**THE APPLICATION OF SPRING WATER GEOCHEMISTRY
AND HYDROGEOLOGY TO A NON-RENEWABLE RESOURCE ASSESSMENT
OF THE SOUTH NAHANNI RIVER AREA, NWT.**

by

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Frontispiece "White Aster hot spring" (#082), the largest of the thermal springs discovered during the 1986 and 1987 field seasons. It is located in a remote area near the Meilleur River, west of the Headless Range.

ABSTRACT

A regional spring sampling program was conducted in the southern Mackenzie Mountains during 1986 and 1987 as part of a resource assessment of proposed extension areas of Nahanni National Park. The region under study crosses the structural grain of the northern Cordillera and consequently encompasses a variety of geologic terranes.

A number of factors, including lithology and known mineral occurrences, were found to be associated with variations in the geochemical character of the groundwater. Three methods of classification were attempted in order to determine the subsurface geochemical processes in the study areas, and to group waters in types for comparison of trace metal anomalies. A field classification system, based on field measurements and observations, including host lithology, was found to group springs which were excessively varied in their geochemistry. Two geochemical classification methods, one a pattern recognition system and the other a form of cluster analysis, produced consistent results. Samples were separated into seven major water types, six of which had direct or indirect application to the resource assessment.

Several areas of high interest were identified. A number of springs located in the Ragged Ranges are enriched in Zn and Ni, suggesting potential for buried base metal skarns or stratiform sulphides. A small thermal spring in the Ragged Ranges has geochemistry consistent with an underlying buried pluton (elevated W, Mo, As, F and Si). Springs of two different classes in the Meilleur River area have very high concentrations of base metals in their water and/or precipitates. One particularly

metalliferous spring suggests an underlying large body of sediment-hosted sulphides, perhaps of Mississippi Valley or shale-hosted type. The Meilleur River area is also anomalous in similar elements in stream silts and heavy mineral concentrates.

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CHAPTER 1 - INTRODUCTION

1.1 Background

The concept of spring sampling as an exploration tool is not a new one. It has been used for a number of years at the Geological Survey of Canada as an aid to stream water and sediment surveys by workers such as R.W. Boyle, I.R. Jonasson and W.D. Goodfellow. Some aspects of hydrogeochemistry have produced promising results. Hoag and Webber (1976) suggested sulphate content in groundwater could be used to detect shallowly buried sulphide bodies and tested the model on a mine in the Eastern Townships of Quebec. One of the most successful applications was in a study by deGeoffroy et al. (1967) where a detailed spring sampling program in Southwest Wisconsin led to the discovery of 56 zinc anomalies, 30 of which had previously been unknown. A number of them were drilled and found to contain economic grades of Pb-Zn mineralization. Despite this earlier work, spring sampling has rarely before been used on a regional scale. The present project covers a variety of geologic terranes and, even with more than 100 springs sampled, has relatively little coverage in any given unit.

The study involves a regional spring sampling program done in 1986 and 1987 as part of a non-renewable resource assessment of proposed extensions to Nahanni National Park Reserve conducted by Dr. C.W. Jefferson of the Geological Survey of Canada for Environment Canada, Parks. The spring sampling program was one of three aspects of the resource assessment. A detailed stream sediment survey of

both silt and heavy minerals is presently being conducted as part of a masters thesis by W.A. Spirito, and a review of the geology and mineral occurrences of the area, including the mapping of both, was conducted by Dr. Jefferson and the writer. The availability of data from all three aspects provides a good opportunity to compare the results and relative merits of each. In particular, it provides an opportunity to compare the relatively unproven method of regional spring geochemistry with that of the proven technique of stream sediment geochemistry.

1.2 Previous Work

Several previous investigations in the region of study have included hydrogeological components in their research. Virtually all of the springs in the region which are cited in literature were sampled during the present study. Most of the ones previously described are thermal. The three-digit number in parentheses in the following summary refers to the corresponding sample number used in the present study.

Atchison (1964) studied four springs in the area: Rabbitkettle Hot Spring (001), Wild Mint Hot Spring (027), Cantung East (060), and Cantung West (018). Brandon (1965) provided detailed descriptions of Rabbitkettle and Kraus (063,064) Hot Springs; the latter was then known as Clausen Creek hot spring. van Everdingen (1973) has also described Rabbitkettle and Kraus Hot Springs, as well as Twisted Mountain iron spring (069).

Gabrielse et al. (1973) reported on the various springs in the Flat River and Glacier Lake map sheets. They referred to the Hole-in-the-wall Hot Springs (052,

053) (no quantitative data are given), Wild Mint (027) and surrounding hot springs (029, 030), and Old Pot mineral springs (028). On the accompanying Flat River geologic map a cold spring (056) is noted in the central portion of the Flat River Valley a few kilometres southwest of the junction of Pass Creek and Flat River.

Crandall and Sadlier-Brown (1978) conducted a sampling program of thermal and potentially thermal springs in the Yukon and adjacent NWT and BC. They sampled the following springs in this study area: Rabbitkettle, Wild Mint, Cantung West, Cantung East, Cantung North (044), Hole-in-the-wall, Nahanni North (033), Nahanni Headwater (038), Broken Skull (040, 041) and Grizzly Bear (043) Hot Springs. Also sampled were Flat Fruit Mineral Springs (058) and Glacier Lake Iron Spring (015). They noted the occurrence of, but did not sample, three large travertine and iron-hydroxide precipitating cold springs in the Flat River valley (055, 056, 059).

Brook (1976) studied the karst landform development in the region referred to in this study as the Nahanni Karst study area. Several cold springs were referred to, including White Spray (065), Bubbling Spring (076) and a small travertine precipitating spring (125).

All of the above reports contain geochemical analyses of the waters, although none of their trace element analyses were comprehensive enough to be used in this study. The chemical analyses of waters in this study were similar to those reported in the previous studies where comparison was possible and, therefore, chemical analyses published by the above authors are not included herein.

1.3 Objectives and Scope

As noted earlier, this study is part of a non-renewable resource assessment for proposed extensions to Nahanni National Park Reserve. The region under study (Figure 1.1) encompasses part of eight NTS map sheets (105H, 105I, 95B, 95C, 95E, 95F, 95G, 95L), approximately 8000 km² in area. The spring sampling program was extended beyond the resource assessment boundaries in the Ragged Ranges area because springs of interest were known to occur nearby which could provide relevant information.

The objectives of this study are twofold: to determine the usefulness of regional spring geochemistry in judging the mineral potential of an area, and to determine the hydrogeochemical processes occurring in groundwater in the southern Mackenzie Mountains, particularly those processes which pertain to the first stated objective.

A total of 114 different springs and surface waters were sampled in the two field seasons and a number of these were sampled during both field seasons to make a total of 124 analyses obtained. Approximately three quarters of the springs had been previously unreported, eleven of which are thermal. One large hot spring, at Meilleur River (082), was discovered during the present investigations.

This thesis examines and discusses major ion and trace element analyses of the waters. Stable isotope data including ¹⁸O, ²H, ¹³C, and ³⁴S were collected for many of the springs in this study, although results of the ³⁴S are not rigorously discussed in this thesis. Stable isotopes have not previously been employed in studying springs in this region and, therefore, were of great help in the study.

Figure 1.1
Location map showing the three study areas.

CHAPTER 2 - GEOLOGIC SETTING

Nahanni National Park and the adjacent study areas cross the structural grain of the southern Mackenzie Mountains fold and thrust belt. Consequently, a large number of units are structurally repeated in the three study areas. For the purpose of this discussion, the geology as summarized in Hall *et al.* (1988) and Morrow and Cook (1987) has been simplified into 8 packages based on age and lithology (Figures 2.1 and 2.2). Only the more important formations and groups in each are mentioned below.

Proterozoic strata are the oldest in the study areas and comprise the Windermere and Mackenzie Mountain Supergroups. These are exposed in the Ragged Ranges study area and adjacent terrane, but not in the eastern study areas. In Figure 2.1, Proterozoic rocks have been simplified as platformal and basinal strata, the first mostly carbonates and the latter shales and shaly facies. Carbonate units within the Proterozoic basinal strata host a number of skarn deposits where they are intruded by plutons near the Ragged Ranges study area, most notably the Cantung tungsten deposit.

Early Paleozoic strata are the most widely exposed in the study areas. These have also been simplified into platformal (carbonate-dominated) and basinal (shale-dominated) facies. The platformal strata include such units as the Rabbitkettle, Sunblood, Whittaker, Nahanni, Arnica and Headless Formations. The deep river canyons near the eastern park boundary and the karst topography in the Nahanni Karst study area are developed in early Paleozoic platformal carbonates. The

Figure 2.1
Simplified geology in the Ragged Ranges study area and surrounding region.
From Jefferson *et al.* (1989).

Figure 2.2
Simplified geology in the eastern study areas and surrounding region. From Jefferson *et al.* (1989). For legend, see Figure 2.1.

Rabbitkettle limestone hosts the Lened tungsten skarn.

The early Paleozoic basinal strata include units such as the Road River Group and Cadillac and Funeral Formations. Siluro-Devonian shales underlie the western part of the Tlogotsho Plateau study area and form the Prairie Creek Embayment (Morrow and Cook, 1987) that lies just west of Nahanni Karst. The embayment opens westward into Selwyn Basin which predominates beneath the Ragged Ranges study area. The shaly strata, in particular the Road River Group, are host to numerous zinc-dominated stratiform base metal deposits, such as the Howard's Pass and Vulcan deposits. Cambrian to Ordovician platformal carbonates underlie the northeastern part of the Ragged Ranges study area and all of the Nahanni Karst and Tlogotsho Plateau study areas. The Manitou Facies of the Nahanni Formation and possibly several other of these formations are host to small Mississippi Valley type lead-zinc occurrences. West of the Nahanni Karst study area, the Prairie Creek Ag-Zn-Pb vein deposit is hosted in Whittaker Formation carbonates in the hanging wall of an east-directed reverse fault.

Late Devonian and younger strata occupy synclinal troughs in the Ragged Ranges study area and underlie much of the Nahanni Karst and Tlogotsho Plateau study areas. They have been simplified into basinal shale-dominated and platformal continental sandstone-dominated units. The basinal package comprises units such as the Earn Group and the Besa River, Fort Simpson, Clausen and Garbutt Formations, all of which are black shales. The Earn Group is host to numerous stratabound barite - base metal - silver deposits (Gordey et al, 1982). The platformal unit consists exclusively of the Mississippian Mattson Formation. Its lithology is

unique in the study areas (continental sandstone).

Cretaceous quartz monzonite plutons, which transect the Ragged Ranges study area and the westernmost regions of the park in a broad north-west trending belt, are the youngest rocks in the study area. They are associated with skarn deposits in regions bordering the park and study area. Base metal skarns have been reported in the area and the world class tungsten skarn deposits of Tungsten and Mac Pass are nearby. A number of hot springs are also related to these intrusions.

CHAPTER 3 - HYDROGEOLOGIC SETTING

3.1 Hydrogeologic controls

The western and eastern study areas are physiographically very different; controls on groundwater flow and discharge therefore also differ. In the Ragged Ranges study area (Figure 3.1), quartz monzonite plutons form jagged peaks up to 3100 m in elevation with small upland areas in cirques. The Ragged Ranges glacier field covers the highest parts of these upland areas. Deep U-shaped valleys cut through the region and contain numerous post-glacial alluvial fans and rock glaciers which alter the profiles of the valleys. The South Nahanni River valley to the east of the Ragged Ranges is wide, relatively flat, and inferred to be fault-controlled. Glacial and post-glacial drift features dominate the topography of this valley and a number of large fault-associated hot and cold springs are located along it. This phenomenon is seen in other fault-controlled valleys throughout the study areas. The mountains on the eastern side of the South Nahanni River valley are lower, more rounded and expose no intrusions. In this area, springs tend to occur in valleys, commonly at the break in slope or at a contact between rock units. Within the Ragged Ranges, springs occur both in the valleys and the upland areas, probably due to the influence of the relatively unfractured intrusions affecting the flow systems. Many of the groundwaters discharging in the upland areas have flow systems through contact metamorphosed rocks, and therefore their geochemical character is important for this study.

A small amount of active karst development was discovered in the Ragged

Figure 3.1
Spring locations plotted over geology for Ragged Ranges study area. Geology from Jefferson *et al.* (1989).

Ranges area. A disappearing stream, sinkholes, caverns and several large, apparently karstic springs were found during the course of sampling in the area. Most of these were found at one locality, near spring 104. Here the discharge from the spring flows into a small lake which drains via a stream into a series of sinkholes. The sound of roaring water is audible as it discharges into the cavern system below. The water may exit from a large unsampled spring near spring 105. The flow system appears to recharge near the contact of the Road River shale with a pluton and to continue through underlying Sunblood Formation carbonates from which it discharges. Although other evidence of karstic flow systems was found within these carbonates, karstic flow systems are uncommon in the Ragged Ranges where hornfelsed shale and crystalline rocks dominate.

The Nahanni Karst study area (Figure 3.2) is dominated by the First Canyon Anticline and the Ram Anticline. The large, gentle First Canyon Anticline forms an overall flat, but dissected, upland area. The South Nahanni River cuts through the southern portion of this upland, its incised meanders occupying the deep, vertical-walled First Canyon. Tributaries, such as Prairie Creek and Lafferty Creek, which occupy the uplands, also have deeply incised valleys.

On the gently sloping to flat-lying synclinal area between the Ram and First Canyon Anticlines, karst topography has developed (Brook, 1976). Numerous sinkholes, caves, solution-formed scarps, poljes, disappearing streams, and springs are located throughout this part of the study area. Flat-lying to southeast-dipping shales mantle the central part of the Sun Dog Syncline and the eastern part of the study area. Small springs are localized along contacts between the shales and the uplifted

Figure 3.2

Spring locations plotted over geology for eastern study areas. Geology from Jefferson *et al.* (1989). For legend, see Figure 3.1.

carbonates and sandstones on the limbs of the adjacent anticlines. Large regional springs draining the karst network are located within the Early Paleozoic carbonates. In both First Canyon and the canyons of the various tributaries, springs with very high flow rates are associated with karstic flow systems.

Groundwater flow within the Nahanni Karst area is dominated by karstic flow. Surface water in the area of greatest karst development appears to drain vertically downward and most of the lateral flow is subterranean. Important examples of this are discussed in subsequent chapters.

The Tlogotsho Plateau study area is south of the Nahanni Karst area (Figure 3.2). The plateau is cored by a gentle basin of Mississippian (Mattson Formation) sandstone. Springs are located along the northern edge of the plateau and in deep valleys cutting it. In most cases these are stratigraphically controlled. West of the Tlogotsho Plateau, beyond the Headless Range, an important belt of eastward dipping thrust and reverse faults is transected by the Meilleur River. These faults form northerly trending, parallel ridges. Hot and cold springs are localized along the faults and along the shale / limestone contacts between faults. To the east of the Tlogotsho Plateau, the limbs of several folds form high parallel ridges with rivers, such as the Jackfish, flowing north along intervening valleys. In this area, the springs are restricted to the valleys and only three were sampled.

All three areas receive ample recharge from the abundant rainfall. Both recharge and discharge may be hampered to some extent by the presence of permafrost. This part of the northern cordillera is within the zone of discontinuous permafrost; however, in the upland areas it is more or less continuous. The presence

of permafrost in the lower altitude eastern area is suggested by ground slumps near the Meilleur River.

Permeability is inferred to vary with lithology in the study area. Most of the shaly formations probably have low hydraulic conductivities and flow within these units is probably fracture related. Two examples of units with probable high hydraulic conductivities are the sandstones of the Sekwi and Mattson Formations in the western and eastern study areas, respectively. Coarse-grained talus debris on the mountain slopes and Quaternary fluvial sediments within the valleys act as excellent unconsolidated aquifers for shorter flow systems.

Springs were located using aerial reconnaissance, air photo interpretation, ground traverses and literature citations. Those which were visible from the helicopter at low altitudes were sampled whenever a landing spot could be found. This led to a sampling bias toward springs which had visible precipitates or high discharge rates. Seeps and small springs were more rarely sampled. This may have had a benefit in that visible springs may be more indicative of regional rock types or larger mineral occurrences at depth.

3.2 Hydrochemical controls

The structural grain of the southern Mackenzie Mountains is traversed by the three study areas. Over 50 map units have been subdivided in the study areas (see Hall *et al.* 1988). As lithology is a major factor in groundwater geochemistry, it is therefore not surprising that water types encountered were quite varied. Many other factors are important in the chemistry of groundwaters. The ones considered in this

thesis are briefly introduced below and are discussed in detail in chapters 4 to 6.

Interaction with base metal sulphides and pyrite can alter the water chemistry drastically and change pH and Eh conditions. The resulting chemistry is often distinctive and can be used to detect the presence of mineralization. Trace metal analyses are essential in this application. The presence or absence, in low pH, Fe-rich waters, of trace metals, such as Zn, Ni, Cd and Co, can give an indication of whether the sulphide being dissolved is of interest from an exploration point of view (e.g. Jonasson *et al.*, 1987). The presence of W, Mo, F and As can indicate the presence of skarn mineralization (Hall *et al.*, 1988).

Temperature is also an important factor. Increased temperature increases the solubility of silica and most other solids while decreasing the solubility of gases such as CO₂. The reduced solubility of CO₂ results in a decreased solubility of carbonate minerals.

The definition of "thermal" groundwaters is somewhat problematic. The most commonly used classification system (White, 1957) defines thermal as being 5°C above the yearly mean ambient air temperature (MAAT). The mean ambient air temperature in the study areas is about -4°C (Brook, 1976) and according to this definition, essentially all groundwaters would be considered thermal. Crandall and Sadlier-Brown (1978) classified groundwaters as cold, cool, warm, and hot based on arbitrary temperature limits.

For this study a system was devised to determine the maximum possible average groundwater temperature in the study areas based on some of the results of the stream sediment survey. It was reasoned that during the hottest months of the

year, waters from springs or base flow in streams could only increase in temperature due to solar warming and mixing with precipitation. This hypothesis is supported by the fact that water temperatures in the first and second order streams are always higher than those in the higher order streams which usually contain a larger proportion of groundwater to surface runoff. Stream temperatures measured during July and August over a large area should give an average maximum temperature for the groundwaters; the actual temperature would be lower. All of the temperatures for the third, fourth and fifth order streams in the study area were averaged, with a result of approximately 7°C. For this study it is assumed that groundwaters above 7°C are "thermal". The term "hot spring" is subjective; in this study it is used to refer to springs with water temperatures over 20° C.

The nature of the flow system can also affect the chemistry of the groundwater. In cases where a flow system is short or controlled by karstic flow, the waters can remain relatively oxygenated and open to the loss of plant CO₂. Depending on lithology, this can have different results. In carbonate terrane, the resulting waters can have low total dissolved solids (TDS) values because CO₂ concentrations will not be much higher than atmospheric. In shale terrane with abundant pyrite present, the concentration of SO₄²⁻ and Fe can be increased by extensive flow through the vadose zone where free oxygen is abundant. Shales themselves also alter the chemistry of a water, particularly if divalent cations such as Ca²⁺ and Mg²⁺ are present in the water due to previous dissolution of carbonate. Clay minerals in the shale often adsorb divalent cations from the water and release monovalent cations such as Na⁺ and K⁺ into solution (Wiklander, 1964). In general,

it can be said that waters with more extensive flow systems, particularly fault-controlled systems, will have increased TDS values.

Various combinations of the above factors can result in a great variety of different water types. This was obvious even during the field work. A large portion of this study involved the classification of water types in order to be able to compare similar waters and to detect anomalous water groups or anomalous constituents within groups of similar waters.

3.3 Data collected

Waters were sampled for major ions and trace elements. A one litre bottle for cations and trace elements was acidified with approximately 10 ml of dilute HCl in 1986, and with 5 ml of 1 molar HNO_3 in 1987 to keep ions and metals in solution. A 500 ml sample bottle for anions was not acidified and as a result carbonate minerals precipitated in some of the bottles. Samples were strained through glass wool but not filtered. Special care had to be taken to see that the sample was not contaminated when sampling springs with precipitates.

At the spring vent (where possible) the pH, electrical conductivity and temperature were measured. Unfortunately, equipment for field alkalinity measurement was unavailable and consequently alkalinities were not measured in the field. Estimates of flow rate and various other field observations were also made at the site. The average amount of time spent at a spring was three quarters of an hour. Field measurements and spring locations are given in Appendix 3.

All of the major ions were analyzed, including Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , SO_4^{2-}

and HCO_3^- . Analyses were conducted in laboratories of the Geological Survey of Canada (GSC). In 1986, the cations were re-analyzed as part of a verification of instruments at the GSC. In both years, cations were analyzed on both the acidified and non-acidified samples. Hence for 1986, there are three sets of cation data and for 1987 there are two. Major ion data are given in Appendix 1. The trace elements analyzed include Fe, Mn, Zn, Cu, Cd, Co, Ni, Pb, Al, Mo, W, Ag, Au, U, Sb, As, F, Sr, Si and Ba. These are listed in Appendix 2. Several of these elements were only measured in one year or the other. Detection limits and laboratories are given in Appendix 6.

Gas samples were collected in 1986 using the same plastic Nalgene bottles that the water samples were collected in, because they were the only container available. They proved unsuitable because they allowed exchange between the sample and the atmosphere. Samples taken in 1987 were collected in glass bottles but through a series of mishaps only one sample was finally analyzed, and even that may be in error. The sample from spring 058 reportedly contained 56% CO_2 .

Samples for oxygen-18, deuterium, and tritium isotope analysis were collected in 250 and 125 ml bottles. Samples for isotopic analysis of SO_4^{2-} and dissolved inorganic carbon (DIC) in water were collected in 8 litre bottles. The species were precipitated in the field by the addition of NaOH to raise the pH above 11 followed by the addition of BaCl_2 . After the precipitate had settled, it was decanted, transferred into a smaller container, and packed for transport back to the laboratory for analysis. Sulphur isotopes were determined but only a few are reported, individually, within the text of this study. The results of the isotope analyses are

given in Appendix 5. Laboratories and detection limits are also given there. Oxygen and 1987 carbon isotope analyses were conducted at the stable isotope laboratory of the Ottawa-Carleton Geoscience Centre. Hydrogen isotopes and 1986 carbon isotopes were analyzed at the stable isotope laboratory of the University of Waterloo, Waterloo Ontario.

Spring precipitates were collected for whole rock analysis, trace metal content and isotope analysis. Some of the results of the whole rock and trace metal analyses are included herein. ^{13}C analysis of the travertines has recently been completed as a Bachelor's thesis by Bowman (1990).

CHAPTER 4 - GEOCHEMICAL CLASSIFICATION OF SPRINGS

4.1 Introduction

This chapter deals with the classification of springs and their waters. A cursory glance at the chemistry in Appendices 1 and 2 shows that there is a great deal of variation in both the concentration of elements and the proportion of the TDS composition that any given ion makes up. Appendix 3 lists pH which is also highly variable. There are many factors which can cause variability but in most samples one or two factors appear to dominate.

By classifying spring waters it is possible to indirectly determine the geochemical processes which have affected the waters at depth. This could help in determining whether mineralization has been encountered along the flow path or if other processes are presently occurring which could be of interest to the resource assessment. A related benefit is that trace element anomalies should be much more obvious within groups than if the sample population were examined as a whole.

It is possible to classify springs according to, or with the aid of, factors such as temperature, electrical conductivity, flow rate, rock type encountered (if known), pH, major ions, trace elements, ionic ratios and total dissolved solids. Before any of these parameters are used it is important to differentiate between which are causes and which are effects. Important factors which affect the measurable properties of the water are: lithology, order of encounter, mineralization, subsurface temperature and subsurface residence time. The chemistry, including pH, Eh and TDS, is almost entirely dependent on these factors.

In some cases, controls on chemistry such as lithology or deep fault circulation are apparent by spatial association, but in most cases they are not. Chemistry and field measurements are commonly the only parameters available to aid in determining subsurface processes. It is necessary, therefore, to base the classification system on chemistry rather than subdividing waters according to the processes which have altered them. However, it is important to note here that it is not the chemistry alone which is of interest. The processes which have resulted in the observed chemistry may have relevance to the resource assessment and, therefore, it is these processes which are of greater interest. A classification system based on chemistry is a "means to the end" of understanding the subsurface processes and, therefore, the system may be modified or over-ridden if evidence other than chemistry is available.

Many procedures can be utilized for grouping chemical data. Diagrams such as that devised by Piper (1944) are designed to show multivariant data. However, the Piper diagram can only display the 7 major ions and becomes very cluttered with more than just a few samples. The most powerful tools available for grouping multivariant data are computer routines such as factor analysis, discriminate analysis and cluster analysis (Koch and Link, 1970).

Factor analysis ascertains whether a series of multivariant observations occupies the number of dimensions equal to the number of variables measured or if they occupy fewer dimensions. For example, if a series of points plotted in three dimensions lie on a line, they need only be represented by a single dimension; or if they plot on a plane, two dimensions will suffice. The purpose of factor analysis is

to "group the variables" thereby reducing their total number and making them more manageable and understandable.

Discriminant analysis requires an a priori grouping of samples. The characteristics (including centre) of each group must be known so that subsequent samples can be pigeon-holed into one of the previously known groups based on distance calculations.

Cluster analysis requires no previous knowledge of how samples are grouped. It classifies multivariant data into groups based on how closely samples plot to each other in multidimensional space. Cluster analysis is extremely useful in cases like this when the causes of groupings are not known. The technique will be explained in detail in section 4 of this chapter. Section 3 deals with Kleiner-Hartigan trees, a crude but effective form of cluster analysis which relies on pattern recognition to discern groups. Section 2 is an explanation of the classification system used in the field. This was a necessary working classification, based mostly on field observations, but was modified after chemical data became available.

In section 4.5, a final classification of springs is outlined which is based mostly on cluster analysis but also uses elements of the other two methods. This classification will be used in Chapters 5 and 6 where a detailed analysis of the geochemical factors which result in these groups will be given. Such an analysis has not been done for each classification system in sections 4.2 - 4.4 in the interest of space and because the results of this thesis are based on the final grouping given in section 4.5.

The term "cluster" is synonymous with "group" but for consistency it will only

be used when describing groups discerned by computer methods and "group" will refer to groups decided by other methods.

4.2 Physical grouping

4.2.1 Field Classification

In the course of sampling during the 1986 and 1987 field seasons, it became apparent that many of the springs had similar characteristics. Factors such as temperature, conductivity, pH, flow rate, underlying lithology and spring precipitates (Appendix 3) were used to classify approximately 3/4 of the 124 springs and surface water samples into one of five groups which are listed in Table 4.1. The remaining 25% were not classified and are simply grouped as "P6". The groups are explained below along with the characteristics used to identify them. Chemical data were not available at the time of sampling but have been included in the descriptions below as an aid to further discussion. Hamilton *et al.* (1988a) provided a more detailed description of the "physical" classification system outlined here but it had not yet been modified to include the 1987 results.

Tufa springs - group P1

Springs which precipitate tufa are located throughout the study area, particularly in carbonate terrane. A number are situated along major faults such as the Broken Skull Fault in the South Nahanni River Valley. Many of the other tufa springs are probably associated with faults, mapped or unmapped. The tufa varies

Group	Sample	Group	Sample	Group	Sample
P1	001	P2	070	P5	045
P1	021	P2	071	P5	065
P1	023	P2	072A	P5	066
P1	026	P2	072B	P5	068
P1	027	P2	073A	P5	075
P1	028	P2	073B	P5	076
P1	029	P2	073C	P5	104
P1	031	P2	074	P5	105
P1	040	P2	078		
P1	041	P2	079	"P6"	009
P1	043	P2	080	"P6"	010
P1	046	P2	083	"P6"	013
P1	047	P2	100	"P6"	020
P1	056	P2	103	"P6"	022
P1	057	P2	108	"P6"	024
P1	058	P2	109	"P6"	032
P1	059	P2	110	"P6"	044
P1	082	P2	112	"P6"	048
P1	111	P2	116	"P6"	050
P1	113	P2	121	"P6"	051
P1	114			"P6"	061
P1	115	P3	011	"P6"	067
P1	125	P3	018	"P6"	081
		P3	019	"P6"	101
P2	012A	P3	020	"P6"	102
P2	012B	P3	033	"P6"	106
P2	012C	P3	034	"P6"	107
P2	015	P3	038	"P6"	117
P2	017	P3	052	"P6"	118
P2	025	P3	053	"P6"	119
P2	030	P3	060	"P6"	124
P2	035			"P6"	126
P2	036	P4	063	"P6"	127
P2	037	P4	064	"P6"	128
P2	042	P4	122		
P2	049	P4	123		
P2	054				
P2	055	P5	004		
P2	062	P5	006		
P2	069	P5	007		

Table 4.1 Results of the field classification of spring waters based on physical characteristics such as lithology and associated deposits. "P6" represents ungrouped samples.

in colour from buff to bright orange depending on how much Fe and Mn oxides and hydroxides have been co-precipitated. Deposits such as Rabbitkettle Hot Spring are large terraced structures. Other tufa springs form small crumbly deposits which line channels draining a vent. The large size of most of the deposits and the colour of the precipitates aid in aerial identification.

The pH of tufa spring waters is usually slightly acidic to slightly basic but invariably rises sharply with distance from the vent due to exsolution of CO_2 . Gas (mostly CO_2) was observed in many vents either bubbling or clinging to objects in the vent as it exsolved. The conductivity is usually moderately high ($> 500 \mu\text{S}/\text{cm}^1$). Temperatures are mainly low, but some of the springs are thermal (up to 48°C).

The chemical analyses have shown that all springs in this group have Ca-HCO_3 dominated waters but the total concentrations of these elements varies. TDS content is usually moderate to high and in cases where it is high there are often significant quantities of other ions, such as SO_4^{2-} or Cl^- , which suggest deeper circulation (021, 040, 041, 043, 082). The concentrations of most trace metals (Fe, Mn, Cu, Co, Cd, Ni and Zn) are low.

Iron springs - group P2

Springs precipitating iron hydroxides are located in shale terrane throughout the study area and are also in areas underlain by the Mattson Formation, a Mississippian sandstone in the Tlogotsho Plateau study area. The springs range from

¹ $\mu\text{S}/\text{cm}$ is a unit of electrical conductivity and is the inverse of micro ohms (resistance).

small reddish seeps to large springs with deposits covering an extensive area. The precipitate is usually a floccular ooze which dries into a red, poorly vegetated soil. The precipitate can also take the form of calcium carbonate, iron hydroxide or gypsum cemented ferricrete. Also sampled were streams with unusually low pH or the presence of iron oxide (red) or sulphate (white) precipitate in the stream bed. In some cases a stream was found to precipitate iron hydroxides downstream of a particular spot along its course (eg. 042, 049, 071). Investigation revealed springs or small spring-fed streams entering the larger streams. Differences in pH or Eh between the spring and the larger stream obviously caused the immediate precipitation.

Most waters from iron precipitating springs are neutral to strongly acidic and, except in several cases (including the Flat River Springs), pH does not tend to rise after waters leave the vent. This indicates that sulphuric acid rather than carbonic acid is causing the acidity. Conductivity has a wide range from 50 $\mu\text{S}/\text{cm}$ to over 3000 $\mu\text{S}/\text{cm}$ and the temperature, when measured at the vent, is low ($< 7^\circ\text{C}$), except in the case of spring 069 (11.5°C).

Chemically, the group is quite variable. Most of the samples have high to very high Fe (500 to 122,000 ppb) and Mn (50 to 5400 ppb) concentrations. A large number of the springs in this group also have elevated trace metal (Cu, Co, Cd, Ni and Zn) concentrations. Of the major ions, commonly SO_4^{2-} is elevated and Ca/Mg- SO_4 dominates. The springs discharging from the Mattson Formation have unusually high Mg^{2+} .

Included in this group at the time of sampling were several of the tufa

precipitating springs of the Flat River Valley (017, 030, 055). They were included because the iron-hydroxides which co-precipitate have a bright orange colour and because the pH at the time of sampling was low. This is one example of how the field classification was lacking. These springs have very high concentrations of Ca^{2+} and HCO_3^- and precipitate CaCO_3 . They will be discussed in Section 5.4.

Hot springs in quartz monzonite terrane - group P3

The springs in this category are all thermal and are spatially associated with Cretaceous quartz monzonite plutons. There is no precipitate, but a white, kaolin-like alteration product coats cobbles and boulders of quartz monzonite around most vents making them easily visible from the air. Vegetation does not grow where the water flows but surrounds the vent; it is unusually lush with ferns, wild mint and stands of deciduous trees. These springs are so easily visible that most of the ones sampled had been previously discovered.

The waters are also quite distinct. The pH is high at the vent, in most cases between 8.5 and 9.2, and does not drop appreciably after sampling. The conductivity is always quite low ($<400 \mu\text{S}/\text{cm}$) and temperature, ranging from 40 to 65°C, is the highest of any of the groups.

Chemical analyses show that the waters are Na-HCO_3 dominated, with very little Ca^{2+} . Elevated trace elements include F, Si, As, Mo, and W, the latter has very high concentrations for natural waters. Two water samples from the Tungsten mine (019,020) show very similar results, although Ca^{2+} and SO_4^{2-} are high in one of them. The two samples of mine water are somewhat thermal (16°C) and have high pH.

Therefore, they were included in the hot springs category in the field.

Clausen Creek hot springs - group P4

Clausen Creek is located within the Tlogotsho Plateau study area and flows north into the national park. Near its mouth are the famous Kraus Hot Springs (063, 064). They have a high flow rate, which is large enough to produce a small stream flowing into the South Nahanni River and which has been extensively dammed by beavers. There are no deposits but a suspended precipitate of CaSO_4 gives the water flowing from them a milky white appearance. Gas bubbles rise from a number of vents in the beaver pond. Smaller springs (122, 123 and at least one other unsampled) with similar characteristics are found from about 2 km south of the river to just north of it, across from Kraus itself. All of the springs have a very strong H_2S smell associated with them. The odour from Kraus was detectable more than 5 km down wind in the helicopter.

The waters are quite distinct in that the conductivity is always high, ranging from 2000-9000 $\mu\text{S}/\text{cm}$, indicating the brackish nature of the water. pH was slightly acidic at the time of sampling but rose to above neutral by the time samples were analyzed. The temperatures of all four sampled springs in this group are elevated and range from 12 to 36°C.

Chemical analyses show a high salt content as was expected. NaCl and CaSO_4 are the most common salts present but HCO_3^- is also present. Most trace metals have detectable concentrations.

High discharge cold springs - group P5

This group includes many of the very large springs sampled throughout the study area. Some are re-emergent streams (007, 069, 104, 105) and the rest are mostly large springs in carbonate terrane with probable karstic flow systems (004, 065, 066, 075, 076). They seldom have precipitates and are visible mainly because of the very large flow. Estimated flow rates ranged from 100 to >10000 l/s in July-August.

Despite the differences in the two environments, the waters from both types of high discharge springs have similar properties. The pH is high, generally >7.5 and <8.3, which indicates equilibration with atmospheric or near-atmospheric levels of CO₂. Temperature and conductivity are always low.

The chemical analyses show Ca-HCO₃ dominated waters but Ca²⁺ and HCO₃⁻ concentrations rarely exceed 50 and 150 ppm, respectively. Therefore, these waters are undersaturated with respect to calcite. Concentrations of other major ions and trace elements vary over a wide range.

4.2.2 Discussion

While working in the field it was inevitable to have developed some subjective criteria for classification of the springs. Physical similarities are quite obvious and many of the factors which caused them, such as fault-control and lithology, were postulated in the field. The lithology in particular was thought important because all but one of the groups (high discharge cold springs) were observed to be related to rock units. During the attempt to regroup the springs after chemical data became

available, underlying lithology was used as a criterion in establishing the groups (Hamilton *et al.*, 1988b). A number of problems arose from this. First, the area is mapped at a scale of 1:250,000 and it is often unclear which exact unit or sub-unit hosted the flow system. Secondly, many of the waters are travelling both laterally and upward from depth and possibly pass through more than one rock unit. Multiple host rocks are certain in the many cases where springs are located along fault traces. Another problem is that not all springs in a given geologic terrane have the same geochemical features. Other factors such as residence time, temperature and the presence or lack of mineralization also influence the geochemical signature of the waters.

An even more important concern with both the original and modified physical classification system was that more than 25% of the samples remained unclassified. When chemical data became available many of the unclassified samples had important geochemical similarities to groups already formed, even though having dissimilar physical characteristics, such as the underlying lithology or the presence or absence of precipitates.

4.3 Kleiner-Hartigan Trees - grouping by pattern recognition

4.3.1 Introduction

The above physical classification and modified physical classification were both based on criteria observed in the field. The chemistry was secondary - used mainly to show that the groups produced had chemical similarity. In order to geochemically classify the groundwaters, an objective geochemical grouping method is necessary. The following section describes a method of grouping multivariant chemical data known as Kleiner-Hartigan Trees (Kleiner and Hartigan, 1981).

The chemical analyses (Appendices 1&2) include the seven major ions and 20 trace elements. Three of the trace elements (Au, Sb and Pb) were only analyzed in 1987 and two others (Ag and Ba) had so few samples above detection that they can not be dealt with statistically. This leaves a total of 22 elements (plus pH) which can be used to produce a geochemical classification of the waters.

A common way of grouping data is to graph it and pick out obvious groupings. However, more than just a few variables are difficult to represent in two dimensions and it becomes increasingly more difficult as the number of variables increases. One method of dealing with this problem is to produce an individual plot for each case (sample), the shape of which is dependent on the data (elements). The plots can then be grouped on the basis of their shapes. There have been many variations on this theme which have produced a number of different type of representative shapes.

One of the more successful shapes is that of a tree. A computer is used to

generate the plots and samples are then grouped by pattern recognition. Similar shaped trees represent waters with similar chemistry. It is only a computer-aided method because the decisions as to what constitutes a group and which samples fit into that group are still left up to the investigator. A program to plot "Kleiner-Hartigan trees" was made available to the author by R.W. Garret at the Geological Survey of Canada. This section deals with the method used by the computer to produce a pattern, followed by a discussion of the results.

4.3.2 Methodology

Tree plots were developed by Kleiner and Hartigan (1981). They also reviewed most of the existing pattern recognition systems such as castles, boxes, glyphs, star plots, profiles and faces. The principle behind all of these systems is similar to that of the tree system which is as follows. Correlation coefficients are calculated for the variables, followed by cluster analysis (explained in detail in section 4.4) on the correlation matrix. The variables which vary together are placed on the same "branch" of the tree. Therefore the configuration of the tree is determined by how the variables vary with respect to each other throughout the whole data set. The variables represent "leaves", the lengths of which are proportional to concentration. The length of the supporting branch is proportional to the combined concentrations of all the leaves on the branch. This produces a tree with the same configuration of variables but with a different shape for each case, provided the chemistry of the water is different.

The 22 variables already mentioned were used to produce the trees; pH was

not included. A summary of the steps employed to produce an output is shown below followed by an explanation of each step:

Data were inputted from a file and down-loaded into a CYBER computer from a micro-computer. The program was then run by having the computer read stacks of cards with the instructions typed onto them. In the program used, data can be inputted in any form and in this case were inputted as they were received from the laboratory (i.e., as ppm and ppb). The potential problem of differing scales is avoided by instructing the computer to perform a 0-1 transformation. This is a type of standardization that involves a simple linear transformation of the data such that

Figure 4.1

Tree plot with the configuration produced by using '86 and '87 geochemical data. Elements which vary most together are placed on the same branch. The length of each leaf represents the concentration relative to the log of the total range within that element for all samples. The size of the branch is proportional to the sum of the relative concentrations of all the leaves on the branch.

the lowest value in the data set is set to zero and the highest takes on a value of one. If the magnitude of a given variable varies greatly among samples then a log transformation of data may also be necessary. Both the 0-1 and the log transformation were found to be necessary because of the differing scales and the large variation in the concentration of the elements. A more detailed description of transformation and standardization methods is given in the following section on cluster analysis.

Figure 4.1 shows the resulting configuration. The tree has 6 major branches or sub-branches, each having a number of co-variant elements on them. Because elements which vary together throughout the sample set were positioned close together, groups of similar waters tend to have one or several enlarged branches. The six sub-branches are discussed below and contain trace element associations which are significant with respect to the genesis of the waters. Results of the grouping are shown in Table 4.2.

4.3.3 Discussion

Figures 4.2 and 4.3 show the results of visual pattern recognition on the tree-plots. Ungrouped samples are shown on Figure 4.4. It can be seen from the figures that the variation in shape of the plots makes some water types easily identifiable.

On branch (A) (Figure 4.1) Ca^{2+} , Mg^{2+} , SO_4^{2-} , U (surprisingly) and HCO_3^- vary together. Uranium forms soluble carbonate complexes such as $\text{UO}_2(\text{CO}_3)_3^{4-}$ which may result in its observed co-variability with HCO_3^- . The most important feature of groups T1 to T3 (Figures 4.2 & 4.3) is that this branch is enlarged and the

Figure 4.2
Tree plots of samples in the eastern study areas arranged into groups by pattern recognition.

Figure 4.3
Tree plots of samples in the Ragged Ranges study area arranged into groups by pattern recognition.

Figure 4.4 Samples in the tree classification which were left ungrouped, which had duplicates and samples from the possible 8th group("T8") which apparently results from ion exchange in shales or clay-rich units.

Group	Sample	Group	Sample	Group	Sample
T1	004	T3	041	T5	108
T1	007	T3	043	T5	112
T1	009	T3	055	T5	121
T1	013	T3	056		
T1	028	T3	057	T6	011
T1	045	T3	058	T6	018
T1	051	T3	082	T6	019
T1	065	T3	082	T6	020
T1	066			T6	033
T1	068	T4	015	T6	034
T1	075	T4	037	T6	038
T1	101	T4	054	T6	052
T1	104	T4	059	T6	053
T1	113	T4	061	T6	060
T1	119	T4	062		
T1	120	T4	078	T7	063
		T4	079	T7	064
T2	001	T4	081	T7	122
T2	006	T4	103	T7	123
T2	023	T4	109		
T2	027			"T8"	074
T2	029	T5	012A	"T8"	083
T2	030	T5	012B	"T8"	110
T2	031	T5	012C	"T8"	116
T2	032	T5	025		
T2	044	T5	035	"T9"	010
T2	046	T5	042	"T9"	022
T2	047	T5	048	"T9"	024
T2	050	T5	049	"T9"	026
T2	076	T5	069	"T9"	036
T2	106	T5	070	"T9"	067
T2	107	T5	071	"T9"	077
T2	111	T5	072A	"T9"	078
T2	115	T5	072B	"T9"	102
T2	125	T5	073A	"T9"	114
T2	127	T5	073B	"T9"	117
		T5	073C	"T9"	118
T3	017	T5	080	"T9"	124
T3	021	T5	100	"T9"	126
T3	040	T5	105	"T9"	128

Table 4.2 Results of classification of spring waters by pattern recognition of "Kleiner-Hartigan Trees". "T9" represents ungrouped samples. See text for explanation of "T8".

relative size of the branch determines which of the three groups the sample will be in. The groups represent Ca-HCO_3 dominated waters but from three different environments. A characteristic of T3 is that several of the other branches are also enlarged.

Branches (B) and (C) both contain only trace metals. (B) contains Al, Cd, Co, Ni and Zn while (C) contains Fe, Mn and Cu. Group T4 results from branch (C) being enlarged, mostly due to elevated Fe and Mn. T5 results from both (B) and (C) being enlarged which is due to trace metals being elevated. The major difference between the two groups (although not visible from the figure) is that waters in T5 are acidic to highly acidic whereas most waters in T4 are near neutral. High SO_4^{2-} indicates that the characteristics of both groups may be due to contact with sulphides. T4 may be a result of mixing with T1 and T5 type waters.

Branch (D) contains the ions Sr^{2+} , K^+ and Cl^- . Na^+ is not included in this branch, as might be expected since it contains Cl^- , for reasons discussed below. In T7, several of the branches are enlarged but the group's most important feature is (D) which is greatly enlarged due to the high salt content. (D) is somewhat enlarged in T3, also indicating a significant salt component in those waters.

Branch (E) contains the elements Mo, W, As, Si, Na^+ and F. (E) is actually made up of two sub-branches, but as they vary so closely together they can be considered to be one. Group T6 results from increased concentrations of the elements in these two sub-branches which gives the tree a right skew. All the waters in T6 are Na-HCO_3 dominated and have a high pH resulting from dissolution of felsic intrusive rocks.

In Figure 4.4 and Table 4.2, a number of samples have been left ungrouped. Some of these are examples of surface waters (022, 024, 077, 117, 118, 124, 128) which could have been left out. Two samples (10, 36) had incomplete analyses and could not be included in the calculations. Sample 067 is water from the Prairie Creek Mine and had such unnaturally high concentrations of certain trace metals that it had to be removed from the calculations. Sample 026 was taken from the same spring as 046 but farther from the vent and therefore was not included twice. The rest of the unclassified samples (102, 114, 126) are unusual waters which would not fit into the groups made.

Similarities between the above groups and those of the physical grouping are apparent. They will be discussed in section 4.5.

Grouping by pattern recognition has a number of advantages. It allows one to see immediately what is causing the groupings. For instance, the differences in elemental associations of groups T2, T6 and T7 are obvious in Figures 4.2 & 4.3, but would not be obvious using methods such as cluster analysis. Another advantage is that when producing the trees the process correlates and then clusters variables and not samples. This results in the use of far less computer time and memory than would be necessary for other computer methods which correlate and cluster samples.

A third advantage is the flexibility which results from the subjectivity of the method. During the selection of samples one has the ability to use criteria which may be known from other data to be important. One can decide what will constitute a group and can also use judgement as to what fits into that group based on factors such as temperature or spring precipitates. The latter point can be important in cases

where mixing of water types is known or suspected. In this case the sample can be included in the group which has the water type of greater interest to the investigator. A non-subjective computer method such as cluster analysis might place it into one of the two groups, but would be more likely to put it into neither since only half the criteria used to determine either group would have been met. Being able to decide what constitutes a group can also be important when the criterion for determining that group are minor relative to other components of the tree. Group T4 is an example of this because the branch containing Fe and Mn has been used as a criteria for choosing waters in that group.

Group "T8" in Figure 4.4 is made up of waters which appear to have undergone cation exchange in shales or clay units. Na^+ from the rock has been exchanged for Ca^{2+} in the water. Only a few waters were found to have been affected by this process and were recognised because they differ in shape from the other, larger groups. The differences are subtle enough that a method such as cluster analysis may not have picked them out and would have forced the waters into a group (probably one like T6) to which they are genetically different.

Subjectivity is a very important factor in this method. It can be argued that samples could fit into more than one group and that some of the groups picked may have little geochemical significance. However, if enough true variation exists in the water types sampled (as in these waters) then this problem is greatly reduced. Cases where subjectivity can be a criticism are where samples have unusual chemistry or in those cases where dilution or mixing has taken place. A more important argument is that the investigator could, willingly or not, establish groupings based on pre-

conceived ideas or models. Admittedly this did play a part in establishing groups T4 and "T8". They do not have very distinctive shapes but they do represent important geochemical processes which are not obvious by looking at the shape alone. It required subjectivity to create the groups and discern which waters have been involved in these processes.

The pattern recognition method invokes several other more technical problems. Different types of waters may have the same elements but have the elements vary in different ways. For example, Group T6 has Na^+ and HCO_3^- varying together but in T7, Na^+ and Cl^- vary together. Because the elements are assigned to a branch once, on the basis of the entire data set, the shape of the tree cannot properly represent the co-variability of elements for all cases. This may or may not prove to be a problem. It is a problem in T6 where the waters are Na- HCO_3 dominated and Na^+ is on one branch while HCO_3^- is on another. This also explains why Ca^{2+} and Mg^{2+} do not vary most closely with HCO_3^- and Na^+ does not vary with Cl^- as would be expected. Pattern recognition systems are also hampered by the difficulty of visually detecting differing shapes with increasing numbers.

Pattern recognition systems were used extensively when computer time was expensive. Their most useful feature is that they can visually display the data.

A classification system based on geochemical characteristics was originally recognized as necessary by the author because of a (negative) critical review of a paper which relied on the field classification system. One of the complaints was the subjectivity of the method and the "Trees" method does not entirely address this problem. Although the method was found to be satisfactory for the data herein, a

non-subjective method was thought to be necessary which would serve, at the very least, as a verification. The next section deals with cluster analysis which addresses these problems.

4.4 Cluster analysis

4.4.1 Introduction

It is clear from some of the uncertainties involved in grouping data by the previous methods and because of their potential biases, that a non-subjective method of classification is required. This can be used as a check, or to modify the previous groups, and it can be used on its own as an independent partitioning method. Mathematical methods for partitioning multivariant data without a priori grouping are known as cluster analyses and have been commonly used since computers have come into widespread use in the mid 1960's. Many types of cluster analyses have been developed particularly for use in medicine and biology. They can be divided broadly into hierarchical and non-hierarchical methods as discussed below.

Statistical packages are available commercially which offer cluster analysis. Two were tried in the present study. Statgraphics by Statistical Graphics Corporation proved to allow insufficient memory for 124 analyses consisting of between 6 and 22 variables. Systat met the requirements and was used with satisfactory results. SPSSX, on the CP6 mainframe was also available and can handle much larger data sets. However, its output (i.e., printout) is poor and difficult to interpret and, therefore, the program was not considered for this application.

Figure 4.5 shows the potential routes which could be taken in inputting and

Figure 4.5 Flow chart to show potential routes for inputting, manipulating and clustering the data using cluster analysis.

manipulating data and the various ways of clustering the data. Different combinations may produce different or possibly erroneous results and, therefore, care had to be taken in finding the path which best suited the data. The following section explains some of the theoretical considerations involved and outlines the choices made to analyze the geochemical data.

4.4.2 Theoretical considerations and methodology

Figure 4.5 shows three stages of data development before the final outcome of grouped data. These will be dealt with individually.

1) Data inputted

In addition to using the six (Na^+ and K^+ represent one) major ions to partition samples, it is also possible to use trace elements as was done with the "Trees" grouping method. The most important of the trace metals is iron, the presence of which (in the form of hydroxide precipitates) was used as a criterion in the field classification. Other trace metals, such as Ni, Co, Zn, Cd, Cu, W and Mo could aid in the discrimination of clusters. However, as a number of these trace metals will be used to differentiate within groups in the chapter on hydrochemical processes (Chapter 5) it is desirable to leave them out of the initial partition.

It was found by experimentation that Systat is capable of handling 120 cases with 7 variables. More cases would mean the number of variables would have to be reduced and more variables (trace elements) would mean the total number of cases would have to be reduced. With 6 major ions it is possible to include only one extra

variable. If this had not been satisfactory SPSSX would have had to have been used. Fortunately, 7 variables are sufficient for initial partitioning purposes.

By experimenting with different combinations, it was determined that H^+ is the most revealing trace element (i.e., pH converted into mg/l H^+) and, therefore, was used as the seventh variable. High H^+ concentrations are often associated with the presence of Fe, which is probably the next most revealing element. Because of this association, the H^+ concentration can help to discern waters which have come into contact with iron sulphides.

All the geochemical data used herein were reported by the laboratory in mass ratios (ppm, ppb, pptr). In this form it is difficult to compare different ions because mass ratios are partially controlled by the atomic weight of the ion and do not take into consideration its charge. Equivalence units are more desirable because they allow comparison of all ions on the same scale. Another consideration is that the maximum magnitude of each of the major ions in the data set is (coincidentally) similar when using equivalence units, although their statistical means differ considerably. The importance of this will be explained later in this section, but it will suffice to say here that most clustering methods require that variables have similar scale and magnitude.

When dealing with trace elements, particularly metals, equivalence cannot be used because the dissolved species (usually a complex) in which it is contained is often not known and neither is its valence. The scale and magnitude of the mass ratio units (ppb, pptr), therefore, present a problem since they can vary by orders of magnitude both within and between variables. H^+ concentration, with respect to

that of major ions, is an example of this. This problem can be solved by using two techniques, standardization and log transformation, covered under the next heading.

The third possible way of inputting the major ion data is as cation and anion percentages. This will have a different result than the other two methods in that it completely eliminates the effect of the magnitude of the variables. This type of method is used when plotting Piper diagrams. Converting data to percentages has a similar result to some forms of data manipulation and, therefore, it will also be dealt with under the next heading.

2) Data manipulation

There are three reasons for manipulating the raw geochemical results before cluster analysis is attempted. The first two, to standardize scale and magnitude across variables, have already been mentioned. The other one is to weight individual variables so as to give them more or less significance with respect to the others.

Standardization of scale and magnitude must be considered for the variables when any sort of distance calculations are used in the clustering method, as is the case in all the methods considered herein. When calculating Euclidean (and other types of) distances between points, each element is a variable in its own dimension and contributes to the distance as a whole. If a particular variable is on a different scale than the others, such as ppb vs. ppm, or has a drastically different magnitude, it will contribute a disproportionate amount to the distance calculation. This may result in groupings which rely more on some variables or completely ignore others. Standardization can be used to prevent this effect.

Standardization is a form of proportional scaling which normally involves re-scaling of variables to a common scale. The standardization option in Systat computes z-scores. Z-scores re-scale variables and centre them by subtracting the mean and dividing by the standard deviation of the variable. This has the result of giving all variables approximately equal significance regardless of scale and overall magnitude. If only selected variables need to be standardized then they should be scaled manually (i.e., without z-scores) so as to match the scales of other variables.

There are a number of considerations when standardizing the data. Standardization may mask true groupings by reducing the significance of important variables. Conversely, it may give too much significance to variables which are not important in natural groupings. For example, if trace metals were included in the variables and all were standardized, then Mo, which is usually present in only minute amounts, would have the same significance as Ca^{2+} which is almost always an important component. This problem is avoided if only selected variables are standardized and done so with care.

Another form of data manipulation is the log transformation of variables. This is a process which finds the highest and lowest values in a sample population. It then re-scales the whole sample population to a fixed scale with the lowest value being 1 and the highest being, say 100. The log of each value is then taken. This reduces, but does not eliminate the effect of magnitude. It is an especially useful procedure when dealing with a variable or variables which vary by orders of magnitude. It has the possible disadvantages of masking clusters due to magnitude and if all variables are log transformed it eliminates differences due to scale just like standardization.

The results of log transformation can themselves be standardized. Indeed, if only several variables are transformed then one must standardize to a final scale similar to that of the other variables.

If variables are inputted as percentage of total charge it eliminates the effect of magnitude of variables on clustering. A sample with only 50 ppm TDS content can be found in the same group as a sample of 3000 ppm TDS content if the relative proportions of the major ions in each sample are similar. This effect is not desirable because it will eliminate any groupings based on magnitude. Another problem is that samples with very low concentrations (like recent snow melt or rainwater) can have their major ion ratios altered significantly by the addition of very small quantities of one or more of the major ions. This could take place in the soil zone, in a swamp or even by dissolution of aerosols and gases in the atmosphere. Because of this, major ion percentages in waters with very low TDS content may be indicative of processes totally unrelated to those taking place in groups with higher TDS content but which have similar major ion proportions. If major ion percentages are used, then low TDS samples may be included in groups with samples to which they have no genetic similarity.

Bearing in mind the potential problems with standardization and log transformation, it was decided to minimize data manipulation as much as possible. The six major ions all have similar maximum values, around 50 equivalence per million (epm), and, therefore, do not require standardization. H^+ concentration varies by orders of magnitude and needs to be log transformed and subsequently standardized. The process followed in transforming the data is shown below:

$$H' = \{h - (-\ln(\text{"pH 7.5"}))\} \times \{(A_m - A_n)/(h_m - h_n)\} \quad (4.1)$$

$$h = -\ln[H^+]$$

Where H' is the standardized and transformed H^+ value, h_m and h_n are the maximum and minimum values, respectively, of h and A_m and A_n are the average maximum and minimum values, respectively, of the major ions when expressed in equivalence units. Subtracting $-\ln(\text{"pH 7.5"})$ centres the variables. The mean value of pH in all the samples is somewhere between 7 and 8, which results in transformed and standardized values between 25 and 35. It was found to be necessary to centre the values because this range is considerably higher than the average values for most of the major ions. It resulted in H^+ distances dwarfing those of the major ions in cases where the TDS content is low. The groups which formed were based more on pH than on major ion chemistry. Centering the data at approximately pH 7.5 solved this problem.

3) Clustering Method

Both hierarchical and non-hierarchical clustering methods may be suitable for analyzing geochemical data and the statistics package used (Systat) offers one of each. The "Joining" method is hierarchical and the "K-means" is non-hierarchical. Both methods are explained below.

Two requirements must be met before the **joining** algorithm can be employed. First, there must be a method for calculating "distance" between clusters in multidimensional space. Second, there must be a "linkage" method which will amalgamate two clusters (which consist of one or more samples). The linkage

method must include a definition of where the cluster is centred in order to calculate distance between it and other clusters. The term "joining", as used herein, includes a number of different clustering methods. They differ largely in their distance calculation and linkage methods. They are similar in that they are all hierarchical, i.e., they partition points into a series of sets which are joined together to form nested sets which depend on how closely they resemble each other.

The earliest and best known linkage method is single linkage. In calculating the distance between two clusters it uses the smallest distance between any of the points in the two clusters, i.e., only a single link is needed between them. If that distance is sufficiently small, the clusters are joined.

Complete linkage is similar to single linkage, except that it uses the two most distant points between two clusters to establish a distance between them i.e., all the points in each cluster can be considered linked. Again, if the established distance is sufficiently small the two clusters are joined.

Single and complete linkage were the only two linkage methods considered, although a number of others are offered by Systat. Some of the others are unsuitable for use with the geochemical data because they require standardization or other forms of data manipulation which may affect the final result. Complete linkage produces clusters which are more compact and farther apart than single linkage, which means that they represent more "ideal" groups. As a result, complete linkage was considered more discriminating and preferable to single linkage. Both methods were tried and complete linkage indeed produced the best results.

Distance calculations can be made on any number of different matrices such

as tables of Pearson coefficients, correlation coefficients or simply matrices of linear data in Euclidean space. The Systat default distance metric is Euclidean, although other distance metrics are available for special applications which input processed matrices of various types. The geochemical data were in a simple rectangular data matrix and, therefore, Euclidean distances were desirable. Euclidean distances are calculated using the standard formula (Hartigan, 1975):

$$D(S,T) = \left(\sum_{j=1} \{A(S_j) - A(T_j)\}^2 \right)^{1/2} \quad (4.2)$$

Where $D(S,T)$ is the distance from samples S to T and $A(S_j)$ is the value of the j^{th} variable of sample S . Two variable (pythagorean) and three variable distance calculations are special cases of the above formula.

Joining methods begin by considering every sample within a group of " n " samples to be a cluster. The algorithm is fairly simple and is outlined below.

Any group of n clusters is capable of producing up to $2n-1$ clusters upon joining, hence the restriction shown above.

Joining major ions and standardized (or weighted) H^+ using complete linkage in Euclidean space produced good results. The method discriminated well between waters with differing chemistry and the results will be discussed in section 4.5 of this chapter.

In order to use the **K-means** clustering algorithm, two requirements must be met. First, there must be a method for calculating distance between a point and a cluster. This is equal to the sum of the squared distances between each variable and the mean value of that variable within the cluster. In other words, it is the Euclidean distance between the point and the centre (mean) of the cluster. Secondly, there must be a method for determining an error factor for indicating the validity of a cluster. The error for the whole partition is equal to the sum of the squared distances between each sample and the centre of the cluster which the sample is in.

Once these are satisfied the following algorithm can be employed:

The K-Means method is non-hierarchical and, therefore, produces a partition in which each point is assigned to only one cluster. Each point within a cluster must be closer to the cluster centre than to the centre of any other cluster. Since the partitioning is wholly based on distance, it is essential that either a similar scale be used for each variable, or that data are standardized.

The K-Means method was tried and found to be unsatisfactory. Results are given in Appendix 4.

4.4.3 Discussion

Based on the field evidence and on geochemical consistency within groups the "joining" method of clustering produced very satisfactory results. Figure 4.6 shows the

Figure 4.6

Output of cluster analysis with groups defined from C1 - C9t in decreasing order of significance. "Distance", measured on the horizontal axis, between one cluster and the vertical line joining it to its neighbour is a measure of significance of the group.

hierarchical clustering of all points (except 026, 050, 117 and 118) using complete linkage in Euclidean space. The printout is organized hierarchically and gives visual representation of the process of clustering the data. Every sample starts off as a separate cluster and these clusters are joined in successive iterations until all samples are included in sets and all sets are joined into larger sets, the largest set being the sample population itself. The samples with the smallest distance between them are the most similar and are the first ones joined. The horizontal lines on the figure represent distances from a point or a cluster centre to the centre of the larger cluster in which it is contained. The vertical lines join samples or clusters together to form a new cluster and are positioned on the horizontal axis so as to give a representation of the distance that the new cluster centre is from the origin. The most significant groups of springs are the ones whose cluster centres are farthest from the centre of the cluster in which they are contained. For example, the most distinct group of springs is the one shown on the bottom, right hand side of the figure (group C1). This group has by far the largest distance between it and the higher cluster. Groups have been numbered on the figure in descending order of significance.

Clusters C1 to C6 are very distinct and show clustering which is indicative of known hydrogeologic conditions. C1 contains saline waters from hot springs in the Clausen Creek area. C2 contains sulphate rich, largely acidic waters from various vents at sample sites 072, 073 and 112. C3 contains CO₂ charged waters from springs in the upper Flat River valley. C4 contains acidic waters which have been in contact with sulphides (C2 is a more extreme example). C5 represents travertine precipitating, mostly thermal springs from across the study area. C6 contains waters

from hot springs which are spatially associated with plutons. All of these groups have been identified before by at least one of the other two classification systems.

The first six groups can be considered to represent "ideal" water types because they neatly pick out each of the distinctive groups of springs. They include 60% of all the samples taken. The remaining samples belong to the tentative groups C7t, C8t and C9t which have been re-clustered. These show small total distances between samples and their clusters, which is mostly a result of low TDS contents. Definite hydrogeochemical environments are not apparent in any of the three groups because low TDS content causes poor differentiation of water types and because mixed and diluted waters from the above groups tend to be included here. Included in this manner are Fe-rich, neutral-pH waters which, as was mentioned in the last section, may be the result of mixing of C4 (or T5) type waters with high alkalinity waters from carbonate terrane (C5, or C7). The best chance of finding any environment-specific groups within C7t-C9t is to re-cluster the data outside the context of the larger spring groups.

Samples 11 and 34 were removed from the second run because these are known from field evidence to be examples of dilution of C6 type waters. The four samples removed in the first run for reasons of space (26, 50, 117 and 118) were added here. Three of these are thought to be examples of re-emergent surface water and, therefore, would likely have plotted in C7t-C9t. H^+ was re-standardized to a range equivalent to the range of major ion concentrations in clusters C7t-C9t. Log transformed and standardized Fe was added in the hope that it would help discern springs with water having iron above saturation limits.

Two runs were attempted: one with variables as described above, and one with SO_4^{2-} and Fe increased by 50%. It was hoped that this weighting would help discern the samples with a character or component of C4 type waters. C4 type waters are particularly interesting because they indicated dissolution of sulphides. They are also problematic because most of the ones with neutral pH tend not to plot in C4.

Systematic weighting of variables is subjective and requires experimentation to see what will give the best results. It is important to note that the method is subjective only in the way the samples are to be chosen, not in their actual grouping.

The results for each run are shown in Figure 4.7. The weighting improved the grouping slightly as can be seen by the increased distances between groups. However, it still did not clearly discern waters with a C4 component. Only a small number of the samples in the second run fit into reliable groups. The first group in the unweighted run (C7) contains many of the same samples as the first group in the weighted run. In both cases, there is a significantly larger distance between this group and the main group. The samples in the two groups are collectively referred to as C7 because they are considered to be significant. Beyond this, groups have less significance and are collectively referred to as C8. The only common characteristic is that nearly all of the samples have low TDS contents.

Low TDS content can result from a number of subsurface conditions. The waters may not have had sufficient contact with the host rock to allow water-rock interaction due to short residence times. Oxidizing conditions may persist in the subsurface due to permeable media or a lack of reducing species for reaction. This will result in low concentrations of metals and other species which have low

Figure 4.7

Output of cluster analysis on samples from groups C7t, C8t and C9t of Figure 4.6. The run on the right is the unweighted run and the one on the left has had SO_4^{2-} and Fe increased by 50%.

solubility under oxidizing conditions. The system may be closed to the input of CO_2 or open to the loss of CO_2 (such as karstic systems) which will lower the solubility of carbonates. Surface water samples have similar chemistry to many of the low TDS samples and most are grouped among them in C8.

Thus, the low TDS samples in C8 cannot, with any degree of reliability, be grouped further using cluster analysis. With a few exceptions, it is probably better to examine these as one group than to force them into some of the previously made groups, even though they may have been in contact with the same rock types.

The results of cluster analysis are shown in Table 4.3. These are probably the best results which can be expected using computer methods and indeed they are quite satisfactory. The majority of samples plot into one of 6 or 7 major groups which are indicative of the subsurface hydrogeochemical environment. Knowing these groups will help to determine the dominant processes occurring in the area.

There are, however, several cases when the system breaks down: when waters have been mixed or diluted by waters of another type, when more than one dominant process takes place during the flow history, or when waters have too low a TDS content for their chemistry to be a reliable indicator of their environment. The first two of these cases can be overcome by carefully examining each case with the understanding gained from the 6 or 7 dominant groups. Careful decisions can be made to place this type of sample into groups representing waters of similar environment. In the next section, final groups will be decided upon based on the results of cluster analysis and the other two classification systems and these groups will be used in chapter 5.

Group	Sample	Group	Sample	Group	Sample
C1	063	C5	040	C7	081
C1	064	C5	041	C7	102
C1	064 *	C5	043	C7	113
C1	123	C5	059	C7	114
		C5	067	C7	115
C2	072A	C5	074	C7	125
C2	072B	C5	078	C7	126
C2	072B *	C5	082		
C2	073A	C5	082A *	C8	004
C2	073B	C5	082B *	C8	009
C2	073C	C5	083	C8	012B
C2	112	C5	110	C8	013
		C5	111	C8	015
C3	017	C5	122	C8	028
C3	017 *	C5	127	C8	035
C3	055			C8	044
C3	056	C6	018	C8	045
C3	057	C6	18A	C8	048
C3	058	C6	18B	C8	050
C3	058 *	C6	019	C8	051
		C6	020	C8	054
C4	012	C6	033	C8	065
C4	012A *	C6	033 *	C8	066
C4	012C	C6	038	C8	068
C4	025	C6	052	C8	075
C4	036	C6	053	C8	076
C4	042	C6	053 *	C8	077
C4	049	C6	060	C8	079
C4	062	C6	060 *	C8	101
C4	069	C6	116	C8	104
C4	070	(C6	011)	C8	105
C4	071	(C6	034)	C8	106
C4	080			C8	107
C4	100	C7	006	C8	109
C4	103	C7	107	C8	117
C4	108	C7	010	C8	118
C4	121	C7	022	C8	119
		C7	023	C8	120
C5	001	C7	024	C8	124
C5	021	C7	026	C8	128
C5	027	C7	031		
C5	027 *	C7	032		
C5	029	C7	046		
C5	030	C7	047		
C5	037	C7	061		

Table 4.3 Results of classification of spring waters by hierarchical cluster analysis. Samples marked with an asterisk are repeat samples from 1987.

4.5 Results of spring classification

4.5.1 Introduction

This section uses the results from the various classification schemes described to produce a classification of the samples which best suits the purposes of this study. Here it will be useful to restate the reasons for clustering the data. The 124 spring and surface water samples from the study areas show a large variation in chemistry. Grouping the samples accomplishes two things. First, it separates samples into geochemical and (ideally) into genetically similar waters to help determine what subsurface processes are occurring, particularly with respect to mineral deposits. Secondly, it puts data into a homogeneous form for definition of trace metal anomalies.

4.5.2 Discussion of grouping methods

The physical grouping was based to a large extent on underlying lithology, spring precipitates and field measurements. This created the following problems: (1) The geology was not always known and at depth it was rarely known; (2) More than one lithology may have been encountered, especially if the spring is fault localized and rock units are rarely geochemically homogenous. (3) Similar lithology and similar precipitates do not necessarily indicate similar subsurface processes.

Even where waters have encountered only one lithology, and this is known, it is the subsurface processes involving mineral deposits which are of greatest interest and these may occur in differing host rocks. When the chemical results became

available, they displayed some similarities within groups, but also some important differences, which made it difficult to compare trace metal anomalies with any confidence.

The physical grouping method is not without merit. It is fast, cheap and requires little subsequent data manipulation. If samples are collected and particular care is taken in noting regional rock types and factors such as pH and spring precipitates, then the system could be used as an exploration tool, particularly for sulphides. The only difficulty in looking for anomalous waters in this way would be in establishing background values for the regional rock types. This might be overcome by looking at average values in the published literature for similar rock types.

In the following discussions, the physical groupings will be used as an aid in discussing the two geochemical groupings, but will not be considered on their own.

The "Trees" method is inherently better than the field classification because it is based on the geochemical character of the water. It is more consistent within groups, shows greater distinction between groups and has fewer ungrouped samples. It also picked out several important groups which were missed or misidentified by the field grouping. However, it has several problems which should be addressed.

The main argument against using pattern recognition systems to group data is that they can be subjective both in what constitutes a group and what samples fit into that group. This can also be an advantage in cases where some small component of the whole set of variables is of interest. One can treat this component as more important within groups and produce results which objective methods cannot. It is

to the credit of the system that the non-subjective method of cluster analysis produced similar results.

The "Trees" method cannot be used with much more data than were available in this study. With more than 100 samples, pattern recognition becomes difficult. It also has difficulty (as does factor analysis) when an element varies with more than one other element due to differing chemistry between groups.

The "Trees" method has two important merits. First, it visually represents the data and allows immediate identification of the variables which control the grouping. The result is somewhat like a visual representation of factor analysis and cluster analysis combined. It is similar to doing factor analysis on the variables because the variables which vary together are put on the same branch, thereby reducing the number of components. It is similar to cluster analysis because samples are sorted into similar groups after printing. Its second strength is that, as opposed to cluster analysis (with most software), it can use all the available data, both major ions and trace elements. Increasing the number of variables does not reduce the number of samples that can be analyzed.

As was mentioned in section 4.4, cluster analysis produced very satisfactory results. Part of the reason for this is that there is a good deal of natural variation in the water types in the study area. Less variation, as might occur if the study area encompassed only one lithology, would likely have produced poor results. Some of the problems with the method discussed in the last section are not a result of the method, but of the data. The failure of cluster analysis (or the other two methods) to find any discernable groups in the low TDS samples is probably unavoidable.

Another merit of cluster analysis is that it is available on popular commercial software, most of which is capable of handling at least as many samples (but with fewer variables) as the trees method. The program and equipment for plotting the trees would normally be difficult to find.

The major drawback of cluster analysis (especially joining) is that it is not possible to see in any fast visual way what is causing the clustering. Only with the knowledge of the characteristics of the samples is it possible to guess at the basis of the groups. In the more distinct groups this is not a serious problem because the groupings may already have been postulated from field data. The problem of visualizing the groups has to be overcome by plotting the data on a Piper diagram or similar display, which can be time consuming. In this study the previously generated trees were of great use in visualizing the basis for the cluster groupings.

4.5.3 Discussion of groups

Despite the differences between the three grouping methods, their results have similar elements. This is particularly true with the latter two methods because they are both based on geochemical characteristics. The approximate correlation of groups is shown below. The correlation attempts to show groups which are based on similar geochemical characteristics, such as high concentrations of iron and sulphate in waters or low TDS contents. It cannot, of course, show exact correlation of samples.

P1	=	T2&T3	=	C5&C7
P2	=	T4&T5	=	C4
P3	=	T6	=	C6
P4	=	T7	=	C1
P5	=	T1	=	C8
"P6"	=	"T9"		--
--		"T8"		--
--		--		C2
--		--		C3

Groups such as T8, C2 and C3 have no counterparts in the other two methods although their samples are included in groups within them. The above correlation shows that, with the three exceptions at the bottom, the major groups were picked out by all three methods. What is different is the actual placing of samples.

There are problems with the placing of samples in both geochemical methods. The "trees" method is a problem because it is subjective in the placement of individual samples although most of the groups formed appear to represent actual geochemical processes. The cluster analysis has an opposite problem. The method is so objective that samples with obvious geochemical affinities can be left out of a group if their major ion proportions result in a distance calculation which puts the samples too far from the cluster center. For the final grouping it was decided that it is better to use an objective system for the original grouping and make a few subjective adjustments than to start with a subjective system, the results of which would be difficult to adjust by objective criteria. Cluster analysis, therefore, has been chosen for the basis of the subsequent classification. Adjustments made to the results of cluster analysis are explained below. The samples which have been adjusted are shown in parenthesis in Table 4.4.

The most distinct group by all three methods is that of the Clausen Creek

Group	Sample	Group	Sample	Group	Sample
A	063	C	057	(E	011)
A	064	C	058	E	018
A	064 *	C	058 *	E	019
(A	122)			E	18A *
A	123	D1	001	E	18B
B1	072A	D1	021	E	020
B1	072B	D1	027	E	033
B1	072B *	D1	027 *	E	033 *
B1	073A	D1	029	(E	034)
B1	073B	D1	030	E	038
B1	073C	D1	040	E	052
B1	112	D1	041	E	053
B2	012	D1	043	E	053 *
B2	012A *	D1	059	E	060
(B2	012B)	D1	067	E	060 *
B2	012C	D1	074	E	116
(B2	015)	D1	082		
B2	025	D1	082A *	F	004
(B2	035)	D1	082B	F	009
B2	036	D1	083	F	013
(B2	037)	D1	110	F	028
B2	042	D1	111	F	044
B2	049	D1	127	F	045
(B2	054)	D2	006	F	048
B2	062	D2	007	F	050
B2	069	D2	010	F	051
B2	070	D2	022	F	065
B2	071	D2	023	F	066
(B2	078)	D2	024	F	068
(B2	079)	D2	026	F	075
B2	080	D2	031	F	076
B2	100	D2	032	F	077
B2	103	D2	046	F	101
(B2	105)	D2	047	F	104
B2	108	D2	061	F	106
(B2	109)	D2	081	F	107
B2	121	D2	102	F	117
		D2	113	F	118
		D2	114	F	119
C	017	D2	115	F	120
C	017	D2	125	F	124
C	055	D2	126	F	128
C	056				

Table 4.4 Final results of classification of spring waters, based largely on cluster analysis. Samples in parentheses were placed in the group subsequent to the cluster analysis. Repeat samples are included in the above listing and marked with an asterix.

samples, group A (C1, T7, P4). It contains 5 samples, all of which have elevated NaCl in the waters. Sample 122 has been added to this group, since it is located directly across the river from 063 and 064, has a similar suspended sulphate precipitate in the water, and has similar chemistry, though somewhat diluted. It previously plotted in C5, T7 and P4 (i.e., it was excluded from this group only in the cluster analysis).

Groups B1 and B2 contain waters from C2 and C4, respectively, and the waters show evidence of contact with sulphides. The equivalent groups by the other methods are T5+T4 and P2. B1 contains waters from 5 different vents at two (or arguably three) spring locations. The waters are acidic and have very high trace metal and sulphate concentrations. The group is a special case of B2 type waters and is distinct because of the very high concentrations.

The above two groups which have been amalgamated have had a number of other additions made to them. 012B was from group C8 and has been included because it is similar in character to water from 012A and 012C but has apparently been diluted by mixing with other groundwater. Samples 015 and 037 were added because these are neutral pH, iron hydroxide precipitating springs with very high Fe and SO_4^{2-} concentrations. Samples 035, 054, 079 and 109 are also neutral pH, iron-precipitating springs with elevated Fe and SO_4^{2-} ; the latter two samples discharge from the Mattson Formation. Sample 105 has a very low TDS concentration but a relatively large amount of trace metals. It has an acidic pH and elevated Fe.

Waters of group C belong to C3 and are those of the high pCO_2 , high alkalinity springs of the upper Flat River Valley. Seven samples from 5 different

springs were part of the groups T3 and P1. These waters are similar in composition to those of group D below, except that the Ca^{2+} , Mg^{2+} and HCO_3^- concentrations are greatly increased. They are not included as a more extreme example of group D because they are genetically different, as will be explained in Chapter 5.

Group D1 contains waters which are supersaturated with respect to calcite (and precipitating tufa) and are mostly thermal. The group originates from group C5. Group D2 appears to be made up of waters similar to group D1, but with only moderately high Ca^{2+} and HCO_3^- concentrations; some are above and some below saturation with respect to calcite. The group was defined by cluster analysis (C7) and its rough equivalent would be T2 in the trees classification.

The waters from hot springs in quartz monzonite terrane make up group E. It is identical to group C6 (no additions or removals). Most of the samples in the groups T6 and P3 belong to group E. The waters are NaHCO_3 dominated, have low TDS contents and are high in certain trace metals.

The final group, F, originated as C8 of the cluster analysis. Group F contains low TDS waters which probably cannot be further subdivided. It includes all surface water samples except for acidic streams.

The chemical characteristics of these final groups, both of major ions and trace elements, will be discussed in the following chapter. Their genesis and importance to the resource assessment will also be discussed there.

CHAPTER 5 - HYDROGEOCHEMICAL PROCESSES AND RESOURCE ASSESSMENT IN THE STUDY AREAS

5.1 Introduction

This chapter examines each of the groups in the final classification as described in section 4.5.3 (Table 4.4) and attempts to explain the hydrogeologic processes controlling the chemistry of each. The average values of pH, temperature and TDS content for each group are shown in Figures 5.1, 5.2 and 5.3, respectively. Oxygen and deuterium are discussed in the following section and are plotted in Figure 5.4. Some of the groups have important implications to the resource assessment while others are only important in that they increase our understanding of the various hydrogeologic processes occurring in the region. Each group is discussed in the order given in Table 4.4 and extraneous samples included in the groups are given geochemical consideration.

5.2 Group A - Hot springs at Clausen Creek

The main hot spring area at Clausen Creek has been previously reported by Brandon (1965) and van Everdingen (1973). Although originally referred to as the Clausen Creek Hot Springs, they are presently known as Kraus Hot Springs and are within the bounds of Nahanni National Park. They were sampled during both the 1986 and 1987 field seasons as samples 063 and 064, taken at a vent in the beaver pond and in a small pool beside the river, respectively. At least three other springs are located in the immediate area of Clausen Creek. Spring 122 was sampled across

Figure 5.1

Mean of pH for each group in the final classification (Table 4.4). The number of samples in each group appears in parentheses beside the group number. The root mean squared appears at the top of each bar.

Figure 5.2

Mean of water temperature at vent for each group. The number of samples in each group appears in parentheses beside the group number. The root mean squared appears at the top of each bar.

Figure 5.3

Mean of total dissolved solids concentration for each group, calculated from major ion data. The number of samples in each group appears in parentheses beside the group number. The root mean squared appears at the top of each bar.

Figure 5.4
 ^{18}O and ^2H plot of spring waters in the study areas. Data are taken from Table A5.1 in Appendix 5.

the South Nahanni River from Kraus, 123 was collected about 1.2 km southwest of the river and a third, which lies 1 km southwest of the river, was not sampled. Many of the physical features of these springs are described in section 4.2.

The waters have high TDS values. All major ion concentrations are also high, particularly Ca^{2+} , Na^+ , Cl^- and SO_4^{2-} (Figure 5.5, Table 5.1). Calcium sulphate is above saturation and precipitates as a suspension in the beaver pond and pools. The supersaturation of calcium sulphate is a result of increased available SO_4^{2-} due to the oxidation of H_2S . H_2S discharges in high concentrations as evidenced by the strong odour. Trace metals are slightly elevated, probably due to the availability of ligands to form anion complexes. The presence of H_2S and the immediate precipitation of sulphates indicates that reducing conditions exist in the subsurface. No Eh measurements were taken, but a dissolved oxygen reading of 1 ppm taken at 064 is approximately the detection limit of the instrument.

Waters in sample 122 appear to have been diluted because the concentrations of dissolved species are uniformly lower. Temperature and conductivity are lower and pH higher than in 063 and 064. The vent is approx 1-2 m above river level and the deeper groundwaters have probably mixed with shallower waters.

^{18}O and ^2H analyses (Figure 4) indicate that the waters were recharged under climatic conditions similar to the present and there is no evidence of high-temperature water-rock interaction. Tritium in the waters, analyzed in 064 (20 ± 8 T.U.) and 123 ($11 \& 16 \pm 8$ T.U.) indicates a component of recent meteoric water. This is probably due to mixing in the shallow subsurface.

The sulphur and oxygen isotope data for the dissolved sulphate ($\delta^{34}\text{S} =$

Figure 5.5
Piper diagram showing major ion chemistry for group A. Concentrations are high (Appendix 1).

Element DL(ppm) units method	temp. n/a (°C) n/a	pH n/a (field)	Ca ²⁺ 1 ppm ICP	Mg ²⁺ 1 ppm ICP	Na ⁺ 1 ppm ICP	K ⁺ .2 ppm ICP	HCO ₃ ⁻ .2 ppm T(c)	SO ₄ ²⁻ .2 ppm D	Cl ⁻ .05 ppm D	SiO ₂ 2 ppm ICP	Fe 20/5 ppb AA	Mn 10/2 ppb AA	Zn 5 ppb AA	Ni 2 ppb AA	Mo 0.1 ppb ICP	W 0.1 ppb ICP	Au 1 pptr AA	As 0.3 ppb AA	F 0.04 ppm S
86-063	38.5	6.62	610	114	1168	88.1	194.6	853	2347.00	30	852	75	30	4	0.2	0.4		7.2	0.83
86-064	37.5	6.62	617	116	1118	84.4	224.8	860	2333.00	30	129	57	13	<2	<.1	0.3		1.4	0.82
87-064	36	6.61	502	92	1252	(345)	264.8	829	2368.00	23	163	85	13	<2	0.7	0.5	<1.0	0.3	
87-122	22.5	7.02	157	42	183	(22)	300.9	243	278.00	14	250	78	3	<2	0.3	0.3	2.5	2.4	0.93
87-123	12	7.09	431	93	1164	(334)	367.5	727	2212.00	22	123	230	8	<2	0.3	0.4	1.5	<.3	

Table 5.1 Major ion and selected trace element concentrations for group A springs. Temperature and pH were measured at the vent. DL = detection limit, ICP = inductively coupled plasma mass spectrometry, T(c) = HCO₃⁻, determined by titration in the laboratory and corrected by charge balance techniques; AA = atomic absorption; D = DIONEX ion chromatography. K⁺ in 1987 was measured on ICP and due to serious systematic errors with measuring K⁺ by this method, the above values in parentheses should only be considered relatively high or low. See Appendix 6 for laboratories.

25.07 ‰, $\delta^{18}\text{O} = -9.4$ ‰) provide constraints on source rocks. The underlying carbonates are Devonian in age and the sulphur isotope age curve (Claypool *et al.*, 1980) shows that $\delta^{34}\text{S}$ values in marine sulphate of this age range between 20 and 28 ‰. This suggests that the source of the sulphate in these waters is likely to be marine sulphate from evaporitic deposits in the underlying carbonates. The high concentrations of dissolved NaCl also suggest contact with evaporites. Under normal circumstances, dissolution of marine sulphates would produce sulphate $\delta^{18}\text{O}$ values greater than zero, because $\delta^{18}\text{O}$ in marine sulphate is always positive and there is negligible fractionation during dissolution. However, a large portion of the sulphur in the waters at Clausen Creek is transported in a reduced form as HS^- and is re-oxidized to sulphate during mixing with shallow, meteoric waters. A component of the oxygen in the resulting SO_4^{2-} is derived from the water (-22.4 ‰) and a component from dissolved atmospheric oxygen (23.8 ‰).

The linear arrangement of the four springs suggests fault control. Published geological maps of the area do not show a fault in this area but the outcrop exposure is poor and the surrounding shale terrane would make even a large fault or fracture difficult to detect. Figure 5.6 is a schematic model which would explain the localization and chemistry of the springs. A regionally high hydraulic head would be maintained due to recharge in the First Canyon Plateau immediately to the west (van Everdingen, 1973). This would cause an easterly flow of groundwater at depth. Waters could travel through the gentle easterly dipping strata and encounter unknown evaporites in one of the carbonate units. Manitou Facies dolomite is known to be vuggy and could have hosted this flow. When groundwaters encounter the

Figure 5.6
Schematic model (proposed) to explain the localization and chemistry of the springs in group A. Recharge is in the First Canyon Plateau to the west. Waters travel along easterly gradients in marine carbonate units and encounter unknown evaporites. Upon encountering a fault in the Clausen Creek area, waters move rapidly up from depth and discharge.

inferred fault, they would move rapidly up from depth and discharge. Assuming the global average of 30°C/km for a geothermal gradient, the waters would have to travel up from at least 1.25 km depth (assuming no heat loss during the rise).

Thermal waters at this latitude are a potential geothermal resource. Relatively low-temperature hot springs such as these can be used, either directly or by utilizing heat-pump technology, to heat buildings of all sizes. However, all four of these springs are within Nahanni National Park, which is set aside as a wilderness area, and the springs are not likely to be used for this application.

5.3 Group B - Acidic, high SO_4^{2-} Springs

5.3.1 Introduction

The character of the waters in group B is interpreted to be a result of oxidation of sulphides (see below). Most of the springs in this group have associated iron hydroxide precipitates at the vent but this is not always the case. The group is very important to the resource assessment, but the waters are so diverse that it will be dealt with as sub-groups B1, B2a and B2b. Sub-group B2a includes waters from the Ragged Ranges study area which discharge mostly from shale terrane near intrusions. Sub-group B2b includes waters from the two eastern study areas, all of which discharge from continental sandstones of the Mattson Formation. Subgroup B1 includes acidic waters in the Meilleur River area which have very high concentrations of SO_4^{2-} .

Oxygen isotope data show the waters to be meteoric and recharged under a period of climatic conditions similar to today. Sulphur isotope data ($\delta^{34}\text{S}$ ranges from

-6.2 to 12.5 ‰ CDT) indicate probable dissolution of sulphides because the values are below those of most marine sulphates. Data for sulphides in the area are presently not available.

The oxidation of sulphides increases the concentrations of a number of dissolved species and can be described according to the four formulae below (Stumm and Morgan, 1970):

Reaction 5.1 takes place first and free oxygen must be present for it to occur. Once the process is initiated it cycles through reactions 5.2 and 5.4, with the slowest step in the process being the oxidation of ferrous iron. Free oxygen must also be present for this process to occur because it is an essential component in reaction 5.2. Hoag and Webber (1976) reasoned that the maximum concentration of SO_4^{2-} in groundwater which can be derived from oxidation of sulphides in the phreatic zone is limited to 24 mg/l by the solubility of free oxygen in water¹. This suggests that acidic waters with high SO_4^{2-} and Fe result from oxidation of sulphides in the vadose zone and the source mineralization must be buried at shallow depth. Other redox reactions which oxidize sulphide without the presence of free oxygen can further increase sulphate concentrations in the phreatic zone (van Everdingen *et al.*, 1985).

¹ The phreatic zone is normally considered closed to the input of free oxygen.

A solid phase containing ferric iron, either as an oxide or hydroxide, has to be formed at some stage, such as reaction 5.3, because most waters in group B have greater concentrations of sulphate relative to Fe than could be explained by either reaction 5.1, 5.2 or 5.4.

The above reactions add Fe^{2+} , SO_4^{2-} and H^+ to solution and remove O_2 and Fe^{3+} . Most of the waters in group B have pH values ranging from neutral to strongly acidic. SO_4^{2-} is high in nearly all samples of this group whereas Fe and other metals are commonly present in concentrations ranging from just detectable to very high. Fe and Mn tend to vary together (Figure 5.7), although the abundance of Mn is generally much lower than that of Fe.

The characteristics mentioned above differ greatly from spring to spring due to various factors. Subgroups B1, B2a and B2b all contain samples of acidic waters with high Fe, Mn and SO_4^{2-} but which are low in other metals. Subgroups B1 and B2a have some waters with the above features and with high concentrations of trace metals such as Zn, Ni, Cd, Co or Cu. B2a and B2b contain a number of waters with close to neutral pH and high Fe, Mn, SO_4^{2-} and sometimes detectable HCO_3^- concentrations, but these waters characteristically have low trace metal contents. Figure 5.8 shows the average Zn and Ni concentrations for the various groups, including the three subgroups of group B. The differences between the three are important and are discussed below.

Acidic springs with elevated Fe and Mn, but no other trace elements, usually result from the oxidation of pyrite alone. The stability field for iron in water (Figure 5.9) shows ferrous iron to be the dominant species and the ferric ion to be insoluble

Figure 5.7

Mean of Fe and Mn for each group. "B2a" refers to springs of group B2 from the Ragged Ranges study area and "B2b" to those discharging from the Mattson Formation in the eastern study areas. The sample size appears in parentheses beside the group number and the log of the root mean squared (RMS) is shown at the top of each bar. The correlation of the mean with the RMS allows no rigorous statistical conclusions to be made from this graph. It is intended as a qualitative display only.

Figure 5.8

Mean of Zn and Ni concentrations for each group. "B2a" refers to springs of group B2 from the Ragged Ranges study area and "B2b" to those discharging from the Mattson Formation in the eastern study areas. The sample size appears in parentheses beside the group number and the log of the root mean squared (RMS) is shown at the top of each bar. The correlation of the mean with the RMS allows no rigorous statistical conclusions to be made from this graph. It is intended as a qualitative display only.

Figure 5.9

Stability field for iron in solution (from Hem, 1985). The shaded areas represent solid phases.

at $\text{pH} > 4.0$. Ni and Co tend to be stable under similar conditions as Fe^{2+} and co-precipitate with it (Hem, 1986). It would be unlikely that these elements would precipitate in situations where Fe stays in solution. Early precipitation of Zn is also unlikely in most cases. The solubility of Zn is higher under oxidizing conditions than Fe because Zn depends more on CO_3^{2-} than oxygen. It can be said, therefore, that if waters are acidic and Fe is the only metal present, then sulphides other than pyrite are generally not abundant in the source mineralization.

Acidic springs with significant quantities of Ni, Co, Cu, Cd and Zn likely indicate the presence of sulphides other than pyrite. In cases like this, high concentrations of Fe are common but not always present.

Either mixing with HCO_3^- charged waters or dissolution of sulphides within a unit containing appreciable carbonate (like the Road River Group shales) could cause an increase in pH. Figure 5.9 shows that Fe^{2+} is stable at neutral pH provided that the Eh remains below 0.2 volts. If the oxidation potential increases, for instance by mixing, oxidation of Fe^{2+} to Fe^{3+} would cause precipitation of iron. Co-precipitation of Co and Ni would leave only Zn in solution, provided that the resulting waters are not high in CO_3^{2-} or HCO_3^- .

During routine charge-balance calculations, serious cation deficiencies were found in many of the waters in group B (samples 012A, 025, 036, 042, 049, 069, 071, 072B, 080, 100, 105, 108, 112, 121). This may result from the presence of neutral sulphate species, particularly $\text{FeSO}_4(\text{aq})$. This species is known to occur in appreciable quantities in waters with high concentrations of Fe^{2+} and SO_4^{2-} (Sillen and Martell, 1964). In cases where iron is not present in high concentrations, the

imbalance may be complexed with sulphur anions. Many such complexes have a valence of -1 as opposed to -2 for sulphate, causing an apparent charge imbalance.

In addition to having differing characteristics, the three subgroups are location-specific and are discussed below.

5.3.2 B1 - Metalliferous springs in the Meilleur River area

Subgroup B1 is composed of essentially 2 spring locations, 112 and 072, the latter has at least 5 vents which includes 073. The two spring groups have many chemical similarities (Figure 5.10, Table 5.2) but they also have very important differences. The area of interest is underlain by various shale units and is in a zone of eastward and westward dipping thrust and reverse faults, some of which localize springs. These faults extend northward and southward in a belt that includes the Prairie Creek Pb-Zn-Ag mine, 50 km to the north of the Meilleur River springs. The high concentrations of metals in groundwaters described below coincide with stream sediment (silt) Zn anomalies in the region (Spirito *et al.*, 1988).

Spring 072 is located at the base of the ridge formed by the eastward dipping South Headless thrust fault, just north of the Meilleur River, and very near the fault as mapped by Morrow and Cook (1987). Groundwaters discharge from three vents into an easily visible, opalescent-green pond. The springs are the only source of water for the pond which drains toward the river. The 073 vents occur downhill along the edge of the river bank and appear to represent re-emergent waters draining waters from the pond above. The 073 waters are assumed to have travelled only through shallow overburden in their passage from the pond. A white sulphate

Figure 5.10

Piper plot showing the major ion chemistry of springs from the Meilleur River area (B1), the Ragged Ranges area (B2a) and discharging from the Mattson Formation (B2b). Concentrations are very high in springs from the Meilleur River area (Appendix I).

Element	temp.	pH	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	HCO ₃ ⁻	SO ₄ ²⁻	Cl ⁻	SiO ₂	Fe	Mn	Zn	Ni	Mo	W	Au	As	F
DL(ppm)	n/a	n/a	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppb	ppb	ppb	ppb	ppb	ppb	pptr	ppb	ppm
units	(°C)	n/a	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppb	ppb	ppb	ppb	ppb	ppb	pptr	ppb	ppm
method	n/a	(field)	ICP	ICP	ICP	ICP	T(c)	D	D	ICP	AA	AA	AA	AA	ICP	ICP	AA	AA	S
Subgroup B1																			
86-072A	5	6.29	613	310	18	2.5	115.0	2403.8	16.83	12	136	2824	4977	2318	<1	0.2		0.4	0.49
86-072B	5	3.78	413	268	18	2.1	<0.2	2284.5	2.47	19	1402	5396	5351	2311	0.8	0.1		1.9	0.48
87-072B	5	3.65	253	151	18	(3)	<0.2	1450.8	2.02	14	470	3568	2350	1120	0.3	0.5	3.6		1.30
87-073A	4	6.93	363	212	20	(3)	190.9	1609.7	1.09	7	10	15	1613	768	0.4	0.2		<3	1.32
87-073B	11.5	5.24	299	175	20	(3)	<0.2	1489.7	1.00	10	13	3818	2713	1513	0.3	0.6		<3	2.18
87-073C	3	7.23	354	206	18	(3)	275.1	1507.7	1.00	6	<5	18	155	633	0.4	0.2		<3	1.36
87-112	3	6.09	397	160	254	(7)	31.9	2122.0	14.90	5	98100	3098	538	303	0.2	0.2	<1.0		1.13
Subgroup B2a																			
86-012	1.1	4.77	25	5	1	0.5	<0.2	67.7	0.16	20	<20	135	366	101	0.6	<1		0.8	0.12
87-012	2	5.12	19	4	<1	(1)	<0.2	81.1	1.27	17	60	80	305	130	1.0	0.1	<1.0	<3	0.05
87-012B	1	6.95	26	3	<1	(1)	12.6	62.9	0.10	11	<5	3	220	35	3.0	0.2		<3	0.13
87-012C	1	5.51	22	4	<1	(1)	<0.2	75.4	0.12	16	103	45	445	75	0.1	<1		<3	0.15
86-015	3.5	7.06	92	15	1	0.7	64.3	187.5	0.35	21	14416	430	652	173	2.1	<1		1.4	0.58
86-025	5	4.02	35	3	<1	0.6	<0.2	122.9	0.08	13	147	169	3936	<2	<1	<1		0.4	0.25
86-035	4.4	7.89	28	13	<1	0.4	84.4	26.8	0.09	8	972	10	7	63	<1	0.2		0.5	0.13
86-036		4.29	18	1	<1	0.2	<0.2	181.0	0.10		645	534	640	168	<1	0.2			0.10
86-037	4.2	6.98	171	10	1	0.9	112.5	290.4	0.22	20	19082	425	306	8	0.4	<1		2.2	0.40
86-042	4	4.92	33	9	<1	0.8	<0.2	140.2	0.19	13	5816	225	1488	273	<1	<1		0.6	0.08
86-049	5.5	4.88	122	26	2	1.0	<0.2	562.4	0.16	22	122307	856	331	233	<1	<1		<2	0.98
86-054	10	7.41	8	5	2	0.6	24.8	12.8	0.17	21	3194	152	19	<2	0.5	0.3		4.0	0.19
87-100	0	4.74	8	6	<1	(0)	<0.2	56.1	0.19	8	80	108	98	38	<1	<1		<3	0.04
87-103	4	5.80	40	39	38	(11)	365.4	44.6	1.07	11	6363	305	3	<2	0.1	0.1		12.6	1.54
87-105	4.5	7.75	8	4	<1	(1)	<0.2	40.3	0.63	4	35	48	50	13	<1	<1		<3	0.07
Subgroup B2b																			
86-062	3	6.15	7	21	<1	1.2	16.6	76.4	1.19	10	9721	707	<5	13	<1	0.1		<2	0.13
86-069	11.5	2.91	43	38	71	2.3	<0.2	722.5	20.42	27	51793	1180	86	115	<1	<1		<2	0.28
86-070	6.2	6.77	102	58	10	2.2	<0.2	482.2	3.25	23	2870	1294	67	94	<1	<1		0.2	0.15
86-071	7	3.86	92	71	11	0.9	<0.2	611.3	0.60	16	21517	1047	187	103	<1	<1		1.3	0.34
86-078	1.5	7.00	96	64	<1	2.8	64.9	405.0	0.29	7	63347	1180	15	34	<1	0.2		0.8	0.46
86-079	6.5	8.34	73	41	<1	1.4	211.5	132.3	0.36	7	1942	101	6	<2	<1	<1		1.5	0.27
86-080	12	3.64	12	5	1	1.3	0.2	91.4	2.02	32	9820	217	12	11	<1	<1		0.4	0.09
87-108	1	5.01	1	1	<1	(1)	<0.2	13.4	0.19	4	65	83	10	<2	<1	<1		<3	0.04
87-109	0	6.63	25	45	12	(4)	122.5	168.4	1.70	12	5373	250	3	<2	<1	<1		0.3	0.36
87-121	4	3.76	17	16	<1	(0)	<0.2	211.0	0.24	15	3763	313	58	50	<1	<1	1.2	<3	0.11

Table 5.2 Major ion and selected trace element concentrations for group B springs. See caption to Table 5.1 for details.

precipitate is visible on the bottom of the pond and around the various vents at 073.

The waters from the primary vent (072B) are strongly acidic. They have high Ca^{2+} , Mg^{2+} and very high sulphate concentrations, but the trace metals are of greater interest. Zn, Ni, Co, Cd, Cu, Mn, Al and U all show highly elevated concentrations. Equally important, Fe values are low. The Zn+Ni vs. Fe ratios in waters at this spring are the highest in any of the B group springs (Figure 5.11).

This assemblage of elements is very similar to that of pore waters in the Howard's Pass Pb, Zn deposits (Goodfellow, 1989). The concentrations of Zn in waters from springs 072 and 073 are higher than the average values at Howard's Pass and the concentrations of Ni and SO_4^{2-} are more than an order of magnitude higher in every case. Co, Cd, Cu, Mn and Al were not analyzed at Howard's Pass.

As was explained above, it is possible for iron to be preferentially precipitated, leaving Zn behind in groundwater. However, the author knows of no mechanism which could remove virtually all of the iron from solution and leave such high concentrations of co-precipitating elements such as Co and Ni. It is possible, therefore, that the sulphides from which these elements were derived contain a relatively minor proportion of pyrite.

The total primary flow from the springs is probably about 15 l/s and considering the concentrations in the water, the amount of Zn alone moved to the surface by these waters in a year would amount to 2.5 tonnes. Assuming no input by sedimentary sulphate (a $\delta^{34}\text{S}$ value of 4.34 ‰ supports this), and assuming Zn as the metallic cation, the concentration of SO_4^{2-} in the water indicates that 1.13×10^7 moles of sulphide or 1097 tonnes of sphalerite (for example) is being dissolved in

Figure 5.11
Graph of $\log(\text{Zn} + \text{Ni})$ vs. $\log(\text{Fe})$ for the three subgroups of B.

the subsurface each year. Much of this must be re-precipitated in the shallow subsurface, perhaps in the form of secondary minerals (such as smithsonite), because relative metal concentrations are much lower than those of SO_4^{2-} .

These results indicate, almost with certainty, that a volumetrically large occurrence of sulphides occurs somewhere in the shallow subsurface vicinity of this spring area and that iron sulphides such as pyrite do not make up a significant proportion of it.

The ^{18}O and ^2H data (Figure 5.4) indicate that the water is unaltered precipitation which was recharged under modern climatic conditions. Tritium in the water from 072B indicates relatively young water. Mixing in this case is not as likely because some of the metals are very unstable under oxidizing conditions and would have precipitated at the point of mixing.

Several origins are possible for these waters. The waters may be moving up the South Headless Fault, where they would be in contact with both the footwall Besa River Formation shales and the hanging wall Arnica Formation dolomite. Stratiform sulphides may be located within the shale. Contact with the shales, followed by contact and dissolution of the dolomite, could produce the observed chemistry. The high Mg/Ca ratio in the water (Figure 5.10, Table 5.2) indicates contact with dolomite as opposed to limestone.

Another possibility is that the sphalerite is hosted in the Arnica Formation dolomite. Fluids may have travelled down through this topographically higher unit and encountered a Mississippi Valley type Pb-Zn deposit, or a polymetallic vein deposit such as at Prairie Creek. Zn and Cd are common in both types of deposits

and the presence of Ni and Co could be explained by preferential dissolution. This is perhaps a stronger possibility because the relative lack of cation-exchanged Na^+ in the water mitigates against transport through shale.

In any case, the waters have been in contact with both sulphides and dolomite at some point in their short history. If the fault does control the movement of these fluids, the mineralization must be close to the surface because extensive contact with the hanging wall dolomite after leaving the sulphides would have neutralized the pH.

Spring 112 is also metalliferous and was found during the 1987 field season. It is relatively small with a ferruginous, well-cemented precipitate and a flow rate of about 5 l/s.

The spring discharges from the Besa River shales near the contact with the underlying Funeral-Headless Formation (calcareous) shales which overly the Arnica Formation. The stratigraphy (including age) of the shale units in this area is poorly understood. Descriptions of each formation are not available because both of the above formations are mapped as undifferentiated shales which may include some or all of a number of shale units.

The ^{18}O and ^2H data (Figure 5.4) indicate local meteoric water. Tritium was analyzed and the result was below detection. This indicates that the water has remained in the subsurface for more than 35 years.

The pH of the water (6.1) is relatively high for an iron spring. The major ions show high concentrations of Ca^{2+} , Mg^{2+} , Na^+ and very high SO_4^{2-} . Similarly, Fe and Mn concentrations are very high while Ni, Zn and Co have significantly elevated

concentrations.

The Eh was not measured but must be relatively low due to the limitations of the stability field (Figure 5.9). Fe^{2+} at a pH of 6.1 is stable between 0.3 and -0.1 volts; above this pH, solid ferric hydroxide would precipitate.

Sulphate and carbonate was collected for isotope analysis by the addition of NaOH to raise the pH, followed by the addition of BaCl to precipitate BaSO_4 and BaCO_3 . An unusual thing happened when this was done to sample 112. A bright green precipitate formed in addition to the usual white Ba compounds. This may be a result of co-precipitation of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (ferrous sulphate) which is green when in solid form. The increased pH would have reduced the solubility of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and the addition of BaCl likely triggered co-precipitation.

Fluids from sample 112 have obviously encountered a large concentration of iron sulphides at some point, probably in shales because high Na^+ and low Cl^- concentrations indicate of ion exchange by clay minerals. The high Ca^{2+} and Mg^{2+} concentrations and relatively high pH indicate that they have also encountered carbonates (probably dolomite) at some point. The most likely scenario is that the groundwater first encountered a large body of iron sulphides, thereby lowering the pH and greatly increasing the concentrations of Fe and SO_4^{2-} . This was followed by contact with dolomite, raising the pH somewhat and probably re-precipitating some of the Fe.

There is probably not a significant quantity of sulphides other than pyrite in the source rocks. If a greater amount of Zn was present in solution at this pH, it would not likely have been removed from solution while Fe was left. This spring

indicates the presence of a large iron-sulphide occurrence, probably within shale, in the Meilleur River area. In this case, the sulphide appears to be mostly pyrite.

5.3.3 B2a - Ragged Ranges study area

The Ragged Ranges study area contains 12 springs of subgroup B2a. They mostly occur in metamorphosed Road River shales (hornfels) adjacent to plutons within high upland areas. Abundant pyrite is associated with the hornfelsed shales in the Ragged Ranges and imparts a rusty colour to the rocks. The trace element chemistry of half the waters in this subgroup (015, 035, 037, 054, 103 and 105) appears to be controlled by pyrite mineralization within the hornfels. Each of these springs have high Fe and Mn and low concentrations of other trace metals. They have neutral to acidic pH and high SO_4^{2-} . Major ion chemistry is shown in Figure 5.10 and Table 5.2.

Springs 015 and 037 are good examples of neutral pH iron springs and are used here to show the process which forms waters of this type. The waters from these two springs are chemically distinct and have remarkably similar properties. Both have a fairly high flow rate (20 and 5 l/s, respectively) and precipitate calcareous ferricrete with riffles. Both have neutral pH, but this rises sharply after venting, due to exsolution of CO_2 . Both have significant quantities of Ca^{2+} and HCO_3^- , and very high SO_4^{2-} , as well as high Fe and Mn concentrations. All other trace element concentrations are low compared to Fe. Spring 015 discharges from the Road River Group near an intrusive contact and spring 037 discharges from a Carboniferous siliciclastic unit which is probably within the thermal metamorphic

aureole of the nearby O'Grady batholith.

Dissolution of disseminated pyrite in the hornfels, coupled with the dissolution of accompanying carbonate, would cause increasing concentrations of Ca^{2+} , Mg^{2+} , SO_4^{2-} and Fe as seen in 015 and 037. The relatively high pH is due to dissolution of carbonate. The Road River Group is calcareous in places, and presumably the Carboniferous unit is calcareous as well.

It is unlikely that any of the springs just described have been in contact with significant quantities of base metal sulphides. However, the other half of the waters in subgroup B2a (012, 025, 036, 042, 049, 100) have typical chemistries which are indicative of dissolution of pyrite, but also have elevated concentrations of trace metals. As discussed below, several of these indicate contact with significant amounts of sulphides other than pyrite.

Springs 012A, 012B and 012C are really three separate vents in the same spring area. Spring 012A discharges over a wide area from gravels whereas springs 012B and 012C discharge nearby as discrete points in a small gully. There is no precipitate at 012A, but the other two have a yellowish sulphate precipitate which may be caused by mixing with surface water. Zn, Cu, Co, Cd and Ni concentrations are elevated, especially considering the low TDS contents of the water.

Spring 025 occurs in the upland area northwest of Glacier Lake and has associated red ferric-hydroxide and white sulphate precipitates. Low pH (4.0) and low Ca^{2+} concentration (26 ppm) indicate that carbonates are not present along the flow path. The sulphate concentration is high but iron is not despite the associated precipitate. Trace metal concentrations are low, with the exception of Zn which is

very high (3936 ppb). With the low pH and lack of evidence of carbonate, it is unlikely that Fe has been removed from solution. It is more likely that an incongruent dissolution reaction, such as reaction 5.3, has taken place and that the new iron species has remained behind as a solid.

Samples 036 and 042 were both taken from acidic streams which drain a Devonian shale unit (Road River equivalent) north of the Ragged Ranges study area. The waters have the typical major ion chemistry of acid springs but Zn, Cu, Co, Ni and Cd are elevated for surface waters. The stream from which 036 was sampled drains an extensively hornfelsed portion of the shales. Aronoff *et al.* (1986) have used the presence of this elemental assemblage in acid surface waters in the vicinity of 042 as evidence of a shallowly buried pluton. They state that this assemblage is indicative of surface waters in contact with hornfelsed shales in the area. The occurrence of these waters is not necessarily indicative of any important concentration of sulphides.

Spring 049 discharges immediately adjacent to and within a small, clear river, changing the colour of the river to bright red. It has the highest Fe concentration recorded by this study (122,300 ppb). SO_4^{2-} and Ca^{2+} concentrations are high and pH is low. Trace metal concentrations are elevated but are low relative to Fe. It is included in this half of the B2a samples because the Fe concentrations are so high that disseminated sulphides within the hornfels is an unlikely source for the metals. There is apparently a significant sulphide occurrence in the vicinity, but pyrite is likely the dominant sulphide mineral present.

Spring 100 was collected near the "MB" Pb-Zn mineral showing and was

sampled at the base of the cirque within which the deposit is located. The water has a very low TDS content, barely higher than rainwater, but Ni, Zn and Mn are all elevated (38, 98 and 108 ppb, respectively). SO_4^{2-} is also elevated relative to the other major ions and pH is low. The presence of a mineral deposit in this location was previously known, but this demonstrates how waters with low TDS contents can detect nearby sulphides.

Because all the springs and surface waters in group B2a are probably located within hornfelsed shales, it may be that disseminated pyrite related to the metamorphism influences all these waters to some extent. High trace metal concentrations in waters from the two surface streams to the north may be related to thermal metamorphism in that area. However, the hornfels within the Ragged Ranges study area do not appear to have this assemblage of trace metals as part of their typical geochemical signature. Samples 012, 025 and 100 may be indicative, therefore, of base metal sulphide occurrences. Small base metal skarns are known to be associated with intrusions in the Ragged Ranges area and stratiform Pb-Zn occurrences are common in the Road River shale. Either of these are potential sources for the metals. The latter is probably more common and, therefore, more likely to be a source of the metals. The chemistry of spring 049 indicates a relatively large concentration of sulphides, perhaps pyrite-rich stratiform sulphides, but there is not likely to be a significant proportion of base metal sulphides present in the rock volume through which the waters passed.

5.3.4 B2b - Springs discharging from the Mattson Formation

All B2b springs are located in the eastern study areas (062, 069, 070, 071, 078, 079, 080, 108, 109, 121) and are discharging from the Mississippian Mattson Formation, a continental sandstone with coal measures and abundant pyrite. Pyrite occurs in both disseminated form and in lenses and pods near layers of organic matter in the sandstone. Plant fragments are common throughout the lower two units of the formation whereas the uppermost unit contains calcareous sandstone. The formation outcrops extensively within the Tlogotsho Plateau study area and forms the plateau itself. On the plateau, the flat-lying to gently dipping sandstone strata are underlain by a series of late Paleozoic shale and transitional units.

The sandstone is highly permeable. Springs vent along the base of the plateau at the shale/sandstone contact and in other areas where the formation outcrops. This is the only example in the study area where the localization of springs shows obvious stratigraphic control. The springs all have a floccular Fe-hydroxide precipitate near the vent. Some also have a cemented, tufa-like precipitate probably composed of Fe-hydroxides.

The waters from the Mattson Formation, particularly from the Tlogotsho Plateau area, have high pH, high SO_4^{2-} and high to very high Fe concentrations. For unknown reasons, Mg^{2+} is also unusually high in most of these springs, as can be seen in Figure 5.10. The chemical similarities are remarkable considering the large area represented by the samples. The hydrogeochemical evidence suggests that pyrite is being actively dissolved by oxygenated groundwater in all parts of the formation. Small to moderate sized rivers (071, 121 and many others unsampled), which are

flowing from the plateau have pH values as low as 3.9. The lack of significant concentrations of trace metals relative to Fe (see Figure 5.11) in the springs indicates that only pyrite is being dissolved. These springs are an interesting natural phenomenon but there is little potential for the presence of economic mineralization within the Mattson Formation.

5.4 Group C - High $p\text{CO}_2$ springs in the Flat River Valley

This group represents a very unusual set of travertine-precipitating springs located in the northwestern end of the Flat River valley. They are located along the western margin of the valley starting about 25 km southeast of the town of Tungsten to almost the park boundary. Five springs were sampled in this group (017, 055, 056, 057, 058). Three more have been identified but not sampled.

Waters from three springs in group C were analyzed for ^3H and all were found to contain high levels. This indicates that in these springs a large component of the water was recharged less than 35 years ago. $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values plot very close to the local meteoric water line (LMWL) (Figure 5.4) indicating that the waters are meteoric in origin and were recharged under present climatic conditions.

All of these springs have similar characteristics. The associated travertine deposits are all large. Water temperature is low and a large quantity of gas (mostly CO_2) is being emitted at each of the vents. The major ion chemistry, as seen in Figure 5.12 indicates that all of the waters are Ca-HCO_3 dominated. All have extremely high TDS contents which are almost entirely due to these two ions (Table 5.3). Several other elements, such as Mg^{2+} and Si, and locally, Fe and Mn, also have relatively high concentrations. The pH of the water is invariably low (<6.3) but rises

Figure 5.12

Piper plot of the major ion chemistry of waters in group C. Concentrations of the dominant ions are very high (Appendix 1).

Element DL(ppm) units method	temp. n/a (°C) n/a	pH n/a (field)	Ca ²⁺ 1 ppm ICP	Mg ²⁺ 1 ppm ICP	Na ⁺ 1 ppm ICP	K ⁺ .2 ppm ICP	HCO ₃ ⁻ .2 ppm T(c)	SO ₄ ²⁻ .2 ppm D	Cl ⁻ .05 ppm D	SiO ₂ 2 ppm ICP	Fe 20/5 ppm AA	Mn 10/2 ppm AA	Zn 5 ppm AA	Ni 2 ppm AA	Mo 0.1 ppm ICP	W 0.1 ppm ICP	Au 1 ppt AA	As 0.3 ppb AA	F 0.04 ppm S
86-017	5.5	6.27	791	68	60	8.1	2428.0	55.3	3.05	94	20766	1503	<5	<2	<.1	<.1	0.4	0.92	
87-017	5.5	6.11	635	55	46	(13)	2272.7	49.5	2.74	73	58	1498	8	<2	<.1	<.1	<.3	0.56	
86-055	1.6	5.88	425	53	10	3.4	1099.7	126.2	5.25	25	15850	587	412	125	1.7	<.1	0.9	0.66	
86-056	7.7	6.10	782	138	119	38.0	2235.9	282.8	22.39	12	33	34	<5	16	0.7	<.1	0.5	1.23	
86-057	14.2	6.81	577	119	74	31.5	1721.7	243.2	20.34	10	161	521	<5	8	<.1	0.2	0.2	0.96	
86-058	8.9	6.20	647	66	32	5.6	1918.0	38.0	3.76	15	28	158	<5	<2	<.1	<.1	<.2	0.53	
87-058	11	6.23	484	51	25	(8)	1759.4	26.9	3.10	13	<5	275	8	<2	0.2	0.3	<.3	0.38	

Table 5.3 Major ion and selected trace element concentrations for group B springs. Temperature and pH were measured at the vent. DL = detection limit, ICP = inductively coupled plasma mass spectrometry, T(c) = HCO₃⁻, determined by titration in the laboratory and corrected by charge balance techniques; AA = atomic absorption; D = DIONEX ion chromatography. K⁺ in 1987 was measured on ICP in 1987 and due to serious systematic errors with measuring K⁺ by this method, the above values in parentheses should only be considered relatively high or low. See Appendix 6 for laboratories.

sharply with increasing distance from the vent due to exsolution of CO₂. pCO₂ in all of the vents is very high with values above 1 bar (Figure 5.13).

All of the unusual chemical characteristics of these springs result directly or indirectly from the presence of excess CO₂. The dissolution of limestone is aided by CO₂ according to the reactions:

The exsolution of CO₂ at the surface causes these reactions to proceed to the left and consequently CaCO₃ is precipitated. This process is well known and occurs commonly in waters throughout the study area. However, the presence of such large quantities of CO₂ is not common and there are a number of possibilities as to its source.

Figure 5.14 illustrates the range of $\delta^{13}\text{C}$ concentrations obtained for the various spring groups. The values for $\delta^{13}\text{C}_{(\text{gas})}$ were obtained from the $\delta^{13}\text{C}_{(\text{DIC})}$ data using equilibrium calculations. The calculated $\delta^{13}\text{C}$ concentrations are not necessarily equal to the original gas concentrations because carbon is added during the dissolution of marine carbonates.

Atmospheric and plant CO₂ are the most common sources of CO₂ in groundwater, but the sheer volume of gas (and high partial pressures) no doubt precludes either of these as primary sources. This interpretation is supported by the $\delta^{13}\text{C}_{\text{gas}}$ values for group C which are higher than either of these sources. Potential sources which are capable of producing these high pCO₂ conditions are mantle gases and gases given off during the metamorphic decomposition of carbonates. Most

Figure 5.13

Calculated partial pressure of CO₂ for all samples in the non-acidic groups (i.e., group B is omitted). Calculations are based on concentrations of carbonate species and pH at the time of sampling.

Figure 5.14
 $\delta^{13}C_{(gas)}$ calculated from $\delta^{13}C_{(DIC)}$ for springs in various groups.

authors consider the range of mantle derived CO_2 to be -8 to -4 ‰ and that values above this indicate a metamorphic source. Thermal metamorphism of carbonates produces CO_2 with a similar $\delta^{13}\text{C}$ composition to the original carbonates. In the Flat River valley, the carbonates (Rabbitkettle and Sunblood Formations) range in composition from -2.8 to $+0.7$ ‰. Therefore, the gas in these springs falls into the range of metamorphic CO_2 .

"Soda springs", such as those in group C, are known elsewhere in Canada and the world. Global compilations of known CO_2 discharges by Barnes *et al.* (1978,1984) show them to occur extensively in young orogenic belts and in areas of extensional tectonism, such as the East African Rift. In Canada, they are presently known to occur in three other areas: southern BC, north-central BC at Mt Edziza, and in the St. Lawrence Valley. The latter is the only significant discharge locality in the eastern part of North America.

Most CO_2 discharges can be shown, on the basis of carbon isotopes, to be either mantle derived or derived from the thermal decomposition of carbonate rocks or organic material such as coal (Barnes *et al.*, 1984). Blavoux *et al.* (1982) described springs in France which appear to have a mantle source of CO_2 , with $\delta^{13}\text{C}_{(\text{gas})}$ values ranging between -8 and -3.7 ‰. These are located along major faults or fractures within the Central Massif and some of them are located within or near Tertiary volcanic centres. In areas of recent volcanic activity, contact metamorphism of marine carbonates is common. Clark (1982) found this to be presently occurring at Mount Cayley in southwestern British Columbia, where CO_2 produced through metamorphism is apparently mixing with volcanogenic CO_2 . $\delta^{13}\text{C}_{(\text{gas})}$ values of -4.9 and

-3.6 ‰ were recorded.

In the Flat River valley, carbon isotopes indicate CO₂ from metamorphic sources and little or no input from mantle or volcanogenic CO₂. However, oxygen, deuterium and tritium isotope data indicate that the water discharging from the springs is of meteoric origin and has been recently recharged. In addition, there is no evidence that water-rock interactions have occurred (Figure 5.4). If they had taken place there should have been a detectable shift in the $\delta^{18}\text{O}$ value of the water due to exchange with the isotopically heavier oxygen in the wall rock. These results suggest that a separate CO₂-rich (low in water) metamorphic fluid is travelling upward from depth and mixing with shallow meteoric water.

Figure 5.15 depicts a possible model for the production, transport and venting of the CO₂-rich fluids. First, CO₂ must be produced by thermal decomposition of the carbonate country rocks. The Cretaceous quartz monzonite plutons are known empirically to have high heat flow, although quantitative data are not yet available. Assuming moderately high conductive heat flow rates of 200 mW/m², and a temperature of reaction between 180 and 300°C to decompose carbonates (Muffler and White 1968,1969), the depth range for the production of CO₂ would be approximately 3-5 km. Carbonate minerals react with silicates or dissolved silica to form calc-silicates and liberate CO₂. The simplest of many such reactions takes place during the formation of wollastonite:

The next important requirement of the model is that some pathway exists for the CO₂ to reach the surface. The most likely way to have so many similar discharges

Cross section of the Flat River Valley at spring #N-55

Figure 5.15 Cross section of the Flat River valley showing the possible model for the origin of CO_2 rich fluids. CO_2 is produced in the shallow crust by metamorphism of carbonates in contact with Cretaceous plutons. The CO_2 travels upward along an inferred fault and mixes with shallow meteoric water. The waters dissolve large quantities of carbonates which are re-precipitated on surface upon discharge.

forming a linear pattern is to have a large fault acting as a conduit. There is presently no fault mapped in the valley, nevertheless, one may exist. It could have been missed during the reconnaissance scale mapping of the mid 1960's, due to the thick glacial deposits on the valley floor. Barnes et al. (1984) noted such localization of CO₂ discharges along major faults in California, including segments of the San Andreas Fault.

With a fault as a conduit in the Flat River valley, CO₂ could travel upward into the zone of active meteoric water, remaining as a liquid (or supercritical fluid) to depths of approximately 500 m. This CO₂-rich meteoric water would dissolve large quantities of carbonate which would then re-precipitate upon discharge at the surface as the CO₂ exsolves from the water.

Carbon dioxide is present in many magmatic fluids and consequently is likely to be present in many hydrothermal ore-forming fluids. In the deposition of some metals, particularly Hg, CO₂-charged waters may play an important role. Such waters may or may not play a role in the development of skarn-type mineralization such as is present at Tungsten, Northwest Territories. Skarn mineralization is thought to occur during hydrothermal alteration of limestone or limey pelitic rocks by magmatic fluids emanating from an intruding igneous body. During the alteration process, thermal decomposition of the limestones would necessarily take place, releasing large quantities of metamorphic CO₂. At the springs in group C, there is no isotopic evidence for the presence of magmatic fluids, however, the process of thermal decomposition of carbonate rocks is apparently taking place nonetheless. Heat transfer would likely be conductive rather than convective because the flux of

present-day fluids would be small relative to that which took place during the emplacement of the plutons when most of the volatiles would have been driven off. The presence of these springs provides an excellent opportunity for studying similar fluids to those produced during the genesis of skarn mineralization and in a similar environment.

Metamorphic CO₂ in groundwater is known to cause silica-carbonate alteration of serpentinite in the California Coastal Ranges (Barnes *et al.*, 1973). Cinnabar is commonly associated with this type of alteration and large scale mercury deposits have been mined from silica-carbonate host rocks in California (Barnes *et al.*, 1973).

The springs in this group also have significance with respect to geothermal prospecting. Crandall and Sadlier-Brown (1978) mentioned some of these springs in their report because they precipitate minerals similar to those of hot springs. The presence of metamorphic CO₂, and the spatial association of these springs with the plutons, would suggest that temperatures of at least 180-300° C exist in the shallow crust (<5 km).

Finally, the model proposed here requires that a large, unmapped and relatively "open" fault is located along the Flat River valley. Irwin and Barnes (1980) discussed the close coincidence between regional seismic activity and areas of CO₂ discharge. CO₂ discharges are known to coincide with on-land segments of linear seismicity, i.e., active faults. Examples of this include branches of the San Andreas Fault in California. As CO₂ discharges represent a long-term event relative to the historic record of seismicity, Irwin and Barnes (1980) suggest that the presence of

CO₂ discharges may be useful in detecting areas of potential seismic activity.

5.5 Group D - High TDS springs in carbonate terrane

5.5.1 Introduction

This section includes springs from groups D1 and D2. They occur largely in carbonate terrane, however, many of the springs in both groups are known or inferred to be fault localized and, therefore, may have encountered a number of different rock units. Both groups tend to have Ca-HCO₃ dominated waters although there are exceptions. They differ largely in their concentrations of Ca²⁺ and HCO₃⁻ and in the relative proportions of the other major ions. D1 contains a number of non-thermal waters which were affected by different processes than the thermal, fault-controlled waters. The two groups will be dealt with as subgroups D1a and D1b.

5.5.2 D1a - Fault localized thermal springs

The springs in this subgroup (001, 021, 027, 029, 030, 040, 041, 043, 82) have temperatures which range from 14 to 49°C and precipitate large deposits of tufa. The only non-thermal water included here is that of spring 111 which has a temperature of 7°C and also precipitates tufa. Some of these springs have been referred to in earlier reports (Chapter 1).

The major ion chemistry of D1 is shown in Figure 5.16. The waters generally exhibit elevated concentrations of major ions (Table 5.4). Most waters are Ca-HCO₃/SO₄ dominated and most have a significant component of NaCl. Trace elements, such as Sr²⁺, Si and U, are elevated in some cases, but trace metals,

Figure 5.16
Piper plot of major ion chemistry of subgroups D1 and D2. Concentrations of the major ions are moderate to high.

Element	temp.	pH	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	HCO ₃ ⁻	SO ₄ ²⁻	Cl ⁻	SiO ₂	Fe	Mn	Zn	Ni	Mo	W	AU	As	F
Subgroup D1a																			
86-001	21	6.85	231	46	4	4.9	768.8	32.6	1.21	16	129	13	8	<2	1.8	<.1			0.53
86-021	17	7.03	333	82	25	15.3	476.8	539.6	2.58	50	243	165	<5	<2	0.4	0.2		99.3	0.73
86-027	25	7.32	155	34	1	2.7	496.9	29.5	0.40	20	26	<10	<5	<2	1.2	0.1		0.8	0.31
87-027	28	6.94	128	27	1	(3)	482.9	27.7	0.48	16	15	<2	5	<2	1.7	0.3	2.1		0.33
86-029	14	7.19	151	32	1	3.3	545.9	15.1	0.71	21	24	<10	7	<2	0.6	0.1		0.5	0.34
86-030	17.7	6.75	148	39	6	2.8	445.2	93.0	1.98	11	1710	15	<5	<2	1.6	<.1		1.2	0.38
86-040	49	6.48	216	67	66	33.3	431.4	396.1	23.42	41	65	<10	<5	8	<.1	<.1		1.5	1.52
86-041	30.5	7.03	218	68	68	33.7	726.0	389.2	23.57	41	440	<10	6	3	0.1	0.2		0.8	1.53
86-043	44	6.92	139	35	26	23.2	201.8	218.5	32.15	43	138	30	5	<2	0.1	<.1		5.2	0.91
86-082	38.5	8.2	171	54	31	13.8	320.0	373.3	31.54	41	159	23	44	<2	4.5	1.2		10.9	0.99
87-082	37	6.75	151	46	30	(17)	377.6	297.4	24.81	36	<5	3	18	<2	4.6	1.6	3.8		0.79
87-082B	30	7.58	131	45	29	(16)	305.7	291.0	23.96	35					4.5	1.6			0.76
87-111	7	7.62	278	31	<1	(2)	484.5	373.7	0.23	7	10	<2	353	80	11.0	0.1	2.6	<.3	0.40
Subgroup D1b																			
86-010	22	8.15	114	19	1	0.2	227.0	189.3	0.33		108	12	<5	16	7.3	<.1			0.24
86-059	5.5	7.22	151	26	7	0.9	483.4	13.2	0.44	6	480	157	<5	<2	<.1	0.2		<.2	0.15
86-067	3	7.55	182	67	<1	0.5	271.8	393.0	1.17	6	337	92	61877	65	0.6	<.1		49.6	0.49
86-074	16	7.40	179	57	146	8.8	672.6	301.1	0.51	15	465	633	58	16	0.8	<.1		0.8	0.06
86-083	3.5	8.1	228	45	184	4.6	254.6	451.0	212.65	17	5179	437	15	<2	3.0	0.4		12.7	0.09
87-110	9	7.64	119	49	207	(3)	394.9	552.6	1.76	5	2013	190	8	<2	6.0	<.1		1.2	0.82
87-127	3.5	7.02	135	25	5	(1)	420.9	91.5	0.82	6	33	10	40	<2	1.2	<.1		<.3	0.23
Subgroup D2																			
86-006	11.1	7.52	79	28	2	2.3	270.0	38.3	1.28	8	<20	<10	<5	<2	0.6	<.1		0.5	0.25
86-007	8.8	8.27	25	10	<1	0.2	83.2	13.9	0.18	<2	<20	<10	<5	<2	0.7	<.1		<.2	0.10
86-022	2.5	7.75	94	23	2	0.5	293.4	14.8	0.32	7	33	<10	<5	<2	2.5	<.1		0.7	0.14
86-023	3.8	7.24	98	42	<1	0.7	292.8	69.2	0.55	7	<20	<10	<5	<2	4.0	0.2		2.4	0.24
86-024	11.1	7.82	97	42	<1	0.7	306.7	69.5	0.51	8	<20	<10	<5	<2	8.0	0.4		0.3	0.23
86-026	18	6.36	58	30	2	1.5	212.5	45.5	3.48	15	<20	<10	<5	<2	4.3	0.1		1.0	0.21
86-031	12.1	7.74	127	30	<1	3.1	444.9	24.9	0.78	18	<20	<10	<5	<2	0.9	0.1		0.3	0.46
86-032	54	7.00	93	29	2	3.8	254.0	81.7	0.91	51	460	23	<5	<2	1.4	0.2		2.4	0.42
86-046	8	7.80	71	33	2	1.4	239.0	45.9	3.69	15	36	<10	10	<2	3.1	<.1		1.2	0.22
86-047	13	8.2	81	36	2	1.4	257.6	57.0	2.47	13	72	<10	13	<2	3.0	0.2		0.6	0.23
86-061	8	7.37	56	27	2	0.6	207.8	31.3	0.50	6	1817	123	<5	3	0.6	0.1		0.5	0.20
86-081	4	8.2	103	26	3	1.6	342.4	41.6	0.69	12	705	222	9	5	3.9	<.1		4.5	0.37
87-102	3.5	6.58	76	9	2	(1)	223.1	44.0	0.66	4	<5	<2	<2	<2	0.6	<.1		<.3	0.09
87-113	8	7.96	79	24	<1	(0)	304.6	32.0	0.49	3	18	<2	28	5	6.7	<.1	5.9	0.5	0.16
87-114	3.5	7.69	95	20	2	(1)	305.4	69.2	1.26	6	<5	8	3	<2	5.5	<.1	3.7	<.3	0.25
87-115	3	7.63	116	43	5	(2)	342.7	171.7	3.48	9	8	<2	3	<2	10.2	<.1	<1.0	0.3	0.91
87-125	1	7.61	127	23	<1	(0)	383.0	87.2	0.32	8	<5	<2	58	<2	15.3	<.1	<1.0	<.3	0.21
87-126	6	7.40	49	15	<1	(0)	199.5	15.8	0.80	5	523	10	10	<2	2.8	<.1		0.3	0.16

Table 5.4 Major ions and selected trace element concentrations for group D springs. See caption to Table 5.1 for details.

including Fe, are usually very low. The pH is generally below neutral but rises, in all cases, after the waters leave the vent.

pCO₂ values are consistently lower in this group than in group C (Figure 5.13). However, spring 040 has a considerably higher pCO₂ than the other springs in group D1. $\delta^{13}\text{C}$ values are also uniformly lower in this group than group C and spring 040(=041) is, again, anomalously higher. The lower pCO₂ and $\delta^{13}\text{C}$ values in D1 indicate a smaller input of CO₂ and that this CO₂ is less likely to be derived from deep sources.

¹⁸O and ²H data show no evidence of water-rock isotope exchange and the waters plot on the LMWL (Figure 5.4). This indicates that waters have not experienced very high temperatures. Sample 021 plots close to the LMWL but is considerably more depleted in both ¹⁸O and ²H than any of the other samples in the study area.

All springs in subgroup D1a are interpreted to be localized along major faults (Hamilton *et al.*, 1988a). Springs 001 and 040 (=041) of subgroup D1a and 023, 026 (=046) and 047 of group D2b are localized along the Broken Skull Fault in the South Nahanni and Broken Skull River valleys. The D2 waters along this fault are non-thermal but also precipitate large deposits of tufa. Tritium was measured in 001 and 040. It was detected in 001 (34 ± 8), possibly due to mixing with younger waters in the shallow subsurface. 040 had undetectable tritium and the highest temperatures recorded in this subgroup (49°C). This would indicate that the water has moved up, with little near surface mixing, from a depth greater than 1.5 km, assuming the global average geothermal gradient (30°C/km) and no heat loss. The other waters

discharging along this fault have probably experienced less deep circulation as indicated by the lower temperatures. The anomalously high $p\text{CO}_2$ and $\delta^{13}\text{C}$ values of sample 040 suggests possible input of metamorphic or mantle CO_2 , though to a lesser extent than in group C.

Spring 021 is a large, tufa precipitating seep located at the core of the Broken Skull Anticline. It may be localized along extensional fractures related to the anticline. The anomalously low $\delta^{18}\text{O}$ and $\delta^2\text{H}$ concentrations reported above suggest possible recharge during a cooler climatic period. Tritium is barely above the detection limit (11 ± 8) and its presence may be due to rainwater which had fallen just prior to sampling. Only a small amount of modern rainwater would increase tritium to above the detection limit and this would probably not alter the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values significantly.

Spring 043 and a number of unsampled thermal springs are located in an area of complicated structure near Grizzly Bear Lake and are probably fault-controlled. Springs 027 and 029 of group D1a and 031 of group D2, all of which are thermal, are located in the southeastern Flat River valley. They are thought to be fault-controlled, although the orientation of the fault(s) is unknown.

Spring 082 of group D1 is located near the Meilleur River and appears to be localized along a large fault. This large hot spring (temperature = 37°C) was discovered during the 1986 field season and re-visited during 1987. It has since been visited by Nahanni Park personnel who have tentatively named it the "White Aster Hot Spring". It is described below in more detail than the other springs because it has not been previously reported in published literature and because it has important

implications to the resource assessment.

The spring is 200-300 m above the level of the Meilleur River and 700 m south. The main vents are three large pools in succession. Water flows from the highest to the lower two pools at an increasing flow rate, to reach a combined flow of 40-50 l/s below the third pool. A small, fourth pool, is located 50 m farther up the hill and discharges 1-2 l/s of water into a small, dry creek bed.

Tufa levees are precipitated along the channels from the main pools but the waters do not precipitate large quantities of travertine until 50 m from the first vent. Here the water flows through a series of vegetated terraces after which it flows into fractures in the deposits, oriented normal to the slope of the hill.

These fractures appear to have been recently formed. The soil filling them is very unstable and they cross-cut recent tufa deposits as indicated by the presence, within the deposits, of non-decomposed plant matter (leaves and moss) and wood with a modern ^{14}C age. The strong Nahanni earthquakes of 1985 may have played a role in the formation of the fractures. Beyond the fractures, the water re-emerges (sample 082B) at a lower temperature (30°C) and precipitates tufa for several hundred meters down to the river.

The water chemistry is similar to other D1 hot springs. Ca^{2+} , Mg^{2+} , HCO_3^- and SO_4^{2-} concentrations are high, and Na^+ and Cl^- levels are elevated and approximately equal in epm balance. This balance suggests that these waters have not travelled extensively through shales. The pH is predictably low (6.75), considering the large tufa deposits, and rises with distance from the vent. Eh was not measured, but the strong H_2S odour suggests it is fairly low in the immediate subsurface.

In addition to the buff coloured tufa being precipitated at 082, a dark grey mineral is being precipitated within all four of the vents. It can be seen in the water as a grey-blue suspension and settles around the vents to form a thick mud which has completely filled the uppermost of the three large vents. X-ray diffraction results on the material were inconclusive but modal analysis shows it to be an aluminosilicate, probably a clay mineral. Trace metal composition of this precipitate is even more interesting. Co, Cr, Cu, La, Ni, Pb, V and Zn are all high, and Zn makes up 0.96% of the precipitate. These results and the precipitate type are unique in the study area. Chemical data on precipitates sampled at a number of springs of groups B and D are available. The 082 trace metal results are far higher than any of the others, including 082y, which is the travertine from the same spring.

Although a great deal is not understood about the geochemical processes affecting the groundwaters discharging from spring 082, a few comments can be made. The waters contain elevated concentrations of Zn and U, although they are certainly not high. Considering the very high concentrations of Zn in the proximal precipitate, the change in oxidation potential must be extremely important in the stability of the metals in solution, much more so than pH. The waters discharging from this spring must have come from a significant depth (>1km) and little or no mixing has occurred with shallow groundwaters, based on undetectable tritium. Groundwater flow is probably concentrated along the fault to the south or west of the spring (its exact position near the spring is unclear) and this water would have travelled through the Arnica and Sombre Formations, among others. The waters may have encountered Zn minerals, perhaps in the Arnica Formation, and transported

the metals in solution because of the unusually low redox potential. As H_2S is exsolved and the waters dissolve atmospheric oxygen, the metals are immediately precipitated with the black mud in an unknown form.

Spring 111 is another of subgroup D1a and differs from all the others in that the waters are not thermal (7°C). It is located several km south of 082, probably on the same fault. The waters deposit a hackly, buff coloured tufa which covers a wide, non-vegetated area on a slope. Small channels in the tufa are filled with water from numerous vents.

The waters have higher Ca^{2+} , Mg^{2+} and HCO_3^- , concentrations than the waters at 082, probably because of the lower temperature. The high SO_4^{2-} concentrations are nearly identical with 082, but Na^+ and Cl^- are virtually absent. Zn and Ni concentrations in waters from 111 are the highest in any of the D1 group waters. The tufa was also analyzed and was found to contain very high Zn (the highest in the study area for a tufa sample) and high Ni concentrations, similar to the proximal precipitate at 082. Pb is also elevated in the tufa and U is elevated in the water.

Spring 111 is situated at the contact between the Besa River shales and the over-thrusted Arnica Formation. The lack of evidence of cation exchange indicates that the waters have not had much contact with the shales. It is most likely that this spring is localized along the same fault as 082 and the waters also pass through the Arnica Formation. The low temperature and abundant tritium in the water indicate a relatively short, shallow flow system. The waters probably recharge in the Arnica Formation, topographically higher and to the west, where they encounter Pb-Zn mineralization. They then flow easterly along the fault, with the footwall shales

acting as an impermeable boundary, and discharge where the fault meets the surface.

5.5.3 D1b - Other D1 springs

A number of springs included in group D1 are not necessarily fault-controlled and most of these are non-thermal. Subgroup D1b was created as a convenience to aid in the discussion and the waters are not all genetically related. They were originally clustered with the fault-controlled springs because they have major ion similarities and high TDS contents.

Sample 083 was collected on the limb of a syncline near the contact between uplifted Mattson Formation and the overlying Cretaceous Garbutt Formation shales, which are exposed in the core of the syncline. A number of tufa precipitating springs are located along this contact. The high SO_4^{2-} and Fe concentrates indicate contact with the Mattson Formation. High concentrations of other major ions, particularly Na^+ and Cl^- , may result from sluggish groundwater flow within the Mattson Formation and possibly the underlying marine units. A slight excess of Na^+ to Cl^- in the epm balance indicates cation exchange reactions.

Springs 074 and 110 of group D2 and 116 of group E, have had their chemistry altered by cation exchange within shales. Springs 074 and 110 discharge directly from shales whereas 116 is an apparently spring-fed pond in shale terrane. Waters at 074 precipitate unidentified (highly soluble) salts on the bedrock and those at 110 precipitate a suspension, probably a sulphate. The exchange of Na^+ in the shale for Ca^{2+} in the water permits greater concentrations of dissolved constituents because NaHCO_3 is much more soluble than CaCO_3 . Springs 074 and 110 have been

included with the D1 thermal springs in the cluster analysis because their high major ion concentrations match the latter in all but Ca^{2+} and perhaps Cl^- . Sample 116 was clustered in group E because its NaHCO_3 dominated major ion chemistry is similar to the springs in this group although the processes resulting in this chemistry are very different.

Sample 067 was collected in the Prairie Creek Pb-Zn-Ag mine. It has extremely high concentrations of Zn, Cu, Cd and elevated levels of Co and Ni. It is useful in that it gives insight into the elemental assemblage which could be expected when dissolving sphalerite, galena, and copper minerals such as malachite, azurite and chalcopyrite. As has been shown, this assemblage of trace metals (although different in proportions and concentrations) has been noted in many springs in the area.

Sample 127 is a sample of the Parks Canada well water at Nahanni Butte and, interestingly, was clustered among group D1.

5.5.4. D2 - Moderate TDS springs in carbonate terrane

Group D2 is made up mostly of Ca-HCO_3 -dominated springs, some of which are thermal and some of which are fault-controlled. The major difference between D2 and D1 is the lower concentration of major ions, which results in part from lower pCO_2 (Figure 5.13). Ca^{2+} and HCO_3^- concentrations tend to be near or slightly above saturation levels with respect to calcite. The major ion chemistry is also different from group D1 in that SO_4^{2-} and Na^+ are lower (Figure 5.16, Table 5.4). Some of these springs discharge from overburden (007, 022, 024, 061, 081, 102). The

elevated TDS levels probably result from dissolution of carbonates by soil CO_2 and a relatively long residence time (compared to springs of group F). None of the springs in this group have elevated trace metals and most have values below detection. An exception is sample 125 in the Nahanni Karst study area, which has slightly elevated Zn levels. The significance of this and samples 114 and 115 will be discussed in Section 5.7.

5.6 Group E - Thermal springs related to quartz monzonite

The physical features associated with group E are given in section 4.2. Six are classified as hot springs (018, 033, 038, 052, 053 and 060) with temperatures ranging from 42 to 65°C and all have been previously reported (Crandall and Sadlier-Brown, 1978; Hall *et al.*, 1988). One new spring (011) is thermal, but has a lower temperature (15°C). Spring 034, which was sampled very near 033 has a low temperature (5°C) but shows some geochemical evidence of mixing with nearby thermal waters. The last two in this group (019, 020) are Cantung mine waters and are also thermal. The flow rates of these springs vary considerably. Total flow from "Cantung West" (018) is estimated to exceed 25 l/s while the flow from "Cantung East" (060) is presently only 2 l/s, but may have been much higher in the past judging from the large size of the vent area.

The hot springs and Cantung mine waters in Group E have distinctive chemistries with low TDS contents and high pH. Figure 5.17 and Table 5.5 show the major ion chemistry for the group. The waters are Na-HCO_3 dominated, with the exception of 019 which has a higher proportion of Ca^{2+} than Na^+ and high SO_4^{2-} .

Figure 5.17
Piper plot showing major ion chemistry for springs in group E. Concentrations are relatively low.

Element DL(ppm) units method	temp. n/a (°C) n/a	pH n/a n/a (field)	Ca ²⁺ ppm ICP	Mg ²⁺ ppm ICP	Na ⁺ ppm ICP	K ⁺ ppm ICP	HCO ₃ ⁻ ppm T(c)	SO ₄ ²⁻ ppm D	Cl ⁻ ppm D	SiO ₂ ppm ICP	Fe ppb AA	Mn ppb AA	Zn ppb AA	Ni ppb AA	Mo ppb ICP	W ppb ICP	AU pptr AA	As ppb AA	F ppm S
86-011	14.7	7.67	49	4	13	1.2	84.6	67.7	0.68	31	<20	<10	10	<2	3.8	2.0		0.5	1.33
86-018	41	8.17	8	<1	60	1.0	105.3	26.0	6.48	47	<20	<10	<5	<2	8.0	59.6		1.8	4.09
87-018	41	8.60	6	<1	50	(1)	100.8	25.0	6.59	39	<5	3	<2	<2	9.1	75.1		1.9	4.27
87-0188	43.7	8.60	7	<1	55	(1)	109.4	28.3	7.48	43					9.9	83.0	7.8	1.8	4.71
86-019	16	8.38	36	4	22	0.3	28.2	92.0	2.09	26	199	37	<5	<2	8.1	21.0		5.2	1.10
86-020	16	8.48	4	3	115	0.9	144.1	60.2	25.17	38	65	<10	<5	<2	1.1	169.0		<.2	9.31
86-033	58	9.05	2	<1	80	1.0	103.9	69.3	1.44	63	36	<10	<5	11	19.0	20.8		0.2	2.95
87-033	55	9.24	2	<1	69	(1)	100.5	60.7	1.48	53	<5	<2	<2	<2	18.8	18.0	5.0	0.3	2.94
87-034	5	8.20	39	2	7	(1)	118.4	20.5	0.23	11	<5	<2	<2	<2	9.5	1.8		2.1	0.31
86-038	63.5	7.91	3	<1	68	1.5	79.5	37.9	10.95	83	26	<10	8	<2	30.0	224.0		163.5	7.79
86-052	42	8.51	1	<1	30	0.6	61.4	7.9	2.03	68	57	<10	<5	<2	10.0	14.9		23.7	2.62
86-053	47.5	7.86	1	<1	31	0.5	63.0	8.7	2.18	70	72	<10	8	4	21.0	17.6		25.5	2.77
87-053	46	9.13	1	<1	28	(1)	50.7	6.6	1.90	57	5	<2	<2	<2	20.3	17.1	<1.0	20.9	2.77
86-060	46	9.08	2	<1	75	1.3	111.7	30.2	10.49	82	120	<10	<5	8	19.0	121.0		0.5	6.53
87-060	46	9.30	2	<1	67	(2)	07.0	28.8	10.27	69	<5	<2	<2	<2	17.8	118.4		9.6	6.77
87-116	11	8.54	37	27	247	(3)	429.4	313.3	3.80	<2	105	<2	5	<2	0.4	<.1		0.4	0.91

Table 5.5 Major ion and selected trace element concentrations for group E springs. See caption to Table 5.1 for details.

Sample 019 comes from a drill hole in the mine which intersects a large fault zone. The concentrations of the major ions in group E are low relative to those of most of the other groups. The trace element chemistry of this group is also distinct, with increased concentrations of Si, F, As, Mo and W. The latter element exhibits very high concentrations for natural waters.

The distinct chemistry of Group E is a result of dissolution of minerals within the intrusions, enhanced by the elevated temperatures. The sodium in the water results from sub-surface "weathering" of sodic feldspars according to the reaction:

This reaction also accounts for the high pH and high silica in the waters. The increased concentrations of W, Mo, As and F are due to dissolution of minor associated minerals which are disseminated within the quartz monzonite, such as wolframite and fluorite.

Like most of the other spring groups, ^{18}O and ^2H data (Figure 5.4) in group E indicate that groundwaters are meteoric, and that there is no evidence of water-rock isotope fractionation. Tritium was analyzed for samples 018, 033, 053 and 060. It was undetected in 033 and 060 (<6 T.U.), 018 had 7 ± 8 T.U. and sample 053 had significant tritium (15 ± 8). This may indicate that the water discharging out of 053 is less than 35 years old, but more likely indicates mixing with shallow meteoric water.

The mechanism for heating the water is quite simple, provided a high heat

flow can be assumed within the intrusions as mentioned previously. Precipitation or glacial meltwater infiltrates the plutons in the high upland areas. Only a sparse network of interconnected fractures is necessary to produce very high hydraulic heads, considering the hydraulic gradients in the mountains. Water travels down through the pluton to depth and is eventually discharged in an adjacent valley. Using the same assumption for heat flow as used for group C, the group E waters would not have to travel to more than 1 km depth, and possibly less, in order to reach their discharge temperatures (no heat loss during upward flow is again assumed). This model is compatible with the yearly mean ambient temperature of less than 0°C, the estimated average groundwater temperature of less than 7°C and mine water temperatures in the Cantung mine of 16°C. The mine adit is only a few hundred meters below the surface of the mountain.

The presence of elements such as Mo and W in the thermal spring waters indicates that the host plutons may have associated skarns containing scheelite and molybdenum and would be a favourable site for exploration. It is, of course, already known that the plutons in this area are favourable for tungsten and base-metal skarn mineralization. However, thermal spring waters with this assemblage of elements, and away from any known pluton provide very strong evidence for the presence of a shallowly buried intrusion. One such spring was discovered during the 1986 field season. 011 is a small, thermal spring (14.7°C) located within the Ragged Ranges study area. Its chemistry is similar to that of the hot springs but the water has apparently been diluted with shallow groundwater from the Road River shale from which it discharges. Mo, W, F, and Si levels are all elevated and As is above

detection, despite the low TDS content of the sample. The waters have elevated Na^+ , although Ca^{2+} dominates. These characteristics strongly indicate that the waters from 011 have passed through a quartz monzonite body, although the nearest exposed pluton is 2 km to the south-southeast.

Aronoff *et al.* (1986) discussed the possibility of buried plutons west and northwest of the present Ragged Ranges study area. To infer the plutons they spatially superimposed data sets: 1) they analyzed Landsat images for associated faults and fractures, 2) stream sediment data indicated increased concentrations of associated elements (similar to the element assemblage in the hot springs), and 3) stream water geochemistry provided evidence of hornfelsed slates (increased metals and decreased pH). The added presence of thermal groundwaters with this type of elemental assemblage would also be an extremely good indicator of a buried intrusion. Spring sampling could also be used in other areas where pluton-related hot springs are known, such as western Alaska, to determine if they would be favourable for exploration for W or other metals.

A more direct spin-off of these hot springs is their potential use as a geothermal resource. Some of the springs produce large quantities of water and greater quantities may discharge through overburden in the shallow subsurface. Any new communities, perhaps related to the mining industry, could tap these resources. Using modern heat-pump technology, any one of the larger springs could help to heat entire communities and greatly reduce their necessary use of fossil fuel with its concomitant pollution. Significant savings could also be realized in the mining plant operations.

5.7 Group F - Low TDS spring waters and surface waters

The waters in this group all have very low TDS contents and were clustered together for this reason. Most are Ca-HCO₃ dominated (Figure 5.18, Table 5.6) and are situated in carbonate terrane. Eleven of the 25 samples are known or suspected to be surface water (009, 050, 068, 077, 101, 104, 117, 118, 120, 124, 128). Two thermal springs are associated with this group: 044 and 106. Spring 106 is located near "Honeymoon Hot Spring" (032) and is probably related to the same system. It has a relatively low temperature of 19°C (spring 032 was 54°) while spring 044 has a higher temperature of 32°C. Spring 044 is somewhat mysterious in that it does not appear to be related to a pluton, either geochemically or areally and does not have the geochemical character of typical fault-controlled hot springs.

As has been mentioned, low TDS waters have to be examined in their own context with respect to transported metals. In general, oxygenated, high pH, HCO₃⁻ dominated waters are very poor media for the transport of metals. This is demonstrated by the fact that most of the metal concentrations in these waters are below the detection limit. Some noteworthy exceptions to this are located in the Nahanni Karst study area.

Springs in the Nahanni Karst area which belong to this group are of special interest because they form the largest group of springs found in the Nahanni Karst. The area is underlain by carbonates of the Nahanni Formation and the Arnica Formation and these are overlain in places by shales of the Fort Simpson and Horn River Formations. The Manitou Facies of the Nahanni Formation is known to

Figure 5.18 Piper plot of the very low TDS waters of group F.

Element	temp.	pH	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	HCO ₃ ⁻	SO ₄ ²⁻	Cl ⁻	SiO ₂	Fe	Mn	Zn	Ni	Mo	W	Au	As	F
DL(ppm)	n/a	n/a	1	1	1	.2	.2	.2	.05	ppm	20/5	ppb	ppb	ppb	ppb	ppb	pptr	ppb	ppm
units	(°C)	n/a	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
method	n/a	(field)	ICP	ICP	ICP	ICP	T(c)	D	D	ICP	AA	AA	AA	AA	ICP	ICP	AA	AA	S
86-004	5.2	8.30	21	3	<1	0.3	58.3	6.3	0.15	4	361	12	<5	<2	0.2	<1		1.4	0.07
86-009	5	7.60	29	13	<1	0.2	97.8	24.4	0.29	3	33	<10	<5	<2	1.2	0.1		<2	0.15
86-013	2.1	8.1	56	7	<1	4.3	135.9	30.0	0.64	4	<20	<10	<5	<2	1.0	0.2		32.9	0.14
86-028	10	7.60	63	13	<1	0.7	206.0	12.9	0.34	6	<20	<10	<5	<2	2.0	0.2		0.2	0.12
86-044	32	7.75	35	19	<1	0.8	132.0	18.5	0.38	22	91	<10	<5	<2	0.5	0.1		0.6	0.15
86-045	4	8.1*	33	4	<1	0.6	86.7	6.1	0.29	3	57	<10	6	<2	<1	0.2		0.3	0.11
86-048	1.5	7.4*	7	<1	1	1.2	20.8	0.8	0.13	4	451	11	<5	<2	1.4	0.2		<2	0.04
86-050	3	8.2*	57	2	<1	0.8	83.4	58.1	0.12	7	91	16	92	23	2.4	0.2		1.0	0.09
86-051	6.5	8.3*	73	1	<1	0.7	179.8	2.8	0.29	7	79	<10	8	<2	0.6	0.2		0.6	0.08
86-065	4.3	7.81	46	10	<1	<0.2	147.4	9.0	1.05	3	136	<10	10	6	0.6	0.2		0.3	0.12
86-066	8.2	8.23	38	17	<1	<0.2	160.6	3.9	0.35	3	67	<10	40	3	1.7	0.3		0.6	0.10
86-068	3.3	8.03	33	18	<1	<0.2	132.0	20.4	0.31	<2	81	<10	14	<2	<1	<1		0.2	0.11
86-075	5	7.95	32	14	<1	<0.2	130.8	9.8	1.60	<2	337	<10	36	<2	0.3	0.1		0.3	0.10
86-076	4	7.57	63	13	<1	0.4	196.7	24.3	2.19	5	158	10	<5	8	2.5	0.2		0.4	0.26
86-077	8	7.51	61	22	<1	0.3	220.1	33.3	0.24	4	96	11	23	<2	2.7	<1		3.4	0.24
87-101	2	7.05	61	6	<1	(0)	63.3	114.8	0.15	8	<5	<2	38	<2	5.5	<1		0.9	0.11
87-104	8	7.72	6	<1	<1	(0)	7.3	11.3	0.09	<2	<5	<2	<2	<2	0.5	<1		14.9	0.04
87-106	19	7.50	30	14	1	(1)	130.3	23.2	0.28	8	<5	<2	<2	<2	0.3	<1	1.0	0.3	0.12
87-107	4	7.50	66	20	5	(1)	195.1	87.9	0.84	3	<5	<2	565	<2	1.8	<1		0.7	0.18
87-117		7.95	45	18	<1	(0)	188.5	26.2	0.23	3	<5	<2	<2	<2	1.1	<1		<3	0.10
87-118	3.5	8.20	31	14	<1	(0)	138.4	19.1	0.27	<2	<5	<2	10	<2	1.0	<1		<3	0.09
87-119	3.5	8.31	31	16	<1	(0)	149.6	13.8	0.36	<2	<5	<2	10	<2	1.1	<1	1.0	0.4	0.10
87-120	2	7.79	49	21	1	(1)	215.1	31.8	0.30	3	<5	<2	5	<2	1.4	<1	1.0	<3	0.12
87-124	18	8.20	27	4	<1	(0)	91.6	10.8	0.85	<2	50	<2	<2	<2	4.6	<1	<1.0	0.5	0.12
87-128	12	7.96	39	9	2	(0)	119.8	30.3	2.61	4	115	<2	5	<2	2.3	0.3	<1.0	0.8	0.11

Table 5.6 Major ion and selected trace element concentrations for group F springs. See caption to Table 5.1 for details.

contain Mississippi Valley type Pb-Zn deposits. Extensive karst topography has developed in the carbonates and is described by Brook (1976). Several of the springs sampled have very high flow rates. Springs 065 and 076 have nothing short of rivers discharging from them. White Spray cold spring (065) has an estimated discharge rate of 5000 l/s and Bubbling Spring (076) is at least twice as large. Dead drainage in the karst area results in most of the flow being subterranean. White Spray appears to drain the southern portion of the area (Brook, 1976), while Bubbling Spring drains the northern portion of the region. Additional dead drainage areas are widespread on the Ram Plateau further to the north. Surface and subsurface karst is still developing. A conservative estimate of carbonate removed from the area yearly by these two springs alone is 53,000 tonnes.

Five springs (065, 066, 075, 076 and 119) and a number of surface waters were sampled in the Nahanni Karst area. Four of these (excepting 119) are thought to be related to karstic flow systems. The waters in this area are Ca-HCO₃ dominated, however, detectable Zn, Cu, Co or Ni are found in all five of these springs. The values are not high in comparison with other groups but considering the pH (>7) and Eh (highly oxidizing) conditions of these waters they are significant. In comparison with other waters in this group, from the other study areas, the values are elevated.

Spring 107 is also located in the Nahanni Formation carbonates. It emerges a few hundred meters south and topographically below a Cu-Zn occurrence on Nahanni Butte. Spring 107 contains detectable Cu and a highly elevated Zn concentration (565 ppb) for waters in this group. On the surface of the rocks above

the spring, Zn is contained in hydrozincite and may be related to a Mississippi Valley type sphalerite deposit. The Cu is in small veins as malachite and azurite. Both occur within Manitou Facies dolomites.

It should be mentioned here that three springs from group D2 (114, 115, 125) also discharge in the Nahanni Karst area. Sample 125 discharges near "first polje" and was mentioned by Brook (1976). It has slightly elevated Zn for waters of group D which is consistent with the springs in this area. The other two were collected along "Wretched Creek", a small creek in the centre of the Nahanni Karst study area which appears to flow parallel to a series of normal faults. The chemistry of these springs is somewhat unusual for waters in the Nahanni Karst area. Both have high Ca^{2+} , Mg^{2+} and HCO_3^- concentrations. Spring 115 also has high SO_4^{2-} and detectable Na^+ and Cl^- concentrations. Isotope data are unfortunately unavailable.

Springs 114 and 115 are of particular interest because they occur very near large gold anomalies in the stream sediments. W.A. Spirito and C.W. Jefferson, who are studying these gold anomalies, have suggested nearby fault or fracture associated lode gold as a possible source (pers. comm.). The chemistry of the waters suggest probable fault-control which is unusual in this area of mostly karstic flow systems. Elevated gold was found in a water sample from 114 (3.7 pptr). The five other springs and surface waters (115, 119, 120, 125, 128) in the karst area which were analyzed for gold had concentrations at, or below detection (1.0 pptr). However, the significance of these results is unclear due to the small quantity of Au data.

CHAPTER 6 - CONCLUSIONS

6.1 Classification of springs

The three study areas under consideration in this thesis encompass a large variety of geologic terranes. Grouping water types was an essential component of this study, in order to detect and understand subsurface processes such as dissolution of sulphides and in order to be able to compare trace metal anomalies between samples in homogenous groups. Several methods of classifying the geochemical data were tried and cluster analysis was found to be the most rigorous. Cluster analysis produced groups based on similar characteristics to those produced by the other two methods, but some springs were assigned differently. One of the more important merits of cluster analysis is that it gives non-subjective justification for assigning springs to certain groups. This is very important when their membership in a particular group is used as justification for some further assumption or model, particularly inferring metallic resource potential.

The classification system has outlined six major groundwater types in the region. Each one represents waters with different flow histories or different hydrogeochemical processes occurring in the subsurface.

Group A contains brackish, high sulphate waters of the Clausen Creek area. Group B is composed of waters which have encountered sulphides and aided in their oxidation to produce low pH, high iron and high sulphate waters. The three subgroups in B were: those associated with hornfelsed rocks of the Ragged Ranges, springs associated with pyrite-rich sandstones of the Mattson Formation, and

metalliferous springs of the Meilleur River area. Waters of group C are a very distinct group of high $p\text{CO}_2$, high alkalinity springs in the Flat River Valley, which are influenced by an external input of metamorphic CO_2 in the subsurface. Waters such as these are known to aid in the formation of mineral (Hg) deposits where the country rocks are favourable, but this is not indicated in the region. Group D waters include fault-localized hot springs and other tufa precipitating springs which have characteristically high TDS contents but low trace metal concentrations. Group E waters are thermal springs which are spatially and geochemically associated with Cretaceous quartz monzonite intrusions in the Ragged Ranges study area. Group F are springs with low TDS waters which are generally Ca^{2+} and HCO_3^- dominated. They include most of the surface waters sampled and springs with probable karstic flow systems among others.

6.2 Anomalies

In the Ragged Ranges study area, four type B2 springs are high in trace metals such as Zn and Ni; springs 012, 025 and 100 have Zn-dominated trace metal anomalies and 049 is Fe dominated. Spring 100 is associated with the "MB" stratiform Pb-Zn occurrence and the first two suggest buried deposits, possibly stratiform or skarn associated base-metal occurrences. Spring 049 has an Fe-dominated trace metal anomaly with very large concentrations of Fe and SO_4^{2-} and elevated concentrations of Zn and Ni. A significant volume of sulphide bearing-rock is being oxidized nearby, although it is probably pyrite dominated.

Group E hot springs all occur in the Ragged Ranges study area and are

related to the quartz monzonite intrusions. The chemistry of this group is highly distinctive of flow through quartz monzonite intrusions. One small thermal spring, 011, has a similar chemistry to the hot springs, although greatly diluted. Its location, more than 2 km on surface from the nearest exposed intrusion, may indicate the presence of a buried pluton or stock. This has implications for the exploration of skarn mineralization, which is more liable to be found on a roofed intrusion than an unroofed one.

The Tlogotsho Plateau study area has one highly anomalous region. This is the Meilleur River area, west of the Headless Range, where two very different spring types give similar anomalies. The two group B1 springs occur in this area. Spring 072 has waters with anomalous concentrations of trace metals, such as Zn, Ni, Cd, Co, Cu, Mn, Al and U, but not Fe. Geochemical evidence suggests that large quantities of sulphides (with relatively low pyrite) are being dissolved in the subsurface. The source of the metals in solution is unknown but may be from Mississippi Valley type Pb-Zn mineralization within the Arnica Formation or stratiform base-metal mineralization within the Besa River shales. The first possibility is favoured in this thesis.

Spring 112 is the other B1 spring. It has lower, but still elevated, concentrations of the same trace metals as 072. However, the waters are dominated by very large quantities of Fe. It appears likely that a large and probably shallow pyrite-dominated sulphide-rich rock body occurs in the shallow subsurface of spring 112. The spring discharges from Besa River Formation shales, underlain by Funeral Formation shales. The chemistry indicates extensive contact with shales and also

contact with a carbonate, probably dolomite. Although the mineralization is probably predominantly pyrite, it does indicate the presence of significant stratiform(?) sulphides within the shales in the Meilleur River area.

A large hot spring (082), with D1 type waters, was discovered in the Meilleur River area. This spring, tentatively named "White Aster Hot Spring" by park personnel, will be considered by some to be a resource in itself because of its beauty and unspoiled nature, but it also has bearing on the mineral potential of the area. The waters are relatively low in trace metals, such as Zn and Ni, but their concentrations could be considered high when compared with D1 type waters elsewhere in the study areas. Two types of precipitate are being deposited: (1) a proximal alumino-silicate, probably a clay mineral, which forms a dark grey mud filling the three main vents, and (2) a distal tufa composed of CaCO_3 which is being precipitated starting 50-100 m from the main vents and continuing down to the river, 700 m away. The distal precipitate contains almost no metals but the proximal precipitate has the highest metal values of any of precipitates in the region. It is high in a number of metals, especially Zn, which makes up 0.96%. Another D1 spring (111), with very similar major ion chemistry, is located just over the ridge from 082. It is not thermal but precipitates travertine. The waters and tufa also contain elevated concentrations of Zn and other metals.

The waters from both of these springs (082, 111) must have most or all of their flow paths through Arnica Formation dolomite. The waters from spring 072 are also likely to have a flow path through the Arnica Formation. In the Meilleur River area, this unit (which as mapped, may include the Sombre Formation), therefore has

a high potential for base-metal sulphides, possibly of the Mississippi Valley deposit type. The parallel stream silt survey conducted during this project only shows this region, within the eastern study areas, to be anomalous in Zn (Spirito *et al.*, 1988).

The Nahanni Karst study area produced few elevated trace metal concentrations. Zn and Ni concentrations are higher in group F waters in this area than elsewhere in the study areas, which may indicate small occurrences of Mississippi Valley type Pb-Zn mineralization. These are known to occur in the carbonate units underlying the area. The only D2 type waters which occur in the Karst area are samples 114, 115 and 125. 114 and 115 were collected on "Wretched Creek" in an area dominated by normal faulted limestone and shale. The waters are not associated with karstic flow systems typical of the area, and their chemistry suggests fault control. On Wretched Creek, large gold anomalies in heavy mineral concentrates from stream sediments may be derived from unknown fault and fracture related lode gold deposits nearby. Gold, measured in waters of spring 114, is higher than background but the significance of this is unclear because of insufficient data.

Outside the Nahanni Karst study area, at Nahanni Butte to the east, a significant Zn anomaly in group F waters indicates the presence of a known Zn-Cu occurrence.

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Appendix 1. Major ion analyses and SiO₂

Element DL (ppm) method	-----Ca ²⁺ -----			-----Mg ²⁺ -----			-----Na ⁺ -----			-----K ⁺ -----			-----HCO ₃ ⁻ -----			-----SO ₄ ²⁻ -----			-----Cl ⁻ -----			-----SiO ₂ -----		
	.2	1	1	.2	1	1	.2	1	1	.2	1	1	.2	1	1	.2	1	1	.2	1	1	.2	1	1
	A	B	C	A	B	C	A	B	C	A	B	C	T(c)	T	D	B	C	D	D	B	C	D	B	C
86-001	196.4	231	102	39.2	46	40	3.8	4	4	4.9	768.8	289.7	32.6	51	42	1.21	16	14	1.21	16	14	1.21	16	14
86-004	17.4	21	18	2.4	3	2	0.4	<1	<1	0.3	58.3	43.5	6.3	9	9	0.15	4	<2	0.15	4	<2	0.15	4	<2
86-006	65.5	79	58	22.5	28	23	1.9	2	2	2.3	270.0	230.9	38.3	54	45	1.28	8	6	1.28	8	6	1.28	8	6
86-007	19.9	25	21	7.7	10	8	<0.2	<1	<1	0.2	83.2	83.2	13.9	18	15	0.18	<2	<2	0.18	<2	<2	0.18	<2	<2
86-009	24.2	29	24	11.0	13	11	0.2	<1	<1	0.2	97.8	97.8	24.4	30	27	0.29	3	<2	0.29	3	<2	0.29	3	<2
86-010	114.2			19.3			1.4			0.2	227.0	227.0	189.3			0.33			0.33			0.33		
86-011	39.1	49	40	2.7	4	3	11.7	13	12	1.2	84.6	84.6	67.7	84	66	0.68	31	25	0.68	31	25	0.68	31	25
86-012	18.9	25	20	4.1	5	4	1.0	1	1	0.5	<0.2	<0.2	67.7	111	93	0.16	20	17	0.16	20	17	0.16	20	17
87-012		19	19		4	4		<1	<1	(1)	<0.2	<0.2	81.1	90	90	1.27	17	16	1.27	17	16	1.27	17	16
87-012B		26	26		3	3		<1	<1	(1)	12.6	12.6	62.9	69	69	0.10	11	11	0.10	11	11	0.10	11	11
87-012C		22	22		4	4		<1	<1	(1)	<0.2	<0.2	75.4	81	81	0.12	16	16	0.12	16	16	0.12	16	16
86-013	44.2	56	44	5.6	7	5	0.5	<1	<1	4.3	135.9	135.9	30.0	39	33	0.64	4	4	0.64	4	4	0.64	4	4
86-015	71.8	92	71	11.6	15	11	1.0	1	1	0.7	64.3	64.3	187.5	231	186	0.35	21	14	0.35	21	14	0.35	21	14
86-017	684.6	791	254	57.0	68	53	45.6	60	49	8.1	2428.0	717.6	55.3	93	69	3.05	94	73	3.05	94	73	3.05	94	73
87-017		635	42		55	52		46	40	(13)	2272.7	925.1	49.5	99	57	2.74	73	72	2.74	73	72	2.74	73	72
86-018	<0.2	8	6	0.8	<1	1	48.0	60	52	1.0	105.3	105.3	26.0	33	27	6.48	47	39	6.48	47	39	6.48	47	39
87-018		6	6		<1	<1		50	45	(1)	100.8	100.8	25.0	27	27	6.59	39	39	6.59	39	39	6.59	39	39
87-018B		7	6		<1	<1		55	51	(1)	109.4	109.4	28.3	33	33	7.48	43	43	7.48	43	43	7.48	43	43
86-019	30.6	36	28	2.9	4	2	18.6	22	19	0.3	28.2	28.2	92.0	117	96	2.09	26	19	2.09	26	19	2.09	26	19
86-020	3.8	4	4	2.1	3	2	84.5	115	106	0.9	144.1	144.1	60.2	615	60	25.17	38	34	25.17	38	34	25.17	38	34
86-021	251.3	333	266	65.2	82	64	19.2	25	21	15.3	476.8	326.6	539.6	663	582	2.58	50	41	2.58	50	41	2.58	50	41
86-022	72.8	94	72	17.0	23	18	1.9	2	2	0.5	293.4	239.9	14.8	24	18	0.32	7	6	0.32	7	6	0.32	7	6
86-023	72.4	98	64	31.6	42	32	0.6	<1	<1	0.7	292.8	246.5	69.2	99	72	0.55	7	6	0.55	7	6	0.55	7	6
86-024	76.6	97	57	31.9	42	31	0.6	<1	<1	0.7	306.7	228.1	69.5	96	69	0.51	8	6	0.51	8	6	0.51	8	6
86-025	26.3	35	30	1.9	3	2	0.3	<1	<1	0.6	<0.2	<0.2	122.9	153	129	0.08	13	11	0.08	13	11	0.08	13	11
86-026	46.0	58	48	23.1	30	24	1.9	2	2	1.5	212.5	212.5	45.5	57	48	3.48	15	13	3.48	15	13	3.48	15	13
86-027	129.4	155	80	26.6	34	27	1.3	1	1	2.7	496.9	272.0	29.5	45	39	0.40	20	17	0.40	20	17	0.40	20	17
87-027		128	55		27	26		1	<1	(3)	482.9	331.0	27.7	45	36	0.48	16	16	0.48	16	16	0.48	16	16
86-028	55.3	63	57	10.3	13	11	0.7	<1	<1	0.7	206.0	194.2	12.9	18	15	0.34	6	5	0.34	6	5	0.34	6	5
86-029	139.7	151	76	26.3	32	28	1.5	1	2	3.3	545.9	294.2	15.1	27	21	0.71	21	20	0.71	21	20	0.71	21	20
86-030	128.1	148	110	31.2	39	32	6.0	6	6	2.8	445.2	289.7	93.0	117	102	1.98	11	10	1.98	11	10	1.98	11	10
86-031	113.6	127	74	24.4	30	25	1.8	<1	1	3.1	444.9	274.4	24.9	36	30	0.78	18	16	0.78	18	16	0.78	18	16
86-032	77.6	93	78	22.1	29	23	2.4	2	2	3.8	254.0	208.4	81.7	105	90	0.91	51	43	0.91	51	43	0.91	51	43
86-033	20.7	2	2	<0.2	<1	<1	64.3	80	73	1.0	103.9	103.9	69.3	147	66	1.44	63	55	1.44	63	55	1.44	63	55
87-033		2	2		<1	<1		69	62	(1)	100.5	100.5	60.7	60	66	1.48	53	53	1.48	53	53	1.48	53	53
87-034		39	38		2	2		7	7	(1)	118.4	118.4	20.5	27	24	0.23	11	12	0.23	11	12	0.23	11	12
86-035	23.9	28	25	9.6	13	10	0.7	<1	<1	0.4	84.4	84.4	26.8	36	30	0.09	8	7	0.09	8	7	0.09	8	7
86-036	18.1		19	17.1		18	0.4		<1	0.2	<0.2	<0.2	181.0		183	0.10			0.10			0.10		

Appendix I (contd.)

Element DL (ppm) method	Ca ²⁺			Mg ²⁺			Na ⁺			K ⁺			HCO3 ⁻			SO4 ²⁻			Cl ⁻			SiO2 ⁻		
	.2	1	1	.2	1	1	.2	1	1	.2	1	1	.2	1	1	.2	1	1	.2	1	1	.05	2	2
	A	B	C	A	B	C	A	B	C	A	B	C	T(c)	T	T	D	B	C	D	D	D	B	B	C
86-037	135.1	171	138	7.1	10	8	1.1	1	<1	0.9	112.5	112.5	290.4	342	273	0.22	20	14	0.22	20	14	20	14	
86-038	30.0	3	3	<0.2	<1	<1	53.4	68	62	1.5	79.5	79.5	37.9	60	39	10.95	83	72	10.95	83	72	83	72	
86-040	168.2	216	148	51.8	67	52	49.7	66	57	33.3	431.4	337.5	396.1	492	390	23.42	41	33	23.42	41	33	41	33	
86-041	26.1	218	139	6.1	68	52	50.7	68	57	33.7	726.0	281.9	389.2	510	393	23.57	41	33	23.57	41	33	41	33	
86-042	25.9	33	28	6.1	9	7	0.5	<1	<1	0.8	<0.2	<0.2	140.2	183	141	0.19	13	11	0.19	13	11	13	11	
86-043	108.7	139	107	25.4	35	27	21.9	26	22	23.2	201.8	201.8	218.5	276	219	32.15	43	34	32.15	43	34	43	34	
86-044	26.7	35	28	13.2	19	14	1.0	<1	<1	0.8	132.0	132.0	18.5	24	21	0.38	22	17	0.38	22	17	22	17	
86-045	27.1	33	27	2.8	4	3	<0.2	<1	<1	0.6	86.7	86.7	6.1	9	9	0.29	3	3	0.29	3	3	3	3	
86-046	57.4	71	59	24.4	33	26	1.8	2	2	1.4	239.0	239.0	45.9	60	51	3.69	15	13	3.69	15	13	15	13	
86-047	65.9	81	63	26.9	36	28	1.5	2	1	1.4	257.6	257.6	57.0	75	60	2.47	13	12	2.47	13	12	13	12	
86-048	6.2	7	6	0.2	<1	<1	1.0	1	<1	1.2	20.8	20.8	0.8	<3	<3	0.13	4	<2	0.13	4	<2	4	<2	
86-049	96.7	122	96	18.8	26	21	1.9	2	1	1.0	<0.2	<0.2	562.4	630	567	0.16	22	17	0.16	22	17	22	17	
86-050	44.5	57	45	1.7	2	1	0.4	<1	<1	0.8	83.4	83.4	58.1	72	57	0.12	7	5	0.12	7	5	7	5	
86-051	58.5	73	59	1.1	1	<1	0.2	<1	<1	0.7	179.8	179.8	2.8	6	6	0.29	7	6	0.29	7	6	7	6	
86-052	15.1	1	2	<0.2	<1	<1	28.1	30	27	0.6	61.4	61.4	7.9	9	9	2.03	68	58	2.03	68	58	68	58	
86-053	12.2	1	1	<0.2	<1	<1	28.8	31	29	0.5	63.0	63.0	8.7	9	9	2.18	70	59	2.18	70	59	70	59	
87-053	1	1	1	<1	<1	<1	28	25	25	(1)	50.7	50.7	6.6	9	6	1.90	57	58	1.90	57	58	57	58	
86-054	6.0	8	6	3.5	5	4	1.8	2	2	0.6	24.8	24.8	12.8	15	12	0.17	21	17	0.17	21	17	21	17	
86-055	345.0	425	338	42.0	53	44	10.1	10	10	3.4	1099.7	447.3	126.2	171	147	5.25	25	20	5.25	25	20	25	20	
86-056	579.2	782	285	111.3	138	110	84.9	119	107	38.0	2235.9	806.9	282.8	372	306	22.39	12	10	22.39	12	10	12	10	
86-057	456.4	577	250	95.3	119	94	56.2	74	74	31.5	1721.7	633.3	243.2	306	306	20.34	10	13	20.34	10	13	10	13	
86-058	530.0	647	250	54.5	66	52	29.1	32	30	5.6	1918.0	487.7	38.0	66	51	3.76	15	13	3.76	15	13	15	13	
87-058	484	484	53	19.9	26	21	6.9	7	7	(8)	1759.4	685.9	26.9	69	33	3.10	13	11	3.10	13	11	13	11	
86-059	127.9	151	84	<0.2	<1	<1	61.7	75	70	0.9	483.4	285.8	13.2	24	21	0.44	6	5	0.44	6	5	6	5	
86-060	21.7	2	2	<0.2	<1	<1	61.7	75	70	1.3	111.7	111.7	30.2	432	33	10.49	82	71	10.49	82	71	82	71	
87-060	2	2	2	<0.2	<1	<1	61.7	75	70	(2)	07.0	107.0	28.8	24	30	10.27	69	70	10.27	69	70	69	70	
86-061	44.5	56	44	20.0	27	21	2.2	2	1	0.6	207.8	207.8	31.3	51	33	0.50	6	5	0.50	6	5	6	5	
86-062	69.0	7	6	15.2	21	17	0.4	<1	<1	1.2	16.6	16.6	76.4	93	72	1.19	10	8	1.19	10	8	10	8	
86-063	509.6	610	467	93.0	114	89	1168.0	601	1099	88.1	194.6	194.6	853.9	705	819	2347.00	30	23	2347.00	30	23	30	23	
86-064	502.0	617	492	94.1	116	94	1118.5	601	1100	84.4	224.8	224.8	860.4	711	819	2333.00	30	24	2333.00	30	24	30	24	
87-064	502	499	499	92	93	93	1252	1570	1570	(345)	264.8	264.8	829.0	1650	828	2368.00	23	24	2368.00	23	24	23	24	
86-065	39.0	46	38	7.9	10	8	0.3	<1	<1	<0.2	147.4	147.4	9.0	6	12	1.05	3	<2	1.05	3	<2	3	<2	
86-066	32.2	38	32	13.2	17	14	0.2	<1	<1	<0.2	160.6	160.6	3.9	<3	6	0.35	3	3	0.35	3	3	3	3	
86-067	148.4	182	150	54.1	67	55	0.5	<1	<1	0.5	271.8	271.8	393.0	441	390	1.17	6	5	1.17	6	5	6	5	
86-068	27.3	33	28	13.8	18	15	<0.2	<1	<1	<0.2	132.0	132.0	20.4	24	21	0.31	<2	<2	0.31	<2	<2	<2	<2	
86-069	35.9	43	36	30.0	38	31	59.4	71	67	2.3	<0.2	<0.2	722.5	651	597	20.42	27	23	20.42	27	23	27	23	
86-070	86.4	102	85	45.4	58	52	9.4	10	11	2.2	<0.2	<0.2	482.2	507	477	3.25	23	19	3.25	23	19	23	19	
86-071	77.8	92	76	56.5	71	58	9.6	11	10	0.9	<0.2	<0.2	611.3	672	627	0.60	16	14	0.60	16	14	16	14	
86-072A	516.2	613	504	241.2	310	260	14.4	18	17	2.5	115.0	115.0	2403.8	711	939	16.83	12	5	16.83	12	5	12	5	

Appendix 1 (contd.)

Element DL(ppm) method	-----Ca ²⁺ -----			-----Mg ²⁺ -----			-----Na ⁺ -----			-----K ⁺ -----			-----HCO ₃ ⁻ -----			-----SO ₄ ²⁻ -----			-----Cl ⁻ -----			-----SiO ₂ -----		
	.2	1	1	.2	1	1	.2	1	1	.2	1	1	.2	1	1	.2	1	1	.2	1	1	.05	2	2
	A	B	C	A	B	C	A	B	C	A	B	C	T(c)	T	D	D	B	C	D	D	B	D	B	C
86-072B	344.2	413	346	212.4	268	227	14.8	18	17	2.1	17	17	<0.2	<0.2	2284.5	711	939	2.47	19	17		2.47	19	17
87-072B		253	257		151	154		18	18	(3)	18	18	<0.2	<0.2	1450.8	1602	1521	2.02	14	15		2.02	14	15
87-072BH		253			149			18		(3)						1233				13				
87-073A		363	360		212	210		20	18	(3)	20	18	190.9	190.9	1609.7	1737	1653	1.09	7	7		1.09	7	7
87-073B		299	280		175	164		20	19	(3)	20	19	<0.2	<0.2	1489.7	1632	1494	1.00	10	9		1.00	10	9
87-073C		354	336		206	194		18	18	(3)	18	18	275.1	275.1	1507.7	1710	1596	1.00	6	6		1.00	6	6
86-074	157.5	179	141	47.3	57	48	122.7	146	150	8.8	150	150	672.6	256.2	301.1	339	303	0.51	15	13		0.51	15	13
86-075	27.7	32	28	10.5	14	11	<0.2	<1	<1	<0.2	<1	<1	130.8	130.8	9.8	9	9	1.60	<2	<2		1.60	<2	<2
86-076	54.1	63	53	10.1	13	10	0.5	<1	<1	0.4	<1	<1	196.7	196.7	24.3	21	21	2.19	5	4		2.19	5	4
86-077	54.0	61	54	17.5	22	19	1.1	<1	<1	0.3	<1	<1	220.1	220.1	33.3	39	39	0.24	4	4		0.24	4	4
86-078	87.5	96	85	52.6	64	54	0.9	<1	1	2.8	1	1	64.9	64.9	405.0	453	411	0.29	7	5		0.29	7	5
86-079	66.1	73	65	33.4	41	35	0.6	<1	<1	1.4	<1	<1	211.5	211.5	132.3	153	141	0.36	7	7		0.36	7	7
86-080	10.6	12	11	4.1	5	5	1.7	1	2	1.3	2	2	0.2	<0.2	91.4	102	90	2.02	32			2.02	32	
86-081	91.6	103	77	21.1	26	22	3.5	3	3	1.6	3	3	342.4	240.2	41.6	51	45	0.69	12	11		0.69	12	11
86-082	151.7	171	153	45.9	54	47	30.2	31	33	13.8	33	33	320.0	289.4	373.3	348	333	31.54	41	38		31.54	41	38
87-082		151	99		46	44		30	30	(17)	30	30	377.6	377.6	297.4	330	303	24.81	36	36		24.81	36	36
87-082 H		147			45			30		(16)						324				34				
87-082B		131	103		45	44		29	29	(16)	29	29	305.7	305.7	291.0	327	306	23.96	35	36		23.96	35	36
86-083	208.0	228	182	38.7	45	39	152.1	184	193	4.6	193	193	254.6	254.6	451.0	483	441	212.65	17	15		212.65	17	15
87-100		8	8		6	5		<1	<1	(0)	<1	<1	<0.2	<0.2	56.1	60	57	0.19	8	8		0.19	8	8
87-101		61	56		6	6		<1	<1	(0)	<1	<1	63.3	63.3	114.8	138	120	0.15	8	8		0.15	8	8
87-102		76	72		9	8		2	2	(1)	2	2	223.1	223.1	44.0	57	51	0.66	4	4		0.66	4	4
87-103		40	37		39	36		38	37	(11)	37	37	365.4	365.4	44.6	54	48	1.07	11	10		1.07	11	10
87-104		6	5		<1	<1		<1	<1	(0)	<1	<1	7.3	7.3	11.3	12	12	0.09	<2	<2		0.09	<2	<2
87-105		8	8		4	4		<1	1	(1)	<1	1	<0.2	<0.2	40.3	45	42	0.63	4	5		0.63	4	5
87-106		30	28		14	13		1	1	(1)	1	1	130.3	130.3	23.2	27	24	0.28	8	9		0.28	8	9
87-107		66	61		20	18		5	4	(1)	4	4	195.1	195.1	87.9	99	90	0.84	3	3		0.84	3	3
87-108		1	1		1	1		<1	<1	(1)	<1	<1	<0.2	<0.2	13.4	15	12	0.19	4	5		0.19	4	5
87-109		25	23		45	43		12	12	(4)	12	12	122.5	122.5	168.4	183	168	1.70	12	11		1.70	12	11
87-110		119	111		49	48		207	198	(3)	198	198	394.9	394.9	552.6	639	618	1.76	5	4		1.76	5	4
87-111		278	175		31	29		<1	<1	(2)	<1	<1	484.5	322.1	373.7	438	408	0.23	7	8		0.23	7	8
87-112		397	392		160	158		254	251	(7)	251	251	31.9	31.9	2122.0	2277	2295	14.90	5	4		14.90	5	4
87-112H		402			161			260		(8)						2301				5				
87-113		79	75		24	23		<1	<1	(0)	<1	<1	304.6	304.6	32.0	48	42	0.49	3	4		0.49	3	4
87-114		95	90		20	19		2	<1	(1)	<1	<1	305.4	305.4	69.2	84	75	1.26	6	6		1.26	6	6
87-115		116	91		43	42		5	4	(2)	4	4	342.7	342.7	171.7	204	189	3.48	9	9		3.48	9	9
87-116		37	28		27	25		247	229	(3)	229	229	429.4	429.4	313.3	351	333	3.80	<2	<2		3.80	<2	<2
87-117		45	43		18	17		<1	<1	(0)	<1	<1	188.5	188.5	26.2	33	30	0.23	3	3		0.23	3	3
87-118		31	30		14	14		<1	<1	(0)	<1	<1	138.4	138.4	19.1	24	21	0.27	<2	<2		0.27	<2	<2

Appendix 1 (contd.)

Element DL(ppm) method	-----Ca ²⁺ -----			-----Mg ²⁺ -----			-----Na ⁺ -----			-----K ⁺ -----			-----HCO3 ⁻ -----			-----SO4 ²⁻ -----			-----Cl ⁻ -----			-----SiO2-----		
	.2	1	1	.2	1	1	.2	1	1	.2	1	1	.2	1	1	.2	1	1	.2	1	1	.05	2	2
	A	B	C	A	B	C	A	B	C	A	B	C	T(c)	T	T	D	B	C	D	B	C	D	B	C
87-119		31	29		16	15		<1	<1	(0)			149.6	149.6		13.8	18	15	0.36		<2	<2		
87-120		49	47		21	21		1	<1	(1)			215.1	215.1		31.8	42	36	0.30		3	3		
87-121		17	17		16	16		<1	<1	(0)			<0.2	<0.2		211.0	231	222	0.24		15	15		
87-122		<u>157</u>	131		42	41		183	180	(22)			300.9	300.9		243.0	252	249	278.00		14	15		
87-123		431	381		93	89		1164	<u>1065</u>	(334)			367.5	367.5		727.0	720	729	2212.00		22	23		
87-124		27	26		4	4		<1	<1	(0)			91.6	91.6		10.8	15	12	0.85		<2	<2		
87-125		127	83		23	21		<1	<1	(0)			383.0	383.0		87.2	105	93	0.32		8	9		
87-126		49	46		15	14		<1	1	(0)			199.5	199.5		15.8	24	18	0.80		5	4		
87-127		135	83		25	24		5	5	(1)			420.9	420.9		91.5	111	99	0.82		6	7		
87-128		39	37		9	9		2	2	(0)			119.8	119.8		30.3	36	33	2.61		4	4		

Abbreviations:

A = A A on acidified samples; B = ICP on acidified samples; C = ICP on non acidified samples; D = Dionex (ion chromatography); T = HCO₃⁻ determined by titration; T(c) = HCO₃⁻ corrected by major ion charge balance; DL = detection limit H = duplicate samples acidified with HCl instead of HNO₃. Underlining refers to data with significant analytical errors. Errors were more common in the 1986 analyses because water standards were not available for the ICP at the Geological Survey of Canada laboratories and therefore rock standards were used instead. (K⁺) data analysed on the ICP (1987 K⁺ results) can be considered only relatively high or low due to serious systematic problems with analysing K⁺ on the ICP.

See Appendix 6 for analytical methods.

Appendix 2 (contd.)

Element	-----Fe-----	-----Mn-----	Zn	Cu	Cd	Co	Ni	Pb	Al	Mo	W	Ag	Au	U	Sb	As	F	Sr	Ba
D.L.	20/5 (.)	10/2 (.)	5	2	2	2	2	5	(.)	0.1	0.1	2	1	0.01/1	0.3	0.3	0.04	(.)	(.)
units	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppm	ppb	ppb	ppb	pptr	ppb	ppb	ppb	ppm	ppm	ppm
method	AA	ICP	AA	AA	AA	AA	AA	AA	ICP	ICP-MS	ICP-MS	AA	AA	FLUOR.	AA-Sil.	AA-Sil.	D	ICP	ICP
86-036	645	534	640	4	<2	46	168			<1	0.2	<2		0.40		0.10			
86-037	19082	425	306	3	<2	<2	8		0.2	0.4	<1	<2		4.00		2.2	0.40	0.5	<1
86-038	26	<1	8	5	<2	<2	<2		<1	30.0	224.0	<2		0.40		163.5	7.79	<1	<1
86-040	65	<10	<5	5	3	<2	8		0.3	<1	<1	<2		3.80		1.5	1.52	4.0	<1
86-041	440	<10	6	6	<2	<2	3		0.5	0.1	0.2	<2		5.20		0.8	1.53	4.0	<1
86-042	5816	225	1488	25	39	29	273		8.0	<1	<1	<2		3.20		0.6	0.08	0.2	0.1
86-043	138	30	5	<2	<2	6	<2		0.2	0.1	<1	<2		5.00		5.2	0.91	1.8	<1
86-044	91	<10	<5	3	<2	<2	<2		0.1	0.5	0.1	<2		2.40		0.6	0.15	0.1	<1
86-045	57	<10	6	4	<2	<2	<2		<1	<1	0.2	<2		0.24		0.3	0.11	<1	<1
86-046	36	<10	10	3	<2	<2	<2		0.1	3.1	<1	<2		3.20		1.2	0.22	0.2	0.2
86-047	72	<10	13	3	<2	<2	<2		0.2	3.0	0.2	<2		3.40		0.6	0.23	0.3	<1
86-048	451	<11	<5	5	3	11	<2		0.5	1.4	0.2	<2		3.60		<2	0.04	<1	<1
86-049	122307	856	331	<2	3	50	233		28.4	<1	<1	<2		4.40		<2	0.98	0.7	<1
86-050	91	16	92	<2	3	<2	23		0.3	2.4	0.2	<2		2.60		1.0	0.09	0.2	<1
86-051	79	<10	8	<2	<2	<2	<2		<1	0.6	0.2	<2		2.80		0.6	0.08	<1	<1
86-052	57	<10	<5	4	<2	<2	<2		0.2	10.0	14.9	<2		7.40		23.7	2.62	<1	<1
86-053	72	<10	8	3	<2	15	4		0.1	21.0	17.6	<2		7.20		25.5	2.77	<1	<1
87-053	5	<2	<2	<2	<2	<2	<2	<5	<1	20.3	17.1	<2	<1.0	6.6	0.4	20.9	2.77	<1	<1
86-054	3194	152	19	4	<2	<2	<2		0.5	0.5	0.3	<2		2.00		4.0	0.19	<1	<1
86-055	15850	587	412	6	<2	18	125		0.3	1.7	<1	<2		6.60		0.9	0.66	0.8	0.1
86-056	33	34	<5	4	<2	8	16		0.3	0.7	<1	<2		4.88		0.5	1.23	3.3	<1
86-057	161	521	<5	4	<2	10	8		0.3	<1	0.2	<2		3.00		0.2	0.96	2.5	<1
86-058	28	158	<5	5	<2	4	<2		0.2	<1	<1	<2		1.44		<2	0.53	2.0	0.2
87-058	<5	275	8	<2	<2	<2	<2	8	<1	0.2	0.3	<2		1.1	<3	<3	0.38	1.6	0.2
86-059	480	157	<5	<2	<2	3	<2		0.1	<1	0.2	<2		0.66		<2	0.15	0.5	0.1
86-060	120	<10	<5	6	<2	3	8		0.1	19.0	121.0	<2		0.27		0.5	6.53	<1	<1
87-060	<5	<2	<2	3	<2	<2	<2	<5	<1	17.8	118.4	<2	9.6	1.2		6.77	<1	<1	<1
86-061	1817	123	<5	6	<2	<2	3		<1	0.6	0.1	<2		0.74		0.5	0.20	0.1	<1
86-062	9721	707	<5	6	<2	13	13		<1	<1	0.1	<2		0.10		<2	0.13	<1	<1
86-063	852	75	30	19	3	6	4		0.6	0.2	0.4	<2		15.60		7.2	0.83	15.0	<1
86-064	129	57	13	16	3	<2	<2		0.5	<1	0.3	<2		5.40		1.4	0.82	15.3	<1
87-064	163	85	13	8	<2	<2	<2	25	0.2	0.7	0.5	<2		15.2	<3	0.3		14.1	<1
86-065	136	<10	10	4	<2	6	6		0.1	0.6	0.2	<2		1.20		0.3	0.12	<1	<1
86-066	67	<10	40	9	<2	<2	3		0.1	1.7	0.3	<2		2.00		0.6	0.10	<1	<1
86-067	337	92	61877	448	135	9	65		0.3	0.6	<1	3		3.80		49.6	0.49	0.2	<1
86-068	81	<10	14	8	3	<2	<2		0.1	<1	<1	<2		2.00		0.2	0.11	<1	0.1
86-069	51793	1180	86	6	<2	58	115		30.3	<1	<1	<2		3.00		<2	0.28	0.4	<1

Appendix 2 (contd.)

Element	-----Fe-----	-----Mn-----	Zn	Cu	Cd	Co	Ni	Pb	Al	Mo	W	Ag	Au	U	Sb	As	F	Sr	Ba
D.L.	20/5	10/2	5	2	2	2	2	5	(.1)	0.1	0.1	2	1	.01/.1	0.3	0.3	0.04	(.1)	(.1)
units	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppm	ppb	ppb	ppb	pptr	ppb	ppb	ppb	ppm	ppm	ppm
method	AA	AA	AA	AA	AA	AA	AA	AA	ICP	ICP-MS	ICP-MS	AA	AA	Fluor.	AA-Sil.	AA-Sil.	D	ICP	ICP
86-070	2870	2.6	1294	1.5	67	11	<2	45	6.9	<1	<1	<2		3.12		0.2	0.15	0.5	<1
86-071	21517	21.0	1047	1.2	187	18	<2	46	21.5	<1	<1	<2		2.40		1.3	0.34	1.0	<1
86-072A	136	0.4	2824	3.2	4977	14	34	170	43.0	<1	0.2	4		5.40		0.4	0.49	5.3	<1
86-072B	1402	1.7	5396	5.8	5351	49	30	405	57.2	0.8	0.1	<2		26.00		1.9	0.48	4.5	<1
87-072B	470	0.8	3568	3.9	2350	15	13	268	29.2	0.3	0.5		3.6	13.2			1.30	3.2	<1
87-072BH		0.9	3.8						28.8									3.1	<1
87-073A	10	0.2	15	<1	1613	<2	3	<2	0.1	0.4	0.2			12.4	<3	<3	1.32	3.8	<1
87-073B	13	0.2	3818	4.0	2713	3	15	95	15.0	0.4	0.6			9.8	<3	<3	2.18	3.5	<1
87-073C	<5	0.2	18	<1	155	<2	3	<2	0.2	0.3	0.2			12.7	<3	<3	1.36	3.4	<1
86-074	465	0.6	653	0.7	58	11	4	10	0.5	0.8	<1	<2		4.40		0.8	0.06	3.5	0.1
86-075	337	0.3	<10	<1	36	9	<2	<2	<1	0.3	0.1	<2		2.40		0.3	0.10	<1	<1
86-076	158	0.2	10	<1	<5	6	<2	<2	<1	2.5	0.2	<2		2.40		0.4	0.26	0.1	0.1
86-077	96	<1	11	<1	23	10	<2	<2	<1	2.7	<1	<2		4.60		3.4	0.24	0.2	0.6
86-078	63347	35.2	1180	1.3	15	5	<2	18	0.1	<1	0.2	<2		0.66		0.8	0.46	0.2	<1
86-079	1942	1.8	101	0.1	6	8	<2	4	<1	<1	<1	<2		0.92		1.5	0.27	<1	<1
86-080	9820	9.6	217	0.2	12	9	<2	5	3.5	<1	<1	<2		0.44		0.4	0.09	<1	<1
86-081	705	0.7	222	0.3	9	4	<2	<2	<1	3.9	<1	<2		2.40		4.5	0.37	0.4	<1
86-082	159	0.2	23	<1	44	9	<2	<2	0.2	4.5	1.2	<2		5.00		10.9	0.99	1.4	<1
87-082	<5	0.1	3	<1	18	<2	<2	<2	<1	4.6	1.6		3.8	14.0			0.79	1.6	<1
87-082 H		0.1	<1	<1					<1									1.5	<1
87-082B		0.1	<1	<1					<1	4.5	1.6						0.76	1.5	<1
86-083	5179	5.1	437	0.5	15	11	<2	4	0.3	3.0	0.4	3		5.40		12.7	0.09	1.7	<1
87-100	80	0.1	108	0.2	98	8	<2	3	2.9	<1	<1			3.5	<3	<3	0.04	<1	<1
87-101	<5	<1	<2	<1	38	<2	<2	<5	<1	5.5	<1			6.9	<3	0.9	0.11	<1	<1
87-102	<5	<1	<2	<1	<2	<2	<2	<5	<1	0.6	<1			2.5	<3	<3	0.09	0.2	<1
87-103	6363	9.5	305	0.5	3	<2	<2	<5	0.5	0.1	0.1			0.5	0.3	12.6	1.54	0.7	<1
87-104	<5	<1	<2	<1	<2	<2	<2	<5	<1	0.5	<1			0.3	0.4	14.9	0.04	<1	<1
87-105	35	<1	48	<1	50	3	<2	3	1.1	<1	<1			0.7	<3	<3	0.07	<1	<1
87-106	<5	<1	<2	<1	<2	<2	<2	<5	<1	0.3	<1		1.0	0.7	<3	0.3	0.12	<1	<1
87-107	<5	<1	<2	<1	565	3	<2	<2	<1	1.8	<1			5.8	0.7	0.7	0.18	0.3	0.1
87-108	65	<1	83	<1	10	<2	<2	<5	0.8	<1	<1			<1	<3	<3	0.04	<1	<1
87-109	5373	8.6	250	0.4	3	<2	<2	<5	<1	<1	<1			0.8	<3	0.3	0.36	<1	<1
87-110	2013	2.9	190	0.2	8	3	<2	3	<1	6.0	<1			20.0	<3	1.2	0.82	1.3	<1
87-111	10	0.2	<2	<1	353	<2	<2	<2	<1	11.0	0.1		2.6	27.9	<3	<3	0.40	0.8	<1
87-112	>20000	98.1	3098	2.8	538	5	<2	60	0.2	0.2	0.2		<1.0	7.7			1.13	3.4	<1
87-112H		96.1	2.9						0.2										
87-113	18	<1	<2	<1	28	<2	<2	<2	<1	6.7	<1		5.9	11.2	<3	0.5	0.16	0.2	0.1

Appendix 2 (contd.)

Element	-----Fe-----	-----Mn-----	Zn	Cu	Cd	Co	Ni	Pb	Al	Mo	V	Ag	Au	U	Sb	As	F	Sr	Ba
D.L. units method	20/5 ppb AA	(.1) ppm ICP	10/2 ppb AA	(.1) ppm ICP	2 ppb AA	2 ppb AA	2 ppb AA	5 ppb AA	(.1) ppm ICP	0.1 ppb ICP-MS	0.1 ppb ICP-MS	2 ppb AA	1 pptr AA	1 ppb Fluor.	0.3 ppb AA-Sil.	0.3 ppb AA-Sil.	0.04 ppm ISE	(.1) ppm ICP	(.1) ppm ICP
87-114	<5	<.1	8	<.1	<2	<2	<2	<5	<.1	5.5	<.1	<.1	3.7	7.9	<.3	<.3	0.25	0.2	<.1
87-115	8	<.1	<2	<.1	<2	<2	<2	<5	<.1	10.2	<.1	<.1	<1.0	4.7	0.4	0.3	0.91	0.7	<.1
87-116	105	0.2	5	<.1	<2	<2	<2	<5	0.2	0.4	<.1	<.1	14.4	<.3	0.4	0.91	1.1	<.1	<.1
87-117	<5	<.1	<2	<.1	<2	<2	<2	<5	<.1	1.1	<.1	<.1	1.4	<.3	<.3	<.3	0.10	<.1	<.1
87-118	<5	<.1	10	<.1	<2	<2	<2	<5	<.1	1.0	<.1	<.1	1.4	<.3	<.3	0.09	<.1	<.1	<.1
87-119	<5	<.1	10	<.1	<2	<2	<2	<5	<.1	1.1	<.1	<.1	1.0	3.1	0.4	0.4	0.10	<.1	0.2
87-120	<5	<.1	<2	<.1	<2	<2	<2	<5	<.1	1.4	<.1	<.1	1.0	6.0	<.3	<.3	0.12	0.2	0.1
87-121	3763	6.3	313	0.5	<2	<2	<2	<5	14.7	<.1	<.1	<.1	1.2	2.5	<.3	<.3	0.11	<.1	<.1
87-122	250	0.3	78	<.1	<2	<2	<2	<5	<.1	0.3	0.3	<.1	2.5	16.8	0.4	2.4	0.93	2.9	<.1
87-123	123	0.3	230	0.2	<2	<2	<2	<5	0.1	0.3	0.4	<.1	1.5	6.6	<.3	<.3	12.3	<.1	<.1
87-124	50	0.1	<2	<.1	<2	<2	<2	<5	<.1	4.6	<.1	<.1	<1.0	0.7	0.4	0.5	0.12	<.1	1.0
87-125	<5	<.1	<2	<.1	<2	<2	<2	<5	<.1	15.3	<.1	<.1	<1.0	12.2	0.6	<.3	0.21	0.3	<.1
87-126	523	1.0	10	<.1	<2	<2	<2	<5	0.5	2.8	<.1	<.1	1.7	<.3	0.4	0.3	0.16	0.1	0.2
87-127	33	0.1	10	<.1	<2	<2	<2	<5	<.1	1.2	<.1	<.1	4.2	<.3	<.3	<.3	0.23	0.6	0.3
87-128	115	0.3	<2	<.1	<2	3	<2	<5	0.2	2.3	0.3	<.1	<1.0	7.6	0.4	0.8	0.11	0.2	0.3

See Appendix 1 for list of Abbreviations. Appendix 6 lists analytical methods.

Appendix 3 - Field data

Sample	temp. (°C)	pH (field)	pH (lab)	cond. µS/cm	flow l/s	Easting	Northing	Comments.
86-001	21	6.85	7.80	580	9	595,400	6,868,800	Carbonate
86-004	5.2	8.30	7.76	98	>10000	567,400	6,868,900	Carbonate
86-006	11.1	7.52	7.89	385	1000	572,100	6,920,200	Local spr.
86-007	8.8	8.27	8.02	152	>10000	585,700	6,922,200	Local spr.
86-009	5	7.60	8.10	186	10	583,800	6,923,000	Local spr.
86-010	22	8.15	7.95	600	<1	569,500	6,914,300	
86-011	14.7	7.67	7.81	262	1	562,900	6,895,000	Granite CS
86-012	1.1	4.77	4.37	183	5	560,500	6,889,200	Granite CS
87-012	2	5.12	4.20	180	20	560,500	6,889,200	Granite CS
87-012B	1	6.95	7.10	161	6	560,500	6,889,200	Granite CS
87-012C	1	5.51	4.80	169	2	560,500	6,889,200	Granite CS
86-013	2.1	8.1	8.09	250	5	568,500	6,881,500	Local spr.
86-015	3.5	7.06	8.21	415	20	573,600	6,885,000	Shale
86-017	5.5	6.27	7.87	1000	5	583,100	6,831,000	Carbonate
87-017	5.5	6.11	7.80	2730	15	583,100	6,831,000	Carbonate
86-018	41	8.17	8.22	252	10	540,800	6,868,600	Granite HS
87-018	41	8.60	8.00	242	4	540,800	6,868,600	Granite HS
87-018B	43.7	8.60	8.00	268	10	540,800	6,868,600	Granite HS
86-019	16	8.38	7.73	240	1000	539,200	6,870,000	Granite HS
86-020	16	8.48	8.39	440	<1	539,200	6,870,000	Granite HS
86-021	17	7.03	8.14	1180	1	599,500	6,899,000	Carbonate
86-022	2.5	7.75	8.22	400	3	591,300	6,891,800	Carbonate
86-023	3.8	7.24	8.15	480	5	572,000	6,902,700	Carbonate
86-024	11.1	7.82	8.39	488	0	572,700	6,904,000	
86-025	5	4.02	4.10	246	3	574,000	6,888,900	Granite CS
86-026	18	6.36	8.39	378	10	285,000	6,883,500	Carbonate
86-027	25	7.32	8.12	457	30	629,300	6,812,300	Carbonate
87-027	28	6.94	7.90	586	30	629,300	6,812,300	Carbonate
86-028	10	7.60	8.12	323	1000	633,400	6,824,400	Carbonate
86-029	14	7.19	8.04	475	3	627,000	6,813,200	Carbonate
86-030	17.7	6.75	8.17	575	5	620,900	6,808,600	Carbonate
86-031	12.1	7.74	8.14	440	<1	628,000	6,807,200	Carbonate
86-032	54	7.00	8.16	458	5	543,800	6,911,700	
86-033	58	9.05	9.30	310	15	516,800	6,915,400	Granite HS
87-033	55	9.24	9.10	301	15	516,800	6,915,400	Granite HS
87-034	5	8.20	8.10	216	5	516,800	6,915,400	
86-035	4.4	7.89	7.89	181		510,000	6,951,700	Shale
86-036		4.29	4.29	318		510,000	6,951,700	Shale
86-037	4.2	6.98	8.12	630	5	550,400	6,957,800	Shale
86-038	63.5	7.91	8.96	390	20	508,000	6,964,200	Granite HS
86-040	49	6.48	8.11	1090	15	543,800	6,958,400	Carbonate
86-041	30.5	7.03	8.11	800	10	543,800	6,958,400	Carbonate
86-042	4	4.92	4.12	280		542,600	6,959,200	Shale
86-043	44	6.92	8.11	775	10	556,800	6,949,200	Carbonate
86-044	32	7.75	8.17	230	5	530,500	6,886,600	
86-045	4	8.1	8.10	142	40	546,600	6,881,800	Local spr.
86-046	8	7.80	8.36	397	10	585,000	6,883,500	Carbonate
86-047	13	8.2	8.23	453	<1	586,200	6,882,400	
86-048	1.5	7.4	7.43	40	2	574,600	6,874,500	
86-049	5.5	4.88	3.00	1080	2	574,800	6,879,700	Shale
86-050	3	8.2	8.11	238		574,800	6,879,700	
86-051	6.5	8.3	8.33	263	<1	571,200	6,875,400	Shale
86-052	42	8.51	7.81	121	10	588,700	6,850,200	Granite HS
87-052	40.5	9.18		130	10	588,700	6,850,200	Granite HS
86-053	47.5	7.86	7.86	124	20	588,700	6,850,200	Granite HS
87-053	46	9.13	8.10	130	20	588,700	6,850,200	Granite HS
86-054	10	7.41	7.41	68	<1	593,000	6,851,500	Shale
86-055	1.6	5.88	8.10	961	5	597,200	6,824,700	Carbonate

Appendix 3 (contd.)

Sample	temp. (°C)	pH (field)	pH (lab)	cond. μS/cm	flow l/s	Easting	Northing	Comments.
87-055	6	6.04		1820	5	597,200	6,824,700	Carbonate
86-056	7.7	6.10	8.06	1587	<1	583,600	6,832,700	Carbonate
86-057	14.2	6.81	8.08	1256	0	583,600	6,832,700	Carbonate
86-058	8.9	6.20	8.07	870	<1	573,600	6,839,000	Carbonate
87-058	11	6.23	7.70	2010	<1	573,600	6,839,000	Carbonate
86-059	5.5	7.22	8.16	870	5	570,900	6,841,600	Carbonate
86-060	46	9.08	8.66	295	2	542,400	6,879,400	Granite HS
87-060	46	9.30	8.80	282	2	542,400	6,879,400	Granite HS
86-061	8	7.37	8.29	346	<1	404,700	6,770,300	
86-062	3	6.15	7.41	181	15	405,000	6,761,500	Sandstone
86-063	38.5	6.62	7.89	7780	5	442,700	6,791,500	
86-064	37.5	6.62	7.95	9100	<1	442,700	6,791,500	
87-064	36	6.61	7.80	8030	<1	442,700	6,791,500	
86-065	4.3	7.81	8.27	770	5000	438,700	6,797,000	Carbonate
86-066	8.2	8.23	8.15	239	50	435,700	6,825,800	Carbonate
86-067	3	7.55	8.21	937	<1	404,500	6,825,800	Carbonate
86-068	3.3	8.03	8.23	232	30	408,900	6,822,100	
86-069	11.5	2.91	2.91	1342	<1	465,300	6,783,600	
86-070	6.2	6.77	4.93	800	3	465,000	6,777,300	Sandstone
86-071	7	3.86	3.34	1062		420,900	6,782,600	Sandstone
86-072A	5	6.29	7.72	2970	<1	405,000	6,785,200	Shale
86-072B	5	3.78	3.57	2730	3	405,000	6,785,200	Shale
87-072B	5	3.65	3.50	2040	5	405,000	6,785,200	Shale
87-073A	4	6.93	8.00	2390	2	405,000	6,785,200	Shale
87-073B	11.5	5.24	4.80	2080	1.5	405,000	6,785,200	Shale
87-073C	3	7.23	8.10	2350	8	405,000	6,785,200	Shale
86-074	16	7.40	8.02	1475	10	445,200	6,790,800	Shale
86-075	5	7.95	8.24	218	50	425,800	6,829,100	Carbonate
86-076	4	7.57	8.21	314	>10000	440,000	6,830,200	Carbonate
86-077	8	7.51	8.34	365	0	407,000	6,799,300	
86-078	1.5	7.00	7.99	772	10	425,200	6,751,600	Sandstone
86-079	6.5	8.34	8.34	518	0	434,500	6,762,500	Sandstone
86-080	12	3.64	3.64	285		455,300	6,779,100	Sandstone
86-081	4	8.2	8.16	445	<1	456,000	6,792,900	Local spr.
86-082	38.5	8.2	8.18	1038	0	397,500	6,778,200	Carbonate
87-082	37	6.75	8.10	1032	50	397,500	6,778,200	Carbonate
87-082B	30	7.58	8.10	972	45	397,500	6,778,200	Carbonate
86-083	3.5	8.1	8.15	1632	<1	463,400	6,795,500	Shale
87-100	0	4.74	4.50	129	50	563,300	6,855,000	Local spr.
87-101	2	7.05	7.90	325	2	563,200	6,852,500	
87-102	3.5	6.58	8.00	387	5	576,800	6,836,400	
87-103	4	5.80	7.90	582	5	598,100	6,842,800	Shale
87-104	8	7.72	6.80	38	50	573,600	6,890,700	Local spr.
87-105	4.5	7.75	4.60	97	5000	567,800	6,592,100	Local spr.
87-106	19	7.50	8.10	235	25	546,100	6,912,800	
87-107	4	7.50	8.30	430	3	482,300	6,770,900	Local spr.
87-108	1	5.01	4.50	41	50	418,000	6,781,900	Sandstone
87-109	0	6.63	7.80	482	2	400,600	6,763,100	Shale
87-110	9	7.64	8.20	1517	50	398,400	6,774,000	Shale
87-111	7	7.62	7.80	1204	25	397,600	6,776,200	Carbonate
87-112	3	6.09	7.00	3060	5	400,000	6,776,000	Shale
87-113	8	7.96	8.30	475	5	401,400	6,782,300	Carbonate
87-114	3.5	7.69	8.30	541		450,600	6,811,000	Carbonate
87-115	3	7.63	8.30	751		450,300	6,811,400	Carbonate
87-116	11	8.54	8.40	1178	0	447,000	6,773,600	Shale
87-117		7.95	8.20	316	5	397,000	6,788,000	Local spr.
87-118	3.5	8.20	8.20	238	50	406,800	6,822,400	
87-119	3.5	8.31	8.10	241	5	406,800	6,822,400	Carbonate

Appendix 3 (contd.)

Sample	temp. (°C)	pH (field)	pH (lab)	cond. μS/cm	flow l/s	Easting	Northing	Comments.
87-120	2	7.79	8.30	353	15	407,400	6,829,000	Local spr. Sandstone
87-121	4	3.76	3.30	500	200	427,000	6,779,500	
87-122	22.5	7.02	8.00	1862	10	443,100	6,791,900	
87-123	12	7.09	8.00	7480	1	441,800	6,788,700	Carbonate
87-124	18	8.20	7.90	160	0	443,400	6,827,400	
87-125	1	7.61	8.30	658	3	443,600	6,825,400	
87-126	6	7.40	8.30	319	5	415,500	6,798,600	
87-127	3.5	7.02	8.10	731		480,500	6,768,200	
87-128	12	7.96	8.00	253		480,500	6,768,200	

Appendix 4 - RESULTS OF K-MEANS CLUSTER ANALYSIS

Major ions in the following table are reported in ppm. H⁺ is given in standardized units which are explained in more detail in section 4.4.2.

SUMMARY STATISTICS FOR 10 CLUSTERS

VARIABLE	BETWEEN SS	DF	WITHIN SS	DF	F-RATIO	PROB
CA	6750.851	9	516.874	109	158.182	0.000
MG	1622.048	9	157.441	109	124.776	0.000
NA	10618.326	9	428.641	109	300.017	0.000
HCO3	5932.774	9	559.940	109	128.322	0.000
SO4	10286.479	9	740.614	109	168.213	0.000
CL	16332.056	9	101.320	109	1952.215	0.000
HST	9258.779	9	1725.493	109	64.987	0.000

CLUSTER NUMBER: 1

MEMBERS		STATISTICS				
CASE	DISTANCE	VARIABLE	MINIMUM	MEAN	MAXIMUM	ST.DEV.
004	1.26	CA	0.06	1.83	5.70	1.46
006	1.59	MG	0.00	0.85	2.75	0.78
007	1.08	NA	0.00	0.78	9.99	1.64
009	1.12	HCO3	0.00	2.49	7.29	1.64
010	2.03	SO4	0.02	0.90	6.91	1.09
011	0.96	CL	0.00	0.06	0.71	0.11
013	0.58	HST	29.00	36.40	46.25	4.16
018	1.09					
019	1.47					
020	2.17					
022	1.32					
024	1.49					
028	1.17					
031	2.46					
033	3.26					
035	1.40					
038	1.13					
044	0.71					
045	1.43					

Appendix 4 (contd.)

046	0.95
047	1.64
048	2.89
051	1.44
052	1.82
053	3.05
054	2.86
060	3.32
061	1.73
065	0.58
066	0.87
068	0.46
075	0.45
076	1.21
077	1.40
079	1.24
081	2.06
128	2.97
18A	1.99
188	2.00
33	3.74
34	0.78
53	3.40
60	3.88
101	2.71
104	1.35
105	1.28
106	1.33
107	1.50
113	1.34
114	1.70
116	4.81
119	1.05
120	0.79
124	0.89
126	1.64
128	0.34

CLUSTER NUMBER: 2

MEMBERS		STATISTICS				
CASE	DISTANCE	VARIABLE	MINIMUM	MEAN	MAXIMUM	ST.DEV.
063	0.83	CA	21.50	24.24	25.42	1.59
064	1.14	MG	7.57	7.67	7.74	0.06
64	1.45	NA	50.79	53.32	56.63	2.11
123	2.05	HCO3	3.19	4.31	6.02	1.07
		SO4	15.20	17.03	17.91	1.09
		CL	62.31	65.21	66.70	1.71
		HST	26.50	27.42	30.02	1.50

Appendix 4 (contd.)

 CLUSTER NUMBER: 3

MEMBERS		STATISTICS				
CASE	DISTANCE	VARIABLE	MINIMUM	MEAN	MAXIMUM	ST.DEV.
73A	1.56	CA	14.91	16.90	18.12	1.42
73B	3.75	MG	14.41	16.26	17.43	1.32
73C	2.28	NA	0.80	0.84	0.85	0.02
		HCO3	0.00	2.55	4.51	1.89
		SO4	31.09	32.90	34.40	1.37
		CL	0.03	0.03	0.03	0.00
		HST	16.44	25.45	31.05	6.43

CLUSTER NUMBER: 4

MEMBERS		STATISTICS				
CASE	DISTANCE	VARIABLE	MINIMUM	MEAN	MAXIMUM	ST.DEV.
017	3.34	CA	22.76	28.01	34.14	4.02
056	2.56	MG	4.19	5.82	9.16	1.94
057	3.45	NA	1.23	2.66	5.58	1.46
058	1.43	HCO3	28.22	33.70	39.80	4.42
17	2.12	SO4	0.66	2.53	6.35	2.28
58	2.59	CL	0.08	0.26	0.63	0.24
		HST	22.76	24.13	27.97	1.78

CLUSTER NUMBER: 5

MEMBERS		STATISTICS				
CASE	DISTANCE	VARIABLE	MINIMUM	MEAN	MAXIMUM	ST.DEV.
012	0.83	CA	0.06	1.42	4.82	1.37
025	2.29	MG	0.10	1.07	3.74	1.09
036	1.50	NA	0.02	0.19	1.67	0.43
042	0.41	HCO3	0.00	0.45	5.99	1.54
049	3.43	SO4	0.28	3.32	11.70	3.28
062	3.75	CL	0.00	0.02	0.09	0.03
070	2.99	HST	4.40	13.41	23.12	5.16
080	3.48					
12A	1.05					
12C	2.02					
100	0.97					
103	3.67					
108	1.42					
121	3.01					

Appendix 4 (contd.)-----
CLUSTER NUMBER: 6

MEMBERS		STATISTICS				
CASE	DISTANCE	VARIABLE	MINIMUM	MEAN	MAXIMUM	ST.DEV.
072B	3.27	CA	12.63	14.90	17.17	2.27
72B	3.27	MG	12.46	14.97	17.48	2.51
		NA	0.70	0.73	0.76	0.03
		HCO3	0.00	0.00	0.00	0.00
		SO4	31.65	39.60	47.54	7.94
		CL	0.06	0.06	0.07	0.01
		HST	4.77	5.25	5.73	0.48

CLUSTER NUMBER: 7

MEMBERS		STATISTICS				
CASE	DISTANCE	VARIABLE	MINIMUM	MEAN	MAXIMUM	ST.DEV.
001	3.27	CA	1.23	6.94	13.87	2.80
015	2.52	MG	0.58	2.93	5.37	1.20
021	3.42	NA	0.00	1.62	8.99	2.55
023	2.00	HCO3	1.05	6.06	12.60	2.90
027	1.99	SO4	0.31	4.85	12.86	3.49
029	2.15	CL	0.01	0.65	7.83	1.75
030	1.71	HST	25.55	30.34	36.70	2.69
032	1.98					
037	2.03					
040	2.46					
041	3.53					
043	1.37					
059	1.99					
067	2.02					
074	2.62					
078	2.67					
082	1.30					
083	4.33					
27	1.93					
82A	1.26					
82B	1.46					
102	2.78					
109	3.08					
110	4.39					
111	3.39					
115	1.62					
122	3.80					
125	1.90					
127	1.33					

Appendix 4 (contd.)-----
CLUSTER NUMBER: 8

MEMBERS		STATISTICS				
CASE	DISTANCE	VARIABLE	MINIMUM	MEAN	MAXIMUM	ST.DEV.
055	0.00	CA	17.21	17.21	17.21	0.00
		MG	3.46	3.46	3.46	0.00
		NA	0.53	0.53	0.53	0.00
		HCO3	18.03	18.03	18.03	0.00
		SO4	3.02	3.02	3.02	0.00
		CL	0.15	0.15	0.15	0.00
		HST	21.14	21.14	21.14	0.00

CLUSTER NUMBER: 9

MEMBERS		STATISTICS				
CASE	DISTANCE	VARIABLE	MINIMUM	MEAN	MAXIMUM	ST.DEV.
069	1.40	CA	1.79	2.84	3.88	1.04
071	1.40	MG	2.47	3.56	4.65	1.09
		NA	0.44	1.54	2.64	1.10
		HCO3	0.00	0.00	0.00	0.00
		SO4	11.97	12.34	12.72	0.38
		CL	0.02	0.30	0.58	0.28
		HST	0.00	3.16	6.31	3.16

CLUSTER NUMBER: 10

MEMBERS		STATISTICS				
CASE	DISTANCE	VARIABLE	MINIMUM	MEAN	MAXIMUM	ST.DEV.
072A	2.65	CA	19.80	22.77	25.75	2.98
112	2.65	MG	13.18	16.51	19.85	3.34
		NA	0.69	5.87	11.05	5.18
		HCO3	0.52	1.20	1.88	0.68
		SO4	47.76	48.89	50.03	1.13
		CL	0.42	0.45	0.47	0.03
		HST	22.68	23.42	24.15	0.73

Appendix 4 (contd.)

K-Means

The above tables are printouts of K-means cluster analysis which was "seeded" by arbitrarily instructing the computer to start with 10 clusters. When a larger number was tried, the results were similar except the more significant groups were further subdivided. One of the main problems with K-means is that it bases its calculations and output entirely on distance measurements (the error factor). Groups are made, based on total distance (magnitude) and this results in a classification based more on TDS content than on similar variability of elements. All the samples which have low to moderate TDS content were grouped together because several groups (such as A, C and B1 in the final grouping) had very high TDS concentrations. This also happens with cluster analysis but the lower TDS groups are subdivided hierarchically which displays the further grouping of the samples. There is no way to subdivide groups when using K-means except to instruct it to produce (or "seed") more groups. The result is that it further subdivides all the groups high TDS samples because relatively small differences in the concentration of the elements in these groups will be greater than any differences possible within the low TDS groups.

Appendix 5 - Isotope data - Table A5.1

Sample number	$^{18}\text{O}-\text{H}_2\text{O}$ ‰	$^2\text{H}-\text{H}_2\text{O}$ ‰	^3H (T.U.)	$^{13}\text{C}_{(\text{DIC})}$ ‰	Temp. °C	HCO_3^- mg/l	H_2CO_3 mg/l	PCO_2 bars	$^{13}\text{C}_{(\text{gas})}$ calc.
86-001	-23.0	-181	34	-2.32	21	768.8	262	-0.96	-2.32
86-004	-23.1	-179		-5.43	5.2	58.3	1	-3.61	-5.43
86-006	-23.3	-184		-4.09	11.1	270.0	24	-2.13	-4.09
86-007	-23.5			-4.51	8.8	83.2	1	-3.41	-5.51
86-011	-23.6								
86-012	-23.4	-185							
87-012B	-23.4			-11.34	1	12.6			
86-015	-23.4	-186		-8.36	3.5	64.3			
86-017	-23.4	-184	87	-0.44	5.5	2428.0	4346	0.05	-0.54
86-017	-23.2			-0.54					
86-018	-23.1	-180	7	-9.32	41	105.3	1	-3.46	-9.32
86-019	-22.7			-7.19	16	28.2	0	-3.95	-7.19
86-020	-23.4	-186		-5.42	16	144.1	1	-3.34	-5.42
86-021	-24.8	-191	11	-5.56	17	476.8	115	-1.37	-5.56
86-022	-23.0								
86-023	-23.1	-188		-8.83	3.8	292.8	59	-1.85	-8.83
86-025	-23.5	-184		-19.51	5	0.2			
86-027	-22.6			-2.10	25	496.9	55	-1.21	-2.10
87-027	-22.5	-180	15	-3.20	28	482.9	123	-1.59	-3.20
86-028	-22.6	-180		-7.23	10	206.0	15	-2.34	-7.23
86-029	-22.4			0.60	14	545.9	97	-1.48	0.60
86-030	-22.6	-181	8	-5.15	17.7	445.2	202	-1.11	-5.98
86-031	-23.1			-1.73	12.1	444.9	23	-2.13	-1.73
86-032	-23.3	-183		-5.98	54	254.0	49	-1.36	-5.98
86-033	-23.8	-186	<6	-7.83	58	103.9	0	-4.00	-7.83
86-034	-22.8	-183							
86-036	-22.0	-177							
86-037	-21.8	-170		-5.76	4.2	112.5			
86-038	-22.8	-182		-6.37	63.5	79.5	2	-2.71	-6.37
86-039	-21.8	-171	24						
86-040	-23.0	-186	<6	-3.62	49	431.4	281	-0.65	-3.62
86-041	-23.0			-1.96	30.5	726.0	146	-1.10	-1.96
86-042	-22.6			-23.53	4	0.2			
86-042				-19.76					
86-043	-23.7	-186	<6	-3.59	44	201.8	48	-1.45	-3.59
86-044	-23.1	-182							
86-044		-183							
86-045	-22.5	-179							
86-046	-23.4			-7.81	8	239.0	12	-2.48	
86-049	-23.3	-184		-10.64	5.5	0.2			
86-050	-23.1								
86-052	-22.9	-181	15	-10.74	42	61.4	0	-3.57	-10.74
86-055	-22.9	-183		2.48	1.6	1099.7	5357	0.08	0.93
86-056	-21.6		12						
86-057	-20.8			3.94	14.2	1721.7	728	-0.60	2.48
86-058	-22.5	-179	55	0.37	8.9	1918.0	3686	0.03	3.94
86-059	-22.3								
86-060	-23.9	-187	<6	-6.44	46	111.7	0	-3.86	-6.44
86-060		-186							
86-062	-22.0	-178		-13.69	3	16.6			
86-063	-22.4	-180		-9.34	38.5	194.6	95	-1.21	-9.34
86-064	-22.4		20						
86-065	-21.4	-170							
86-066	-20.5								
86-067	-21.8	-172		-6.95	0	271.8	27	-2.20	-6.95
86-068	-21.5								
86-070	-22.0	-176	43	-11.99	6.2	0.2			
86-072A	-22.4			-17.51	5	115.0			

Appendix 5 (contd.)

Sample number	$^{18}\text{O}-\text{H}_2\text{O}$ ‰	$^2\text{H}-\text{H}_2\text{O}$ ‰	^3H (T.U.)	$^{13}\text{C}_{(\text{DIC})}$ ‰	Temp. °C	HCO_3^- mg/l	H_2CO_3 mg/l	PCO_2 bars	$^{13}\text{C}_{(\text{gas})}$ calc.
86-072B	-22.2	-180	27						
87-073A	-21.9	-175							
86-074	-23.4	-179		-6.55	16	672.6	71	-1.59	-6.55
86-075	-21.6	-170							
86-076	-22.3	-176		-10.41	4	196.7	18	-2.35	-10.41
86-076		-178							
86-077	-21.9			-7.13	8	220.1	21	-2.23	-7.13
86-078	-21.6	-169		-4.02	1.5	64.9			
86-079	-22.0								
86-080	-22.1								
86-081	-21.1								
86-082	-23.0	-181	<6	-5.74	38.5	320.0	21	-1.06	-5.74
87-100	-22.1	-176							
87-106	-22.4	-180							
87-107	-21.6	-169							
87-109	-22.2			-15.29	0	122.5			
87-111	-22.5	-180	59	-12.46	7	484.5	37	-2.00	-12.46
87-112	-21.5	-171	<6						
87-116	-19.6								
87-119	-21.6								
87-122	-22.4	-176							
87-123	-22.4	-180	11(&16)						
87-124	-15.4								
87-125	-22.4	-179		-14.54	1	383.0	35	-2.12	-14.54
87-127	-22.2								

DISCUSSION:

Oxygen-18 and Deuterium

^{18}O and ^2H are expressed in ‰ SMOW (Standard Mean Ocean Water) in the above table. Not all waters in the study area were analyzed for these two isotopes. 79 analyses were obtained for ^{18}O and 51 for ^2H .

When concentrations of both of these isotopes have been determined for a water sample, the results can be plotted on a graph. When worldwide precipitation data are plotted, they define a line known as the global meteoric water line (GMWL). The line results from the proportional distillation process of ^{18}O and ^2H as water vapour moves away from the ocean where it originated. Precipitation falling

Appendix 5 (contd.)

over the ocean and very near coasts tend to have $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of close to that of seawater (0 ‰ SMOW). As a vapour mass moves inland, preferential condensation

of the heavier isotopes results in the a depletion of oxygen-18 and deuterium in precipitation which increases with distance from the coast. The isotopic signature of precipitation is also affected by factors such as temperature and altitude. Cooler climates have precipitation which is more depleted in both these isotopes than warmer climates. Increased altitude has the same effect.

Shallow meteoric waters in a given region, in most cases, plot along a line near the GMWL known as the local meteoric water line (LMWL). This is produced by fitting a line through precipitation data from an area which has been plotted on a graph. Precipitation data are not available for the Nahanni region and therefore an approximation was made by plotting a regression through the spring water data (Figure 5.4). The similarity in the slope of the resulting line and the GMWL (Gat, 1980) is close enough to suggest that this is a good approximation of the LMWL.

Data from the study area all fall close to the "LMWL" in Figure 5.4 and within a fairly small range. This would suggest little or no water-rock exchange reactions have taken place, even in the C, D1 or E group springs (see Chapter 5, text).

Appendix 5 (contd.)

Tritium

^3H is the radioactive isotope of hydrogen and is produced naturally in the upper atmosphere by cosmic ray bombardment of hydrogen in water vapour. Natural levels are in the order of 1-2 T.U. (tritium units). Anthropogenic tritium, however, has been introduced into the atmosphere in much larger quantities (more than 4 orders of magnitude higher than natural levels) since atmospheric testing of thermonuclear weapons began in 1952. The half life of Tritium is approximately 12 years and the levels in the atmosphere have been steadily dropping since atmospheric nuclear testing was ended in 1961. The presence of tritium in groundwater, indicates that a component of the water is less than 35 year old (samples were taken in 1986 and 1987).

If the record of tritium has been kept over a period of time for an area, it is possible, using the decay equation of tritium, to make approximations of the age of groundwaters. This assumes that there has been no subsurface mixing or dilution of the groundwater. This calculation works better on waters from wells than on spring waters because springs are often located at the break in slope or on a fault where many flow systems may merge prior to discharge. In many cases in this study it is likely that waters have been mixed in the subsurface and for this reason age calculations have not been attempted on the water. Knowing the exact age of the groundwaters was not essential to the project but tritium analyses, nonetheless proved very useful in determining whether a spring had relatively old or young groundwater.

Appendix 5 (contd.)

Carbon-13

^{13}C was measured on the dissolved inorganic carbon (DIC) in the water. DIC in groundwater usually comes from both dissolution of carbonate rocks and from CO_2 according to equations 5.6 and 5.7. Calculations can be made to determine the equilibrium concentrations of $^{13}\text{C}_{(\text{gas})}$ based on known enrichment factors between dissolved CO_2 and the various carbonate species in solution (H_2CO_3 , HCO_3^- , CO_3^{2-}). Isotopic exchange reactions between dissolved CO_2 and carbonate species in solution have very fast reaction rates and therefore, the calculations can be a good measure of the ^{13}C composition of the gas phase.

In order to calculate the ^{13}C composition of the gas, the concentrations of the major carbonate species in solution must first be known. These can be calculated based on the following formulae provided their respective equilibrium constants are known.

$$K_1 = [\text{H}_2\text{CO}_3]/\text{PCO}_2$$

$$K_2 = [\text{H}^+] \times [\text{HCO}_3^-]/[\text{H}_2\text{CO}_3]$$

$$K_3 = [\text{H}^+] \times [\text{CO}_3^{2-}]/[\text{HCO}_3^-]$$

Therefore, knowing the pH and HCO_3^- concentration it is possible to calculate PCO_2 and H_2CO_3 and CO_3^{2-} concentrations.

Appendix 5 (contd.)

Equilibrium constants (K) for the above formulae were obtained for the various temperatures from (Hem, 1985) which allowed the molarities of the various carbonate species to be calculated (see above Table).

$$\epsilon(\text{H}_2\text{CO}_3\text{-CO}_2) = -0.373 \times 10^3 \times \text{T}^{-1} + 0.19$$

(Mook et al., 1974)

$$\epsilon(\text{HCO}_3^-\text{-CO}_2) = 9.483 \times 10^3 \times \text{T}^{-1} - 23.89$$

(Mook et al., 1974)

$$\epsilon(\text{CO}_3^{2-}\text{-CO}_2) = 0.87 \times 10^6 \times \text{T}^{-2} - 3.4$$

(Deines et al., 1974)

In waters with pH less than 8, CO_3^{2-} can usually be neglected because it makes up such a small proportion of the DIC. With the molarities of the carbonate species and the enrichment factors of the exchange reactions, $^{13}\text{C}_{(\text{gas})}$ can now be calculated using the below formula:

$$\delta^{13}\text{C}_{(\text{DIC})} \text{M}_{(\text{DIC})} = [\text{M}_{(\text{H}_2\text{CO}_3)} (\delta^{13}\text{C}_{(\text{CO}_2)} + \epsilon_{(\text{H}_2\text{CO}_3\text{-CO}_2)}) + \\ [\text{M}_{(\text{HCO}_3^-)} (\delta^{13}\text{C}_{(\text{CO}_2)} + \epsilon_{(\text{HCO}_3\text{-CO}_2)})]$$

Where M = concentration of the species. Calculated $^{13}\text{C}_{(\text{gas})}$, H_2CO_3 and PCO_2 concentrations are shown in Table A5.1. PCO_2 and $^{13}\text{C}_{(\text{gas})}$ for each of the spring groups are given in Figures 5.12 and 5.13 respectively.

Appendix 5 (contd.)

Laboratories

^{18}O and the 1987 ^{13}C analyses were conducted at the Stable Isotope Laboratory, Ottawa-Carleton Geoscience Centre. A mass spectrometer was used and the detection limit for both isotopes is ± 0.2 ‰.

^2H and 1986 ^{13}C were analyzed at the Stable Isotope Laboratory, Department of Earth Sciences at the University of Waterloo. Analyses were conducted using a mass spectrometer with detection limits of ± 2.0 and 0.2 ‰ respectively. ^3H was also analyzed at the University of Waterloo. Tritium analysis was conducted using direct counting liquid scintillation with a detection limit of 6 ± 8 T.U..

The ^{34}S and $^{18}\text{O}_{(\text{SO}_4)}$ results reported in the text were analyzed by Dr. R. Krouse at the Stable Isotope Laboratory, Department of Physics, University of Calgary. The analyses were conducted on a mass spectrometer with detection limits of 0.2 ‰ for both isotopes.

Appendix 6 - ANALYTICAL TECHNIQUES

Element	Method	Detection limit
Ca 1986	AA	0.2 ppm
Ca 1987	ICP MS	1 ppm
Mg 1986	AA	0.2 ppm
Mg 1987	ICP MS	1 ppm
Na 1986	AA	0.2 ppm
Na 1987	ICP MS	1 ppm
K 1986	AA	0.2 ppm
K 1987	Not analyzed	
HCO ₃ 1986 & 1987	titration	0.2 ppm
SO ₄ 1986 & 1987	DIONEX	0.2 ppm
Cl 1986 & 1987	DIONEX	0.05 ppm
Si 1986 & 1987	ICP MS	2 ppm
F 1986 & 1987	DIONEX	0.04 ppm
Sr 1986 & 1987	ICP MS	0.1(±) ppm
Ba 1986 & 1987	ICP MS	1 ppm
Al 1986 & 1987	ICP MS	1 ppm
Cr 1986 & 1987	ICP MS	1 ppm
Fe 1986	AA	20 ppb
Fe 1987	AA	5 ppb
Mn 1986	AA	10 ppb
Mn 1987	AA	2 ppb
Cu 1986 & 1987	AA	2 ppb
Ni 1986 & 1987	AA	2 ppb
Co 1986 & 1987	AA	2 ppb
Cd 1986 & 1987	AA	2 ppb
Zn 1986	AA	ppb
Zn 1987	AA	2 ppb
Ag 1986	AA	2 ppb
As 1986	AA-silica	0.2 ppb
As 1987	AA-silica	0.3 ppb
U 1986	Fluorometric	0.02 ppb
Mo 1986 & 1987	ICP MS*	0.1 ppb
W 1986 & 1987	ICP MS*	0.1 ppb

AA = atomic absorbtion

ICP MS = inductively coupled plasma mass spectography

titration = acid titration to pH end point

DIONEX = DIONEX ion chromatography

Fluorometric = uranium fluorometric

ICP MS* = ICP MS after preconcentration with activated charcoal

All the above analyses were conducted at the laboratories of the Geological Survey of Canada or contracted-out through the GSC to Bondar Clegg Ltd. of Ottawa.