superior Province. The Abitibi deposits fall in the range of 100 to 1000 ppm Sr in scheelite, while the Wabigoon scheelites contain 5000 to 10,000 ppm Sr and the Lake Head (Shebandowan) scheelites contain almost 8000 ppm Sr.

Table 2.1 reveals a difference in the dominant host rocks to the mineralization in the Abitibi area compared to the other greenstone belt deposits studied. The Abitibi deposits have mafic extrusive rocks as important hosts for mineralization, while in the other greenstone belts clastic and chemical sedimentary rocks appear to be more important hosts to ore. Felsic intrusive rocks are important hosts to ore in both groups of deposits and, in the deposits studied, are apparently lacking only at the Lake Head mine.

There is some evidence that the wallrock of the veins may influence the Sr content in the scheelites. In the Val d'Or camp, the Pascalis scheelites, which are from veins hosted entirely within the quartz diorite Bourlamaque batholith have a slightly higher average Sr content, and a more restricted range in values, than those from the Sigma mine, which is hosted in extrusive mafic volcanic rocks and porphyritic diorite intrusions. A detailed geochemical study of alteration profiles in porphyritic dykes at the Sigma mine (Ludden et al., 1984) suggests that Sr is released from breakdown of mafic mineral phases in the wallrocks and precipitated in vein minerals such as tourmaline.

The inhomogeneity of Sr within individual scheelite samples suggests that local controls such as alteration of immediate wallrocks, and the influence of co-precipitating phases, may play a role in determining the Sr content of the scheelite. To examine the Sr content in associated minerals, 6 polished thin sections of carbonate-bearing vein samples from the Sigma mine were submitted to J. Stirling at the Geological Survey of Canada for electron microprobe analysis. The data are presented in Table 3.7. In five of the six samples, carbonates entirely hosted within the vein were analysed. In sample S-10b, carbonate in the wallrock, approximately 1 cm from the vein margin, was analysed. Samples S-06, -07, -08 have Sr contents slightly greater than the Sr in scheelites from the same vein, while the carbonates in samples 85-011 and -014 have Sr contents very similar to the scheelite in the same samples (Table 3.1). A tourmaline and a carbonate sample from the Pascalis mine have also been analysed by ID for Sr and they both have Sr contents similar to the scheelite samples from the same veins. Surprisingly, the carbonate in the wallrock had no detectable Sr. This would suggest that Sr was not derived by the breakdown of wallrock minerals, but was introduced by the mineralizing fluid. The reasons for the differences in strontium content between districts, and within samples, are not entirely clear. These will be discussed further in light of the REE data below, and isotopic data presented in subsequent chapters.

The Sr contents are, in all cases, sufficiently high to directly measure the initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the ore-forming fluids. Because of the low Rb/Sr ratios of the scheelites, the Sr isotopic ratio should have remained relatively unaffected by

Table 3.7 Electron Microprobe Analyses of Carbonate

Sample # S-06

SrO	MgO	MnO	FeO	CaO	CO	Total
.080	2.098	1.487	2.139	56.038	27.963	89.806
.083	2.064	1.471	2.184	56.038	27.963	89.804
.091	2.101	1.493	2.164	56.038	27.963	89.850
.089	2.111	1.478	2.100	56.038	27.963	89.799
.086	2.134	1.500	2.146	56.038	27.963	89.868
.101	2.073	1.392	2.046	56.038	27.963	89.612
.096	2.071	1.395	2.139	56.038	27.963	89.702
.050	1.718	1.352	1.964	56.038	27.963	89.085
.013	1.749	1.280	1.912	56.038	27.963	88.955

n = 9

x (SrO%) = 0.0766

x (Sr ppm) = 650

Range (ppm) = 110 - 854

Sample # S-07

SrO	MgO	MnO	FeO	CaO	CO	Total
.001	0.673	1.038	0.539	56.038	27.963	86.253
.000	1.562	1.123	2.031	56.038	27.963	88.718
.086	1.817	1.294	1.966	56.038	27.963	89.165
.091	1.988	1.392	2.093	56.038	27.963	89.566
.080	1.754	1.269	1.937	56.038	27.963	89.043
.000	1.613	1.108	2.934	56.038	27.963	89.657
.064	1.250	1.170	2.211	56.038	27.963	88.697
.078	1.743	1.265	1.921	56.038	27.963	89.008

n = 8

x (SrO%) = 0.0500

x (Sr ppm) = 423

Range (ppm) = 0 - 770

Sample # S-08

SrO	MgO	MnO	FeO	CaO	CO	Total
.078	1.791	1.280	1.721	56.038	27.963	88.871
.080	2.209	1.487	2.286	56.038	27.963	90.064
.085	2.227	1.485	2.313	56.038	27.963	90.111
.093	1.749	1.349	1.950	56.038	27.963	89.144
.086	2.061	1.392	2.136	56.038	27.963	89.676
.089	2.137	1.380	2.231	56.038	27.963	89.839
.058	1.826	1.331	1.878	56.038	27.963	89.094
.072	1.796	1.369	1.846	56.038	27.963	89.084
.069	1.925	1.318	1.958	56.038	27.963	89.271
.083	2.003	1.360	2.027	56.038	27.963	89.474

n = 10

x (SrO%) = 0.0793

x (Sr ppm) = 670

Range (ppm) = 490 - 786

Sample # S-10b

SrO	MgO	MnO	FeO	CaO	CO	Total
.000	0.315	1.007	0.349	56.038	27.963	85.672
.000	0.043	0.868	0.054	56.038	27.963	84.966
.000	0.028	0.766	0.032	56.038	27.963	84.827
.000	0.172	0.881	0.198	56.038	27.963	85.253
.000	0.181	0.719	0.117	56.038	27.963	85.018

n = 5

x (SrO%) = 0.0000

x (Sr ppm) = 0

Range (ppm) = 0 - 0

Sample # 85-011

SrO	MgO	MnO	FeO	CaO	CO	Total
.011	0.119	1.311	0.134	56.038	27.963	85.576
.026	0.172	1.852	0.268	56.038	27.963	86.319
.012	0.161	1.433	0.371	56.038	27.963	85.978
.002	0.045	0.892	0.051	56.038	27.963	84.992
.015	0.091	1.048	0.067	56.038	27.963	85.223
.014	0.075	1.072	0.073	56.038	27.963	85.235

n = 6

x (SrO%) = 0.0133

x (Sr ppm) = 110

Range (ppm) = 20 - 220

Sample # 85-014

SrO	MgO	MnO	FeO	CaO	CO	Total
.004	0.201	1.291	0.223	56.038	27.963	85.719
.009	0.171	1.117	0.102	56.038	27.963	85.400
.071	1.353	1.487	1.611	56.038	27.963	88.524
.047	0.156	1.003	0.309	56.038	27.963	85.517
.032	0.980	1.342	0.987	56.038	27.963	87.342
.043	1.048	1.557	1.137	56.038	27.963	87.786

n = 6

x (SrO%) = 0.0343

x (Sr ppm) = 290

Range (ppm) = 35 - 600

2

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radiogenic addition of Sr throughout time. Petrographic studies indicate that the scheelite samples from the Val d'Or camp have not been affected by significant later deformation (other than fracturing), alteration or metamorphic effects, and thus the Sr isotopic composition should give a fairly reliable indication of the primary fluid composition, and perhaps help to resolve the problem as to whether the Sr and hence Au, is derived from mantle or crustal sources.

The scheelites from the Hollinger-McIntyre-Coniaurum, however, show evidence of more than one period of scheelite deposition, and in some cases, significant deformation subsequent to deposition. It could well be that the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios have been affected, but the apparent chemical resistivity of scheelite may prevent remobilization of the REEs and Sr by later events.

3.6.3 REE

The INAA REE analyses are presented in Tables 3.8, 3.9, 3.10 and 3.11. In addition, Sm and Nd contents of 37 scheelite samples have been determined by isotope dilution and these results are summarized in Table 3.12.

The REE contents within a single deposit or district are generally fairly uniform, but significant variations exist between groups of deposits. Maximum, minimum and average total REE (minus La (-La), due to the poor reproducibility of these data) are tabulated in Table 3.13. Plots of total REE content of scheelites, and plots of average chondrite-normalized REE patterns for each of the deposits sampled are presented below. The chondrite values of Taylor and Gorton (1977) are used.

Table 3.8 Rare Earth Element Neutron Activation Analyses of Val d'Or Scheelites.

LOCATION	SAMPLE	La	La(CN)	Ce	Ce(CN)	Nd	Nd(CN)	Sm	Sm(CN)	Eu	Eu(CN)	Tb	Tb(CN)	Yb	Yb(CN)	Lu	Lu(CN)
			0.315		0.813		0.597		0.192		0.0722		0.043		0.208		0.0323
SIGMA	D	85-009	108.0	342.9	46	57	69	116	53.5	278.7	38.1	527.7	25.5	520.4	10.1	48.6	27.24
SIGMA	D	85-010	102.0	323.8	26	32	37	62	29.9	155.7	27.3	378.1	20.3	414.3	10.6	51.0	26.32
SIGMA	C	85-011	7.9	25.1	33	41	47	79	29.0	151.0	34.3	475.1	19.2	391.8	11.4	54.8	24.77
SIGMA	B	85-011	7.8	24.8	38	47	48	80	27.7	144.3	37.0	512.5	16.0	326.5	6.3	30.3	25.39
SIGMA	C	85-012	14.2	45.1	81	100	149	250	38.6	201.0	53.1	735.5	21.1	430.6	12.0	57.7	35.60
SIGMA	B	85-012	9.6	30.5	57	70	68	114	40.0	208.3	47.0	651.0	16.0	326.5	11.0	52.9	33.75
SIGMA	B	85-013	7.2	22.9	11	14	5	8	9.1	47.4	15.0	207.8	8.6	175.5	14.0	67.3	34.30
SIGMA	C	85-014	11.9	37.8	33	41	15	25	37.9	197.4	31.7	439.1	21.7	442.9	14.4	69.2	60.06
SIGMA	B	85-014	9.9	31.4	36	44	45	75	37.0	192.7	34.0	470.9	30.0	612.2	13.0	62.5	27.86
SIGMA	D	87-049	13.0	41.3	46	57	61	102	52.6	274.0	32.9	455.7	22.1	451.0	10.6	51.0	33.75
SIGMA	D	87-050	90.7	287.9	35	43	58	97	49.7	258.9	28.1	389.2	24.1	491.8	11.6	55.8	32.20
SIGMA	D	87-051	19.8	62.7	72	89	100	168	64.5	335.9	56.3	779.8	27.7	565.3	3.0	14.4	47.99
PASCALIS	D	86-036	53.7	170.5	20	25	45	75	42.3	220.3	16.0	221.6	27.4	559.2	15.1	72.6	49.85
PASCALIS	D	86-037	42.8	135.9	17	21	41	69	36.1	188.0	15.2	210.5	25.8	526.5	12.7	61.1	40.87
PASCALIS	F	P-06	19.0	60.3	63	77	65	109	32.7	170.3	33.6	465.4	26.3	536.7	16.5	79.3	38.70
PASCALIS	F	P-09	15.0	47.6	61	75	72	121	36.7	191.2	37.2	515.2	29.5	602.0	20.4	98.1	51.39
PASCALIS	F	P-15	8.0	25.4	28	34	53	89	40.3	209.9	39.5	547.1	31.4	640.8	18.0	86.5	37.77
PASCALIS	F	P-16	9.5	30.2	24	30	40	67	35.8	186.5	33.8	468.1	30.8	628.6	17.9	86.1	39.94
PASCALIS	F	P-19	18.6	59.1	51	63	61	102	53.8	280.2	46.2	639.9	44.9	916.3	17.8	85.6	39.32
PASCALIS	F	P-20	7.0	22.2	27	33	45	75	32.8	170.8	34.0	470.9	28.7	585.7	14.5	69.7	33.75
PASCALIS	F	P-21	9.0	28.6	26	32	49	82	33.1	172.4	30.9	428.0	26.1	532.7	15.9	76.4	31.58
PASCALIS	F	P-27	25.5	81.0	92	113	107	179	78.9	410.9	59.8	828.3	45.0	918.4	18.6	89.4	53.25
PASCALIS	F	P-28	12.7	40.3	35	43	60	101	46.5	242.2	42.6	590.0	29.3	598.0	17.4	83.7	47.37
PASCALIS	F	P-29	14.1	44.8	52	64	106	178	78.6	409.4	54.9	760.4	39.1	798.0	17.9	86.1	49.23
PASCALIS	F	P-30	12.1	38.4	44	54	65	109	47.9	249.5	41.1	569.3	26.8	546.9	12.5	60.1	34.98
PASCALIS	F	P-32	8.7	27.6	26	32	57	95	40.0	208.3	36.0	498.6	25.5	520.4	13.9	66.8	37.77
PASCALIS	F	P-37	10.1	32.1	41	50	62	104	45.9	239.1	38.2	529.1	30.6	624.5	16.0	76.9	41.18

Table 3.9 Rare Earth Element Neutron Activation Analyses of Hollinger-McIntyre-Coniaurum Scheelites.

LOCATION	SAMPLE	La	La(CN) 0.315	Ce	Ce(CN) 0.813	Nd	Nd(CN) 0.597	Sm	Sm(CN) 0.192	Eu	Eu(CN) 0.0722	Tb	Tb(CN) 0.049	Yb	Yb(CN) 0.208	Lu	Lu(CN) 0.0323	
CONIAURUM	A	85-022	27.8	88.3	84	103	17	28	3.9	20.4	87.3	1209.1	2.4	49.0	15.30	73.56	1.38	42.72
HOLLINGER	B	86-018	28.0	88.9	81	100	38	64	15.0	78.1	50.0	692.5	4.7	95.9	6.59	31.68	0.43	13.31
HOLLINGER	D	87-048	25.8	81.9	73	90	58	97	30.6	159.4	51.5	713.3	14.3	291.8	4.34	20.87	0.36	11.15
MCINTYRE	B	85-019	14.6	46.4	38	47	38	64	26.0	135.4	72.0	997.2	9.1	185.7	11.90	57.21	1.83	56.66
MCINTYRE	C	85-019	18.6	59.1	39	48	42	70	28.6	149.0	81.4	1127.4	9.6	195.9	15.70	75.48	2.73	84.52
HOLLINGER	E	87-059	50.0	158.7	110	135	60	101	25.1	130.7	55.2	764.5	8.0	163.3	6.40	30.77	0.40	12.38
HOLLINGER	E	88-040H	40.0	127.0	60	74	40	67	20.0	104.2	62.0	858.7	7.0	142.9	10.00	48.08	1.20	37.15
HOLLINGER	E	86-039	50.0	158.7	80	98	40	67	23.0	119.8	56.7	785.3	8.0	163.3	5.90	28.37	0.40	12.38
HOLLINGER	E	86-040	30.0	95.2	60	74	40	67	21.9	114.1	62.5	865.7	7.0	142.9	11.10	53.37	1.00	30.96
HOLLINGER	E	86-042	50.0	158.7	110	135	50	84	22.0	114.6	53.9	746.5	7.0	142.9	6.30	30.29	0.40	12.38

Table 3.10 Rare Earth Element Neutron Activation Analyses of Dome Mine and Preston East Dome Mine Schedules.

LOCATION	SAMPLE	La	La(CN)	Ce	Ce(CN)	Nd	Nd(CN)	Sm	Sm(CN)	Eu	Eu(CN)	Tb	Tb(CN)	Yb	Yb(CN)	Lu	Lu(CN)	
			0.315		0.813		0.597		0.192		0.0722		0.049		0.208		0.0323	
DOME	C	85-017	27.5	87.3	37	46	12	20	6.26	32.60	22.3	308.9	1.6	32.7	6.53	31.39	0.59	18.27
DOME	B	85-017	22.5	71.4	47	58	16	27	3.75	19.53	23.6	326.9	2.2	44.9	5.58	26.83	0.84	26.01
DOME	D	86-033-1	58.0	184.1	59	73	33	55	11.10	57.81	36.6	506.9	4.5	91.8	5.77	27.74	2.35	72.76
DOME	D	86-033-2	137.0	434.9	95	117	48	80	17.10	89.06	26.7	369.8	7.3	149.0	9.91	47.64	1.10	34.06
DOME	D	86-033-3	68.6	217.8	121	149	63	106	23.80	123.96	30.3	419.7	8.0	163.3	10.60	50.96	1.09	33.75
DOME	D	87-033-4	50.1	159.1	125	154	54	90	3.86	20.10	9.0	124.7	8.1	165.3	14.20	68.27	1.45	44.89
DOME	F	86-033-5	68.0	215.9	160	197	101	169	27.10	141.15	72.3	1001.4	8.1	165.3	11.40	54.81	1.06	32.82
DOME	F	86-033-6	60.5	192.1	122	150	72	121	21.10	109.90	67.5	934.9	8.2	167.4	11.00	52.88	1.05	32.51
DOME	B	85-003	23.0	73.0	100	123	45	75	12.70	66.15	31.0	429.4	5.5	112.2	12.00	57.69	1.14	35.29
DOME	C	85-003	67.5	214.3	119	146	64	107	8.23	42.86	41.3	572.0	5.7	116.3	9.10	43.75	1.10	34.06
Preston E.	D	86-035-2	92.1	292.4	75	92	49	82	20.50	106.77	30.5	422.4	7.9	161.2	6.21	29.86	0.64	19.81

Table 3.11 Rare Earth Element Neutron Activation Analyses of Wabigoon Subprovince and Pickle Crow mine schistities.

LOCATION	SAMPLE	La	La(CN)	Ce	Ce(CN)	Nd	Nd(CN)	Sm	Sm(CN)	Eu	Eu(CN)	Tb	Tb(CN)	Yb	Yb(CN)	Lu	Lu(CN)
			0.315		0.813		0.597		0.192		0.0722		0.049		0.208		0.0323
Hard Rock	C	85-002	10.5	33.3	52	64	55	92	20.20	105.21	17.70	245.15	8.1	165.3	3.15	15.14	0.29
Hard Rock	B	85-002	8.9	28.3	44	54	39	65	20.20	105.21	19.00	263.16	6.5	132.7	2.78	13.37	0.20
Hard Rock	D	86-032-1	82.1	260.6	61	75	65	109	19.70	102.60	18.90	261.77	7.7	157.1	2.28	10.96	0.20
Hard Rock	D	86-032-2	74.7	237.1	46	57	42	70	19.00	98.96	16.10	222.99	6.5	132.7	2.04	9.81	0.24
L.L.L.	A	85-021	3.1	9.8	10	12	-10	-17	0.46	2.40	2.58	35.73	15.0	306.1	-0.80	-3.85	-0.01
L.L.L.	C	85-021	3.0	9.5	3	4	-3	-5	-0.01	-0.05	1.86	25.76	0.1	2.0	0.39	1.88	0.03
Leitch	B	85-001	20.0	63.5	16	20	10	17	3.71	19.32	6.00	83.10	1.2	24.5	6.30	30.29	0.27
Leitch	C	85-001	26.2	83.2	11	14	16	27	5.65	29.43	7.16	99.17	1.2	24.5	3.56	17.12	0.36
Leitch	C	85-015	6.7	21.3	9	11	9	15	2.14	11.15	7.72	106.93	1.4	28.6	2.03	9.76	0.21
Leitch	B	85-015	4.1	13.0	9	11	8	13	2.45	12.76	6.67	92.38	1.2	24.5	1.76	8.46	0.17
Lake Head	C	85-020	15.4	48.9	3	4	-3	-5	-0.01	-0.05	1.37	18.98	0.2	4.1	0.31	1.49	0.03
Lake Head	A	85-020	1.9	6.0	-4	-5	-3	-5	0.42	2.19	1.80	24.93	5.2	106.1	1.20	5.77	-0.01
Pickle C.	A	85-016	8.3	26.4	38	47	-10	-17	3.61	18.80	8.70	120.50	1.3	26.5	5.20	25.00	-0.24
Pickle C.	C	85-016	99.7	316.5	27	33	15	25	11.7	60.94	7.79	107.89	2.1	42.9	4.22	20.29	0.53

Table 3.12 Summary of Sm and Nd Analyses by ID and INAA.

LOC	Sample	INAA Nd	ID Nd	INAA Sm	ID Sm	LOC	Sample	INAA Nd	ID Nd	INAA Sm	ID Sm
S	D 85-009	69	168.2	53.5	97.1	C	A 85-022	17	50.5	3.9	16.5
S	D 85-010	37	168.2	29.9		C	85-022r		51.6		16.7
S	C 85-011	47		29.0		H	B 85-018	38	87.7	15.0	32.2
S	B 85-011	48		27.7		H	E 86-039	40	89.8	23.0	35.0
S	C 85-012	149	162.1	38.6	92.8	H	E 86-040	40	74.6	21.9	30.4
S	B 85-012	68	162.1	40.0		H	E 88-040H	40	74.6	20.0	30.4
S	B 85-013	5		9.1		H	E 86-042	50	100.6	22.0	32.5
S	C 85-014	15		37.9		H	D 87-048	58		30.6	
S	B 85-014	45		37.0		H	E 87-059	60		25.1	
S	D 87-049	61	139.3	52.6	80.9	H	EW-167		77.1		26.5
S	87-049II		138.7		80.4	H	EW-168		23.3		9.0
S	D 87-050	58		49.7		H	EW-169		106.9		46.7
S	D 87-051	100	205.2	64.5	120.6	M	B 85-019	38	94.6	26.0	54.2
S	S-01		29.1		17.4	M	C 85-019	42	94.6	28.6	54.2
S	S-03		30.6		18.4	M	88-060w		155.8		82.4
S	S-04		34.7		21.5	D	C 85-017	12		6.3	
S	S-05		33.7		20.6	D	B 85-017	16		3.8	
S	S-08		23.7		15.4	D	D 86-033-1	33		11.1	
S	S-09		29.0		19.7	D	D 86-033-2	48		17.1	
S	S-10		33.2			D	D 86-033-3	63		23.8	
S	S-11		31.1		20.7	D	D 86-033-4	54		3.9	
P	D 86-036	45	102.0	42.3	76.7	D	F 86-033-5	101		27.1	
P	D 86-037	41		36.1		D	F 86-033-6	72		21.1	
P	87-055		120.7		40.7	D	Av. 033	62	149.6	17.3	43.5
P	F P-06	65	77.6	32.7	54.0	D	B 85-003	45	93.4	12.7	27.6
P	F P-09	72		36.7		D	C 85-003	64	93.4	8.2	27.6
P	F P-15	53		40.3		PED	D 86-035-2	49		20.5	
P	F P-16	40	72.1	35.8	59.6	PED	86-035-1		258.1		105.8
P	F P-19	61		53.8		HR	C 85-002	55		20.2	
P	F P-20	45	70.6	32.8	56.9	HR	B 85-002	39		20.2	
P	P-20r					HR	D 86-032-1	65		19.7	
P	F P-21	49		33.1		HR	D 86-032-2	42		19.0	
P	F P-27	107		78.9		L	B 85-001	10		3.7	
P	F P-28	60		46.5		L	C 85-001	16		5.7	
P	F P-29	106		78.6		L	C 85-015	9		2.1	
P	F P-30	65	122.3	47.9	90.0	L	B 85-015	8		2.5	
P	F P-32	57	107.5	40.0	80.3	LLL	A 85-021	-10	2.8	0.5	0.94
P	F P-37	62	97.7	45.9	78.1	LLL	C 85-021	-3	2.8	0.0	0.94
SE	SE-1		130.0		43.5	LH	C 85-020	-3	2.5	0.0	0.85
SE	SE-1(A)		137.2		48.3	LH	A 85-020	-3	2.5	0.4	0.84
						PC	A 85-016	-10		3.6	
						PC	C 85-016	15		11.7	

Table 3.13. Maximum, Minimum and Average Total REE(-La) for Each Deposit by INAA.

DEPOSIT	SUM REE(-La)			n	Notes
	MAX.	MIN.	AVG.		
Sigma	356	64	210	12	
Pascalis	403	182	234	15	
Coniaurum	-	-	211	1	
Hollinger	265	196	223	7	
McIntyre	219	197	208	2	
Dome	381	86	216	10	
Preston E.D.	-	-	190	1	
Hard Rock	175	132	145	4	
Little L.L.	20	7	13	2	1
Leitch	45	29	37	4	
Lake Head	12	6	9	2	1
Pickle Crow	68	62	65	2	2

Notes: 1. The INAA analyses for these samples are poor, with several elements reported below detection limits. Isotope dilution analyses of Sm and Nd confirm the low REE contents of these scheelites. Where analyses reported below detection limit, one half of the DL value is used in the Sum calculation.

2. Sm and Lu values for one of the duplicate analyses were reported below detection limits. These values are treated as in Note 1.

3.6.3.1 REE abundances in Scheelites

The Val d'Or and Timmins area scheelites have similar, and high, average total REE(-La) values. The Val d'Or scheelites have average total REE(-La) contents of 210 and 224 ppm for Sigma and Pascalis respectively (one Sigma sample, 85-013, has an anomalously low total REE relative to the other samples; excluding it from the calculation yields an average of 223 ppm, essentially equivalent to the Pascalis average). Ludden et al. (1984) report INAA results for REE in one scheelite from the Sigma mine, which give total REE(-La) of 345 ppm, which is within the range of data reported here.

The Timmins average total REE(-La) contents fall in a narrow range from 208 ppm (McIntyre) to 223 ppm (Hollinger), with the exception of the single Preston East Dome sample (190 ppm). Figure 3.3 illustrates the remarkable similarity of total REE in the scheelites from the Abitibi subprovince deposits.

The Wabigoon, Shebandowan and Uchi subprovince scheelites have significantly lower average total REE(-La) contents than the Abitibi samples, ranging from the 9 ppm in the Lake Head samples to 149 ppm in the Hard Rock samples.

The total REE (-La) are fairly consistent for duplicate analyses with some exceptions. The Lake Head and Little Long Lac duplicates are not in good agreement, and in both cases this may be due to analytical problems for samples with low REE contents (several elements reported below detection limits) and very different reported Tb in duplicate samples. For the Lake Head, Little Long Lac and Pickle Crow

Figure 3.3. A) Average total REE (minus La, see text) abundance in scheelite (analysed by INAA) for each deposit studied. (See caption to Fig. 3.1A for explanation of symbols and abbreviations.); B) Maximum, minimum and mean values of data presented in (A).

samples, where REE are below the detection limit, the total REE is calculated on the basis of one-half the less than value reported (to give an approximate maximum estimate of the total REE for comparison with the scheelites from other areas). Isotope dilution analyses of Sm and Nd contents of the Lake Head and Little Long Lac samples confirm the very low REE abundances in these samples (Table 3.12).

3.6.3.2 Chondrite-normalized REE Patterns

The chondrite-normalized average REE patterns shown in Figures 3.4A, B, C, D, and E indicate that:

a) scheelites from all deposits sampled, except those in Val d'Or, have a significantly positive Eu anomaly. This is in contrast to data for scheelite samples from some magmatic and skarn deposits, which have a distinctive negative or no Eu* anomaly (Cottrant, 1981; Guion et al., 1985; Raimbault, 1985). Note that the La values are inconsistent between duplicate analyses, and the elevated patterns at La may be due to analytical interference, or possible included La-rich phases such as apatite; and,

b) The REE patterns can be separated into two groups on the basis of the patterns shown by the normalized data. Samples from Val d'Or have a pattern with a broad positive hump in the intermediate REE's with nearly equivalent chondrite-normalized Eu and Tb, and a distinctive LREE depletion, while all other samples, including those from Timmins, have relatively flat LREE, and distinctly HREE depleted profiles, with the distinctive positive Eu anomaly mentioned earlier.

Figure 3.4. Chondrite-normalized REE plots for average scheelite REE values for each deposit studied (Tables 3.8 to 3.11): A) Sigma and Pascalis, B) Hollinger-McIntyre-Coniaurum, C) Dome and Preston East Dome, D) Hard Rock, Little Long Lac and Leitch, E) Lake Head and Pickle Crow.

3.6.3.3 Eu Anomalies

The Eu/Eu^* ratio is a measure of the degree of enrichment or depletion of Eu relative to the neighbouring REE, Sm and Gd (Taylor and McLennan, 1985). Eu is the measured elemental abundance in the sample, and Eu^* is the theoretical concentration for Eu if no anomaly was present. Eu^* is calculated by Taylor and McLennan (1985) assuming a smooth REE pattern in the region of Sm-Eu-Gd, using the formula

$$\text{Eu}/\text{Eu}^* = \text{Eu}(\text{cn})/[(\text{Sm}(\text{cn}))\times(\text{Gd}(\text{cn}))] \times 10^{0.5},$$

where (cn) represents the chondrite-normalized values. In this study, Gd values were not determined so they are replaced in the formula by Tb for a very rough calculated estimate of Eu^* . Values of Eu/Eu^* of less than 1 indicate depletion, while values greater than 1 indicate enrichment, of Eu relative to the neighbouring REE. (The chondrite-normalized REE patterns presented in Figure 3.4 also illustrate the positive Eu anomaly in the scheelites.)

All of the scheelites analysed have calculated Eu/Eu^* greater than 1.1, except two Pascalis samples which have values of 0.6 and 0.7. The Sigma and Pascalis average calculated Eu/Eu^* values are 1.7 and 1.3 respectively. The Timmins samples have the highest Eu/Eu^* . The Eu/Eu^* values calculated for the very low REE samples (Lake Head, Pickle Crow and Little Long Lac) are considered unreliable due to the anomalous reported Tb content (see Appendix 5). These Tb analyses are suspect as they are not supported by the duplicate analyses.

3.6.3.4 Significance of Er Anomaly and REE Content in Scheelites

Europium has two oxidation states, Eu^{2+} and Eu^{3+} . The behaviour of Eu in solution is complex and may be influenced by many factors, including: pressure, temperature, composition, pH and/or redox state of the fluids. The presence or absence of a Eu anomaly in a hydrothermal mineral phase may be influenced by the above factors and also, a crystallochemical preference for Eu^{2+} over the trivalent REE (for example in Ca-plagioclase, due to similarity in charge to Ca^{2+}), a Eu anomaly in the fluid source area, and/or REEs contributed to the fluid from breakdown of minerals in the wallrocks.

A Eu anomaly in a mineral phase precipitated in equilibrium with an aqueous phase may be the result of a crystallochemical preference for the divalent Eu^{2+} over the rest of the trivalent REE, or the presence of a Eu anomaly in the fluid phase itself. The aqueous geochemistry of Eu at elevated pressures and temperatures is not well understood. Sverjensky (1984) used available thermochemical data to estimate the behaviour of Eu in aqueous solutions, and concluded that the $\text{Eu}^{2+}/\text{Eu}^{3+}$ redox equilibria displays a strong temperature dependence, such that above 250°C any Eu in an aqueous phase should be divalent. From this observation Sverjensky (1984) concludes that most minerals in equilibrium with an aqueous phase at temperatures above 250°C should have either a positive or a negative Eu anomaly depending on whether they discriminate against the divalent or the trivalent REE.

The similarity in charge of Eu^{2+} to Ca^{2+} may make the divalent Eu more easily incorporated into the scheelite structure than the other trivalent REE. However,

scheelite from other high temperature ore deposits does not necessarily exhibit a positive Eu anomaly (Cottrant, 1981; Richard, 1980; Uspensky et al., 1989).

Uspensky et al. (1989) examined 200 scheelite specimens from 45 ore deposits of various types (including Au, Cu-Mo, W, Sn and polymetallic mineralization) and concluded that scheelite from gold deposits was unlike all other ore deposit sources in having a distinctive positive Eu anomaly.

Most of the lode gold deposits in the Superior Province have been shown through fluid inclusion studies and stable isotope analyses, to have been formed at approximately the same temperature, pressure and bulk fluid compositions, yet the degree of Eu enrichment, relative to Sm and Tb, is distinctly different between the Val d'Or samples and the other districts. Thus, fluid pressure and temperature probably did not control the Eu anomaly in gold deposits.

If the wallrocks contain a Eu-enriched phase that was breaking down during alteration and mineralization, then Eu may be preferentially added to the fluid and incorporated into the scheelite. However, Ludden et al. (1984) concluded that the Au, W and REE's in the veins at the Sigma mine were derived from an external source and were not derived from the decomposition of wallrock mineral phases during alteration. In addition, the scheelite REE patterns from the Sigma and Pascalis mines are very similar even though these deposits are hosted in different rock types. These observations indicate that the REE in the veins in the Val d'Or area were derived from a source external to the local wallrocks.

Several Bourlamaque batholith samples from the Pascalis mine were analysed for REE, by INAA, for comparison with the scheelites. The chondrite-normalized REE whole rock patterns from the batholith are relatively flat with minor LREE enrichment and small negative Eu anomalies and, therefore, do not appear to provide suitable precursors for the REE in scheelite. However, breakdown of plagioclase during phyllic (quartz-sericite-pyrite) alteration, typical of these veins, may release some Eu to the fluids.

A Eu anomaly in a hydrothermal mineral phase may also reflect a Eu anomaly in the fluid that was inherited from its source, i.e. the source is enriched in Eu, and/or the fluid is selectively enriched in Eu when it is derived. A fluid that is enriched in Eu at source, for example due to breakdown of Ca-plagioclase, would be reflected as a Eu anomaly in minerals, such as scheelite, that incorporate the REE systematically. The Eu enrichment of the fluid at source may also be a reflection of the redox conditions under which the fluid phase was derived and/or the anionic complexes available to transport the REE.

Without knowing the relative partition coefficients from Eu^{2+} versus Eu^{3+} in scheelite it is difficult to assess whether the observed Eu anomaly is due to the preferential incorporation of the divalent Eu over the rest of the trivalent REE, or if the fluid had a positive Eu anomaly when it was formed. Future REE studies of other hydrothermal mineral phases in the veins may elucidate this problem.

Ionic radius and charge conditions which control the REE distribution in scheelite are relatively constant for all of the REE, with the exception of Eu as noted

above. The differences in the shapes of the patterns from one district to another suggest that the fluids had different compositions from one area to another. Although the relatively large size of the REE, especially the LREE, tends to inhibit complexing of the REE, in solution the REE can form ion-pair associations with ligands such as CC^- , Br^- , I^- , NO_3^- and SO_4^{2-} , and they appear to be particularly mobile in CO_2 -rich solutions (Henderson, 1984). CO_2 -rich solutions are characteristic of gold deposits, and the REE may therefore have been derived from the same source as the CO_2 . The stability of REE complexes appears to vary depending on the pH and the water/rock ratio, but there are very few studies of REE complexing in high temperature aqueous solutions.

Although there are no experimentally determined partition coefficients for the REE between scheelite and fluid, Raimbault (1985), on the basis of REE analyses of coexisting hydrothermal mineral phases, estimated partition coefficients for scheelite/fluid in a mainly chlorine- and fluorine- bearing media for temperatures in the range 350-500°C. This work suggested that scheelites show a slight preference for the LREE. Raimbault (1985) also suggested that scheelite/fluid partition coefficients are so high that the scheelite probably effectively reflects the fluid REE content. Similarly, Cottrant (1981) found regular substitution of Ca by the REE with conservation of site local symmetry. Some deviations exist for the heavier REE. Cottrant (1981) attributed the strong difference in REE patterns between scheelites from skarn deposits and those from other deposit types, to distinct characteristics of mineralizing fluids. These studies support the observations made above that the

scheelite REE patterns are probably reflecting the REE pattern of the fluid.

Considering the scheelite/fluid partition coefficients presented by Raimbault (1985) the Val d'Or patterns require a fluid strongly depleted in LREE, with flat to moderately depleted HREE, and a positive Eu anomaly. Given the apparent preference for LREE in scheelite, the patterns from the other areas may reflect a fluid derived from a source with a relatively flat to slightly LREE depleted pattern with a Eu anomaly either in the source, or produced during fluid generation.

Another factor that may influence the REE pattern in the scheelites, other than the original pattern inherited from the source, is the presence of co-precipitating phases. The veins at Val d'Or are distinct from other Superior Province gold deposits in the abundance of tourmaline as a gangue and alteration mineral in the veins and wallrocks. Some veins and alteration envelopes are composed of almost 100% tourmaline. The distinctive LREE-depleted and low Eu anomaly patterns of scheelites from the Val d'Or area may possibly be due to the co-precipitation of large amounts of tourmaline. Tourmalines from Archean lode gold deposits have not been analysed for their REE contents, however Jolliff et al. (1987) have examined the REE content of tourmaline from pegmatites. These tourmalines exhibit slightly LREE enriched and HREE depleted chondrite-normalized patterns and relatively low REE abundances, and in some cases negative Eu anomalies (Jolliff et al., 1987). In addition a very small amount of a LREE-enriched phosphate phase was recently found during SEM examination of a Pascalis quartz vein sample (no Ca detected, therefore not apatite, D. Marshall, Univ. Lausanne, pers. comm. 1991). However, the Val d'Or scheelite REE

patterns are remarkably consistent, which suggests that a minor associated phase is probably not responsible for the REE distribution.

3.6.3.5 Relationship Between Sr and REE in Hydrothermal Scheelites

A plot of average Sr contents of scheelites versus their average Eu/Eu* does not yield a correlation (Figure 3.5). Eu/Eu* versus total REE (-La) also reveals no correlation between total REE and the Eu anomaly. A plot of Sr content versus total REE does indicate a crude negative correlation (Figure 3.6).

Richard et al. (1980) noted that for scheelites analysed from different deposits (n=4), those with the highest Sr content (3600 ppm) corresponded to the strongest positive Eu anomaly and the scheelite with a distinct negative Eu anomaly corresponded with the lowest Sr content (16 ppm). They concluded that this correlated behaviour reflected the similarity in charge and ionic radius between Sr^{2+} and Eu^{2+} , 1.21 and 1.25 Å respectively (Richard et al., 1980).

Abitibi scheelites have higher average REE contents and generally lower Sr than the scheelites studied from other areas in the Superior province. The lack of correlation between Eu/Eu* and Sr content in the scheelites indicate that the Eu and Sr in the fluid are probably not coming from the same source, and that the scheelites reflect differences in the REE and Sr contents in the fluid.

The Sm and Nd content of the scheelites is sufficient to permit isotopic analysis of these minerals, and these data may provide more insight on the source and composition of the hydrothermal fluids.

Figure 3.5. Average Eu/Eu* (calculated, see text) versus average Sr (ppm) for scheelites from selected gold deposits. The Coniaurum Eu/Eu* is 38 and was not included on the plot. (The Lake Head sample was excluded due to poor analytical data. The Pickle Crow and Hard Rock samples are estimated values.)

Figure 3.6. Average Sr (ppm) versus average total REE(-La) (ppm) for scheelites from selected gold deposits. (Note, on this plot the symbol for the Wabigoon subprovince includes the Lake Head sample from the Shebandowan subprovince. Also, the values reported as less than have been converted to one-half their reported detection limit values for samples 85-020 (LH), 85-021 (LLL) and 85-016 (PC) to provide maximum estimates of total REE(-La) for comparison with the other scheelites.)

3.7 SUMMARY AND CONCLUSIONS

1. As, Au, Co, Cr, Fe and Sb in the scheelites analysed are probably in included phases within the scheelite, probably sulphides such as pyrite and arsenopyrite. The other trace elements (excluding Sr and REE) are low in abundance and therefore few conclusions can be drawn from the data. Ni, however, appears to be slightly higher in concentration in the Timmins scheelites than those from other areas.
2. The range of Sr contents in scheelites from individual deposits is more restricted than the total range of Sr contents in all scheelites analysed.
3. There appear to be significant differences in Sr contents of scheelites from deposits in the Abitibi greenstone belt (Val d'Or and Timmins average values range from 200 to 2000 ppm) versus those in the Wabigoon and Shebandowan belts (8000 to 16000 ppm). The Wabigoon and Shebandowan subprovince (Geraldton-Beardmore and Lake Head areas, respectively) scheelites have considerably higher Sr contents than the scheelites from the Abitibi Subprovince.
4. EMP analyses indicate that Sr is inhomogeneously distributed in the scheelites, with a wide variation in those samples with high Sr concentrations, and much more restricted ranges in those scheelite samples with low Sr. EMP analyses also indicate that there is no zoning with respect to Sr within the scheelites.
5. The REE contents of scheelites within a single deposit or district are generally fairly uniform, but significant variations exist between groups of deposits. The Wabigoon and Shebandowan subprovince scheelites have significantly lower average

total REE(-La) contents than the Abitibi samples.

6. Scheelites from all deposits sampled, except those in Val d'Or, have significant positive Eu anomalies. This contrasts with data from scheelites associated with some magmatic and skarn deposits, which have either a distinctive negative, or no, Eu anomaly.

7. The REE patterns can be separated into two groups on the basis of the patterns shown by the normalized data. Samples from Val d'Or have a pattern with a broad positive hump in the intermediate REE's with nearly equivalent chondrite-normalized Eu and Tb, and a distinctive LREE depletion, while all other samples, including those from Timmins, have relatively flat LREE, and distinctly HREE depleted profiles, with a distinct positive Eu anomaly.

8. The Val d'Or deposits are distinctive in their low calculated Eu/Eu^* .

9. The inhomogeneity of Sr within individual scheelites, and differences in average Sr content between different gold mining camps, suggest that some or all of the Sr may be contributed to the fluid from a local (wallrock or underlying crust) source.

10. Homogeneity of patterns and REE abundances in scheelites from individual deposits suggest a relatively homogeneous, external source (ie. not wallrocks or rock types immediately underlying the deposits, may be lower crust or upper mantle?) for most of the REE, consistent with the results of alteration studies at the Sigma mine (Ludden et al., 1984).

11. The variation in scheelite Sr contents and REE patterns between districts, including the Eu anomaly, indicate that the scheelites are reflecting composition of the fluids that they precipitated from, although the patterns may be modified by co-precipitating phases, and that crystallographic controls are not solely responsible for REE patterns and Sr abundances in these hydrothermal scheelites.

Chapter 4. Rb-Sr ISOTOPIC ANALYSES OF SCHEELITES

4.1 INTRODUCTION

One of the most important problems in understanding the genesis of Archean gold deposits is determining the "source" of the Au and the fluid(s) responsible for its transport. Host rocks for gold deposits in the Superior Province are extremely variable and include mafic and ultramafic through felsic and alkaline volcanic and intrusive rocks, metasedimentary rocks, including chemical sediments such as chert and iron formation, and lamprophyric intrusive rocks. All of these rocks types have been considered as possible sources for the Au, as have the lower crust and the mantle. A summary of the host rocks for the deposits sampled in this study is presented in Table 2.1.

A powerful method for studying the possible source(s) of hydrothermal fluids associated with mineral deposits involves studying the initial isotopic compositions of Sr, Nd and Pb of hydrothermal minerals found in the veins. Because of the very low Rb/Sr ratios of scheelites, their measured $^{87}\text{Sr}/^{86}\text{Sr}$ are very similar to initial ratios. The scheelite initial ratios provide information on the Sr isotopic composition of the fluid from which they were precipitated, and may be used to place some constraints on the possible source(s) of these fluids.

4.1.1 Evolution of Strontium in the Earth

Radiogenic Sr is produced from the decay of radioactive ^{87}Rb , which decays by emission of a negative beta particle to ^{87}Sr . The growth of the radiogenic daughter, ^{87}Sr , can be described by the equation:

$$^{87}\text{Sr} = ^{87}\text{Sr}_i + ^{87}\text{Rb} (e^{\lambda t} - 1)$$

where ^{87}Sr and ^{87}Rb are the total number of these atoms in a unit weight of the mineral at the present time (i.e. the measured quantities), $^{87}\text{Sr}_i$ is the number of atoms incorporated into the mineral at the time of its crystallization, λ is the decay constant of ^{87}Rb (in units of reciprocal years), and t is the time elapsed since the formation of the mineral (Faure, 1986).

The $^{87}\text{Sr}/^{86}\text{Sr}$ in the Earth's crust and mantle has evolved at different rates due to the difference in Rb/Sr ratios in these two reservoirs. The formation of the continental crust, through differentiation from the mantle, is thought to have begun around 4 billion years ago (Faure, 1986). Rb is concentrated in crustal material relative to Sr, because of the more lithophile nature of Rb. Therefore the mantle has a lower Rb/Sr ratio, and the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio has evolved more slowly, than that of the continental crust. The Rb/Sr ratio of the upper continental crust is a factor of ten times greater than that of the lower crust and mantle. Most present-day $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the mantle are thought to fall in the narrow range of 0.704 ± 0.002 . The isotopic composition of Sr in the continental crust is more difficult to describe because of the unknown number of geological systems continental material may have passed through, and the variety of geological processes which may have acted upon it

to change the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio. However, the $^{87}\text{Sr}/^{86}\text{Sr}$ of the continental crust, at any given time, should in most cases be significantly greater than that of the upper mantle. The present day $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of continental material, differentiated from the mantle about 2.9 Ba, having a Rb/Sr ratio of 0.15, if it remained in a closed system, would be approximately 0.720 (Faure, 1986).

Large-scale reservoirs such as the crust and mantle are considered to have been derived from primitive, undifferentiated material, referred to as CHUR ("chondritic uniform reservoir") and bulk Earth. The CHUR model is based on the assumption that the primitive material from which the Earth's crust and mantle are derived has the same Sm-Nd ratio as that found in chondritic meteorites (0.32). The present day $^{143}\text{Nd}/^{144}\text{Nd}$ ratio of CHUR is 0.512638 (for $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$), and the $^{147}\text{Sm}/^{144}\text{Nd}$ ratio is 0.1967 (Faure, 1986). The bulk Earth model is based on the correlation of $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in young basalts, mainly from oceanic environments. This correlation is referred to as the 'mantle array' and it is used to define the $^{87}\text{Rb}/^{86}\text{Sr}$ and the $^{87}\text{Sr}/^{86}\text{Sr}$ parameters that are complementary to the CHUR model. The $^{87}\text{Sr}/^{86}\text{Sr}$ for the bulk Earth model is 0.7045 and the $^{87}\text{Rb}/^{86}\text{Sr}$ is 0.0816, assuming the primordial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the Earth is 0.69899 and the age of the Earth is 4600 Ma (Faure, 1986).

Bell and Blenkinsop (1987) studied the $^{87}\text{Sr}/^{86}\text{Sr}_i$ and $^{143}\text{Nd}/^{144}\text{Nd}_i$ ratios of carbonatites and related alkaline rocks that are hosted in the Canadian Shield. These samples define a development line on a plot of age versus initial ratio that intersects

the development line for bulk Earth and CHUR at approximately 2900 Ma. Bell and Blenkinsop (1987) interpreted this age in terms of a model which involved the differentiation of a CHUR- and bulk Earth-like mantle into crustal rocks of the Superior province and a LIL-depleted, residual upper mantle. They also suggest that this depleted sub-continental reservoir appears to have remained intact and coupled to the continental crust until at least 110 Ma ago (Bell and Blenkinsop, 1987).

4.1.2 Strontium Isotope Tracer Studies - General Comment

It may be possible to identify the source(s) of the mineralizing fluids by analysing the Sr isotopic composition of hydrothermal minerals which incorporate Sr into their crystal structures. The Sr isotopic signature of the hydrothermal minerals may allow a distinction to be made between mantle-derived and crustal-derived Sr in the fluids that precipitated the minerals. However, distinguishing a mantle from a crustal source in rocks of Archean age is more difficult than in younger rocks because of the relatively short period of time that has elapsed from the hypothesized mantle-crust differentiation event (ca. 2900 Ma; Bell et al., 1989, or earlier as evidenced by older crustal material in the Superior Province; Davis and Corfu, 1991) to the hydrothermal event responsible for gold mineralization (also Archean, 2400 Ma or older). Depending on the Rb/Sr ratios in each reservoir, the time between separation of crustal material from the mantle, and derivation of the gold-bearing fluids, may not be sufficient to evolve distinctive $^{87}\text{Sr}/^{86}\text{Sr}$ ratios.

In this chapter, Sr isotopic measurements on scheelite from several gold deposits in the Superior Province are reported. Scheelite, as discussed earlier, is a common gangue mineral in Archean lode gold deposits and an integral part of the hydrothermal mineralization in the gold bearing veins. Alteration studies by Ludden et al. (1984) at the Sigma mine indicate that the W is derived from an external source and not from the wallrocks, therefore the scheelite is clearly not a remobilized phase from the country rock, nor is it a later alteration of some other phase. Paragenetic studies by other researchers at the Val d'Or and Timmins camps (Robert and Brown, 1986b; Wood, 1986; Allen and Folinsbee, 1944) identify scheelite as being introduced earlier than, or co-precipitated with, gold in the veins.

Scheelite is an ideal mineral for Sr isotope tracer studies because of its variable Sr contents (100 to over 10,000 ppm, Tables 3.1 to 3.6) and low Rb contents (<3 ppm). Minerals with high Sr abundances and low Rb/Sr ratios will not experience large changes in $^{87}\text{Sr}/^{86}\text{Sr}$ since the time of their crystallization, assuming closed system conditions. Scheelite is also a favourable mineral for Sr isotopic tracer studies because of its apparent resistance to alteration.

4.1.3 Previous Work on Strontium Isotopic Composition of Scheelites

The feasibility of Sr isotopic analyses of hydrothermal scheelites was demonstrated by von Quadt (1985a,b) who investigated the Sr and Pb isotopic compositions of scheelites from the Felbertal deposit in Austria. Twelve scheelites were analysed for their Rb and Sr contents and isotopic ratios. The Sr concentrations

in the scheelite ranged from 62.5 ppm to 338.4 ppm. In 9 of the 12 samples Rb was less than 3.5 ppm, the other three samples had Rb contents ranging from 23.6 to 66.2 ppm. Von Quadt (1985a) found that the Sr contents and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the scheelites are negatively correlated and that the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are negatively correlated with the $^{206}\text{Pb}/^{204}\text{Pb}$ ratios in the scheelites. Von Quadt (1985a,b) used these isotopic variations to make some inferences about the fluid chemistry from which the different generations of scheelite were precipitated.

Kerrick et al. (1987) studied the Rb and Sr contents and isotopic compositions of tourmaline, scheelite, actinolite and peimontite from Archean gold deposits. In their study the three scheelite samples are from the Macassa, Dome and Deep Dome mines. Their data indicate that different Sr-rich minerals from the same locations have the similar Sr initial ratios. Given that Sr isotopic tracer studies in Archean rocks are commonly equivocal because there has been insufficient time for separate reservoirs to evolve distinct isotopic signatures, Kerrich et al. (1987) nevertheless conclude that the Sr isotopic data requires a more radiogenic source for the scheelites than komatiites or contemporaneous mantle.

Bell et al. (1989) report Sm-Nd and Rb-Sr isotopic analyses for eight scheelites from gold deposits in the Canadian Shield. The variation observed of Sr_i ratios in these scheelites also indicates that a more evolved reservoir than depleted mantle contributed Sr to the fluids. Variable initial Sr ratios at the Hollinger-McIntyre-Coniaurum deposit in Timmins indicate that more than one fluid was involved in the

formation of this deposits and/or the fluids interacted to some degree with the wallrocks during scheelite precipitation.

4.2 ANALYTICAL METHODS

4.2.1 Samples

Thirty-four samples of scheelite (plus one tourmaline and one carbonate) from gold-mineralized veins, representing 7 different deposits in the Superior Province, were analysed on a mass spectrometer for their $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios, and their Sr and Rb concentrations.

The twenty-three samples analysed from the Val d'Or camp were collected (17 of them by the author) from underground exposures, including 12 scheelites from the Sigma mine, 8 from the Pascalis mine (plus a tourmaline and a carbonate sample), and one from the Siscoe Extension deposit. The samples from the Sigma mine labelled S-01 through to S-11, were taken from one continuous "flat" or extension vein on the 1700 level where the vein crosscuts a series of wallrock types including mafic volcanics, porphyritic (subvolcanic) diorite, and feldspar porphyry dykes (Figures 2.4 and 2.5). Samples 85-009 and 85-012 are chips from the same hand sample (provided by F. Robert) from a vein on the 3300 level. Samples 87-049 and 87-051 (provided by D. Burrows) are from two different locations on the 2800 level.

The Pascalis mine samples P-06 to P-20 and P-35 were all taken from the same "flat" vein where it is exposed continuously in one drift (888XC N) over 50 to 60

metres (Figures 2.7 to 2.12). The wallrock at the Pascalis mine is almost exclusively the quartz diorite of the Bourlamaque batholith; however, minor mafic dykes and very minor aplitic dykes are observed. The control on the location of the samples from the Val d'Or should allow the influence, if any, of different types of wallrock on the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the scheelites to be determined.

Ten samples from the Timmins camp were obtained from the collections of the Geological Survey of Canada (GSC), mine tailings dumps, and from other geologists. These samples include 8 from the Hollinger-McIntyre-Coniaurum vein system, 1 from the Dome mine and 1 from the Preston East Dome mine (however, this last sample has been analyzed only for Rb and Sr concentration). The data for 6 of the Hollinger-McIntyre-Coniaurum samples are taken from Bell et al. (1989). In addition, one sample of scheelite from the Lake Head (LH) deposit near Thunder Bay, and one from the Little Long Lac (LLL) deposit in Geraldton were obtained from the GSC collections. The data for these two samples are also from Bell et al. (1989). The Timmins LH and LLL samples are not precisely located relative to their wallrocks and structural or paragenetic setting.

All scheelites come from veins that contained economic concentrations of gold. The geologic setting of the areas included in this study and descriptions of the samples are given in Appendix 1 and in Chapter 2. These deposits encompass a wide variety of host lithologies, including ultramafic-mafic volcanic rocks, intrusions of mafic, granitic, trondhjemitic, alkalic and lamprophyric composition, and volcanoclastic and chemical sediments.

Petrographically, the Val d'Or, Lake Head and Little Long Lac scheelites show no evidence of zonation or alteration. Several of the Timmins samples do, however, show evidence of zoning, and patches of varying cathodoluminescence may indicate some variation in trace element (most likely REE) concentrations within these samples (A. Mariano written comm. 1988). Electron microprobe analysis indicate that the Sr concentration varies considerably across sections of massive scheelite, and the Sr distribution within the scheelites appears to be random.

4.2.2 Analytical Methods

Twenty scheelite samples were analysed for Rb and Sr concentration and Sr isotopic compositions. (In addition, four samples were analysed for Sr isotopic compositions only, two for Sr isotopic ratio and concentration, and two for Sr and Rb concentrations only.) One tourmaline sample and one carbonate sample from the Pascalis mine were also analysed.

Present-day $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were determined from unspiked dissolutions of sample splits. Concentrations of Rb and Sr were determined by isotope dilution using ^{87}Rb - and ^{84}Sr -enriched spikes. More details on the analytical method are given in Bell et al. (1989) and in Appendix 3. The estimated uncertainties, quoted at the two-sigma level, for the $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios are about 0.003% and for the Rb and Sr concentrations are approximately 1% and 0.5% respectively.

4.3 RESULTS

Data from the Val d'Or scheelites (21 samples including two duplicate analyses) plus the Pascalis tourmaline and carbonate data are given in Table 4.1. Table 4.2 includes data from 4 scheelites from the Timmins area done for this study (two $^{87}\text{Sr}/^{86}\text{Sr}$ analyses from Hollinger scheelites and one Dome scheelite, plus Rb and Sr concentration determinations on a Preston East Dome scheelite), and Timmins, Lake Head and Little Long Lac data given in Bell et al. (1989). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of all samples analysed are presented in Figure 4.1, and the isotope dilution Sr concentrations are plotted in Figure 4.2.

4.3.1 Val d'Or Area

Present-day $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of Val d'Or scheelites range from 0.70135 (Siscoe Extension) to 0.70174 (Sigma, 85-012) (Figure 4.1). The Sr content of the scheelites ranges from 210 ppm for S-11 to 1856 ppm in SE-1. The average Sr content of all Val d'Or scheelites by ID is 463 ppm ($n=19$). The tourmaline and carbonate samples from the Pascalis mine have Sr contents (543 and 461 ppm respectively) that are similar to those of the Val d'Or scheelites, but these are at the low end of the range of Sr ppm in the Pascalis scheelites (546 to 698 ppm). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the tourmaline and carbonate are within the analytical error of scheelites from the same locations.

Table 4.1. Val d'Or Rb-Sr Scheelite Analyses.

sample			$^{87}\text{Sr}/^{86}\text{Sr}^+$ (atomic)	Sr (ppm)	Rb (ppm)	$^{87}\text{Rb}/^{86}\text{Sr}$ (atomic)	$^{87}\text{Sr}/^{86}\text{Sr}^*$ (initial)	1/Sr
	S	85-009	0.70170	338	2.15	0.01841	0.70101	0.00296
	S	85-012	0.70174	320	0.23	0.00194	0.70166	0.00313
	S	87-049	0.70158	312	0.82	0.00739	0.70130	0.00321
r	S	87-049(II)	0.70163	316	0.19	0.00169	0.70157	0.00316
	S	87-051(II)	0.70165	350	0.06	0.00051	0.70163	0.00286
r	S	87-051	0.70163	na	na	na	0.70163	na
	S	S-01	0.70144	231	0.20	0.00269	0.70134	0.00433
	S	S-03	0.70146	na	na	na	0.70146	na
	S	S-04	0.70149	221	0.16	0.00200	0.70142	0.00452
	S	S-05	0.70148	244	0.21	0.00255	0.70139	0.00410
	S	S-08	0.70150	238	0.04	0.00037	0.70149	0.00420
	S	S-09	na	253	0.07	0.00074	na	0.00395
	S	S-10	0.70150	214	0.02	0.00041	0.70149	0.00467
	S	S-11	0.70151	210	0.10	0.00127	0.70146	0.00476
	P	86-036	0.70151	678	na	na	0.70151	0.00147
	P	87-055	0.70154	661	0.15	0.00067	0.70152	0.00151
	P	P-06	0.70148	546	2.10	0.01104	0.70107	0.00183
	P	P-16	0.70162	560	0.32	0.00165	0.70156	0.00179
	P	P-20	0.70151	555	0.02	0.00011	0.70150	0.00180
i	P	P-20	0.70154	563	na	na	na	0.00178
	P	P-30	0.70152	676	0.02	0.00008	0.70152	0.00148
	P	P-32	0.70158	667	na	na	na	0.00150
	P	P-37	0.70154	698	0.00	0.00000	0.70154	0.00143
	SE	SE-1	0.70135	1856	0.02	0.00003	0.70135	0.00054
Val d'Or carbonate and tourmaline								
tm	P	P-31	0.70156	543	0.13	0.00067	0.70153	0.00184
cbt	P	P-35	0.70157	461	0.02	0.00013	0.70156	0.00217

FOOTNOTES:

S = Sigma mine, P = Pascalis mine, SE = Siscoe Extension mine,

tm = tourmaline, cbt = carbonate, r = repeat dissolution

i = replicate on separate chip from same hand sample, na = not analysed,

+ = normalised to a $^{86}\text{Sr}/^{88}\text{Sr}$ of 0.1194, * = initial $^{87}\text{Sr}/^{86}\text{Sr}$ calculated at 2600 Ma.

Table 4.2. Rb-Sr Analyses of Scheelites from Timmins, Lake Head and Little Long Lac.

sample			$^{87}\text{Sr}/^{86}\text{Sr}^+$ (atomic)	Sr (ppm)	Rb (ppm)	$^{87}\text{Rb}/^{86}\text{Sr}$ (atomic)	$^{87}\text{Sr}/^{86}\text{Sr}^*$ (initial)	1/Sr
Timmins area								
b	C	85FRA022	0.70166	643	1.66	0.00750	0.70138	0.00156
b	H	85FRA018	0.70159	1260	0.67	0.00150	0.70153	0.00079
b	H	86FRA039	0.70165	1248	0.28	0.00066	0.70163	0.00080
b	H	86FRA040	0.70183	1523	0.03	0.00005	0.70183	0.00066
b	H	86FRA042	0.70165	1571	0.02	0.00003	0.70165	0.00064
	H	89-IRJ-1	0.70150	na	na	na	na	na
	H	EW-167	0.70179	1278	na	na	na	0.00078
b	M	85FRA019	0.70227	121	0.02	0.00042	0.70225	0.00826
	D	86-033	0.70146	1129	0.01	0.00003	0.70146	0.00089
	PE	86-035-1	na	1355	0.05	0.00010	na	0.00074
Wabigoon and Shebandowan Subprovince samples								
b	LH	85FRA020	0.70184	6862	0.51	0.00210	0.70176	0.00015
b	LL	85FRA021	0.70179	11260	0.12	0.00003	0.70179	0.00009
b,r	LL	85FRA021	0.70174	na	na	na	na	na

FOOTNOTES:

C = Coniaurum mine, H = Hollinger mine, M = McIntyre mine, D = Dome mine, PE = Preston East Dome mine,

LH = Lake Head mine, LL = Little Long Lac mine, b = from Bell et al. (1989), na = not analysed,

r = repeat dissolution, + = normalised to a $^{86}\text{Sr}/^{88}\text{Sr}$ of 0.1194,* = $^{87}\text{Sr}/^{86}\text{Sr}$ initial ratios calculated at 2600 Ma.

Figure 4.1. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of scheelites. Symbols represent scheelite sample localities and are labelled in the box insert on the graph. The Pascalis tourmaline and carbonate determinations are included for comparison.

Figure 4.2. Isotope dilution determinations of Sr abundance in scheelites. Labels are the same as for Fig. 4.1. The Pascalis tourmaline and carbonate determinations are included for comparison.

Most Val d'Or scheelites have Rb contents less than 0.4 ppm and have an average Rb/Sr ratio of 0.0010. Replicate dissolutions of sample 87-049 (87-049(II)) indicate good reproducibility of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio measurements but poor reproducibility of Rb analyses (0.82 and 0.19 ppm respectively). The Rb/Sr ratios are 0.0026 and 0.0006, respectively. The highest Val d'Or Rb concentration was obtained on Sigma sample 85-009 (Rb = 2.15 ppm). Sigma sample 85-012 is from chips of scheelite from the same hand sample as 85-009 and yielded a Rb concentration of 0.23 ppm. The measured $^{87}\text{Sr}/^{86}\text{Sr}$ of these two samples are 0.70170 and 0.70174 for samples 85-009 and 85-012 respectively, and these values fall within analytical uncertainty of each other; however, the Rb/Sr ratio of sample 85-009 (0.0064) is quite different from 85-012 (0.0007) and most of the other Sigma scheelites. Only one other Val d'Or sample has Rb content greater than 0.40 ppm (sample P-06, Rb = 2.1 ppm) and this sample was not repeated; however the Rb/Sr ratio of 0.0038 is also anomalous with respect to all the other Pascalis samples whose Rb/Sr ratios range from 0.00000 to 0.0006. Only three of 21 Rb analyses (including the tourmaline and carbonate analyses) have Rb concentrations greater than 0.4 ppm. This, and the poor reproducibility of Rb determinations, suggests that the higher Rb contents are due to small inhomogeneous component of Rb-bearing contaminant in the scheelite concentrate, and/or analytical difficulties with measuring Rb isotopic composition in samples with such extremely low Rb concentrations.

Initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (Table 4.1) were calculated assuming an age of 2600 Ma which is the U-Pb age obtained from a hydrothermal rutile from the alteration

envelope of a gold-bearing vein at the Sigma mine and represents the best independent estimate of the time of mineralization (see Table 2.2). The calculated Sr initial ratios at 2600 Ma range from 0.70101 (Sigma, 85-009, Rb = 2.15 ppm) to 0.70166 (Sigma, 85-012, Rb = 0.23 ppm) (Table 4.1). These two extreme values come from the same hand sample and the lower Sr_i is considered unreliable (see above). All but three of the scheelite samples have Rb/Sr ratios that are less than 0.0009. The correction to the $^{87}\text{Sr}/^{86}\text{Sr}$ present-day ratios is less than 0.0001 using an age of 2600Ma. The present-day $^{87}\text{Sr}/^{86}\text{Sr}$ ratios thus provide a reasonable estimate of the Sr_i ratios in scheelite, carbonate and tourmaline.

Samples from the Sigma mine have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios that range from 0.70144 to 0.70174. The Pascalis scheelites exhibit a range of $^{87}\text{Sr}/^{86}\text{Sr}$ from 0.70148 to 0.70162. The Pascalis tourmaline and carbonate fall within this range (0.70156 and 0.70157). The tourmaline sample, P-31, comes from the same vein as scheelite samples P-30 and P-32 and the present-day $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of these samples are almost identical to that of the P-31 tourmaline. The carbonate sample P-35 was taken from the same locality as scheelite sample P-20 where carbonate and scheelite deposition appear to have been contemporaneous. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are 0.70157 for the carbonate and 0.70151 and 0.70154 for two analyses of the scheelite. These ratios are essentially identical.

The Siscoe Extension deposit has the lowest $^{87}\text{Sr}/^{86}\text{Sr}$ (0.70135) and the highest Sr content (1856 ppm) of the samples analysed from Val d'Or.

4.3.2 Timmins Area

The Timmins camp is geologically more complex than the Val d'Or area. The gold mineralization in the Timmins camp has been suggested by different workers to represent different mineralizing processes including, syngenetic exhalative (Karvinen, 1982 and others), porphyry Cu-Mo-Au related to the felsic porphyritic intrusions (Pearl Lake Porphyry, McIntyre mine, Mason and Melnik, 1986), and late structurally-controlled shear zone hosted mineralization related to magmatism and devolatilization in the lower crust (Fyon et al., 1989; Jemielita et al., 1990). Considerable evidence has been put forward in the literature for the presence of syngenetic- and porphyry-related mineralization in the Timmins area and the controversy has yet to be resolved.

The majority of scheelites analyzed from the Timmins camp have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the range 0.70146 (Dome) to 0.70182 (Hollinger) (Table 4.2). One sample has an anomalously (with respect to all other scheelites analysed) high value of 0.70277 (McIntyre). The initial ratios are calculated at 2600 Ma in Table 4.2 for comparison with the Val d'Or samples. The initial ratios, however, are not particularly sensitive to the choice of age, given their low Rb/Sr ratios. Only one sample (Coniaurum) has a sufficiently high Rb/Sr ratio (0.0026) to significantly change the present-day $^{87}\text{Sr}/^{86}\text{Sr}$ ratio. The Rb content of 1.66 ppm is much higher than the other Timmins scheelites which have Rb contents < 0.70 ppm, similar to the majority of Val d'Or scheelites. The Sr contents of the Timmins scheelites range from 121 ppm (McIntyre) to 1571 ppm (Hollinger, 86-042), with an average of 1125 ppm (1251 ppm excluding the McIntyre sample).

4.3.3 Other Areas

Two samples, one from the Lake Head mine in the Shebandowan greenstone belt, and one from the Little Long Lac mine in the Wabigoon greenstone belt, have also been analysed for their Sr isotopic compositions (Table 4.2). The Lake Head scheelite has a Rb/Sr ratio of 0.00007 and a present-day $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.70184. The Little Long Lac scheelite has a Rb/Sr ratio of essentially zero and a $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.70177. These ratios are at the high end of the range of values shown by the Timmins scheelites, excluding the one McIntyre sample.

4.3.4 Sr Abundance in Scheelite

The Sr content, as determined by ID, of the Val d'Or scheelites, and the Pascalis tourmaline and carbonate samples, confirm the neutron activation and electron microprobe results. The "provinciality" of Sr concentration in the scheelites from the different deposits is illustrated in Figure 4.2. The Sr analyses of Sigma scheelites range from 210 to 350 ppm, with good agreement between replicate dissolutions (049 and 049II) and corresponding sample chips (85-009 and 85-012). The Pascalis scheelites, distinct from the Sigma samples, have Sr values that range from 546 to 698 ppm Sr. The Pascalis tourmaline and carbonate contain 543 and 461 ppm Sr respectively. The Siscoe Extension scheelite has a Sr content of 1856 ppm, distinctly higher than the Pascalis vein minerals, and also has a relatively low $^{87}\text{Sr}/^{86}\text{Sr}$ ratio.

The Timmins samples have significantly higher Sr concentrations than the Val d'Or samples. These samples have a range of Sr contents from 1129 ppm (Dome) to

1571 ppm (Hollinger), with the exception again of the McIntyre sample which has relatively low Sr content (121 ppm), and the highest $^{87}\text{Sr}/^{86}\text{Sr}$ measured. The Lake Head sample contains 6862 ppm Sr and the Little Long Lac sample has the highest Sr measured, for any of the scheelites studied, with 11260 ppm.

4.4 DISCUSSION AND INTERPRETATION

4.4.1 Sr Isotopic Composition of Different Mineral Phases

The similarity of the Sr isotopic compositions from three different hydrothermal mineral phases (scheelite, tourmaline and carbonate) at the Pascalis mine supports the hypothesis that these minerals are reflecting the isotopic composition of the fluid from which they were precipitated, and that they have retained their isotopic signature since the time of crystallization. A later event would be expected to affect scheelite (a tungstate), tourmaline (a borosilicate) and carbonate differently, unless they were subjected to complete recrystallization, which is not indicated by field relationships, petrography or vein paragenesis. Therefore, the Sr isotopic compositions have probably not been altered by a subsequent event and these minerals have remained as closed systems with respect to Rb and Sr.

The very low Rb/Sr ratios of the scheelites, as well as the tourmaline and carbonate make these minerals extremely useful for Sr initial ratio studies, particularly for deposits of unknown age, because their calculated initial ratios are relatively

insensitive to the time of mineralization. The $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios of scheelites reflect the Sr isotopic ratios of the fluid at the time of mineralization.

4.4.2 $^{87}\text{Sr}/^{86}\text{Sr}$ versus 1/Sr

Diagrams involving both isotope compositions and elemental abundance data can yield useful information about the evolutionary history of igneous and hydrothermal systems. One such diagram involves a plot of $^{87}\text{Sr}/^{86}\text{Sr}$ versus 1/Sr (ppm). Samples from this study are plotted on Figs 4.3 (Val d'Or samples) and 4.4 (Timmins, LH and LLL samples). Note that the present-day $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are plotted. On this type of plot the data may yield a straight line, if the Sr isotopic compositions are the result of mixing between two homogeneous end-members (Faure, 1986).

The Val d'Or data form discrete clusters on the plot of $^{87}\text{Sr}/^{86}\text{Sr}$ versus 1/Sr. The Sigma samples seem to fall into two groups, the lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratio group contains samples collected from the 1708W stope. The Pascalis scheelites, tourmaline, and carbonate, form a discrete cluster independent of the Sigma samples, while the Siscoe Extension has a lower $^{87}\text{Sr}/^{86}\text{Sr}$ and higher Sr ppm than other Val d'Or samples. It is interesting that the 1708W stope "flat" vein is bordered by several different rock types. S-01 and S-08 are scheelites from this vein where it crosscuts mafic volcanic rock, S-04 and S-05 are taken from where the vein cuts G-dyke rock (porphyritic diorite), and samples S-10 and S-11 are from the vein where the wallrock

Figure 4.3. $^{87}\text{Sr}/^{86}\text{Sr}$ versus $1/\text{Sr}$ (ppm), Val d'Or scheelites.

Figure 4.4. $^{87}\text{Sr}/^{86}\text{Sr}$ versus $1/\text{Sr}$ (ppm), Timmins, Lake Head and Little Long Lac scheelites.

is C-porphyry (feldspar porphyry dykes). All six samples cluster fairly tightly on the plot of $^{87}\text{Sr}/^{86}\text{Sr}$ versus $1/\text{Sr}$, suggesting that their $^{87}\text{Sr}/^{86}\text{Sr}$ was not obtained from their immediate wall rocks.

This contrasts with the distribution of the Pascalis mine scheelites, where the dominant host rock is the quartz diorite of the Bourlamaque batholith, and the scheelites have a slightly greater range in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios than the 1708W vein samples. However, samples from elsewhere in the Sigma mine (samples 85-009, 85-012, 87-049 and 87-051) form a cluster distinct from the 1708W stope samples. The Siscoe Extension sample sits in a unique position of low $^{87}\text{Sr}/^{86}\text{Sr}$ and high Sr (low $1/\text{Sr}$) compared to the other Val d'Or samples, in spite of the fact that the rock types which host this deposit are similar to those observed at the Sigma mine.

More detailed study of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of wallrock and vein samples will be required to determine how much of the Sr isotopic signature of the mineralizing fluid is inherited from the source, and how much may be derived from interaction with the wallrocks, but the distribution of $^{87}\text{Sr}/^{86}\text{Sr}$ in the vein minerals studied here, particularly those samples from the 1708W stope, suggests that the fluid $^{87}\text{Sr}/^{86}\text{Sr}$ dominates that of the hydrothermal minerals, as there is no systematic difference in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios that can be related to immediate wallrock type. Alternatively, the wallrocks may have had similar $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, 0.7014 to 0.7018, and this requires further testing.

The inhomogeneous distribution of Sr content within the scheelites shown by electron microprobe analysis seems to indicate a local fluctuation in the Sr content of

the fluid. Duplicate analyses of the $^{87}\text{Sr}/^{86}\text{Sr}$ on splits of the sample powder suggest either the powders are remarkably well-mixed, or the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in the scheelites is not as variable as the Sr content.

The Timmins data, with the exception of the Coniaurum scheelite, may be interpreted as defining a linear array on a plot of $^{87}\text{Sr}/^{86}\text{Sr}$ versus $1/\text{Sr}$ (Figure 4.4). The McIntyre sample has a low Sr and very high $^{87}\text{Sr}/^{86}\text{Sr}$ ratio and is anomalous relative to all other scheelites analysed from the Timmins area. The Hollinger samples tend to form a cluster distinct from the Coniaurum samples, but close to the Dome sample. There is a tendency for the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio to decrease as the Sr content decreases, which may indicate a mixing between two end-members; however, the Coniaurum sample falls well off this trend.

The Lake Head and Little Long Lac samples both have high Sr contents and relatively high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios compared to the Val d'Or and most of the Timmins data.

4.4.3 Comparison of Scheelite and Tourmaline Sr Isotopic Compositions

Kerrick et al. (1987) examined the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of vein minerals characterized by $\text{Rb}/\text{Sr} \leq 0.02$ including, tourmaline, piemontite, actinolite and scheelite from eleven gold deposits in the Abitibi greenstone belt. King and Kerrich (1989) continued this work with additional $^{87}\text{Sr}/^{86}\text{Sr}$ analyses of tourmalines from 21 gold deposits in the Abitibi. They used the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the vein minerals to

estimate initial Sr ratios of the fluids for comparison with contemporaneous Sr reservoirs such as the upper mantle, volcanic rocks, and granitoid batholiths.

Kerrich et al.'s (1987) and King and Kerrich's (1989) tourmaline data are plotted, for comparison with the scheelite data presented in this study, in Figures 4.5 and 4.6. The reported Rb values of Kerrich et al. (1987) and King and Kerrich (1989) are generally higher than most values determined by isotope dilution analysis of the scheelites. The present-day $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were used for comparison, because the Rb/Sr ratios in these minerals are very low. The tourmaline data from Kerrich et al. (1987) and King and Kerrich (1989) is included in Appendix 6.

Val d'Or tourmaline data from Kerrich et al. (1987) and King and Kerrich (1989) are plotted with the Val d'Or scheelite analyses on an $^{87}\text{Sr}/^{86}\text{Sr}$ versus $1/\text{Sr}$ (ppm) diagram (Figure 4.5). The tourmaline data compare well with the range of $^{87}\text{Sr}/^{86}\text{Sr}$ versus $1/\text{Sr}$ determined for the scheelites, with a few exceptions. Three $^{87}\text{Sr}/^{86}\text{Sr}$ values sit above, and one below, the range defined by the Val d'Or scheelites. These values were obtained for tourmalines from the Bras d'Or mine and one from the Bevcon mine (mines that were not examined in this study, therefore, no further specific comment will be made on these data points). The average of the Val d'Or tourmaline Sr abundances of Kerrich et al. (1987) and King and Kerrich (1989) is 410 ppm ($n=19$), while that determined on scheelites in this study is 463 ppm ($n=19$).

The Timmins tourmaline Sr isotope data are plotted in Figure 4.6 along with the Timmins scheelite data. They are also in fairly good agreement with the scheelite

Figure 4.5. $^{87}\text{Sr}/^{86}\text{Sr}$ versus $1/\text{Sr}$ (ppm), Val d'Or scheelites and tourmalines. (Tourmaline data from Kerrich et al. (1987) and King and Kerrich (1989) are denoted in the legend with the prefix 'K'.)

Figure 4.6. $^{87}\text{Sr}/^{86}\text{Sr}$ versus $1/\text{Sr}$ (ppm), Timmins scheelites and tourmalines. (Tourmaline data from Kerrich et al. (1987) and King and Kerrich (1989) are denoted in the legend with the prefix 'K'.)

data in this study, but the tourmalines have slightly lower Sr contents (average of 865 ppm, n=10) than that determined in the scheelites (average of 1125 ppm, n=9). This is particularly evident for the Coniaurum samples which have identical $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.70166 scheelite, 0.7017 tourmaline) but very different Sr contents (643 and 335 ppm respectively). The Dome samples analysed by Kerrich et al. (1987) include two scheelite analyses which have the highest $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the Dome samples plotted on Figure 4.6. The Dome scheelites and tourmalines analysed by Kerrich et al. (1987) and King and Kerrich (1989) have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios above and below the Dome scheelite analysed in this study, however, the scheelite analysed in this study has a higher Sr content. The Hollinger tourmaline is anomalous in that it has a slightly higher Sr content than the Hollinger scheelites, but the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio falls within the range determined on the scheelites. None of the tourmalines analyzed from the Timmins deposits studied here yielded a similar $^{87}\text{Sr}/^{86}\text{Sr}$ value to that of the McIntyre scheelite, however, King and Kerrich (1989) did obtain some similarly high values from other deposits in the Timmins mining camp.

In summary, the tourmaline Sr isotope data presented by King and Kerrich (1989) and Kerrich et al. (1987) are in good general agreement with the Sr isotope data on scheelites from the same mines, although, the tourmalines commonly have lower Sr contents than the scheelites. These data support the hypothesis that the Sr isotopic signature of the fluid is accurately reflected in the hydrothermal minerals, and that these minerals have remained closed systems to Rb and Sr. King and Kerrich

(1989) state that the Sr initial ratios of the tourmalines do not relate to Sr content or Rb/Sr ratios of their contiguous wallrocks.

4.4.4 Comparison of Hydrothermal Fluid Sr Isotopic Composition with Possible Source Reservoirs

The initial strontium isotopic ratios of hydrothermal minerals may be compared with the Sr isotopic signatures of potential reservoirs such as the upper mantle, lower crust, mafic volcanic rocks and granitic batholiths. Interpretation of the Sr isotope data requires information on the timing of mineral precipitation and the age and initial ratios of the source reservoirs. Calculated initial ratios of the scheelites, however, are not sensitive to the choice of age for mineralization because of their low Rb/Sr ratios, therefore present-day values are used.

Initial ratios may be compared with the characteristics of the bulk Earth reservoir at the time of mineralization by use of the epsilon (ϵ) notation of DePaolo and Wasserburg (1976) in which the initial Sr at time t , R_i , is compared to the bulk Earth value at the same time R_t :

$$\epsilon\text{Sr}(t) = [(R_i / R_t) - 1] \times 10^4.$$

Negative ϵSr values indicate derivation from a source with a lower Rb/Sr ratio than the chondritic reservoir (bulk Earth) indicating a source depleted in Rb and other large ion lithophile (LIL) elements, such as depleted upper mantle. Positive ϵSr values indicate an "enriched" source, with higher Rb/Sr ratios than bulk Earth, such as sialic crustal material.

Using this notation, and an age of 2600 Ma as an estimate of age of mineralization, the Val d'Or Sr ratios (0.70135 to 0.70174) correspond to epsilon values of - 1.1 to + 4.4. Similarly, the Timmins samples have epsilon values that range from - 3.0 to + 9.0 at 2400 Ma (Bell et al. (1989) Sm-Nd isochron age for Timmins scheelites). The Lake Head scheelite yields an epsilon value of + 5.8 at 2600 Ma, and the Little Long Lac sample yields + 4.9. These values are variable and range to values significantly more positive than those obtained from the 2700 Ma Poohbah Lake syenites in northwestern Ontario (Bell and Blenkinsop, 1987) which are interpreted to have been derived from a depleted sub-continental mantle source. Bell et al. (1989) interpreted the variable Sr epsilon values from the Timmins scheelites as indicating that some of the Sr was contributed to the fluids from a more evolved reservoir than depleted mantle, i.e. continental crust, and that the fluids responsible for scheelite deposition probably reacted with their wallrocks to varying degrees.

Kerrich et al. (1987) compiled selected $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of various rock units in the Superior Province, which indicate that mafic volcanic rocks of the Superior Province have $^{87}\text{Sr}/^{86}\text{Sr}$ initial ratios in the range of 0.70105 to 0.70180. This is in agreement with pyroxenes from alkaline rocks at Kirkland Lake with $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the range of 0.7008 to 0.7018 (Hattori and Hart, 1991). The Poohbah Lake syenites, representative of depleted sub-continental mantle at 2700 Ma, have $^{87}\text{Sr}/^{86}\text{Sr}$ initial ratios of 0.70119 to 0.70124 (Bell and Blenkinsop, 1987).

The data compiled by Kerrich et al. (1987) for Superior Province intrusive rocks (ages from 2735 to 2160 Ma) ranges from 0.7008 to 0.7015. As analogues to

possible basement to the greenstone sequences Kerrich et al. (1987) compiled data on gneisses which have retained old Rb-Sr ages. These rocks have $^{87}\text{Sr}/^{86}\text{Sr}$ initial ratios ranging from 0.7014 to 0.7028, more radiogenic than the estimated contemporaneous mantle, and the Superior Province volcanic and intrusive rocks. They point out that the presence of 3.0 Ga detrital zircons in the Pontiac Sediments in the Abitibi, suggests that this greenstone belt was either underlain or flanked by older felsic crust.

Comparison of the scheelite $^{87}\text{Sr}/^{86}\text{Sr}$ ratios with the data compiled by Kerrich et al. (1987), and the Poohbah Lake syenites (Bell and Blenkinsop, 1987), indicate that the gold vein fluid initial ratios are more radiogenic than 2700 Ma depleted upper mantle, they overlap the high end of Superior Province 2650 to 2700 Ma volcanic and intrusive rocks and overlap the low end of possible Superior Province basement rocks.

4.4.5 Regional Variation in Sr Isotopic Ratios of Scheelites

It is interesting that, with the exception of the McIntyre scheelite, the scheelite samples show a slight but significant increase in measured $^{87}\text{Sr}/^{86}\text{Sr}$ from the Val d'Or through Timmins to the Geraldton (Little Long Lac) and finally Shebandowan (Lake Head) area. This corresponds to a rough southeast to north and west trend in increasing $^{87}\text{Sr}/^{86}\text{Sr}$, that may possibly reflect subtle difference in the age and/or composition of the source of the gold mineralizing fluid(s). Davis and Corfu (1991) note that within the Superior Province there appears to be a variation in the age of

greenstone belts, with ages generally decreasing towards the south and east. In addition, there is evidence for ca. 3 Ga arc, rift and plutonic rocks in the northern Superior Province (including the Uchi subprovince) and the Wabigoon subprovince. Evidence of this older crustal material has only been found in detrital zircons in the Pontiac sediments of the southern Superior Province (Abitibi subprovince). Thus there is some geological evidence for the existence of potentially different source areas underlying the Abitibi subprovince deposits (Timmins and Val d'Or) versus the deposits in the other subprovinces. The link between the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the fluid and the age and composition of possible source rock material requires more study; however, it would appear that the gold mineralizing fluids may be inheriting their Sr isotopic compositions from crustal material underlying the deposits, as opposed to the mantle, or immediate wallrocks, although both may contribute some Sr to the fluid.

Bohlke and Kistler (1986) examined the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of Sr-rich, Rb-poor hydrothermal minerals from the 140 to 100 Ma gold mineralization in the northern Sierra Nevada Foothills in California. The deposits sampled represent four districts located along the 200 kilometer strike length of the Foothills metamorphic belt. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the fluids which precipitated the vein and alteration minerals varied between 0.7039 to 0.7183, and the variations of $^{87}\text{Sr}/^{86}\text{Sr}$ within mines are generally small compared to large regional variations. They conclude that the Sr isotopic compositions of the mineralizing fluids were relatively homogeneous on a district or subdistrict scale, despite the fact that the veins traverse wallrocks of different compositions, age and metamorphic grade. These data were interpreted to be

consistent with "packets" of Sr isotopically homogeneous fluids flowing through fracture systems on the order of at least 4 km². On the other hand, the large regional variations observed in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the hydrothermal fluids from different districts they conclude to be related to regional variations in host rock ages and lithologies.

The Archean gold mineralizing systems studied here have less variation in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios than those deposits in the Paleozoic to Jurassic Sierra Nevada Foothills Belt studied by Bohlke and Kistler (1986). However, the general similarities between the Californian lode gold deposits and the Archean deposits studied here, suggest that similar processes may be controlling the fluid isotopic composition.

4.5 SUMMARY AND CONCLUSIONS

1. Most of the scheelite samples have Rb/Sr ratios less than 0.0010. Back-calculating present-day $^{87}\text{Sr}/^{86}\text{Sr}$ ratios to 2600 Ma results in a decrease in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of less than 0.0001. The present-day $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are, therefore, taken as a reliable estimate of the Sr_i ratios.
2. The scheelites from different areas have different ranges of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. The Val d'Or scheelites range from 0.70135 to 0.70174, the Timmins scheelites from 0.70146 to 0.70182 (excluding the McIntyre sample), and the Lake Head and Little Long Lac scheelites have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.70184 and 0.70177 respectively.

3. Tourmaline and carbonate samples from the Pascalis mine have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios similar to those in scheelites from the same locations.
4. Val d'Or samples have generally lower Sr contents (210 to 698 ppm, one sample with 1856 ppm), Timmins samples range from 1129 to 1571 ppm (excluding the McIntyre sample with 121 ppm), and the Lake head and Little Long Lac samples contain 6862 and 11260 ppm Sr respectively, indicating a 'provinciality' in the Sr abundances as well as isotopic composition.
5. The similarity in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios between scheelite, tourmaline and carbonate from gold-bearing veins, including the data given in Kerrich et al., 1987 and King and Kerrich, 1989, indicate that these minerals probably reflect the isotopic composition of the fluid from which they precipitated, and have retained their isotopic signature since the time of crystallization.
6. Tourmalines from the veins have lower average Sr contents than scheelites.
7. Plots of $^{87}\text{Sr}/^{86}\text{Sr}$ versus $1/\text{Sr}$ for Val d'Or scheelites do not yield linear arrays, suggesting that the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the fluids is probably not the result of mixing between two discrete end-members. Plots of $^{87}\text{Sr}/^{86}\text{Sr}$ versus $1/\text{Sr}$ for Timmins scheelites indicate some evidence for a trend from high $^{87}\text{Sr}/^{86}\text{Sr}$ -low Sr to low $^{87}\text{Sr}/^{86}\text{Sr}$ -high Sr values. However, the trend is based on very few samples and the Coniaurum sample falls well off the trend.
8. The scheelite data form clusters on plots of $^{87}\text{Sr}/^{86}\text{Sr}$ versus $1/\text{Sr}$ by deposit, primarily on the basis of Sr content.

9. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the hydrothermal minerals do not appear to correlate with wallrock types, suggesting that the Sr isotopic ratio of the fluid is dominated by an external (with respect to immediate wallrocks) source, although there may be some influence from local sources.
10. The Sr isotopic ratio of the gold-bearing fluids appears to be slightly more radiogenic than depleted upper mantle, similar to the conclusion made by Bell et al. (1989).
11. With the exception of the McIntyre sample, the scheelites show a slight but significant regional variation in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. There appears to be a progressive increase in the ratios from southeast to north and west. This may reflect a progressive shift in age and/or composition of the gold-bearing fluid source reservoir, although this hypothesis requires further testing.

Chapter 5 - Sm-Nd ISOTOPIC ANALYSES OF SCHEELITES

5.1 INTRODUCTION

One of the most controversial aspects of Archean lode gold deposits research is the timing of emplacement of the mineralization. Traditionally, the timing of mineralization has had to be inferred from the relative superpositioning of intrusive, structural, metamorphic and alteration events, combined with dating of the host rocks by conventional U-Pb zircon. The present study was initiated to evaluate the Sm-Nd isotopic system using hydrothermal vein minerals. Since this study was initiated, titanite in veins at Camflo (Zweng, 1991; Jemielita et al., 1990) and hydrothermal rutile in alteration envelopes at Sigma (Wong et al., 1989) have been dated in the Val d'Or area and are interpreted to yield the age of mineralization. These dates provide important constraints for testing the accuracy of results by the Sm-Nd method.

The Sm-Nd isotopic systematics of scheelite from Archean gold deposits in the Timmins area were examined by Bell et al. (1989) to test the feasibility of using this isotopic system for dating auriferous hydrothermal activity. The results of the study were promising in terms of the technique, but yielded a much younger age of hydrothermal activity (approximately 2400 Ma) than was anticipated or previously indicated by $^{40}\text{Ar}/^{39}\text{Ar}$ analysis of alteration minerals from these deposits (2560 to 2633 Ma, Masliwec et al., 1985). In order to further test the applicability of the

method for dating of Archean hydrothermal gold deposits, scheelite samples were collected from gold-bearing veins underground in the Val d'Or camp.

5.1.1 Samarium-Neodymium Isotope Systematics - General Comment

Radiogenic neodymium is produced from decay of radioactive ^{147}Sm , which decays by emission of an alpha particle to ^{143}Nd . The growth of the radiogenic daughter, ^{143}Nd , can be described by the equation:

$$^{143}\text{Nd} = ^{143}\text{Nd}_i + ^{147}\text{Sm} (e^{\lambda t} - 1)$$

where ^{143}Nd and ^{147}Sm are the total number of these atoms in a unit weight of the mineral at the present time (ie. the measured quantities), $^{143}\text{Nd}_i$ is the number of atoms in the same unit weight that were incorporated into the mineral at the time of its crystallization, λ is the decay constant of ^{147}Sm (in units of reciprocal years), and t is the time elapsed since the formation of the mineral (Faure, 1986). The decay constant of ^{147}Sm is generally accepted to be $6.54 \times 10^{-12} \text{ yr}^{-1}$, as calculated from the means of the most recent determinations of the half-life of ^{147}Sm . The error on the ^{147}Sm half-life of 106 Ga is on the order of ± 1 Ga (DePaolo, 1988). This represents an approximately 1 per cent uncertainty in the decay constant which should be taken into account when comparing Sm-Nd ages with those determined by other decay systems. Over geologic time, the decay of ^{147}Sm to ^{143}Nd results in systematic increase in the abundance of ^{143}Nd relative to the other Nd isotopes, which can be measured on a

mass spectrometer. The magnitude of the isotopic variations that are observed are a function of the variation of Sm/Nd in nature and the time elapsed since the system became closed.

The rare earth elements are particularly useful for petrogenetic studies because of their chemically coherent behaviour. They differ only with respect to ionic radius, which tends to decrease regularly with atomic number, referred to as the "lanthanide contraction". The fractionation that occurs within the lanthanide group therefore tends to be systematic. The very similar chemical behaviour of the REE, particularly Sm and Nd as they are both light REE, results in a limited variation in the Sm/Nd ratio, typically 0.1 to 0.5, and therefore variations in the abundance of ^{143}Nd in nature is on the order of only a few tenths of a per cent (DePaolo, 1988).

Use of the Sm-Nd system for dating requires that the following criteria be met by the system under consideration: 1) the geological system has remained chemically closed to exchange of parent and daughter elements, 2) the rocks or minerals analysed were crystallized or precipitated at the same time, t , and 3) the rocks or minerals analysed had the same initial Nd ratios at time t . If these assumptions are satisfied, then the isochron model may be applied to the system to calculate the time of crystallization using the above equation. This equation corresponds to that of a straight line of slope $(e^{\lambda t} - 1)$ and intercept $^{143}\text{Nd}_i$. The present-day isotopic composition of Nd in a mineral is a function of the Sm/Nd ratio of the mineral, and the time elapsed since the crystallization of the mineral (ie. until the mineral became a closed system to Sm and Nd).

Neodymium tends to be slightly more incompatible than Sm, thus Nd is concentrated in the liquid relative to Sm during fractional crystallization of a magma, and typical crustal rocks have lower Sm/Nd ratios than those derived from the upper mantle. Similarly, in silicate liquids derived by partial melting, Nd is enriched in the liquid phase relative to Sm. This is due to the lower ionic potential (charge/radius) of Nd^{3+} relative to Sm^{3+} (Faure, 1986).

Neodymium in the Earth's crust and mantle has evolved at different rates due to the difference in Sm/Nd ratios in these two reservoirs. The formation of the continental crust through differentiation from the mantle is thought to have begun around 4 billion years ago (Faure, 1986). Since that time, the $^{143}\text{Nd}/^{144}\text{Nd}$ ratio of the mantle has grown more quickly than that of the crust, because of the higher Sm/Nd ratio in mantle material. Thus, Nd initial ratios are useful indicators of petrogenetic processes in the Earth's crust.

The evolution of large-scale reservoirs such as the crust and mantle are commonly studied with reference to models called CHUR and bulk Earth (Chapter 4). The CHUR ("chondritic uniform reservoir") model is based on the assumption that the primitive material from which the Earth's crust and mantle are derived has the same Sm-Nd ratio as that found in chondritic meteorites (0.32). The present day $^{143}\text{Nd}/^{144}\text{Nd}$ ratio of CHUR is 0.512638 (for $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$), and the $^{147}\text{Sm}/^{144}\text{Nd}$ ratio is 0.1967 (Faure, 1986).

Bell and Blenkinsop (1987) studied the $^{87}\text{Sr}/^{86}\text{Sr}_i$ and $^{143}\text{Nd}/^{144}\text{Nd}_i$ ratios of carbonatites and related alkalic rocks that are hosted in the Canadian Shield. These

samples define a development line on a plot of age versus initial ratio that intersects the development line for bulk earth and CHUR at approximately 2900 Ma. A model was developed which involved the differentiation of a CHUR- and bulk Earth-like mantle into crustal rocks of the Superior Province and a LIL-depleted, residual upper mantle. They also suggested that this depleted sub-continental reservoir appears to have remained intact and coupled to the continental crust until at least 110 Ma ago (Bell and Blenkinsop, 1987). This very significant study provided more information about the nature of the subcontinental upper mantle under the Superior Province than is known from other continental areas in the world.

5.1.2 Previous Studies of Sm-Nd Isotopic Systematics of Hydrothermal Mineralization

Fryer and Taylor (1984) investigated the REE lithogeochemistry of some hydrothermal uranium deposits in Saskatchewan. They demonstrated a relationship between U concentration and REE abundances and a marked enrichment in HREE relative to LREE, including a marked enrichment in Sm relative to Nd, in pitchblendes. They concluded that the REE and U were transported together as carbonate complexes in the hydrothermal mineralizing fluid. The enriched Sm/Nd ratios of the pitchblendes suggested that a natural enrichment of the parent ^{147}Sm isotope might make these minerals suitable for Sm-Nd dating of the hydrothermal mineralization. Their results yielded two linear arrays which define the primary age of mineralization and a remobilization age. The results of their study led Fryer and Taylor (1984) to suggest that Sm-Nd mineral isochrons may be applied to a wide

range of mineral deposits for dating of the hydrothermal ores. They suggested that application of this approach to "Archean lode gold deposits, tungsten skarn mineralization, rare metal granite pegmatites - alkali granites, and numerous other mineralized environments" (Fryer and Taylor, 1984). Recently, Chesley et al. (1991) have studied the Sm-Nd isotopic characteristics of hydrothermal fluorites from granite-hosted tin deposits and were able to determine the age and origin of the deposit on the basis of precise Sm-Nd isochron ages of the fluorites.

Following initial investigations of the REE content of scheelites from Archean lode gold deposits (Ludden et al., 1984; Anglin et al., 1987), which indicated that the scheelites contained sufficient quantities of REE for Sm-Nd isotopic analyses, Bell et al. (1989) tested the suitability of dating scheelites. Bell et al.'s (1989) initial results illustrated that the Sm-Nd dating of scheelite is feasible. A linear array of data was obtained for the Timmins scheelite samples, but the age indicated by interpreting this line as an isochron is much younger than indicated by other geochronological studies that have been done in the area (Table 2.4). The Timmins area is geologically complex, with considerable controversy surrounding the interpretation of the structural setting and relative timing of the gold emplacement in terms of the deformations that have affected these rocks. In addition, considerable evidence has been put forward for more than one mineralizing event at the McIntyre mine, including an early porphyry gold-copper event preceding the main gold mineralization (Mason and Melnik, 1986).

The Val d'Or gold deposits are, by comparison with Timmins, much simpler structurally, and they have been the subject of detailed studies by F. Robert (Sigma)

and A. Tessier (Pascalis). Several mines in the Val d'Or area were accessible for sampling at the time of this study. For these reasons the Val d'Or region was selected as a more constrained test of the Sm-Nd dating method for hydrothermal scheelites associated with lode gold mineralization. The Val d'Or area has also recently been the subject of other geochronological studies, specifically focused on the gold mineralization, and involving the U-Pb dating of hydrothermal rutile and sphene. Such studies provide important constraints for evaluating the Sm-Nd method on hydrothermal scheelite.

5.2 METHODS

5.2.1 Samples

Thirty-six samples of scheelite (plus one tourmaline) from gold-mineralized veins, representing 8 different deposits in the Superior Province, were analysed for their $^{143}\text{Nd}/^{144}\text{Nd}$ isotopic ratios, and their Sm and Nd concentrations.

Twenty-three samples were collected from underground exposures in the Val d'Or camp including 12 scheelites from the Sigma mine, 8 from the Pascalis mine (plus one tourmaline), and one from the Siscoe Extension mine. The samples from the Sigma mine labelled S-01 through to S-11 were taken from one continuous "flat" or extension vein on the 1708 level where it crosscuts a series of wallrock types including mafic volcanics, porphyritic (subvolcanic) diorite, and feldspar porphyry dykes. Scheelites were sampled from locations in the veins adjacent to the three

different rock types (Figures 2.4 and 2.5). Samples 85-009 and 85-012 are chips from the same hand sample, provided by F. Robert, from a vein on the 3300 level. Samples 87-049 and 87-051, provided by D. Burrows, are from two different locations on the 2800 level.

The Pascalis mine samples P-06 to P-20 and P-35 were all taken from the same "flat" vein where it is exposed continuously in one drift (888XC N) over 50 metres (Figures 2.7 to 2.12). The wallrock to the veins at the Pascalis mine is dominantly quartz diorite of the Bourlamaque batholith and mafic dykes which cross-cut the batholith, however, minor aplitic dykes are also observed.

Twelve samples from the Timmins camp were obtained from the collections of the Geological Survey of Canada, mine tailings dumps, and from other geologists. These sample include, 9 from the Hollinger-McIntyre-Coniaurum vein system, 2 from the Dome mine and 1 from the Preston East Dome mine. The data for 7 of the Hollinger-McIntyre-Coniaurum samples are taken from Bell et al. (1989).

In addition, one sample of scheelite from the Lake Head deposit near Thunder Bay, and one from the Little Long Lac deposit in Geraldton were obtained from the GSC collections. The data for these two samples are also taken from Bell et al., (1989). The Timmins and other samples are not precisely located with respect to host lithologies and vein paragenetic relationships.

All of the scheelite samples come from veins that were mineralized with gold. The geologic setting of the areas included in this study and descriptions of the samples are given in Appendix 1. These deposits encompass a wide variety of host lithologies,

including ultramafic-mafic volcanic rocks, intrusions of mafic, granitic, trondhjemitic, alkalic and lamprophyric composition, and volcanoclastic and chemical sediments (Table 2.1 and Appendix 1).

The Val d'Or scheelites show no evidence of zonation or alteration either under transmitted or reflected light, or by cathodoluminescence (T. Mariano, pers. comm., 1988). The Lake Head and Little Long Lac samples also show no evidence of alteration or zoning. Several samples from Timmins do show evidence for zoning, and patches of varying cathodoluminescence were observed indicating trace element (most likely REE) variation within these samples (A. Mariano pers. comm., 1988).

5.2.2 Analytical Methods

Thirty scheelites and one tourmaline were analysed in this study for their Sm and Nd content and isotopic compositions. Present-day $^{143}\text{Nd}/^{144}\text{Nd}$ ratios were determined from unspiked dissolutions of sample splits. Concentrations of Sm and Nd were determined by isotope dilution using ^{149}Sm - and ^{145}Nd -enriched spikes. More detail on the analytical method are given in Bell et al. (1989) and in Appendix 3. The estimated uncertainties, quoted at the two-sigma level, for the $^{143}\text{Nd}/^{144}\text{Nd}$ isotopic ratios are about 0.003% and 0.5% of the quoted values for the Sm and Nd concentrations.

5.3 RESULTS

5.3.1 Val d'Or Area

Twenty-two samples of scheelite from three deposits in the Val d'Or area were analysed, including 12 samples from Sigma, 8 from Pascalis and 2 from Siscoe Extension (different scheelite grains from the same large sample). The data are presented in Table 5.1. One tourmaline from the Pascalis mine was also analysed and is included at the bottom of Table 5.1.

The $^{147}\text{Sm}/^{144}\text{Nd}$ ratios of the Val d'Or scheelites range from 0.203 to 0.499, and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios range from 0.51286 to 0.51795. The Sigma scheelite $^{147}\text{Sm}/^{144}\text{Nd}$ ratios fall between 0.346 and 0.410, and most Pascalis scheelites fall in the range 0.421 to 0.499. One sample, 87-055, has a relatively low $^{147}\text{Sm}/^{144}\text{Nd}$ ratio (0.204). The Siscoe Extension samples have relatively low $^{147}\text{Sm}/^{144}\text{Nd}$ ratios of 0.203 and 0.213. One tourmaline sample from the Pascalis mine, P-06, has a ratio of 0.254.

The Val d'Or Sm-Nd data are plotted on an isochron diagram in Figure 5.1. With the exception of one scheelite sample (85-009) the data form a very good linear array on this diagram.

5.3.2 Timmins Area

Thirteen samples of scheelite from 3 deposits in the Timmins area (the Hollinger-McIntyre-Coniaurum system is considered as one large deposit) have

Table 5.1 Val d'Or Sm-Nd Scheelite Analyses.

Sample			$^{143}\text{Nd}/^{144}\text{Nd}$	$^{147}\text{Sm}/^{144}\text{Nd}$	Nd (ppm)	Sm (ppm)
	S	85-009	0.51562	0.349	168.2	97.1
	S	85-012	0.51535	0.346	162.1	92.8
	S	87-049	0.51544	0.353	139.3	80.9
r	S	87-049(II)	0.51543	0.352	138.7	80.4
	S	87-051(II)	0.51546	0.355	205.2	120.6
r	S	87-051	0.51547	na	na	na
	S	S-01	0.51556	0.363	29.1	17.4
	S	S-03	0.51560	0.362	30.6	18.4
m	S	S-03	0.51557	na	na	na
	S	S-04	0.51584	0.373	34.7	21.5
j	S	S-05	0.51579	0.368	33.7	20.6
j	S	S-08	0.51607	0.394	23.7	15.4
	S	S-09	0.51639	0.410	29.0	19.7
	S	S-10	na	na	33.2	na
	S	S-11	0.51626	0.402	31.1	20.7
j	P	86-036	0.51715	0.453	102.0	76.7
	P	87-055	0.51290	0.204	120.7	40.7
	P	P-06	0.51662	0.421	77.6	54.0
	P	P-06**	0.51665	na	na	na
	P	P-16	0.51795	0.499	72.2	59.6
	P	P-16**	0.51796	na	na	na
	P	P-20	na	0.496	75.6	62.0
i	P	P-20	0.51775	0.488	70.6	56.9
i	P	P-20**	0.51774	na	na	na
	P	P-30	0.51702	0.445	122.3	90.0
	P	P-32	0.51714	0.452	107.5	80.3
	P	P-32**	0.51713	na	na	na
	P	P-37	0.51765	0.483	97.7	78.1
j	SE	SE-1	0.51286	0.203	130.0	43.5
i	SE	SE-1(A)	0.51297	0.213	137.2	48.3
Val d'Or tourmaline						
tm	P	P-06	0.51353	0.254	3.5	1.5

FOOTNOTES

S = Sigma mine, P = Pascalis mine, SE = Siacoe extension mine

tm = tourmaline (NB. larger analytical errors associated with these samples due to relatively low REE contents. Sm and Nd spiked ratio measurement errors approximately .01%, normally .001%)

cbt = carbonate (NB. larger analytical errors, see comment above for tm).

r = repeat dissolution

i = replicate analysis on separate chip from same hand sample

na = not analysed

m = mass spec. rerun

** = second time through REE columns, same dissolution

Figure 5.1. Sm-Nd data for scheelites (small filled squares) and one tourmaline (cross) from the Val d'Or area.

been analysed. The results are presented in Table 5.2 and include 8 analyses from Bell et al. (1989). The Hollinger-McIntyre-Coniaurum samples have $^{147}\text{Sm}/^{144}\text{Nd}$ ratios ranging from 0.195 to 0.347 and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios ranging from 0.51275 to 0.51516. The two Dome samples analysed have very similar $^{147}\text{Sm}/^{144}\text{Nd}$ ratios of 0.176 and 0.178 and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios of 0.51242 and 0.51238, while the Preston East Dome sample yields a $^{147}\text{Sm}/^{144}\text{Nd}$ ratio of 0.248 and a $^{143}\text{Nd}/^{144}\text{Nd}$ ratio of 0.51366.

The Timmins data is plotted on an isochron diagram in Figure 5.2 and show a linear relationship as demonstrated by Bell et al. (1989).

5.3.3 Other Areas

Two other scheelite samples analyzed by Bell et al. (1989) are included here for comparison. One sample each from the Wabigoon Subprovince (Little Long Lac mine), and the Shebandowan Subprovince (Lake Head mine), are included in Table 5.2. These two samples have identical $^{147}\text{Sm}/^{144}\text{Nd}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios.

5.4 DISCUSSION AND INTERPRETATION

5.4.1 Val d'Or Data

5.4.1.1 Age of Val d'Or Scheelite

The scheelite data form an excellent linear array on a Sm-Nd isochron diagram (Figure 5.1), with the exception of one data point (85-009). Sample 85-009 is from

Table 5.2. Sm-Nd Analyses of Scheelites from Timmins, Lake Head and Little Long Lac.

sample			$^{143}\text{Nd}/^{144}\text{Nd}$	$^{147}\text{Sm}/^{144}\text{Nd}$	Nd (ppm)	Sm (ppm)
Timmins area:						
b	C	85FRA022	0.51275	0.197	50.5	16.5
b _r	C	85FRA022	0.51281	0.195	51.6	16.7
b	H	85FRA018	0.51328	0.222	87.7	32.2
b	H	86FRA039	0.51342	0.236	89.8	35.0
b	H	86FRA040	0.51361	0.247	74.6	30.4
b	H	86FRA042	0.51280	0.196	100.6	32.5
	H	EW-167	0.51287	0.208	77.1	26.5
	H	EW-168	0.51333	0.232	23.3	9.0
b	M	85FRA019	0.51516	0.347	94.6	54.2
b	M	88FRA060W	0.51478	0.320	155.8	82.4
	D	85-003	0.51238	0.178	93.4	27.6
	D	86-033	0.51242	0.176	149.6	43.5
	PE	86-035-1	0.51366	0.248	258.1	105.8
Wabigoon and Shebandowan Subprovinces						
b	LH	85FRA020	0.51279	0.206	2.5	0.85
b _r	LH	85FRA020	na	na	2.5	0.84
b	LL	85FRA021	0.51275	0.206	2.8	0.94

FOOTNOTES:

C = Coniaurum mine

H = Hollinger mine

M = McIntyre mine

D = Dome mine

PE = Preston East Dome mine

LH = Lake Head mine, Thunder Bay

LL = Little Long Lac mine, Geraldton

na = not analysed

b = from Bell et al., 1989

r = repeat dissolution

Figure 5.2. Sm-Nd data for scheelites from the Timmins area including Hollinger-McIntyre-Coniaurum samples (small filled squares) and Dome and Preston East Dome samples (crosses).

the same hand sample as 85-012 and has anomalous Rb content and Rb/Sr ratio compared with 85-012 and other Sigma scheelites. Sample 85-009 may have contained some impurity or have been subject to an analytical error during dissolution and therefore is excluded from all calculations.

A straight line on a Sm-Nd isochron plot may represent an isochron or may be produced by mixing of two "end-member" components with different $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{147}\text{Sm}/^{144}\text{Nd}$ ratios. In the case of mixing, the slope of the line simply reflects the $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{147}\text{Sm}/^{144}\text{Nd}$ of the two end members and has no significance in dating the scheelites. If the system fulfils all of the requirements of an isochron, that is to say, the scheelites have remained a "closed system", and all of the scheelites had the same initial $^{143}\text{Nd}/^{144}\text{Nd}$ at the time of crystallization, then the slope of the linear array is proportional to the time at which the scheelites crystallized.

The calculated slope, intercept and corresponding uncertainties for different combinations of the data are tabulated in Table 5.3, using the method of York (1969).

For all Val d'Or scheelite samples (excluding 85-009, and using the average of 049 and 049II), the slope of this array has an MSWD (mean square of weighted deviates, a measure of how close the data fits a straight line) of 1.0 and yields an age of 2611 ± 30 Ma (two sigma) and an initial ratio of 0.50936 ± 0.00004 . The eight Pascalis scheelite samples define an excellent linear array with an MSWD = 0.1 (essentially no analytical scatter in the data), and yield an age of 2591 ± 42 Ma, and an initial ratio of 0.50942 ± 0.00006 , within analytical uncertainty of the combined

Table 5.3. Results of York (1969) Calculations of Slope, Intercept and MSWD from the Val d'Or Sm-Nd Data^{1,2}.

Location	No. of points	MSWD	Age ($\pm 2\sigma$)	initial ratio ($\pm 2\sigma$)
All Val d'Or Scheelites ³	20 scheelites	1.0	2611 (30)	0.50936 (0.00004)
Sigma	11 scheelites	1.2	2504 (182)	0.50962 (0.00022)
Sigma and Siscoe Extension	13 scheelites	1.3	2628 (46)	0.50932 (0.00005)
Pascalis	8 scheelites	0.1	2591 (42)	0.50942 (0.00006)
Pascalis	8 scheelites 1 tourmaline	3.4	2645 (38)	0.50925 (0.00005)
Pascalis and Siscoe Extension	10 scheelites	0.6	2612 (30)	0.50935 (0.00004)

1. Excluding 85-009.
2. Uncertainties at the 2σ level.
3. Using the average of 87-049 and 87-049(ii).

Val d'Or scheelite isochron. The 11 Sigma scheelite data points define a line with an MSWD of 1.2 and the age corresponds to 2504 ± 182 Ma. The uncertainty in the calculated age is much smaller when there is a greater spread in $^{147}\text{Sm}/^{144}\text{Nd}$ ratios.

Plotting the Pascalis tourmaline analysis with the Pascalis scheelites yields an MSWD of 3.4 and a slightly older age of 2639 ± 38 Ma with a slightly lower initial ratio, of 0.50925 ± 0.00005 , than that obtained for the Pascalis scheelites, but again, within analytical uncertainty.

A linear array on an isochron diagram may also be the result of mixing between two discrete end-member compositions with different $^{147}\text{Sm}/^{144}\text{Nd}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios. The linear arrays defined by the Val d'Or scheelite data are interpreted as isochrons rather than as mixing lines for the following reasons:

a) back calculation of the Val d'Or Sm-Nd data to 2690 Ma (the age of zircons found in some of the veins in Val d'Or and suggested by Claoue-Long et al. (1990) to represent the age of mineralization), and plotting these data versus their corresponding value of $1/\text{Nd}$, does not indicate an inherited collinearity, or mixing of two end-members at this time (Faure, 1986), and

b) the homogeneity of REE patterns observed in scheelites from the gold-bearing veins at Val d'Or suggests an external, well-mixed source for the REE in the mineralizing fluids.

The strongest evidence for the Sm-Nd isochron interpretation of these data, however, is the very good agreement between the age represented by the slope of the

scheelite isochron and results obtained recently by U-Pb and Pb-Pb dating on other mineral phases. These studies include U-Pb on rutile in alteration envelopes at Sigma (Wong et al., 1989), and U-Pb and Pb-Pb on titanite from veins at Camflo (Zweng, 1991; Jemielita et al., 1989, 1990). The results of these studies are summarized in Table 2.2 for comparison with the Sm-Nd age. U-Pb dating of rutile at Sigma gives an age of 2592 ± 2 Ma (Wong et al., 1989) and of rutile and titanite at Camflo gives 2625 ± 7 Ma (Zweng, 1991), which are in very good agreement with the Sm-Nd isochron age of 2611 ± 30 Ma determined on the Val d'Or scheelites.

The Sm-Nd isochron technique thus represents a very useful geochronological tool for dating hydrothermal mineralization. The technique is potentially applicable to any hydrothermal mineralizing system in which minerals precipitated that incorporate sufficient quantities of the REE, and in which the minerals have remained closed systems, with respect to Sm and Nd, since crystallization. Recently, the Sm-Nd technique has been applied to fluorite mineralization associated with the granite-related tin deposits in Cornwall, England (Chesley et al., 1991), and yielded precise Sm-Nd isochron ages, interpreted by the authors, as the time of mineralization.

The Sm-Nd data presented here brings into question the recent study by Claoue-Long et al. (1990) who dated, by ion-microprobe, 'hydrothermal' zircons from the veins in several deposits in the Val d'Or camp. They dated zircons from quartz veins, from several deposits spatially associated with the Bourlamaque batholith, and obtained ages within 20 Ma of the age of the Bourlamaque batholith. They suggested that their data constrained the formation of the gold veins to be closely related to the

emplacement of the batholith. This conclusion is inconsistent with field observations that the introduction of gold is related to a structural event that is superimposed on feldspar porphyry dykes that cross-cut the previously deformed Bourlamaque batholith (F. Robert, pers. comm. 1990). It would seem, more likely, that the zircons dated by Claoue-Long et al. (1990) were in fact magmatic zircons entrained in quartz veins during vein formation, and that these zircons were preserved because they are more resistant to alteration than other wall-rock materials. This hypothesis is supported by the observation that the Bourlamaque batholith is very rich in zircons, and that the magmatic zircons have the same optical and crystallographic characteristics as those analysed by Claoue-Long et al. (1990) (D. Davis, pers. comm. 1990).

In summary, the scheelite Sm-Nd isochron age of 2611 ± 30 Ma is in very good agreement with U-Pb ages recently obtained on hydrothermal rutile and titanite from gold-bearing veins in the Val d'Or area. In addition, these ages indicate gold emplacement to have occurred approximately 70 Ma later than the youngest magmatic activity (Camflo syenite), and approximately 60 Ma later than the youngest metamorphic activity, indicated in the Val d'Or area.

5.4.1.2 Initial Ratio of Val d'Or Scheelite Isochron

The Nd initial ratio calculated for the data shown in Figure 5.1 has implications for the source(s) of the REE and the fluids associated with the scheelites, and therefore possibly the gold mineralization, in the Val d'Or area. Initial Nd isotope ratios may be compared using the epsilon notation of DePaolo and Wasserberg (1976). The

epsilon value compares the initial $^{143}\text{Nd}/^{144}\text{Nd}$ ratio at time t (R_i), with that of the reference reservoir, eg. CHUR, at the same time (R_r):

$$\epsilon\text{Nd}(t) = [(R_i / R_r) - 1] \times 10^4.$$

A positive ϵNd indicates derivation of the material from a source that has been depleted, relative to CHUR, in the large-ion lithophile elements (Rb, K, U, Th, Nd, etc) for a significant period of time.

CHUR at 2611 Ma has a $^{143}\text{Nd}/^{144}\text{Nd}$ ratio of approximately 0.50925, slightly lower than the Val d'Or scheelite initial ratio of 0.50936 ($\epsilon\text{Nd} = +2.2$). This is consistent with the REE patterns of the scheelites from Val d'Or which indicate a source depleted in LREE, and is similar to the positive epsilon value found by Bell et al. (1989) for the scheelites from the Timmins area.

5.4.2 Timmins Data

5.4.2.1 Age of Timmins Scheelite

Bell et al. (1989) obtained an MSWD of 0.7, for an isochron made up of seven samples from the Hollinger-McIntyre-Coniaurum deposit. This array yielded an age of 2403 $\pm$ 47 Ma and an initial ratio of 0.50969 $\pm$ 0.00008. The data from Bell et al. (1989) is plotted with two additional Hollinger analyses obtained during this study, and three analyses of scheelites from the Dome mine, on Figure 5.2.

The new data fall on the same linear array defined by Bell et al. (1989). The results of the calculations of slope, age, $^{143}\text{Nd}/^{144}\text{Nd}$ initial ratio (intercept) and MSWD for the data are presented in Table 5.4. The addition of the two Hollinger scheelite determinations to the data of Bell et al. (1989) result in a higher MSWD, a slightly lower initial ratio, and an older age of 2425 ± 68 Ma, within analytical uncertainty of the age obtained by Bell et al. (1989). When the scheelite samples from the Dome and Preston East Dome mines are included the MSWD increases to 3.3 and the age increases to 2479 ± 60 Ma. The two Dome and one Preston East Dome samples alone yield a slope corresponding to an age of 2688 ± 172 Ma. The Dome and Preston East Dome deposits are situated on a separate fracture system from the Hollinger-McIntyre-Coniaurum system, and these scheelites may have been derived from fluids with slightly differing Nd initial ratios, or the Dome and Preston East Dome mineralization may represent an older mineralization event.

The 2403 Ma scheelite isochron age for the Timmins gold deposits presented by Bell et al. (1989) is somewhat controversial. The age of the host rocks in the area has been determined by U-Pb zircon dating (Table 2.3), and a maximum age constraint on the gold mineralization at the Hollinger-McIntyre deposit, is provided by albitite dykes, the youngest lithology crosscut by gold-bearing veins, which yield a date age of 2673 Ma (Marmont and Corfu, 1989). Previous efforts to date the gold mineralization in the Timmins deposits have primarily relied on $^{40}\text{Ar}/^{39}\text{Ar}$ dating of alteration and vein micas. These data (Table 2.3 and references) yield dates of 2633 Ma to 2478 Ma. A date of 2450 Ma has also been obtained which was referred to as a disturbance

Table 5.4. Results of York (1969) Calculations of Slope, Intercept and MSWD from the Timmins area Sm-Nd Data¹.

Location	No. of points	MSWD	Age ($\pm 2\sigma$)	initial ratio ($\pm 2\sigma$)
Combined Timmins area	13 scheelites	3.3	2479 (60)	0.50956 (0.00005)
Hollinger-McIntyre Coniaurum	10 scheelites (2 from Coniaurum)	2.1	2425 (68)	0.50964 (0.00005)
Dome and Preston East Dome	3 scheelites	0.3	2688 (172)	0.50926 (0.00011)
Bell et al., 1989	7 scheelites	0.7	2403 (47)	0.50969

1. Uncertainties at the 2σ level.

in a fuchsite age spectra by McMaster et al. (1987). Additional evidence for a relatively "young" event in the Timmins area is given by a whole rock Rb-Sr isochron on metasomatised fault rocks at the Hollinger mine which defines an age of 2410 Ma and initial ratio of 0.70256 ± 0.00011 (Kerrick et al., 1987). A secondary Pb isochron on galenas from gold mineralization in the Matachewan area also yields a date of 2406 Ma (Sinclair, 1982).

A definitive minimum age constraint for the mineralization at Timmins is not available. The gold deposits are cut by Matachewan-type dykes, but these have yet to be dated in the Timmins camp itself. Gates and Hurley (1973) obtained a Rb-Sr age of 2633 ± 93 Ma for the Matachewan swarm, but Fahrig (1987) correlated the Matachewan dykes with the early Huronian Thessalon and Copper Cliff volcanics and Krogh et al. (1984) dated the latter by U-Pb zircon at 2450 Ma. Recently Heaman (1988) obtained a U-Pb zircon age of 2454 ± 2 Ma for a diabase dyke from the Hearst swarm, located west of the Kapuskasing structure, thought to be correlative of the Matachewan dykes (Ernst and Halls, 1984).

The coincidence of an approximately 2450 Ma old 'event' registered by many different isotopic systems, on different mineral species, is strong evidence for a relatively late Archean event affecting the Timmins area.

The complexity of gold mineralization in the Timmins camp, and the ongoing controversy regarding the primary origin of the mineralization in the area, i.e. syngenetic versus magmatic-porphyry versus later structurally-hosted metamorphic outgassing, suggest that these deposits may well have been subjected to more than one

period of mineralization, and possibly remobilization of gold. However, the Sm-Nd and much of the $^{40}\text{Ar}/^{39}\text{Ar}$ dating indicates mineralization ages significantly younger than the age of volcanism and magmatism in the area.

5.4.2.2 Initial Ratio of Timmins Scheelite Isochron

The initial ratio of the Hollinger-McIntyre-Coniaurum isochron (0.50964) compared with that of CHUR at 2425 Ma (0.509494) corresponds to an ϵ_{Nd} of +2.9 (and is similar to the epsilon value obtained by Bell et al. (1989)). It is interesting to note that this is consistent with the positive ϵ_{Nd} ratio of the Val d'Or scheelite isochron. Positive epsilon values indicate derivation from sources that had a higher Sm/Nd ratio than CHUR, such as LIL-depleted mantle, or material derived from it.

5.4.2.3 Implications of Scheelite Isochron Initial Ratios

The initial ratios of both the Val d'Or and the Timmins scheelite isochrons yield positive ϵ_{Nd} values indicating derivation of the REEs in the fluid (and possibly the fluid itself) from depleted mantle or material derived from it. Bell and Blenkinsop (1987) noted that carbonatites (mantle-derived material) hosted in the Canadian Shield define a development line on a plot of age versus initial ratio that intersects the development line for bulk earth and CHUR at approximately 2900 Ma.

Bell and Blenkinsop (1987) interpreted the 2900 Ma intersection age as the time of differentiation of a CHUR- and bulk Earth-like mantle into crustal rocks of the Superior Province and a LIL-depleted, residual upper mantle. They also suggest that

this depleted sub-continental reservoir appears to have remained intact and coupled to the continental crust until at least 110 Ma ago (Bell and Blenkinsop, 1987). The Timmins and Val d'Or scheelite isochrons define a (two-point) development line that intersects the CHUR development line at approximately 3 Ga based on the calculated intersection of these two lines. It is interesting to note the similarity in CHUR intersection ages of the gold deposit and the carbonatite "development lines". This suggests that Superior Province carbonatites and gold-bearing fluids may both be derived from a depleted mantle layer underlying the Superior Province.

5.5 SUMMARY AND CONCLUSIONS

1. The scheelite data from Val d'Or and Timmins form very good linear arrays on a Sm-Nd isochron diagram. These arrays do not appear to originate from mixing. This is supported by the homogeneity of the REE patterns of the Val d'Or scheelites.
2. For all Val d'Or scheelite samples the slope of the linear array has an MSWD of 1.0, an age of 2611 ± 30 Ma (two sigma) and an initial ratio of 0.50936 ± 0.00004 . The scheelite Sm-Nd isochron age is in good agreement with results obtained recently by U-Pb and Pb-Pb dating on other mineral phases.
3. The Sm-Nd isochron age indicates that gold emplacement occurred approximately 70 Ma later than the youngest magmatic activity, and approximately 60 Ma later than the youngest metamorphic activity, indicated in the Val d'Or area.

4. The Val d'Or scheelite isochron initial ratio of 0.50936 ± 0.00004 corresponds to an epsilon value of + 2.2, indicating derivation of the material from a source depleted in large-ion lithophile elements.
5. New scheelite data from the Hollinger-McIntyre-Coniaurum deposits fall on the same linear array defined by Bell et al. (1989) and yield an age of 2425 ± 68 Ma and initial ratio of 0.50964 ± 0.00005 . The addition of the new data results in a slightly higher MSWD, but the initial ratio, and the age are, within analytical uncertainty, the same as those obtained by Bell et al.(1989).
6. Three scheelites from the Dome and Preston East Dome mines yield a much older Sm-Nd isochron age of 2688 ± 172 Ma and an initial ratio of 0.50926 ± 0.00011 . These data indicate that there may be more than one period of gold mineralization in the Timmins camp. Further work is required to test this hypothesis.
7. The initial ratio of the Hollinger-McIntyre-Coniaurum isochron (0.50964) corresponds to an ϵ_{Nd} at 2425 Ma of +2.9, and this is similar to the ϵ_{Nd} value from the Val d'Or scheelites.
12. The Timmins and Val d'Or scheelite Nd initial ratios define a (two-point) development line that intersects the CHUR development line at approximately 3 Ga, similar to the CHUR intersection age of 2900 Ma of the carbonatite "development line" defined by Bell and Blenkinsop (1987). This may indicate that Superior Province carbonatites and gold-bearing fluids may both be derived from a depleted mantle layer underlying the Superior Province.

13. The Sm-Nd isochron method is a viable geochronological dating tool for hydrothermal mineralization.

Chapter 6 - DISCUSSION AND CONCLUSIONS

6.1 DISCUSSION

6.1.1 Summary of Present State of Knowledge Regarding Genesis of Gold Deposits

Hypotheses for the genesis of mesothermal gold deposits have generated considerable controversy and various models are presently proposed for the origin of mesothermal gold deposits (Keays and Skinner, 1989). Currently, two models dominate the debate concerning the origin of the lode gold mineralization: 1) the magmatic model, which proposes that the close spatial association between gold mineralization and felsic intrusive rocks observed in many gold camps is indicative of a magmatic derivation of the mineralizing fluid and/or gold (Burrows et al., 1986; Burrows and Spooner, 1986; Cameron and Hattori, 1987; Hattori, 1987; Wood et al., 1986); and 2) the metamorphic-replacement model (Groves and Phillips, 1987), which calls upon structural focusing of auriferous fluid from an unknown source which may include metamorphic dewatering of underlying greenstones (Kerrick and Fyfe, 1981) or derivation of fluids during granulite formation in the lower crust (Cameron, 1988, 1989; Colvine et al., 1988).

Recent U-Pb dating of rutiles and titanite associated with the mesothermal gold mineralization in the Val d'Or area (Zweng, 1991, Jemielita et al., 1990, Wong et al., 1989) have provided convincing evidence that the hydrothermal gold mineralization is younger than any identified magmatic or regional metamorphic activity that is spatially

associated with the deposits. In addition, Jemielita et al. (1990) point out that the U-Pb ages of the titanites and rutiles are broadly contemporaneous with growth of zircons in high-grade metamorphic rocks of the Kapuskasing structural zone. These zircons yield ages ranging from 2660 Ma for cores in higher level rocks, to as young as 2504 Ma in titanites in deeper level rocks (Krogh et al., 1988). The Kapuskasing structure is thought to be representative of the lower crust underlying greenstone belt material (Percival and Card, 1983). Jemielita et al. (1990) point out that the correspondence in ages between the gold-mineralizing hydrothermal activity and the metamorphism at deeper crustal levels may indicate that these are related processes. They suggest that fluids derived from devolatilization of the lower crust may be focused along major structural breaks such as the Kirkland Lake - Cadillac fault (Fig. 2.1), and ultimately be involved in the hydrothermal gold mineralizing process.

Fyon et al. (1989) have made a similar suggestion, on the basis of carbon-isotopic data, that granulitization of the lower crust may have played an important role in Archean mesothermal gold mineralization. They point out that a large volume of CO₂-bearing fluid of relatively uniform isotopic composition is required to account for the tremendously large volumes of hydrothermal carbonate minerals precipitated in the vicinity of the gold mineralized zones. Fyon et al. (1989) suggest that the source reservoir for this fluid must have been large and contained significant volumes of CO₂ with a uniform carbon-isotopic composition. The average δC^{13} value of - 4 and the uniformity of the C-isotopic composition would not be expected from prograde

metamorphism of a heterogeneous greenstone pile and are more consistent with a mantle source.

Fyon et al. (1989) noted that fluid inclusions in granulites include CO_2 and H_2O - rich types and they tend to have relatively uniform isotopic compositions, which may in turn reflect derivation from an external source. There is evidence that the formation of some granulites may be related to the influx of heat and/or magmatic CO_2 into amphibolitic precursors. In addition, the P-T-t paths and heat requirements in some granulitic terrains imply a thermal history compatible with magmatic underplating at the base of the crust, or intrusion of magma into the crust (Fyon et al., 1990).

Fyon et al. (1989) presented a genetic model for Archean gold mineralization in which granulitization of the lower crust is induced by an influx of heat and volatiles generated in the upper mantle and lower crust by degassing of silicate magmas (Fig. 6.1). A CO_2 -rich fluid may evolve, as H_2O is preferentially removed by partial melts, and subsequently flow towards higher crustal levels along regional structural zones. This CO_2 -rich fluid would probably be a very effective transporting medium for Au and many other LIL elements. Fyon et al. (1989) note that the incompatible element suite that is commonly enriched in alteration zones around gold veins (K, Rb, Li, B) is similar to the LIL element suite that is commonly depleted from granulites.

Figure 6.1. Composite crustal section illustrating the elements of Fyon et al.'s (1989) genetic model for Archean gold deposits. U = melt material, dashed lines = zones of carbonatization, cross pattern = intrusive rocks. Diagram modified after Fyon et al. (1989).

6.1.2 implication of the Results of this Study for Genetic Models of Archean Mesothermal Gold Deposits

The Sm-Nd data on scheelites from gold-bearing veins in the Val d'Or and Timmins areas yield isochron ages of 2611 Ma and 2425 Ma respectively. The Val d'Or age is in very good agreement with U-Pb dating of titanites and rutiles from the Camflo and Sigma deposits. Although the Timmins age is considered by some authors to be controversial (Claoue-Long et al., 1990), there is abundant evidence from Rb-Sr whole rock isochrons, a Pb-Pb secondary isochron, and some young $^{40}\text{Ar}/^{39}\text{Ar}$ dates on alteration micas, to indicate that some of the gold mineralization in the Timmins camp may in fact be late "Archean" in age.

The presence of zircons and titanites in the Kapuskasing structural zone with ages as young as 2504 Ma indicates that significant "metamorphic" activity and fluid movement continued until very late in the Archean (Krogh et al., 1988). The older Kapuskasing zircons identified by Krogh et al. (1988) indicate that the Kapuskasing structural zone rocks have undergone a protracted history of metamorphism and volatile movement.

In the Red Lake area deformation, alteration and gold mineralization are constrained to between 2718 and 2700 Ma (Corfu and Andrews, 1987), but calc-alkaline volcanism and plutonism were initiated circa 2730 Ma and terminated circa 2700 Ma, which is 20 to 35 Ma earlier than these events took place in the southern Superior Province (Fyon. et al., 1989). The isotopic data presented here suggest that gold mineralization in the southern Superior Province (Abitibi Subprovince) did not

occur contemporaneously in all areas, but that different areas may have been mineralized at different times during the Archean.

The initial Nd ratios of the Val d'Or and Timmins scheelites, and the collinearity of the points on these isochrons, suggest that the REEs in the gold-bearing fluids were derived from an isotopically homogeneous source that had a depleted mantle-like isotopic signature. If the REE's in the gold mineralizing fluids in both these deposits are assumed to have had a similar source, the Val d'Or and Timmins Nd data define a (two-point) line on a Nd_i versus age development diagram that indicates a 3083 Ma age of derivation of the LIL-depleted source from a CHUR-like mantle. This is in good agreement with other isotopic systems that indicate a major mantle differentiation event around 2900 Ma (Bell and Blenkinsop, 1987).

The Sm-Nd isotopic data presented here thus support the hypothesis that depleted mantle may have been the source of some of the constituents of the gold-mineralizing fluids. Mantle degassing of CO_2 may provided an effective transport medium for REEs and gold to higher crustal levels.

Strontium isotopic ratios of scheelites from the Superior Province gold deposits have initial ratios that indicate derivation from a source that appears to be slightly more evolved than contemporaneous upper mantle. There also is a small but consistent shift in the $^{87}Sr/^{86}Sr$ ratios of the scheelites from lower average values in the southern Superior Province deposits, to slightly higher average values in the scheelites from gold deposits in the Wabigoon and Shebandowan subprovinces. The

provinciality in Sr isotopic signature of the hydrothermal fluids may reflect the "average" wallrock that interacted with the fluids in the lower crust. Bohlke and Kistler (1986) recognized this characteristic Sr isotopic provinciality of gold mineralizing fluids in the Mother Lode and related gold districts in California. They found that the Sr isotope ratios of the fluid reflected that of the rocks within a 4 km² area around the district, and they argued that the slight differences in Sr isotopic ratios may indicate the relative ages of the crustal rocks underlying the gold mineralized district. There is evidence that the basement and therefore cratonization ages of the Superior Province increase from southeast to northwest, consistent with the apparent shift in Sr isotope ratios.

Thus the Nd and Sr isotopic data provide evidence that gold mineralizing fluids may have been derived from a depleted mantle source that has interacted with the lower crust on its way to higher crustal levels. In addition, the Sm-Nd isotopic method has proved to be a valuable geochronological tool for dating hydrothermal gold mineralization. This method should prove very useful for dating a variety of types of hydrothermal mineralization.

6.2 SUMMARY AND CONCLUSIONS

1. The range of Sr contents in scheelites from individual deposits is more restricted than the total range of Sr contents in all scheelites analysed. There appear to be significant differences in Sr contents of scheelites between those from deposits in the Abitibi greenstone belt (Timmins and Val d'Or) and those in the Wabigoon, Shebandowan and Uchi Belts. The Wabigoon, Uchi and Shebandowan Subprovince (Geraldton-Beardmore, Pickle Crow and Lake Head areas, respectively) scheelites have considerably higher Sr contents than the scheelites from the Abitibi Subprovince. EMP analyses indicate that Sr is inhomogeneously distributed in the scheelites. The degree of inhomogeneity appears to be greater in the high Sr concentration scheelites.
2. The REE contents of scheelites within a single deposit or district are generally fairly uniform, but significant variations exist between groups of deposits. The Wabigoon, Shebandowan and Uchi subprovince scheelites have significantly lower average total REE(-La) contents than the Abitibi samples. Scheelites from all deposits sampled, except those in Val d'Or, have a significantly positive Eu anomaly, which contrasts with data from scheelites from some magmatic and skarn deposits, which have a distinctive negative or no Eu* anomaly.

3. The REE patterns of the scheelites can be separated into two groups on the basis of the chondrite-normalized data. Samples from Val d'Or have a pattern with a broad positive hump in the intermediate REE's with nearly equivalent chondrite-normalized Eu and Tb values, and a distinctive LREE depletion, while all other samples, including those from Timmins, have relatively flat LREE, and distinctly HREE depleted profiles, with a distinct positive Eu anomaly.
4. The provinciality of scheelite Sr contents suggests a regional control (possibly different source areas or different crustal material underlying the deposits which interacted with the fluids) on the Sr content of the fluids.
5. Homogeneity of patterns and REE abundances in scheelites from the Val d'Or area suggest a homogeneous, external (i.e. not immediate wallrocks) source for most of the REE. The scheelite REE patterns, including the Eu anomaly, appear to be reflecting that of the fluid, which in turn acquired its REE distribution at source, although the patterns may be modified by phases co-precipitating with the scheelites.
6. Replicate dissolutions yield good reproducibility of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios indicating that individual samples are relatively homogeneous with respect to their Sr isotopic compositions. The similarity in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios between scheelite, tourmaline and carbonate from these veins, including data reported on tourmalines by Kerrich et al., 1987 and King and Kerrich, 1989, indicate that these minerals, a) reflect the isotopic composition of the fluid from which they precipitated, and b) have retained their isotopic signature since time of crystallization, that is to say they have behaved as closed systems with respect to Rb and Sr.

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7. The Rb concentrations of all of the analysed scheelites are < 3 ppm, and most samples have Rb/Sr ratios less than 0.0010. If the present-day $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are back-calculated to 2600 Ma this results in a decrease in the ratio of 0.0001 or less. For this reason, the present-day $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are taken as a reliable estimates of the Sr_i ratios.
8. Plots of $^{87}\text{Sr}/^{86}\text{Sr}$ versus $1/\text{Sr}$ for Val d'Or does not yield a linear array, therefore suggesting that the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the fluids is not the result of simple binary mixing i.e between two discrete end-members. The data form clusters on plots of $^{87}\text{Sr}/^{86}\text{Sr}$ versus $1/\text{Sr}$, primarily on the basis of Sr content. The Timmins data may form a linear array on a plot of $^{87}\text{Sr}/^{86}\text{Sr}$ versus $1/\text{Sr}$, from high $^{87}\text{Sr}/^{86}\text{Sr}$ and low Sr to low $^{87}\text{Sr}/^{86}\text{Sr}$ and high Sr; however, the data from the Coniaurum sample falls well off the trend. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the hydrothermal minerals do not appear to correlate with wallrock types, suggesting that the Sr isotopic ratio of the fluid is not dominated by the immediate wallrocks but by an external source.
9. The Sr isotopic ratio of the gold-bearing fluids appears to be slightly more radiogenic than depleted upper mantle which supports the findings of Bell et al. (1989).

10. The scheelites from different districts have distinct $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. The Val d'Or scheelites range from 0.70135 to 0.70174 ($\bar{x}=0.70154$, $n=23$), the Timmins scheelites range from 0.70146 to 0.70227 ($\bar{x}=0.70171$, $n=9$) (excluding the McIntyre sample, $\bar{x}=0.70164$), and the Lake Head and Little Long Lac scheelites have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.70184 ($n=1$) and 0.70177 ($n=2$) respectively. With the exception of the McIntyre sample, the scheelites show a slight but significant shift in $^{87}\text{Sr}/^{86}\text{Sr}$ from lower to higher values from southeast to north and west. This may reflect a progressive shift in age and/or composition of the gold-bearing fluid source reservoir.
11. The Val d'Or scheelite data form a very good linear array on a Sm-Nd isochron diagram. This is not considered to be a mixing line, but an isochron, implying a homogeneous source with respect to the $^{143}\text{Nd}/^{144}\text{Nd}$ and probably all of the REE. This is supported by the homogeneity of the REE patterns of the Val d'Or scheelites. For all Val d'Or scheelite samples the slope of this array has an MSWD of 1.0 and yields an age of 2611 $\pm$ 30 Ma (two sigma) and an initial ratio of 0.50936 $\pm$ 0.00004.
12. The Val d'Or scheelite Sm-Nd isochron age is in very good agreement with results obtained recently by U-Pb and Pb-Pb dating on other mineral phases. The Sm-Nd isochron method therefore appears to be a viable geochronological dating tool for hydrothermal mineralization. The Sm-Nd age indicates that gold emplacement occurred approximately 70 Ma later than the youngest magmatic activity, and approximately 60 Ma later than the youngest metamorphic event, in the Val d'Or area.

13. New scheelite data from the Hollinger-McIntyre-Coniaurum deposits fall on the same linear array defined by Bell et al. (1989). The addition of the new data results in a slightly higher MSWD, but the age and the initial ratio (2425 ± 68 Ma, 0.50964 ± 0.00005) are, within analytical uncertainty, the same. Previous efforts to date the gold mineralization in the Timmins deposits have yielded ages from 2633 Ma to 2450 Ma. Evidence for a relatively "young" event in the Timmins area (2410 Ma) is given by a whole rock Rb-Sr isochron on metasomatised fault rocks at the Hollinger Mine (Kerrick et al., 1987), and a secondary Pb isochron on galenas from gold mineralization in the Matachewan area (2406 Ma, Sinclair, 1982).

14. The Val d'Or scheelite isochron initial $^{143}\text{Nd}/^{144}\text{Nd}$ ratio of 0.50936 corresponds to an epsilon value of + 2.2, indicating derivation of the material from a source depleted in large-ion lithophile elements. The initial ratio of the Hollinger-McIntyre-Coniaurum isochron (0.50964) corresponds to an ϵNd at 2425 Ma of +2.9, which is consistent with the positive ϵNd value from the Val d'Or scheelites and also points to derivation from a depleted mantle-like source. The Timmins and Val d'Or scheelite initial $^{143}\text{Nd}/^{144}\text{Nd}$ ratios define a (two-point) development line that intersects the CHUR development line at 3083 Ma, similar to the CHUR intersection age of 2900 Ma of the carbonatite "development line" defined by Bell and Blenkinsop (1987). This suggests that Superior Province carbonatites and gold-bearing fluids may both be derived from a depleted mantle layer underlying the Superior Province.

15. The Sm-Nd method is a valuable geochronological tool applicable to age dating of hydrothermal mineralization.

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APPENDIX 1 - Sample Locations and Descriptions			
SAMPLE #	LOCATION	LOCATION DESCRIPTION	DESCRIPTION OF SAMPLE
SIGMA MINE			
85-009	Sampled by F. Robert (sample 3302.01)		Coarse scheelite (-60 +80 mesh)
85-010	Sampled by F. Robert (sample 3830.06)		Scheelite and tourmaline, scheelite (-60 +80 mesh) sampled and hand picked by FR
85-011	Sampled by F. Robert (sample 3830.03)		Scheelite with quartz, tourmaline and pyrite
85-012	Sampled by F. Robert (sample 3302.01)		Same hand sample as 009. 3 cm chunk of massive scheelite from FR, uniform under cathodoluminescence, fractured but undeformed?
85-013	Sampled by F. Robert (sample 802.09)		Tourmaline + scheelite + quartz
85-014	Sampled by F. Robert (sample 2103.02) (2103 W2B-02)		Scheelite, quartz and minor pyrite and wall rock, pyrite contamination in the scheelite separate.
87-049	Sampled by D. Burrows (sample 28-59A) Vein# 2804W 10 m East of Station #6179.		Scheelite in a quartz vein at the border of silicified and pyritized light green wall rock.
87-050	Sampled by D. Burrows (sample 28-59B) Same location as "049"		Scheelite in a quartz vein and dark green to black wall rock with pyrite.

87-051

Sampled by D. Burrows
(sample 28-66)
vein # 2802E

Scheelite and quartz with minor tourmaline

S-01 to S-11

16 level, stope 1708W (40 feet below 16 level) from the SE wall of the 1708 W stope where the vein cross cuts all three rock types mentioned above from one "flat vein" (extension vein) exposed in within 15 metres of vein strike the walls of the 1708 W stope. and the 'terminates' (and smaller This vein dips shallowly to an echelon flat veins form) to the the west and crosscuts (see south. Blade shaped carbonate Figs 2.4 and 2.5) all mine crystals grow at 90 degrees to the vein margin contact. Black lithologies including tourmaline is common in the volcanics, C-porphyry and vein particularly where the G-dyke. wallrock is C-Porphyry (see fig. 2.5).

S-01

Less than 15 cm from the A fractured honey-orange scheelite crystal (3 X 5 termination of the main vein, cm) was found at the lower vein margin. Euhedral where vein width is scheelite crystal outlines where scheelite is in contact approximately 4 to 4.5 cm, the with and surrounded by quartz (see fig. 2.6). Some wallrock is the contact between very fine grained (< 1 mm) tourmaline needles are the volcanics to the south and the included in the scheelite. Some chips sampled from G-dyke to the north (Fig. 2.5). the centre of the crystal. The wallrock is buff-green pyritized tourmalinized and albitized volcanics.

S-03

Approximately 2m. north of the Beautiful 5 cm wide orange scheelite crystal. The vein termination, the vein is ~7 crystal is euhedral where its surfaces face upward cm wide. The wall rock is G- into the vein. The crystal is rimmed along one edge dyke (fig 2.5). with very fine grained black tourmaline needles. Scheelite crystal habit presents good evidence for open space filling mechanism of vein material precipitation. No subsequent deformation of vein material (see detail in fig 2.5).

S-04		40 cm north of S-03, vein is 8 cm wide. The wall rock is G dyke.	Small (2 cm wide) scheelite crystal growing upward from a tourmaline plane in the middle of the quartz-rich part of the vein. Sub- to euhedral orange crystal. No evidence of deformation subsequent to the precipitation of the crystal.
S-05	Same as S-01	Same as S-01, G dyke wall rock.	Small approximately 2 cm scheelite crystal growing downward from upper edge of vein.
S-08	Same as S-01	Vein approximately 3 cm. wide, 10 m. N of sample S-01, volcanic wallrock	Light orange scheelite, appears fractured, but retains sub- to euhedral crystal outlines where surrounded by quartz. Some carbonate in vein at this location no tourmaline.
S-09	Same as S-01	Same as S-08	Light orange-grey, small anhedral scheelite mass (1 X 2 cm) in quartz carbonate vein with minor tourmaline. Tourmaline forms elongate needles approximately one millimeter in diameter.
S-10	Same as S-01	Vein approximately 10 cm. wide, approximately 50M. NW of S-01, C porphyry wall rock, altered with tourmaline pyrite and carbonate.	Two scheelite crystals in vein near lower margin which is marked by coarse carbonate crystals growing perpendicular to vein margin, and massive very fine grained tourmaline needles (Fig. 2.6).
S-11	Same as S-01	Approximately two metres south of sample S-10, vein approximately 10 cm wide.	Anhedral 5 X 4 cm mass of scheelite in quartz tourmaline vein.
PASCALIS MINE			
86-036	Sampled by FR. 898 stope	Quartz-tourmaline vein in shear zone (#32 vein in Bourlamaque batholith (BB)).	Massive chunk of orange scheelite (4 X 6 cm).

86-037	Sampled by FR. 637E stope (see fig 2.13)	Quartz-tourmaline vein in shear zone (#32 vein) subvertical 'shear vein'.	Anhedral orange scheelite masses 1-3 cm wide in tourmaline-quartz vein.
87-055	Sample by FR. July 1987 786 stope	'32 type' shear zone vein.	Anhedral orange scheelite mass 1 - 4 cm. wide in tourmaline-quartz vein with minor carbonate and pyrite.
P-06	Samples P-06 through P-25 from crosscut #888 -flat vein exposed in the east wall on the 825 level (Figs 2.8 - 2.12) excluding P-19 which is from the west wall of a shallowly dipping extension (or 'flat') vein.	Area 1. Fig 2.9 (enlarged detail) Scheelite crystal on the upper side of a tourmaline plane in quartz. The scheelite is not in contact with the present wall-rock to the vein.	Sampled part of the scheelite crystal (several pieces 5-10 cm in maximum dimension) with light-orange scheelite in contact with the fine grained tourmaline. Two mm pyrite cubes are present in the quartz vein.
P-09	Same as P-06	Area 1. Fig 2.9 (enlarged detail). A scheelite crystal approximately 3 cm wide between lower vein margin and a tourmaline plane. The wall-rock is light buff coloured with abundant sericite and tourmaline.	Light-orange scheelite with euhedral crystal outlines. The crystal is rimmed by tourmaline in places. Due to the brittleness of the crystal only a few small fragments were sampled.
P-15	Same as P-06	Area 2. Fig. 2-10. Scheelite crystal in vein. The crystal is not in contact with the wall rock and is approximately 7 cm above the lower vein contact.	Subhedral scheelite crystal in contact with fine-grained tourmaline plane approximately 7 cm above the vein contact. The scheelite here is darker orange than other samples taken from this vein. Only a few small chips were sampled.

- P-16** Same as P-06
- Area 2 Figs 2.10 and 2.12. Orange scheelite with euhedral outline projects Scheelite crystal projecting upward from the vein margin. Very convincing evidence for open-space-filling mechanisms of mineral precipitation within the vein. Only small chips of this crystal were obtained as samples. No evidence of deformation of the crystal after precipitation.
- P-19** 'Flat vein' exposed in the Small (< 3 cm) scheelite crystals west wall of crosscut 888N located at the lower margin of the vein. Chips were taken from one of the three small subhedral scheelite crystals. Darker orange scheelite is surrounded by fine-grained tourmaline and carbonate.
- P-20** North wall of entrance to Vein dips at approximately 30°. Two large crystals of light orange scheelite at the raise on the vein exposed in W. There is a lens-shaped lower vein margin with some fine-grained tourmaline and pyrite crystals at the vein margin. Scheelite is bordered by quartz and coarse-grained pink and white carbonate crystals. There are very sharp planar contacts between the scheelite and the carbonate crystals. Some chips samples were taken from the scheelite.
- P-21** Same as P-20
- Same as P-20
- An unusual scheelite crystal growing across the upper vein margin into the wall-rock. It is also unusual that the crystal is located adjacent to the upper margin of the vein. Most of the scheelites in this vein have been observed at or close to the lower vein contact. Only chips from the lower half (the part contained in the vein) of the crystal were sampled.

P-27	637 E stope level 625 Pascalis Mine (Fig. 2.13)	Samples P-27, 28 and 29 were all taken within a one square meter area from the north wall of this very large stope in a quartz-tourmaline shear vein, the equivalent of F. Robert's '32-type' vein. (see also sample 86-037 from the same location).	Light-orange fractured scheelite occurs in irregular anhedral masses 0.5 to 3 cm in width. Seams of tourmaline-carbonate-pyrite-sericite-chlorite less than 2mm wide run through quartz. Some chips of pure scheelite were obtained from the vein material.
P-28	Same as P-27	Same as P-27	Same habit but slightly darker orange than the scheelite of P-27. Samples were taken less than 50 cm away from P-27. Less tourmaline is present at this location than P-27, but fine wisps of fine grained tourmaline and some pyrite were noted in the vein material.
P-29	Same as P-27	Same as P-27	Darker orange anhedral scheelite masses adjacent to an altered wallrock fragment. Scheelite was very fractured and only small chips could be sampled at this locality.
P-30	637 E drift, level 625 Fig. 2.13	North wall of 637 drift, where a shallowly dipping (or flat) extension vein is exposed.	Scheelite occurs as subhedral crystals in quartz with some tourmaline needles.
P-31	Same as P-30. One metre to the east of P-30.	Same as P-30.	Fine grained black tourmaline laminae in a quartz vein with minor carbonate. No scheelite was observed at this locality.
P-32	Same as P-30. One metre east of P-31.	Same as P-30.	Scheelite in a quartz vein. The scheelite is darker orange than sample P-30 and occurs in sub to anhedral crystals 1 to 3 cm across. A 3 to 5 mm rim is developed along the edge of one scheelite crystal, otherwise tourmaline is not as abundant in this sample as in P-30 or P-31.

P-37 Gallerie 631 E Loose sample from the floor of a Anhedra scheelite-tourmaline-quartz shear vein
 Level 625 of the Pascalis small stope in a shear-type vein. material.
 Mine

S I S C O E EXTENSION

SE-1 725 level, East wall of drill South dipping shear vein in Subhedral to anhedral masses of light brownish-
 station B, approximately 60 feldspar porphyry. orange scheelite irregularly distributed in a white
 metres west of shaft. quartz vein with many small (2 - 3 mm wide)
 veinlets of chlorite-pyrite-carbonate-sericite
 roughly parallel to the vein margins. Some of the
 veinlets appear to crosscut scheelite crystals, but
 many also localize some scheelite crystals. Some
 scheelite crystals exhibit euhedral outlines but most
 most of the scheelite occurs in irregular masses.

CONAURIUM MINE

85-022 Coniaurum Mine 2750 level "Dark brown scheelite in dacite Highly sulphidized wall rock, chlorite schist with
 No. 22 vein, sampled by Dr. along 20x2 foot wide vein." Oct stringers of quartz - scheelite, deep orange-brown
 Eardley-Wilmott in 1941. 2/41 colour, fractured, irregular outlines, some
 (sample number 174) deformation. Scheelite fractured and veined by
 quartz and quartz-carbonate bearing veinlets.

HOLLINGER MINE

85-018 Hollinger Mine 1400 M1 ?III vein Sept 22/41 "Massive 12x5x3 cm hand sample of quartz and dark orange
 crosscut Eardley-Wilmott buff WO₃" Eardley-Wilmott brown scheelite. Scheelite forms large sub- to
 sample 161; Sept 22, 1941. anhedral masses, some regular and some disrupted
 contacts are observed with the adjacent quartz.

86-039	Hollinger Mine (Queens Univ. #K467)	Mine location unknown	Large vein 12-15 cm. wide, quartz and scheelite (light and dark orange colour, possibly two generations of scheelite). Wall rock is a chloritic schist with abundant pyrite and some scheelite.
86-040	Hollinger Mine (Queens Univ. #4K62)	#85 vein, 2450 level.	Massive chunk of dark-brown-orange scheelite with some quartz. The scheelite is fractured with carbonate within the fractures. The scheelite appears to have been fractured and then surrounded by quartz. Some patches of the scheelite exhibit distinct cathodoluminescence but no regular zonation or alteration patterns are observed.
86-042	Hollinger Mine (GSC collections)	Location unknown, sample marked "Hollinger mine from the Millerton porphyry. High Grade"	Very fractured massive scheelite, fractures in the scheelite filled with quartz, only one small carbonate crystal observed in thin section.
87-048	Hollinger Mine (18-8301 stope)	Sampled by D. Burrows	Massive scheelite with quartz. The orange-brown scheelite is fractured. These fractures are filled with grey quartz.
87-059	Hollinger Mine (location unknown)	Esso Minerals (Timmins) collection Sample donated by R. Shegelsi.	3x5 cm sample of massive orange scheelite in grey -white quartz, some of the scheelite exhibits euhedral crystal outlines and others are irregular.
89-IRJ-1	Hollinger Mine (location unknown)	From the GSC collections	Quartz with bright orange scheelite crystals, some scheelite has very well developed crystal outlines. Some irregular scheelite along dark seams of chlorite. Abundant visible gold in with scheelite along dark seams in quartz.
EW-167	Hollinger Mine (1400' - 50' W of No. 9)	Eardley Wilmott sample (no 167) GSC collections (Sept 22, 1941) "Buff scheelite in masses and streaks for 100 feet."	

EW-168	Hollinger Mine (3800 [level]? crosscut)	177E 21	Eardley-Wilmott sample (no 168) GSC collections.	Narrow veins of quartz with blebs and fairly big masses of scheelite
EW-169	Hollinger Mine (800 [level] 47 drift)		Eardley-Wilmott sample (no. 169) GSC collections.	"Brown-grey - masses in grey quartzite." Grey-brown scheelite in grey fractured quartz vein.

MCINTYRE MINE

85-019	McIntyre Mine 3700 level, 3772 stope Sampled by Eardley-Wilmott Sept 29, 1941.		Location (as estimated by R. Mason, Queen's Univ.) very close to the top of the 22 vein on south side of Pearl lake porphyry. 3750 level, 72 stope in brecciated pillow lavas, highly altered, highly pyritized. Adjacent to a highly strained zone.	Scheelite is fractured but not highly deformed. Some carbonate-quartz-tourmaline veinlets in scheelite. Some cathodoluminescence zoning.
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88-060W	McIntyre Mine 3700 level, 3771 drift, no. 3 vein 0.5 m S of shaft Sampled by Eardley-Wilmott Sept 29, 1941.		NE striking vein in grey "quartzose" porphyry. This stope was being mined for scheelite and gold. (Au = 6-7 oz/ton.)	Buff-coloured scheelite.
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DOVE MINE

85-003	Sample TQ74-574 sampled by R. Thorpe (GSC)		1102 level, #8 south, vein within the Preston Porphyry	Massive scheelite with included visible gold and minor quartz, from a vein within the Preston porphyry
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85-017	Eardley Wilmott sample no. 25.164 774 crosscut, 538 stope. Sample taken in September of 1925.	Coarse grained very brown-orange scheelite, quartz and chlorite(?) and minor sulphides
86-033	Sample no. 1 from D. Rogers 1104 level no. 8 stope.	Scheelite in a quartz vein from within the Preston Porphyry. Irregular masses of brown-orange scheelite, with euhedral crystal faces preserved in translucent grey quartz. Very distinct cathodoluminescence zoning.
PRESTON E DOME MINE		
86-035-1,2	Loose samples from the mine dump (?)	Orange scheelite irregularly distributed in milky white quartz. Some crystal outlines preserved, and some fracturing observed in the scheelite.
HARD ROCK		
85-002	Sample from the Queen's University collection. (unlocated).	Quartz vein with sericite and scheelite
86-032-1,2	Unlocated samples from the dump of the Hard Rock Mine.	Scheelite in quartz with minor sericite, pyrite and chlorite.
LITTLE LONG LAC MINE		
85-021	Eardley-Wilmott sample 189	Sample taken from the Little Long Lac Stockpile on the 11th October, 1942 (unlocated).

LEITCH MINE

85-001 Leitch Mine Dump Unlocated Quartz vein with scheelite blebs along stringers of chlorite, minor tellurides and gold.

85-015 Eardley-Wilmott sample 188 Selected from ore pile. 15th Oct, 1942 (unlocated). Scheelite with quartz, stringers of chlorite and sulphides (tellurides).

LAKE HEAD MINE

85-020 Eardley-Wilmott sample 198 Vein 2, section A, sampled the 14th of October, 1942. Scheelite in quartz.

PICKLE CROW MINE

85-016 Eardley-Wilmott sample 195 Quartz vein with scheelite, chlorite and sulphides. The chlorite and sulphides are found in narrow stringers in the quartz.

NOTES

FR = Sample donated by Francois Robert (GSC)
GSC = Geological Survey of Canada

APPENDIX 2 - Instrumental Neutron Activation Analytical Method

A2.1 Initial Sample Preparation (same for all analytical methods)

Relatively inclusion-free (based on visual inspection) scheelite chunks were chipped out of hand samples, and initial hand picking of scheelite was done under binocular microscope to select inclusion-free pieces for further crushing. Samples were crushed (crushing was done with a stainless steel jaw crusher, followed by agate cone crusher or agate mortar and pestle, smaller samples were done entirely using agate mortar and pestle) and then sieved into two fractions -200 and -100+200 mesh, using brass mesh (cleaned after each use with compressed air) or nylon mesh (disposed of after each use) sieves. Scheelite -100+200 mesh separates were then further purified using a super-panner, (a few samples were also put through heavy liquids), rinsed with acetone and water, dried and then run through a Frantz magnetic separator to remove any magnetic material. Samples were then checked for purity under binocular microscope.

A2.2 Neutron Activation Analyses of Scheelite

The following description of the analytical technique is taken from Anglin et al. (1987):

Approximately 0.5 grams of sample material was accurately weighed and encapsulated in polyethylene vials. The sample vials and NBS 1632A reference standards were co-radiated for 45 minutes at a thermal neutron flux of $7 \times 10^{12} \text{ n.cm}^{-2}\text{s}^{-1}$ in the rotating RIFLS facility of the McMaster University Nuclear Reactor. After an initial nine day decay period the samples were counted on a high purity 11% relative efficiency germanium detector with a resolution of 1.7 KeV at 1332 KeV.

Data were reduced using a modified version of the TEABAGS computer programme which corrects for inter-element interferences and the rare earths produced by fission of uranium. Internal calibration was based on approximately 30 international standards and normalized to the neutron flux monitored by the flux wire. Additional standards were used for quality control. Samples were recounted after a further 13 days to allow most of the activity from ^{187}W (half-life: $t_{1/2} = 23.9$ hours) to decay, to improve the precision on determination of the long-lived radioisotopes.

^{165}Dy (half-life: $t_{1/2} = 2.33$ hours) was determined by irradiating the samples and standards sequentially for 10 seconds at a thermal neutron flux of $7 \times 10^{12} \text{ n.cm}^{-2}\text{s}^{-1}$ in the microprocessor automated RABBIT system. After a decay of 3600 seconds the samples were counted and compared to international and internal (synthetic) Dy standards also irradiated in the batch.

A2.2.1 The problem of W in INAA

The presence of appreciable quantities of tungsten in scheelite presents a problem in neutron activation analysis. The isotopic composition of tungsten after neutron bombardment consists principally of 3 isotopes:

180W	n,gamma ->	145 days	0.1%
184W	n,gamma ->	70 days	30.6%
186W	n,gamma ->	24 hours	28.4%

The first two isotopes have small effective cross-sections and therefore they are poor activators and are not a significant problem in the analyses. However, the 186W isotope activates strongly and the decay of the 187W isotope (produced from the neutron capture reaction with 186W) interferes with Tb and Yb at 86.79 keV and 396 keV (Cottrant, 1981). However, these two isotopes are normally counted after 15 days, at which time most of the activity from W will have significantly reduced. Because the half-life of 187W is only 24 hours, after 5 days most of the activity will have decayed away.

The two REEs most likely to be affected by the interference caused by the tungsten activity are 140La and 153Sm, whose half-lives are only 40.22 and 46.44 hours respectively. 175Yb, with a half-life of 101 hours may also be affected. Other TEs (and their half-lives) for which the W may cause significant interference include; 24Na (15.03 hours), 99Mo (66.6 hours), 198Au (2.696 days), U (239Np, 2.35 days). In addition, the presence of considerable background radiative activity due to the abundance of tungsten in these samples raises the detection limits for many of the other trace elements. For these reason, the data are treated as qualitative indicators of relative REE and TE abundances.

Uranium and Th also produce interferences with the REE determinations during neutron activation analysis. It is difficult to assess how much of a problem this is in the scheelites analysed in this study because U and Th abundances show poor analytical reproducibility, or are reported as below elevated detection limits (many analyses are reported as "less than" some value).

A2.2.3 Reproducibility of Scheelite REE Abundances

The total REE (minus La) are fairly consistent for duplicate analyses with some exceptions (see Appendix 5). Sample 85-012 batch "C" Ce and Nd analyses are higher than batch "B" results while the rest of the REE are similar. The six replicates of the Dome sample 86-033 show considerable variation, with 86-033-1 lower in all REE except Eu and Lu compared with the other samples, and 86-033-4 with very low reported Sm and Eu. This seems to indicate heterogeneous sample material.

The above discussion points out some problems with the neutron activation analyses of scheelites for the REE (ie underestimation of the LREE, and reported abundances may show significant variation between analytical repeat samples). No scheelite standard was available for use in this study, and repeat analyses are too few in number to calculate a meaningful standard deviation for these analyses.

Qualitative examination of the data from the repeat analyses done allow the following generalizations to be made:

1. the La analyses do not show good reproducibility,
2. the Dome sample repeats (sample 86-033) show much more variability than three analyses (two of one chip and one of another chip) of a Sigma sample, and in fact is more heterogeneous than a suite of scheelites from the Pascalis Mine or from one stope at the Sigma Mine,
3. in the low REE samples (sum REE less than 30) only the Ce, Eu, Yb and Lu analysis appear to be consistent, and
4. the REE patterns, particularly those of scheelites from Val d'Or, show good reproducibility even where abundances do not.

A2.2.4 Reproducibility of Scheelite REE Patterns

Visual inspection of chondrite-normalized REE patterns for scheelites indicate fairly good reproducibility of the 'patterns' ie. the relative amounts of the REE, if not the abundances, by INAA.

Patterns for all scheelites analysed are presented on the next three pages. The scheelites from the Sigma and Pascalis mines show remarkably consistency, with the exception of La analyses. Hollinger, McIntyre and Dome patterns are also very consistent, and distinct from the Val d'Or patterns. The patterns from the Little Long Lac, Lake Head and Pickle Crow deposits show poor reproducibility. These scheelites have the lowest total REE of all the scheelites analysed in this study.

Sigma scheelites

Sigma/Pascalis - 2

Pascalis - 3

Pascalis - 4

Hollinger-McIntyre- oniaurum

Hollinger

DOME

DOME-2

Geraldton-Beardmore

Leitch-LH-PC

Numbers in the preceding plots correspond to the following sample numbers and analytical batches:

1	D 85009	21	F P-21	41	D 86033-2	61	A 85016
2	D 85010	22	F P-27	42	D 86033-3	62	C 85016
3	C 85011	23	F P-28	43	D 86033-4		
4	B 85011	24	F P-29	44	D 86033-5		
5	C 85012	25	F P-30	45	D 86033-6		
6	B 85012	26	F P-32	46	B 85003		
7	B 85013	27	F P-37	47	C 85003		
8	C 85014	28	A 85022	48	D 86035-2		
9	B 85014	29	B 85018	49	C 85002		
10	D 87049	30	D 87048	50	B 85002		
11	D 87050	31	B 85019	51	D 86032-1		
12	D 87051	32	C 85019	52	D 86032-2		
13	D 86036	33	E 87059	53	A 85021		
14	D 86037	34	E 88040H	54	C 85021		
15	F P-06	35	E 86039	55	B 85001		
16	F P-09	36	E 86040	56	C 85001		
17	F P-15	37	E 86042	57	C 85015		
18	F P-16	38	C 85017	58	B 85015		
19	F P-19	39	B 85017	59	C 85020		
20	F P-20	40	D 86033-1	60	A 85020		

APPENDIX 3 - Rb-Sr and Sm-Nd Isotope Dilution Analytical Methods.

The isotope dilution analytical procedures used in this study are essentially those outlined by Bell et al. (1989), and are reproduced here.

Scheelite was dissolved using a slightly modified version of the procedure described by von Quadt (1985a); 100 to 200 mg samples were taken into solution in bombs using a mixture of HF and HNO₃ in a ratio of 9:2. Two separate sample aliquots were taken into solution, one for the determination of present-day ⁸⁷Sr/⁸⁶Sr and ¹⁴³Nd/¹⁴⁴Nd ratios, and the other for spiking and determination of Rb, Sr, Sm and Nd concentrations. The bombs were kept at 150 °C for at least three days, after which the solution was removed and evaporated to dryness. The yellow residue was leached with 5 ml of 6N HCl in a bomb at 150 °C for at least 12 h. The solution was then centrifuged; the liquid evaporated to about 1 ml; water added; and half of the solution used for separation of Rb, Sr and the REE by using ion exchange columns. Dowex 50 cation exchange resin was used to separate Rb, Sr and the REE. Nd and Sm were separated by reverse-phase chromatography (Richard et al., 1976)

Isotopic measurements were made on a multicollector Finnigan-MAT 261 mass spectrometer. Nd ratios were normalized to a ¹⁴⁶Nd/¹⁴⁴Nd ratio of 0.7219. The reproducibility of the isotopic ratios is about 0.003% at the two-sigma level; the precision for the Nd, Sm and Sr concentrations at the two-sigma level is about +/- 0.5% of the quoted values, and that for Rb is about +/- 1%. ... The Eimer and Amend standard gives a ⁸⁷Sr/⁸⁶Sr value of 0.70802 +/- 0.00002, and the La Jolla standard a ¹⁴³Nd/¹⁴⁴Nd value of 0.51186 +/- 0.00002. Blanks during the course of this study averaged 2 ng for Sr, 0.01 ng for Rb, and 0.02 ng for Nd and Sm.

Blanks for Nd determined in the lab. by the author and by A. Simonetti (pers. comm., 1991) in 1990-1991 range from 0.01 to 0.7 ng. Blanks for Sr determined by A. Simonetti (pers. comm., 1991) average less than 2 ng.

The sample dissolution method outlined by Bell et al. (1989) was modified slightly by the author during the course of this study. The use of stainless steel bombs was discontinued due to a problem of repeated leaking and corroding of the bomb (which resulted in the loss of many samples when the bombs corroded shut and could not be opened). SavillexTM PFA Teflon screwtop vials were tested, with teflon tape on the threads to aid in sealing, and it was found that after several days at 150°C, very few of the beakers leaked. These vials were subsequently used for all dissolutions. More detail on the lab procedures can be found in Pollock (1987).

The second column separation (reverse phase chromatography method of Richard et al. (1976)) method used by Pollock (1987) and Bell et al. (1989), and used in the first part of this study, consisted of columns of Supercil quartz tubing, with a 5mm inner bore, approximately 60 cm in height and with a 100 ml quartz glass reservoir at the top. The base of the column was fitted with a fritted polyethylene disk, filled with 10 cm of 325 mesh Teflon powder coated with DEHPA in ratio of 10:1 powder to DEHPA, and covered with a 0.5 cm layer of BioRad 1-X8 anion exchange resin (200 to 400 mesh, nitrate form). Samples were loaded, onto the top of the anion resin, with a micro-pipette through a small port drilled approximately 1 cm above the top of the resin bed.

The column configuration was modified slightly part of the way through this study to remove the necessity of loading samples through the small port, and to determine if a clean separation could be obtained using coarser Teflon powder in a wider/shorter column (and therefore speed separation time). BioRad quartz columns, 30 cm in height, with approximately 6mm bore and teflon fittings, were filled with 6 to 7 cm heights of 100-200 mesh Teflon powder coated as above with DEHPA, and covered as above with a 0.5 cm layer of anion resin. Sixty ml funnels were affixed into the small 15 ml tops for acid reservoirs. These columns were tested, and calibrated, with standard solutions of Sm and Nd and the separations were found to be very good, and faster than the tall Supercil quartz tubing columns.

Sample loading and mass spectrometry procedures are similar to those outlined in Pollock (1987) and Theriault (1990). Unspiked Sr samples were run on double Re filaments with the ionization filament at approximately 1500 to 1600 °C and a minimum ^{88}Sr signal of 3 volts at the start of a run. Ten blocks of ten scans were collected for unspiked Sr. Five blocks of ten scans were collected for spiked Sr analyses. Rubidium samples were run at less than 1500 °C, two blocks of six scans each were collected. Unspiked Nd samples were run at approximately 1900 °C with a minimum ^{146}Nd signal of 1.2 volts at the start of the run. Ten blocks of ten scans were collected for unspiked Nd analyses. Five blocks of eight scans were collected for spiked Nd and spiked Sm analyses.

APPENDIX 4 - Comparison of Sr, Nd and Sm Analyses by Isotope Dilution and Instrumental Neutron Activation Analysis

This appendix provides only a general qualitative comment on the agreement between the Sr, Sm and Nd analyses by the different analytical methods used.

Table (3.6) is a compilation of Sr analyses by INAA, ID and EMP, Table 3.12 is a compilation of Sm and Nd analyses by INAA and ID analysis. These data are used to comment on the comparison of results for scheelite analyses of these elements by the different analytical techniques.

A.4.1. NA versus ID (Sm, Nd, Sr):

Plots of Nd (NA) vs Nd (ID), Sm (NA) vs Sm (ID), Sm/Nd (NA) vs Sm/Nd (ID), and Sr (NA) vs Sr (ID) are given on the following two pages, for samples for which both types of analyses were performed. In several instances, more than one analysis of a sample was done by NA but this sample was not analysed more than once by ID. The different NA results are then compared to the same ID result. See below for linear regression calculations of these data.

Note that for the linear regression calculation of the Sm and Nd data, the average of the 6 repeat analyses of sample 86-033 were used because these data showed a significant amount of variability. It is difficult to assess whether this is an analytical problem, or one of sample heterogeneity because this is the only sample for which this many repeat analyses were done. However, the variability of the data for this one sample by NA is larger than the variability in a suite of samples from one mine (eg. Pascalis samples, 13 analyses ranging from 40 to 72 ppm Nd, and 2 samples with 107 ppm Nd), and a suite from one stope at the Sigma Mine (samples S-01 to S-11) suggests that this particular Dome sample may be quite heterogeneous. (The average 86-033 value is marked on the plots of NA vs ID with an asterisk).

The Sr data regression was done excluding one NA analysis (sample 85-021 Batch "C", marked with an asterisk on the plot of Sr (NA) vs Sr (ID)); however, this analysis is not inconsistent with the range of Sr concentration values obtained by EMP analysis of this sample.

Summary of the Results of the linear regression of NA vs ID data:

Element	x-coefficient	constant	R-squared
Sm	0.54	- 0.11	0.94
Nd	0.46	4.22	0.64
Sm/Nd	1.14	- 0.08	0.65
Sr	1.01	- 121	0.92

There is a fairly good linear correlation between Sm analyses by isotope dilution and by neutron activation analyses, however NA consistently underestimates Sm by a factor of 0.54. The correlation between Nd analysis by ID and by NA is not as good as for Sm. The NA method underestimates the Nd by a factor of 0.46 plus the intercept value of 4.22. However, the Sm/Nd ratio by isotope dilution appears to be in fairly good agreement with that determined by isotope dilution (X-coefficient of 1.14). However, there is more scatter of the data than for the Sm analyses alone.

The Sr analyses by NA and by ID are in good agreement with a correlation factor R-squared of 0.92 and an x-coefficient value of 1.01. The negative constant value indicates that the NA analyses underestimate Sr by approximately 120 ppm.

A.4.2 NA and ID versus EMP (Sr):

The range and mean of values obtained by EMP analysis are listed in Table 3.6 and plotted graphically for comparison with the NA and ID data. These data show a wide range in measured Sr concentrations in the high Sr content scheelites, but a good overall agreement between the average EMP data and the NA and ID analyses in most of the samples with average Sr less than 6000 ppm. Note that sample 022 has 9000 ppm Sr as reported by NA, but 900 ppm would be in much closer agreement with both the ID and EMP analyses. This is probably a reporting error. In the higher Sr content scheelites (greater than 6000 ppm), the EMP average analysis is consistently higher than the ID and NA data.

Nd(NA) vs Nd(ID) (PPM)

Sm(NA) vs Sm(ID) (ppm)

Sm/Nd (INAA) vs Sm/Nd (ID)

Sr(NA) vs Sr(ID) (ppm)

APPENDIX 5 - Table of Calculated Values Used for Plots

(Note that the REE and Sr values reported as "less than" were set to one-half of the "less than" value for plotting purposes.)

SAMPLE	SUMREE (ppm)	SUMREE (-La)	Ce/Yb (CN)	Ce/Nd (CN)	Eu/Eu* calc'd
85-009	351.1	243.08	1.17	0.49	1.4
85-010	254.0	151.95	0.63	0.52	1.5
85-011	182.6	174.7	0.74	0.52	2.0
85-011	181.6	173.82	1.54	0.58	2.4
85-012	370.2	355.95	1.73	0.40	2.5
85-012	249.7	240.09	1.33	0.62	2.5
85-013	71.0	63.808	0.20	1.62	2.3
85-014	167.5	155.64	0.59	1.62	1.5
85-014	205.8	195.9	0.71	0.59	1.4
87-049	239.3	226.29	1.11	0.55	1.3
87-050	298.2	207.54	0.77	0.44	1.1
87-051	344.9	325.05	6.14	0.53	1.8
Sigma avg.	243.0	209.48	1.39	0.54	1.7
86-036	221.1	167.41	0.34	0.33	0.6
86-037	191.9	149.12	0.34	0.30	0.7
P-06	257.4	238.35	0.98	0.71	1.5
P-09	273.5	258.46	0.77	0.62	1.5
P-15	219.4	211.42	0.40	0.39	1.5
P-16	193.1	183.59	0.34	0.44	1.4
P-19	294.6	275.97	0.73	0.61	1.3
P-20	190.1	183.09	0.48	0.44	1.5
P-21	191.0	182.02	0.42	0.39	1.4
P-27	428.5	403.02	1.27	0.63	1.3
P-28	245.0	232.33	0.51	0.43	1.6
P-29	364.2	350.09	0.74	0.36	1.3
P-30	250.5	238.43	0.90	0.50	1.5
P-32	208.3	199.62	0.48	0.33	1.5
P-37	245.1	235.03	0.66	0.49	1.4
Pasc.avg.	251.6	233.86	0.63	0.48	1.3
85-022	239.1	211.29	1.40	3.63	38.3
85-018	223.7	195.72	3.14	1.57	8.0
87-048	257.9	232.1	4.30	0.92	3.3
87-059	315.1	265.1	4.40	1.35	5.2
88-040H	240.2	200.2	1.54	1.10	7.0
86-039	264.0	214	3.47	1.47	5.6

86-040	233.5	203.5	1.38	1.10	6.8
86-042	299.6	249.6	4.47	1.62	5.8
Holl.avg.	262.0	222.89	3.24	1.29	5.6
85-019	211.4	196.83	0.82	0.73	6.3
85-019	237.6	219.03	0.64	0.68	6.6
Mcl. avg.	224.5	207.93	0.73	0.71	6.4
85-017	113.8	86.28	1.45	2.26	9.5
85-017	121.5	98.97	2.15	2.16	11.0
86-033-1	210.3	152.32	2.62	1.31	7.0
86-033-2	342.1	205.11	2.45	1.45	3.2
86-033-3	326.4	257.79	2.92	1.41	2.9
87-033-4	265.7	215.61	2.25	1.70	2.2
86-033-5	449.0	380.96	3.59	1.16	6.6
86-033-6	363.4	302.85	2.84	1.24	6.9
85-003	230.3	207.34	2.13	1.63	5.0
85-003	315.9	248.43	3.35	1.37	8.1
Dome avg.	273.8	215.57	2.58	1.57	5.4
86-035-2	281.9	189.75	3.09	1.12	3.2
85-002	166.9	156.44	4.22	0.69	1.9
85-002	140.6	131.68	4.05	0.83	2.2
86-032-1	256.9	174.78	6.84	0.69	2.1
86-032-2	206.6	131.88	5.77	0.80	1.9
HR avg.	192.7	148.70	5.22	0.74	2.0
85-021	36.5	19.945	6.40	1.47	4.2
85-021	9.9	6.885	1.97	1.47	111.7
LLL avg.	23.22	13.42	4.18	1.47	6.9
85-001	63.5	43.48	0.65	1.17	3.8
85-001	71.1	44.93	0.79	0.50	3.7
85-015	38.2	31.5	1.13	0.73	6.0
85-015	33.4	29.25	1.31	0.83	5.2
Leitch avg.	51.54	37.29	0.97	0.77	4.7
85-020	21.8	6.415	2.48	1.47	58.2
85-020	14.0	12.125	0.43	0.98	1.6
LH avg.	17.92	9.27	1.45	1.22	2.8
85-016	70.2	61.93	1.87	5.58	5.4
85-016	168.0	68.34	1.64	1.32	2.1
PC avg.	119.1	65.14	1.75	3.45	3.1

APPENDIX 6 - Tourmaline data of Kerrich et al. (1987) and King and Kerrich (1989)

Location	Sample No	Mineral	Rb (ppm)	Sr (ppm)	$^{87}\text{Sr}/^{86}\text{Sr}$
VAL D'OR DATA					
Kerrich et al. (1987)					
Pascalie mine	PC-1	T	2.1	813	.70143 ± 10
	PC-6	T	0.5	180	.70105 ± 31
	PC-10	T	0.5	320	.70158 ± 08
Lamaque	LS-1	T	0.5	63	.70396 ± 31
	LS-1a	T			.70398 ± 11
	LS-4D	T	2.0	751	.70439 ± 17
Bras d'Or	BD-1	T	1.2	447	.70168 ± 01
	BD-2	T	1.0	273	.70200 ± 10
	BD-3	T	1.1	441	.70200 ± 11
	BD-4	T	4.0	365	.70343 ± 04
	BD-5	T	0.5	330	.70155 ± 09
	BD-5a	T	1.3	425	.70138 ± 18
	BD-6	T	0.5	331	.70150 ± 07
King and Kerrich (1989)					
Sigma	Type 1	T	1.9	514	.7016
	Type 2	T	1.5	488	.7014
	Type 3	T	1.3	385	.7016
Bras d'Or		T	1.3	485	.7012
Nord Pascalie		T	1.1	823	.7014
New Pascalie		T	0.2	126	.7014
Bevcon		T	0.8	233	.7021
TIMMINS DATA					
Kerrich et al. (1987)					
Dome	D-1	T	0.8	1442	.71362 ± 11
	D-2	S	0.4	594	.70159 ± 08
Deep Dome	D-3	T	1.0	576	.70154 ± 17
	D-4	S	0.6	832	.70157 ± 03
Kerrich and King (1989)					
Dome		T	1.2	492	.7012
Preston	Type 1	T	0.6	655	.7013
	Type 2	T	0.9	582	.7017
	Type 3	T	0.2	1163	.7012
Hollinger		T	1.2	1975	.7016
Coniaurium		T	1.1	335	.7017

END

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