

5. Spring Water Geochemistry and Hydrogeology

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5.1. Introduction

5.1.1. Background - spring sampling as an assessment tool

Spring sampling as an exploration tool has a long history, yet much remains to be learned. It was 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 hydro-geochemistry 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. Michel (1986) reported sulphur source identification in groundwaters of Mackenzie Valley using isotopes. Michel and Van Everdingen (1987) identified a groundwater system passing through a pyrite-rich sulphide zone using isotopes and geochemistry. 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 been used on a regional scale.

The South Nahanni River resource assessment project covers a variety of geologic terranes and, even with more than 100 springs sampled, has obtained relatively sparse coverage of springs in any given unit. Nevertheless, the availability of data from mineral occurrences, regional geology and regional stream sediment geochemistry provides an opportunity to compare the results and develop mutually supportive inferences. In particular, it provides an opportunity to link the relatively unproven method of regional spring geochemistry with the proven technique of stream sediment geochemistry.

5.1.2. Previous hydrogeological studies in the Nahanni region

Several previous investigations in the Nahanni region have included hydrogeological components. Virtually all springs in the region that are cited in literature were sampled here; most being thermal. The three-digit numbers in parentheses (given only to the first mention of the spring name) in the following summary refer to the corresponding sample numbers

used in this resource assessment (Figs. 5.1, 5.2; Tables in this chapter, Appendix 4).

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) detailed the Rabbitkettle (063) and Kraus (064) Hot Springs (then known as Clausen Creek Hot Spring); van Everdingen (1973) 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) sampled springs that were known or thought to be thermal in the Yukon and adjacent NWT and BC, including the following in the Nahanni 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).

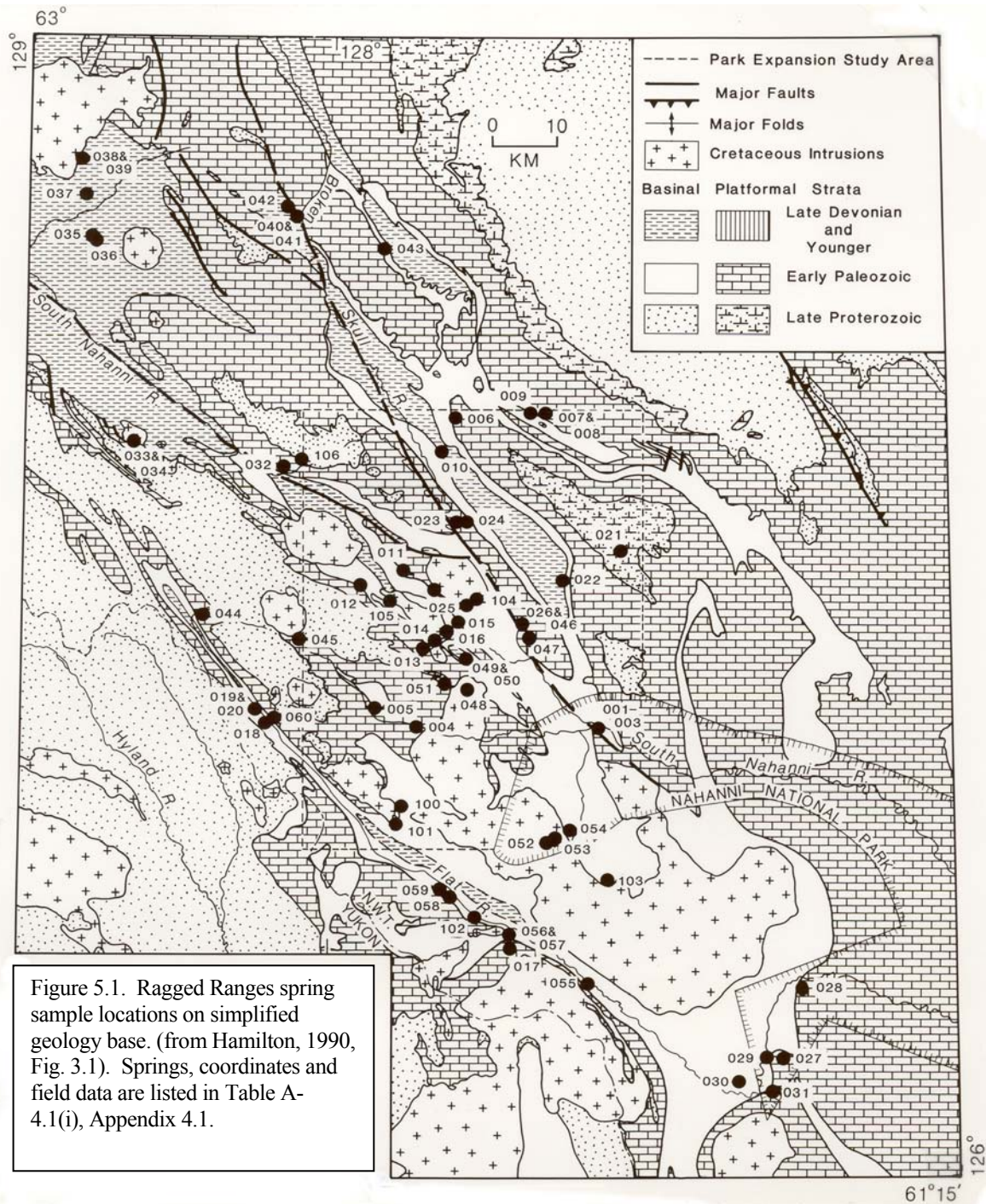
Brook (1976) studied landforms in the Nahanni Karst area, referring to several cold springs, including White Spray (065), Bubbling Spring (076) and a small travertine precipitating spring (125).

All of the above report water geochemistry, although none of their trace element analyses were comprehensive enough to be used in this study. Chemical analyses of waters reported herein are similar to those of previous studies (where comparison is possible) and, therefore, chemical analyses published by the above authors are not included herein.

This chapter and Appendix 4 are slightly revised reproductions from an M.Sc thesis by Hamilton (1990), for which a preliminary report (Hamilton *et al.* 1988) and one follow-up paper (Hamilton *et al.* 1991) were published. As an outgrowth of Hamilton's thesis

work, several additional studies were completed: ^{13}C analysis of the travertines as a B.Sc. thesis by Bowman (1990), cold springs of the Flat River Valley as a B.Sc.

thesis by Timlin (1991), and the Rabbitkettle Hot Springs as an M.Sc by Gulley (1993).



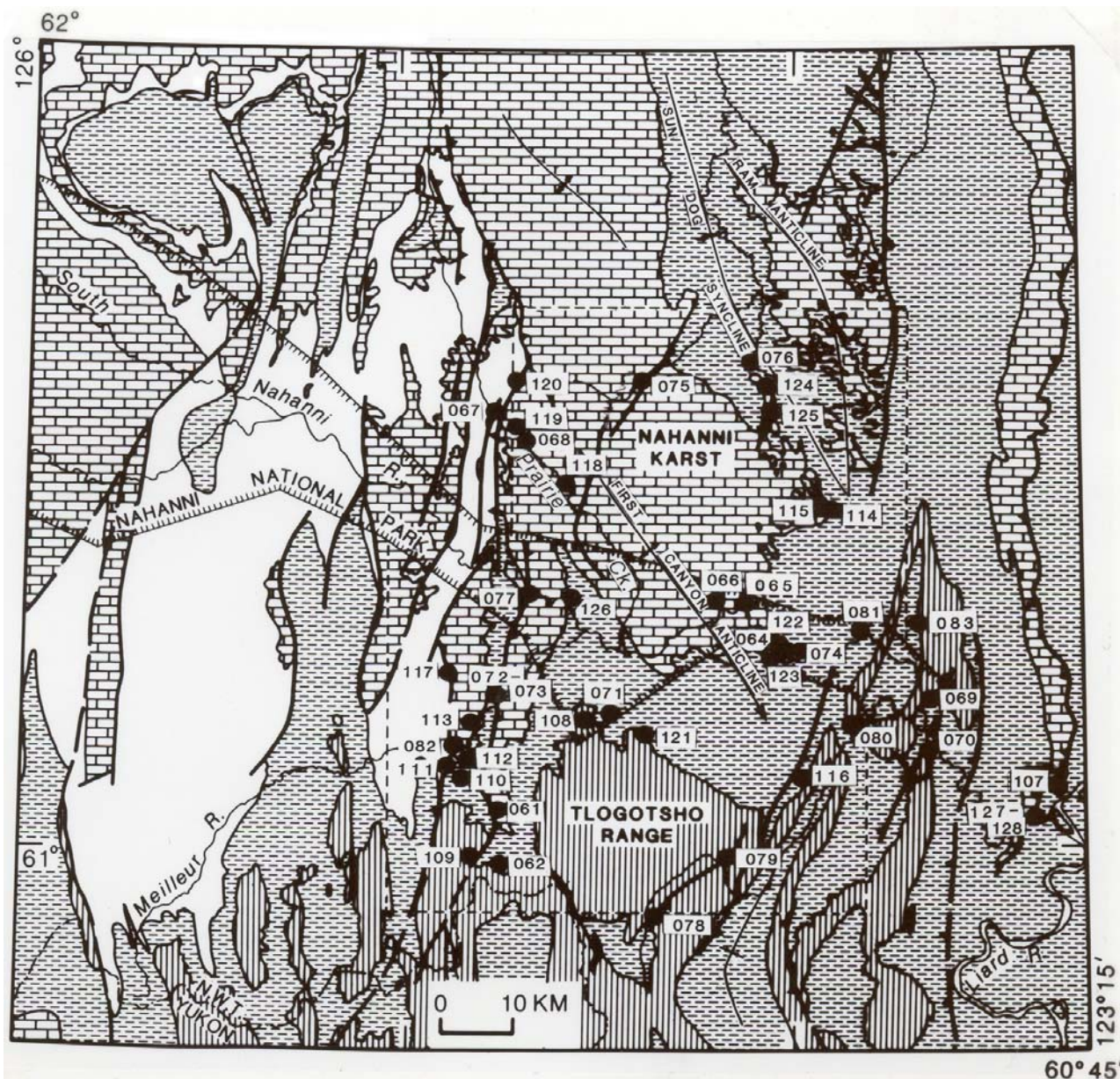


Figure 5.2. Nahanni Karst and Tlogotsho Plateau sample locations on simplified geology base. For legend, see Fig. 5.1 (from Hamilton, 1990, Fig. 3.2). Springs, coordinates and field data are listed in Table A-4.1(i), Appendix 4.1.

5.1.3. Hydrogeologic Objectives and Scope

The objectives of this study are two-fold: (1) to determine the usefulness of regional spring water geochemistry in assessing the mineral potential of an area, and (2) to determine the hydrogeochemical processes in groundwater of the southern Mackenzie Mountains, particularly processes relevant to resource assessment. Spring sampling was conducted mainly in the resource assessment study area, but was extended in the Ragged Ranges because nearby known springs of

interest could provide relevant information.

A total of 114 different spring and surface water sites were sampled in two field seasons (Figs. 5.1 and 5.2). Ten of these were sampled during both field seasons to make a total of 124 samples obtained (Appendix 4.1) for further study. Approximately three quarters of the springs had not been reported in the literature. Eleven of the previously unreported springs are thermal, and of these the "White Aster hot spring" at Meilleur River (082) is quite large and beautiful but the surface architecture and vegetation are very fragile.

Both major ion and trace elements of the waters were analysed and are herein interpreted. Stable isotope data including ^{18}O , ^2H , ^{13}C , and ^{34}S were also collected for many of the springs in this study.

5.2. Hydrogeologic setting

5.2.1. Controls on groundwater recharge, flow and discharge

The western and eastern study areas differ markedly in their physiography, geology, and therefore controls on groundwater flow and discharge. In the Ragged Ranges study area (Fig. 5.1), quartz monzonite plutons form jagged peaks up to 3100 m in elevation with small upland areas in cirques. A number of hot springs are spatially and geochemically related to these intrusions (Section 5.2.2, Hydrochemical influences). 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. 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 terrain was discovered in the Ragged 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 the 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 South Nahanni River Valley to the east of the Ragged Ranges is wide, relatively flat, and inferred to be fault-influenced. 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-influenced 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 a break in slope or a contact between rock units.

The First Canyon Anticline and the Ram Anticline (Fig. 5.2) are the dominant structures that have uplifted and exposed carbonate strata in the Nahanni Karst study area. 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 occupy the deep, vertical-walled First Canyon. Tributaries that drain the uplands, such as Prairie Creek and Lafferty Creek, also have deeply incised valleys.

Karst topography has also developed on the gently sloping to flat-lying Sundog Syncline area between the Ram and First Canyon Anticlines, (Brook, 1976). Groundwater flow within Nahanni Karst area is dominated by karstic flow. 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 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. Surface water in the area of greatest karst development appears to drain vertically downward and most of the lateral flow is subterranean.

The Tlogotsho Plateau, cored by a basin of Mississippian (Mattson Formation) sandstone, hosts springs along its northern edge and incised deep valleys. In most cases, these springs appear to be stratigraphically controlled, although analysis of satellite images indicates that a number of springs are located at intersections of subtle regional lineaments that are interpreted as late brittle fractures with minor offset. West of the Tlogotsho Plateau, beyond the Headless Range, the Meilleur River transects an important belt of eastward dipping thrust and reverse faults. Strata offset along these faults form northerly trending, parallel ridges. Hot and cold springs are localized along the faults and along the shale / limestone contacts between faults. East of the Tlogotsho Plateau, the limbs of several folds form high parallel ridges with intervening valleys along which rivers, such as the Jackfish, flow north. In this area, springs are restricted to the valleys.

All of the study areas receive ample recharge from the abundant annual precipitation (350 mm at Fort Simpson to 650 mm at Tungsten). Both stations receive

almost equal amounts of rain (52%) and snow (48%) (Environment Canada, AES, 1982). Both recharge and discharge are hampered locally by discontinuous permafrost (permafrost above treeline is more 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 shaley formations probably have low hydraulic conductivities and flow within these units is probably related to fractures. 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.

5.2.2. Hydrochemical influences

The three study areas transect the structural and lithologic grain of the southern Mackenzie Mountains that are underlain by more than 50 different map units (Table 3.1). As lithology is a major factor in groundwater geochemistry, it is therefore not surprising that water types encountered are quite diverse. 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 karst, the waters can remain relatively oxygenated and open to the loss of CO_2 . Depending on lithology, the results can differ. In carbonate terrane, the resulting waters can have low total dissolved solids (TDS) values because CO_2 concentrations will not be much higher than atmospheric. In shale terrane with abundant pyrite present, the concentration of SO_4^{2-} and Fe can increase substantially where free oxygen is available. Shales themselves also alter the chemistry of a water through cation exchange.

Interaction with base metal sulphides and pyrite can alter the major and minor ion contents, as well as pH and Eh conditions. These alterations are often distinctive and can be used to detect the presence of mineralization. For example, 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 part of a sediment-hosted base metal deposit that may be worthy of exploration (e.g., Jonasson *et al.*, 1987). Similarly, 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. An increase in temperature increases the solubility of silica and most other solids while decreasing the solubility of

gases such as CO_2 . The reduced solubility of CO_2 results in decreased solubility of carbonate minerals. The definition of "thermal" groundwaters must be relative to their local context. 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 region is about -4°C (Brook, 1976) to -6°C (Environment Canada, AES, 1982); according to this definition, essentially all groundwaters would be considered as thermal. Crandall and Sadler-Brown (1978) classified groundwaters as cold, cool, warm, and hot based on arbitrary temperature limits.

For this study it is assumed that groundwaters above 7°C (the average measured summer temperature of streams in the area) are "thermal", and the term "hot spring" represents springs that exceed 20°C .

5.3. Hydrogeology methods and data collected

Springs were located using descriptions in the literature, air photo interpretation, aerial reconnaissance and ground traverses. 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 bias is thought to be appropriate because the more substantial water volumes and greater amounts of dissolved constituents of visible springs provide greater insight into regional rock types or larger mineral occurrences at depth.

Waters were sampled for major ions and trace elements. A one-litre bottle for cations plus 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.

The pH, electrical conductivity and temperature were measured at the spring vent. Unfortunately, equipment for field alkalinity measurement was unavailable. Flow rate was estimated, and geological setting was noted at the site. These field data and spring locations are listed in Table A-4.1(i), Appendix 4.1.

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. Cations were analyzed on both the

acidified and non-acidified samples. Major ion data are given in Appendix 4.2 (Table A-4.2(ii)). Trace element data include Fe, Mn, Zn, Cu, Cd, Co, Ni, Pb, Al, Mo, W, Ag, Au, U, Sb, As, F, Sr, Si and Ba (Table A-4.2(iii) in Appendix 4.2). Several of these elements were only measured in one year or the other. Detection limits and laboratories are in Appendix 4.2 (Table A-4.2(i)).

Samples for ^{18}O , 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 4.4. The ^{18}O and 1987 carbon isotopes were analysed at the stable isotope laboratory of the Ottawa-Carleton Geoscience Centre. Hydrogen isotopes and 1986 carbon isotopes were analyzed at the Environmental Isotope Laboratory of the University of Waterloo, Ontario.

5.4. Classifications of springs

5.4.1 Introduction to classification methods

Classification is necessary here for context to determine whether high geochemical values are anomalous or just characteristic of a particular hydrogeological setting. Classifying spring waters also helps to indirectly determine the geochemical processes that may have affected the waters at depth. This helps to determine whether a mineral deposit has been encountered along a flow path or if active processes could be relevant to environmental base-line data or other aspects of land use and park management.

Springs may be classified with the aid of factors such as temperature, electrical conductivity, flow rate, rock types encountered, pH, major ions, trace elements, ionic ratios and total dissolved solids (TDS). Before any of these parameters are used, it is important to differentiate which are causes and which are effects. Important factors that affect the measurable properties of the water include: lithology, order of encounter, mineralization, subsurface temperature and subsurface residence time. The chemical attributes, e.g. pH, Eh and TDS, are almost entirely dependent on these factors.

In some cases, chemical influences such as lithology or deep fault circulation are apparent by spatial association, but in many cases they are not. Hydrochemistry 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 that have altered them. However, chemistry is only one of several parameters 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 ultimate 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 chemical composition is available.

Many procedures can be utilized for grouping chemical data. The most powerful tools available for grouping multivariate data are computer routines such as factor analysis, discriminant analysis and cluster analysis (Koch and Link, 1970).

Factor analysis ascertains whether a series of multivariate 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, a single dimension need only represent them; 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 *apriori* grouping of samples. The characteristics (including centre) of each group must be known so that subsequent samples can be assigned to one of the previously known groups based on distance calculations.

Cluster analysis requires no previous knowledge of how samples are grouped. It classifies multivariate data into groups based on how closely samples plot to each other in multidimensional space. Cluster analysis is extremely useful in cases like this study wherein the causes of groupings are not known.

Section 5.4.2 explains the classification system used in the field, initially based mostly on field observations, but later modified using chemical data. Section 5.4.3 deals with Kleiner-Hartigan trees, a crude but effective form of cluster analysis, which relies on pattern recognition to classify groups. Cluster analysis is explained in section 5.4.4.

Final classification of springs is outlined in section 5.4.5, based mostly on cluster analysis but also using elements of the other two methods. This

classification is used in sections 5.5 and 5.6 that analyse in detail the geochemical factors that influence these groupings. The term "cluster" is synonymous with "group" but for consistency it is used here only when describing the computer methods. The term "group" refers here to groups determined in this study by each of the methods.

5.4.2. Field classification

During sampling in 1986 and 1987, it became apparent that many of the springs could be grouped in the field based on similar characteristics such as temperature, conductivity, pH, flow rate, underlying lithology and spring precipitates (Appendix 4.1). These attributes were used to classify approximately $\frac{3}{4}$ of the 124 spring and surface water samples into the five groups listed in Table 5.1. The remaining $\frac{1}{4}$ were not readily classified and were left as an ad-hoc heterogeneous group labelled "P6". Anomalous springs (Table 5.11) include some from the first five groups and all of P6.

The strongest subjective criteria for initial field classification include physical similarities and geological context such as faults and host lithology. All but one of the groups (high discharge cold springs) appear to be related to host lithology (Hamilton *et al.*, 1988b). Laboratory analyses, later added to the field criteria, indicate that the field groups have some chemical similarities. Use of host lithology was tempered by the following: (1) Maps are at a scale of 1:250,000 and it is often unclear which exact unit or sub-unit hosted the flow system. (2) Waters travel both laterally and upward from depth and may pass through more than one rock unit, especially where springs are located along fault traces. (3) Not all springs in a given geologic terrane have the same geochemical features. (4) Residence time, temperature and the presence or lack of mineralization also may influence the geochemical signature of the waters.

Details of the application of the above criteria to the field classification shown in Table 5.1 are provided in Appendix 4.1. The physical classification system left more than $\frac{1}{4}$ of the samples unclassified (Group P6 – Miscellaneous). Many of the unclassified samples have important geochemical similarities to groups already formed, despite dissimilar physical characteristics such as the underlying lithology or the presence or absence of precipitates. It was decided that an objective geochemical grouping method was necessary.

5.4.3. Kleiner-Hartigan Trees Classification - grouping by hydrogeochemical pattern recognition

The following section summarizes the application of a method of grouping multivariate chemical data known as Kleiner-Hartigan Trees (Kleiner and Hartigan, 1981).

Table 5.1 Results of the field classification of spring waters based on physical characteristics. Field data and detailed discussion of groups are in Appendix 4.1

Group	Sample	Group	Sample	Group	Sample
Tufa Springs		P2	62	High - discharge cold springs	
P1	1	P2	69		
P1	21	P2	70	P5	4
P1	23	P2	71	P5	6
P1	26	P2	72A	P5	7
P1	27	P2	72B	P5	45
P1	28	P2	73A	P5	65
P1	29	P2	73B	P5	66
P1	31	P2	73C	P5	68
P1	40	P2	74	P5	75
P1	41	P2	78	P5	76
P1	43	P2	79	P5	104
P1	46	P2	80	P5	105
P1	47	P2	83	Miscellaneous	
P1	56	P2	100		
P1	57	P2	103	P6	9
P1	58	P2	108	P6	10
P1	59	P2	109	P6	13
P1	82	P2	110	P6	20
P1	111	P2	112	P6	22
P1	113	P2	116	P6	24
P1	114	P2	121	P6	32
P1	115	Hot springs in Quartz Monzonite		P6	44
P1	125			P6	48
Iron Springs		P3	11	P6	50
		P3	18	P6	51
	P2	P3	19	P6	61
	P2	P3	20	P6	67
P2	12A	P3	20	P6	67
P2	12B	P3	33	P6	81
P2	12C	P3	34	P6	101
P2	15	P3	38	P6	102
P2	17	P3	52	P6	106
P2	25	P3	53	P6	107
P2	30	P3	60	P6	117
P2	36	Clausen Creek Hot Springs		P6	118
P2	37			P6	119
P2	42	P4	63	P6	124
P2	49	P4	64	P6	126
P2	54	P4	122	P6	127
P2	55	P4	123	P6	128

Details of the method and its application here are provided in Appendix 4.3; results are summarized here in Figures 5.3 to 5.6 inclusive and Table 5.2, and briefly discussed below.

The chemical analyses (Appendix 4.2) include the seven major ions and 20 trace elements. Three of the trace elements (Au, Sb and Pb) were analyzed only in 1987 and two others (Ag and Ba) were detectable in so few samples that they cannot 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 them and visually pick obvious clusters. However, any more than a few variables are difficult to represent in two dimensions. One method of dealing with this problem is to produce an individual plot for each sample, the shape of the plot being dependent on the element abundances. The plots can then be grouped on the basis of their shapes. Many variations on this theme have produced a number of different types of representative shapes.

One of the more successful shapes is that of a tree (Fig. 5.3). A computer program is used to generate the plots and samples are then grouped by pattern recognition. Similar shaped trees represent waters with similar chemistry. It remains 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. R.W. Garrett (pers. com. 1988) provided the computer program used in this study.

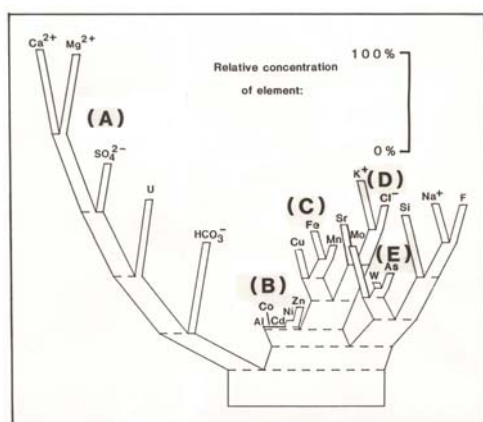


Figure 5.3. Tree plot configuration produced by using all 1986 and 1987 geochemical data. Elements that vary together are placed on the same branch. The length of each leaf represents the concentration relative to the log of the total range within that element for all samples. The size of the branch is proportional to the sum of the relative concentrations of all leaves on the

branch. Letters (A) through (E) label branches for reference in Appendix 4.3 (Hamilton, 1990, Fig. 4.1).

Table 5.2. Results of classification by pattern recognition of "Kleiner-Hartigan Trees". Names of groups retain elements of the original field classification (Table 5-1) for ease of recognition. Groups are summarized in Figures 5.4, 5.5 and 5.6 and discussed in the text and in Appendix 4.3.

Group	Sample	Group	Sample	Group	Sample
Mostly Hi-Discharge Cold Springs		T3	41	T5	112
		T3	43	T5	121
T1	4	T3	55	Hot Springs in Quartz Monzonite	
T1	7	T3	56		
T1	9	T3	57	T6	11
T1	13	T3	58	T6	18
T1	28	T3	82	T6	19
T1	45	T3	82A	T6	20
T1	51	Mostly Iron Springs with high Cu-Fe-Mn		T6	33
T1	65		T6	34	
T1	66	T4	15	T6	38
T1	68	T4	37	T6	52
T1	75	T4	54	T6	53
T1	101	T4	59	T6	60
T1	104	T4	61	Clausen Creek Hot Springs	
T1	113	T4	62		
T1	119	T4	78	T7	63
T1	120	T4	79	T7	64
Mostly Tufa Springs		T4	81	T7	122
		T4	103	T7	123
T2	1	T4	109	Iron Springs with High Na ⁺ -Ca ²⁺ ratios	
T2	6	Mostly Iron Springs with high Al-Co-Cd-Ni-Zn-Cu-Fe-Mn			
T2	23		T8	74	
T2	27		T8	83	
T2	29	T5	012A	T8	110
T2	30	T5	012B	T8	116
T2	31	T5	012C	Unclassified	
T2	32	T5	25		
T2	44	T5	35	T9	10
T2	46	T5	42	T9	22
T2	47	T5	48	T9	24
T2	50	T5	49	T9	26
T2	76	T5	69	T9	36
T2	106	T5	70	T9	67
T2	107	T5	71	T9	77
T2	111	T5	072A	T9	78
T2	115	T5	072B	T9	102
T2	125	T5	073A	T9	114
T2	127	T5	073B	T9	117
Mostly Tufa, high K ⁺ -Cl ⁻ -Si-Na ⁺ -F		T5	073C	T9	118
		T5	80	T9	124
T3	17	T5	100	T9	126
T3	21	T5	105	T9	128
T3	40	T5	108		

Grouping by pattern recognition has a number of advantages. It allows one to see immediately what causes the groupings. For instance, the differences in elemental associations of groups T2, T6 and T7 are obvious in Figures 5.4 & 5.5, but would not be obvious using methods such as cluster analysis. Another advantage is that the tree process correlates and then clusters variables and not samples. This requires far less computer resources than would be necessary for other digital methods that 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 that 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 that 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 assign it to neither as 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 criterion for choosing waters in that group.

Group T8 in Figure 5.6 is made up of waters that 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 minimized. Subjectivity can cause bias where samples have unusual chemistry or dilution or mixing has taken place. A more important argument is that the investigator could, knowingly or not, establish groupings based on pre-conceived ideas or models. Admittedly this did play a part in establishing groups

T4 and T8. Although they do not exhibit very distinctive shapes, they do represent important geochemical processes that are not obvious by the shapes alone. Subjectivity was involved in creating the groups and deciding which waters were involved in which processes.

Use of a pattern recognition method creates other, technical problems. Different types of waters may have the same elements but the elements may vary in different ways. For example, in Group T6, Na^+ and HCO_3^- vary together but in T7, Na^+ and Cl^- vary together. Because the elements are assigned to only one branch, on the basis of the entire data set, the shape of the tree cannot fully represent the co-variability of elements. This is a problem in T6 where the waters are Na-HCO_3 dominated and Na^+ is on one branch whereas 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 visualizing differing shapes with increasing numbers. Although the method was found to be satisfactory for the data herein, a non-subjective method (cluster analysis) was thought to be necessary for verification.

5.4.4. Cluster Analysis

Some uncertainties involved in grouping data by the previous methods and their potential biases require a non-subjective method of classification as an independent check, or to modify the previous groups, or to partition the data from first principles. Mathematical methods for partitioning multivariate data without a priori grouping are known as cluster analyses and are divided broadly into hierarchical and non-hierarchical methods. Cluster analysis has been used commonly since the mid- 1960's. Details of the application of Cluster analysis to this study are in Appendix 4.4.

All of the geochemical data used herein were reported by the laboratory in mass ratios (ppm, ppb, ppt). 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 similar when using equivalence units, although their statistical means differ considerably. Most clustering methods require that variables have similar scale and magnitude.

The geochemical data associated with this study were analysed using both hierarchical ("Joining" method) and non-hierarchical ("K-means") clustering methods (Appendix 4.4). The hierarchical "Joining"

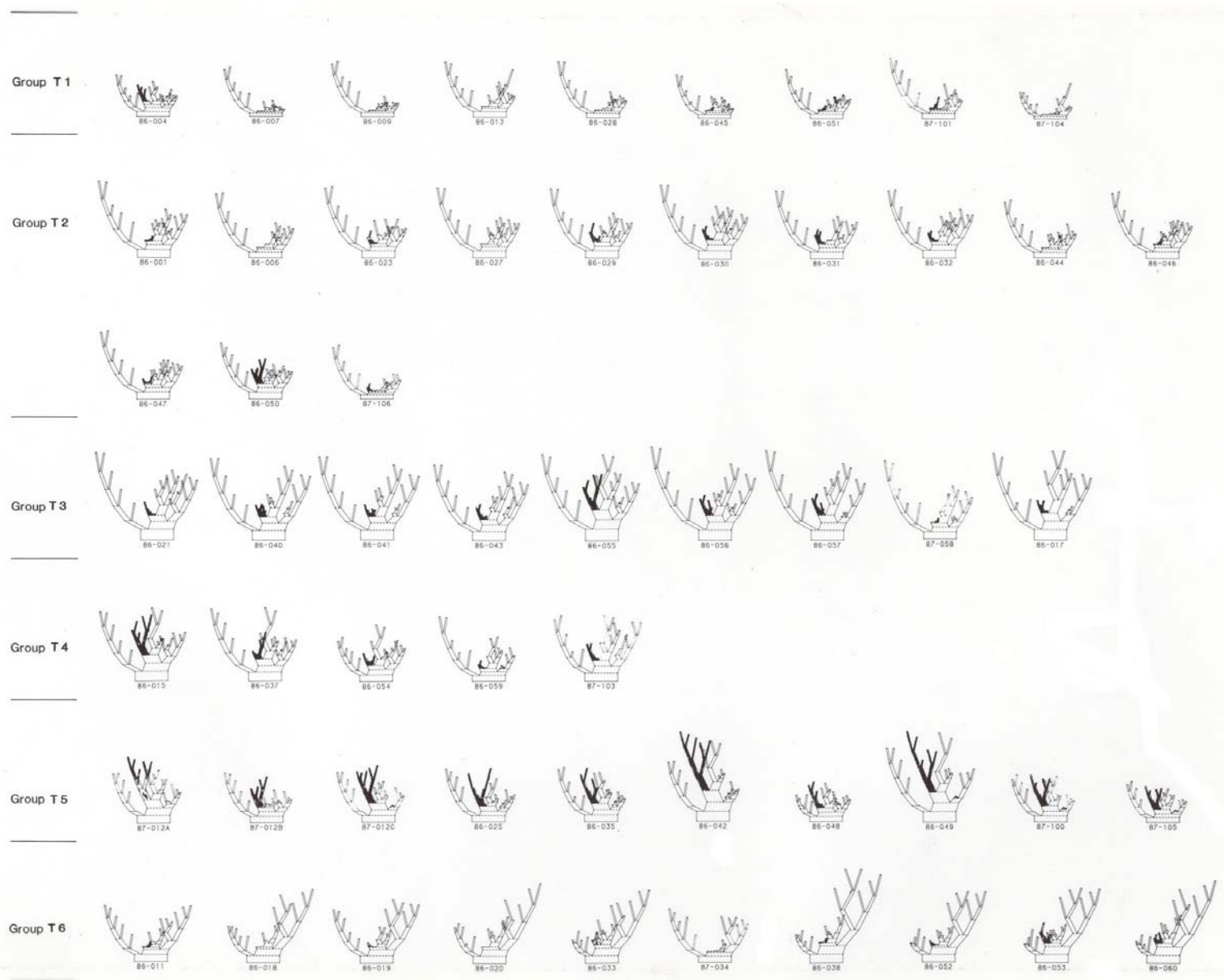
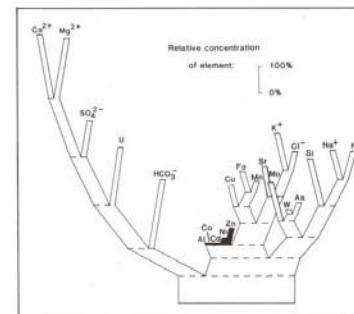
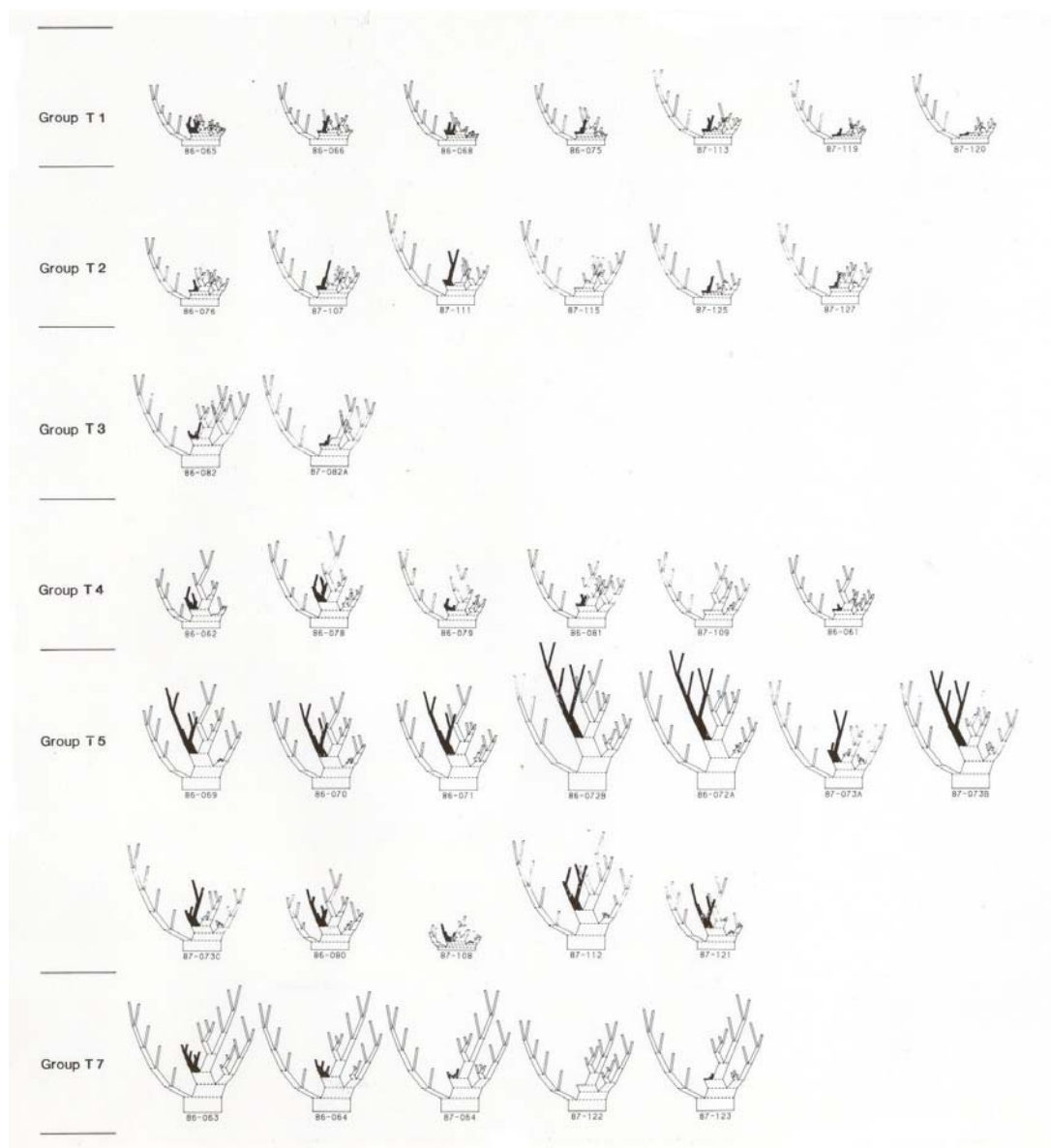


Figure 5.4. Geochemistry of spring water samples from the Ragged Ranges study area graphically represented and arranged into groups by pattern recognition of Kleiner-Hartigan trees. (from Hamilton, 1990, Fig. 4.3). Explanation of branches is in Figs. 5.3 and 5.5. Groups are summarized in Table 5.2. See Appendix 4.3 for detailed discussion of groups.



Hydrochemical classification of spring waters: clustering by tree plots. Size of branch represents individual relative concentration of each element. Overall size of tree is logarithmically proportional to total dissolved solids (TDS).

- Group T 1 mostly from high discharge cold springs alkaline waters with low TDS
- Group T 2 mostly tufa precipitating thermal waters found in carbonate terrane high Ca^{2+} , Mg^{2+} , HCO_3^- , Na^+ , Cl^-
- Group T 3 tufa precipitating waters similar to "Group 2" but with extremely high TDS
- Group T 4 non-acidic Fe-hydroxide precipitating waters probably a result of mixing of waters from "Group 3" and "Group 5"
- Group T 5 mostly acidic Fe-hydroxide precipitating waters very high trace metal concentrations, high SO_4^{2-} chemistry results from dissolution of sulfides
- Group T 6 waters from hot springs spatially related to quartz-monzonite intrusions high Na^+ , Si , Mo , W , F
- Group T 7 thermal waters with very high TDS possibly resulting from dissolution of evaporite minerals (NaCl , CaSO_4)

Figure 5.5. Geochemistry of spring samples from the Nahanni Karst and Tlogotsho Plateau study areas graphically represented and arranged into groups by pattern recognition of Kleiner-Hartigan trees. (from Hamilton, 1990, Fig. 4.2). Groups are summarized in Table 5.2. See Appendix 4.3 for detailed discussion of groups.

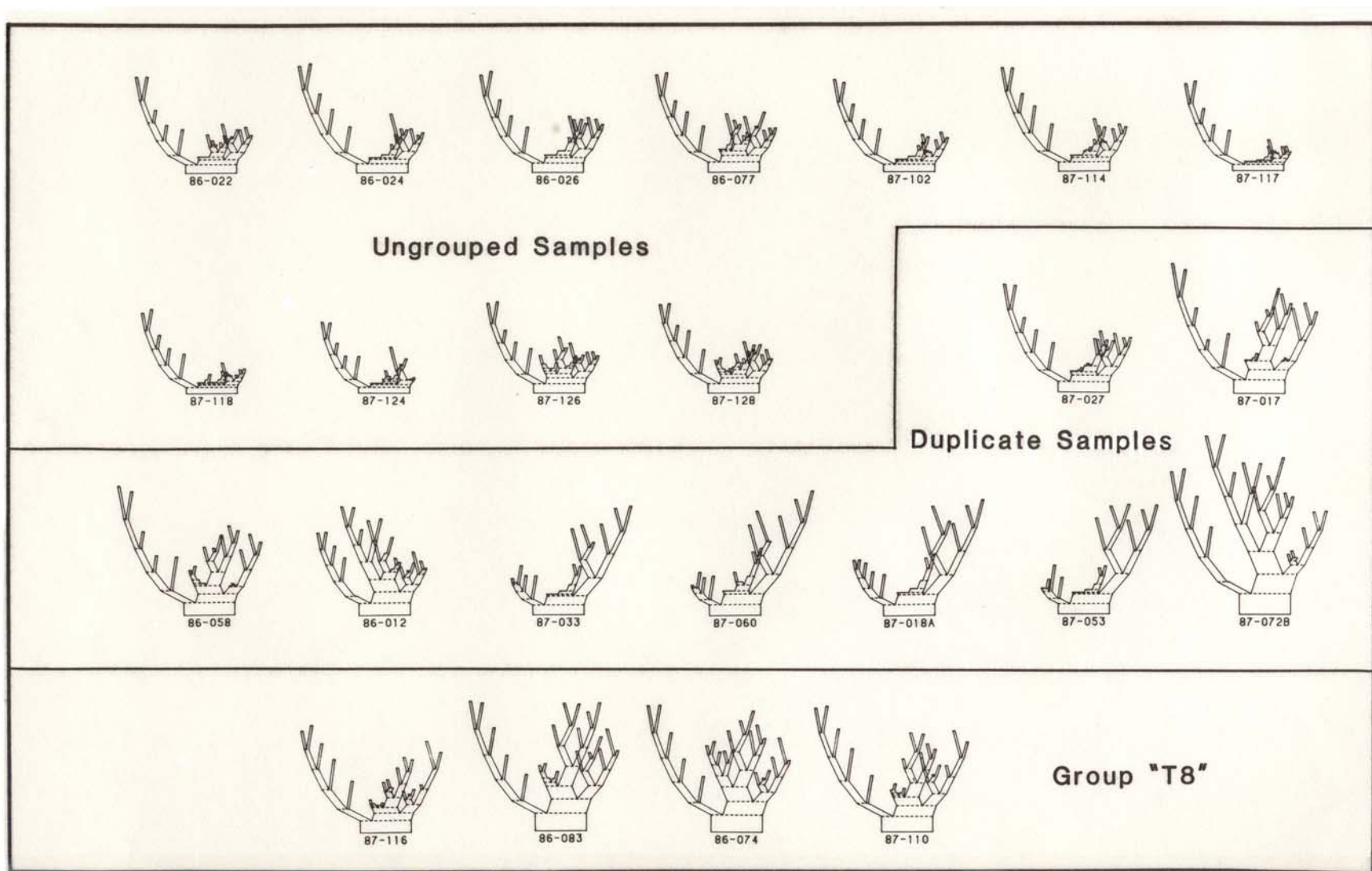


Figure 5.6. Samples in the Kleiner-Hartigan tree classification which were left ungrouped, which had duplicate analyses and which possibly belong to an 8th group("T8") of high $\text{Na}^+ : \text{Ca}^{2+}$ ratios which are interpreted to result from ion exchange in shales or clay-rich units. (from Hamilton, 1990, Fig. 4.4). Branches are explained in Fig 5.3 and 5.5.

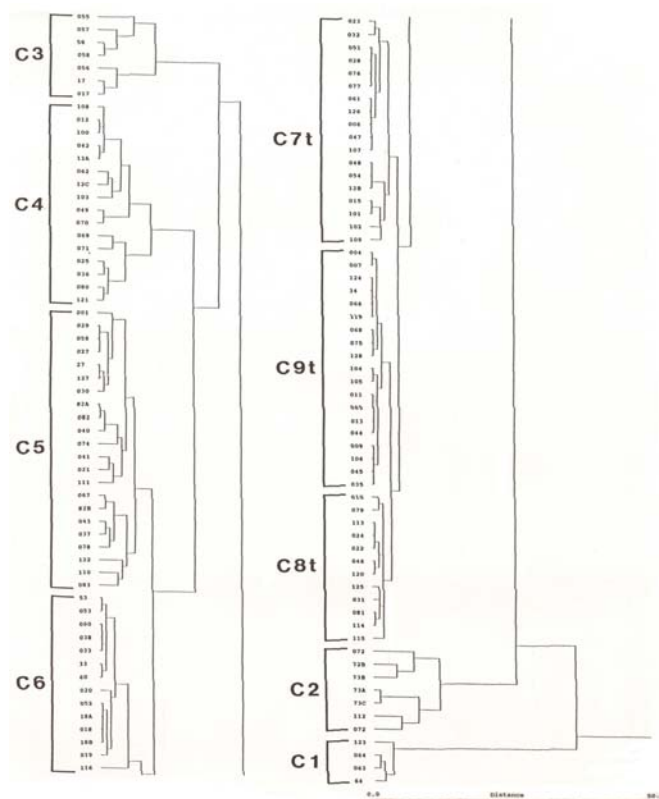


Figure 5.7 Results of the hierarchical cluster analysis (from Hamilton, 1990, Fig. 4.6). Summary statistics for this plot are listed in Table A-4.4 (i).

method discriminated between waters with differing chemistry, whereas the non-hierarchical “K-Means” method did not. The results of hierarchical clustering of all points (except 026, 050, 117 and 118) are shown in Figure 5.7. and listed in Table 5.3. Most samples plot into major groups that reflect the subsurface hydrogeochemical environment. Knowing these groups will help to determine the dominant hydrogeochemical processes and metallogenic inferences in the three study areas.

The samples with the smallest distance between them are the most similar and are the first ones joined. The horizontal lines 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 to give a representation of the distance that the new cluster centre is from the origin. The most significant group 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

Table 5.3. Results of classification by hierarchical cluster analysis. Titles of groups respect wording of discussions in text and Appendix 4.4, with some continuity from tables 5.1 and 5.2. Samples marked with an asterisk are repeat samples of the 1986 sites taken in 1987. Analytical data are listed in Appendix 4.2.

Group	Sample	Group	Sample	Group	Sample
Clausen Creek hot springs		Mixture of tufa & iron springs		C7	24
				C7	26
C1	63	C5	1	C7	31
C1	64	C5	21	C7	32
C1	64 *	C5	27	C7	46
C1	123	C5	27 *	C7	47
Meilleur River valley cold iron springs with high Al-Co-Cd-Ni-Zn-Cu-Fe-Mn		C5	29	C7	61
		C5	30	C7	81
		C5	37	C7	102
		C5	40	C7	113
		C5	41	C7	114
C2	072A	C5	43	C7	115
C2	072B	C5	59	C7	125
C2	072B *	C5	67	C7	126
C2	073A	C5	74	Springs with low total dissolved solids (TDS)	
C2	073B	C5	78		
C2	073C	C5	82		
C2	112	C5	82		
CO ₂ -charged, upper Flat River valley (mostly tufa & high K ⁺ -Cl-Si-Na ⁺ -F)		C5	082A *	C8	4
		C5	082B *	C8	9
		C5	83	C8	012B
		C5	110	C8	13
C3	17	C5	111	C8	15
C3	17 *	C5	122	C8	28
C3	55	C5	127	C8	35
C3	56	Hot springs in quartz monzonite		C8	44
C3	57			C8	45
C3	86-58	C6	18	C8	48
C3	87-58 *	C6	18A	C8	50
Acidic iron springs with high Al-Co-Cd-Ni-Zn-Cu-Fe-Mn		C6	18B	C8	51
		C6	19	C8	54
		C6	20	C8	65
C4	12	C6	33	C8	66
C4	012A *	C6	33 *	C8	68
C4	012C	C6	38	C8	75
C4	25	C6	52	C8	76
C4	36	C6	53	C8	77
C4	42	C6	53 *	C8	79
C4	49	C6	60	C8	101
C4	62	C6	60 *	C8	104
C4	69	C6	116	C8	105
C4	70	(C6 11)		C8	106
C4	71	(C6 34)		C8	107
C4	80	Fe-rich, neutral-pH, mixed C4 & C5 / C7		C8	109
C4	100			C8	117
C4	103	C7	6	C8	118
C4	108	C7	107	C8	119
C4	121	C7	10	C8	120
		C7	22	C8	124
		C7	23	C8	128

springs, C1, is shown on the bottom, right hand side of Figure 5.7). This group has the largest distance between it and the next highest cluster.

Groups have been numbered from C1 to C9 in descending order of significance. The significance of the group, "distance", is measured on the horizontal axis between one cluster and the vertical line joining it to its neighbour. Clusters C1 to C6 are very distinct and show clustering which indicates distinct hydrogeologic conditions. C1 contains saline waters from hot springs in the Clausen Creek area. C2 contains sulphate-rich, largely acidic waters from sample sites 072, 073 and 112 in the Meilleur River Valley. C3 contains CO²-charged waters from springs in the upper Flat River valley. Cluster C4 contains acidic waters which have been in contact with sulphides (C2 is a more extreme example). Cluster C5 represents travertine precipitating, mostly thermal springs from across the study area. Cluster C6 contains waters from hot springs, which are spatially associated with plutons.

There are, however, several cases where the cluster analysis is weak: where the waters have been mixed or diluted by waters of another type, where more than one dominant process takes place during the flow history, or where waters have too low a TDS content for their chemistry to be a reliable indicator of their environment. The first two cases can be overcome by careful examination of low TDS samples, with the understanding gained from the 7 dominant groups.

Careful decisions can be made to place low-TDS or mixed-water types of sample into groups representing waters of similar environment. Final groups (Table 5.4 and Discussion) were decided based on the results of cluster analysis and the other two classification systems.

5.4.5. Discussion of individual classifications

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. Second, it puts data into a homogeneous form for definition of trace metal anomalies. The results from the various classification schemes described (see appendices) have been combined to produce a final classification of the samples that best suits the purposes of this study.

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; and (2) more than one lithology may have been encountered, especially if the spring is fault localized, and rock units are rarely geochemically homogenous.

Even where waters are known to have encountered only one lithology, it is the subsurface processes involving mineral deposits, which are of the greatest interest in this study. 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 has merits. It is fast, inexpensive and requires little subsequent data manipulation. If spring water 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.

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 that were missed or misidentified by the field grouping. However, it has several problems, which need to 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 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, 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.

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.

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. In this study the previously generated trees were of great use in visualizing the basis for the cluster groupings.

5.4.6. Comparisons among groups

Despite differences among the three preliminary grouping methods, their results have similar elements. The approximate correlation of groups is shown in Table 5.4. The correlation shows that groups are broadly similar by each method, based on similar geochemical characteristics, such as high concentrations of iron and sulphate in waters, or low TDS contents.

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

There are problems with the placement 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

Table 5.4. Evolution of classifications in this study, ordered by final groupings. Correlations between groups are only approximate, because individual springs shift from one group to another as the method changes. Final spring groups are subdivided as shown in Table 5.5 and explained in text.

Field	Tree	Cluster	Final Spring Groups
P4	T7	C1	A – Kraus Hot Springs (at Clausen Ck.)
n/a	n/a	C2	B1 – Acidic high-SO ₄ ²⁻ Meilleur R. Valley
P2	T4, T5	C4	B2a & B2b – Acidic high-SO ₄ ²⁻ Ragged Ranges and Mattson Fm.
n/a	n/a	C3	C – High-pCO ₂ springs in upper Flat R. Valley
P1	T2,	C5, C7	D – High TDS springs
P3	T6	C6	E – Thermal in quartz monzonite terrane
P5	T1	C8	F – Low-TDS springs and surface waters
“P6”	“T9	n/a	Allocated some to each
n/a	“T8	n/a	Allocated some to each

cluster center. For the final grouping it was decided to create a primary grouping using an objective system and then make a few subjective adjustments. An initial subjective system would be difficult to adjust by objective criteria. Cluster analysis has thus been chosen as the basis of the final classification. Adjustments made to the results of cluster analysis are explained below as part of the analysis of processes and their implications for resource assessment. The samples which have been adjusted after cluster analysis are shown in parentheses in Table 5.5.

5.5. Final Spring Groups, Hydrogeochemical Processes and Applications to Resource Assessment

5.5.1. Introduction

Certain hydrogeologic processes are interpreted from the chemistry of each group in the final classification (Tables 5.4, 5.5) as discussed in the following sections. The average values of pH, temperature and TDS content for each group are shown in Figures 5.8, 5.9 and 5.10, respectively. Oxygen and deuterium data are plotted in Figure 5.11. Together, these important data increase our understanding of the various hydrogeologic processes in the region.

Some of the groups have important implications for the resource assessment. When placed

in the context of the hydrologic processes affecting these groups, it becomes possible to assess the importance of the trace element anomalies and their significance for determining resource potential. Each group is discussed in the order given in Table 5.5.

5.5.2. Group A – Kraus Hot Springs (at Clausen Creek)

Brandon (1965) and van Everdingen (1973) reported the main hot spring area at Clausen Creek. Although originally referred to as the Clausen Creek Hot Springs, they are presently known as Kraus Hot Springs and are within the boundaries of Nahanni National Park Reserve (NNPR). 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 the South Nahanni River from Kraus and a sample from Spring 123 was collected about 1.2 km southwest of the river. A third spring in this cluster lies 1 km southwest of the river and was not sampled. Many of the physical features of these springs are described in section 5.4.2 – Field Classification and in Appendix A-4.1.

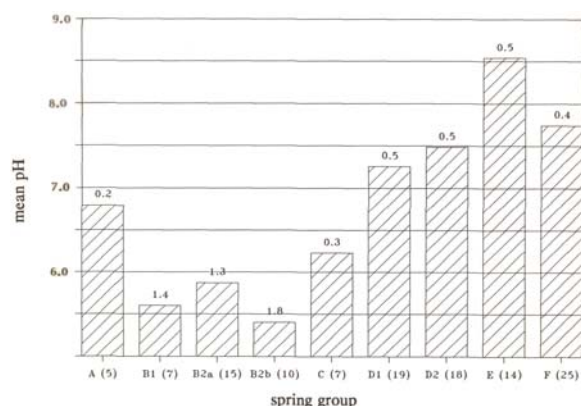


Figure 5.8 Mean pH for each group in the final classification (Table 5.5). The number of samples in each group is in brackets beside the group number. The root mean squared of each group is at the top of each bar (from Hamilton, 1990, Fig. 5.1).

The Clausen Creek waters have high TDS values. All major ion concentrations are high, particularly Ca^{2+} , Na^+ , Cl^- and SO_4^{2-} (Fig. 5.12, Table 5.6). Calcium sulphate is above saturation and precipitates as a suspension in the beaver ponds and pools. The supersaturation of calcium sulphate is a result of increased available SO_4^{2-} due to the oxidation of H_2S , which 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

Water from spring 122 appears to have been diluted because the concentrations of dissolved species, temperature and conductivity are lower and pH higher than in springs 063 and 064. The vent is approximately 1-2 m above river level and the deeper groundwaters have probably mixed with shallower waters.

The sulphur and oxygen isotope data for the dissolved sulphate ($\delta^{34}\text{S} = 25.07 \text{ ‰}$, $\delta^{18}\text{O} = -9.4 \text{ ‰}$) provide constraints on source rocks. The underlying carbonates are Devonian in age. The sulphur isotope curve for marine sulphate of this age (Claypool *et al.*, 1980) shows that $\delta^{34}\text{S}$ values 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.

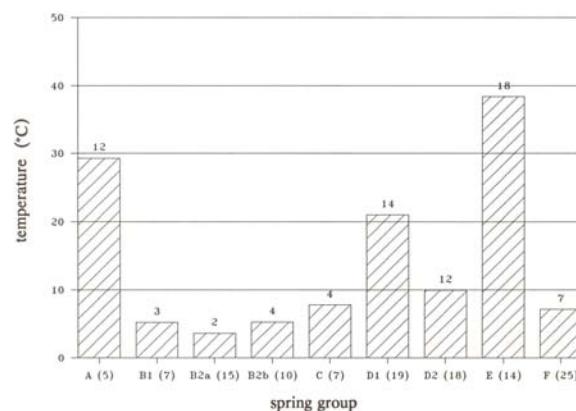


Figure 5.9. Mean water temperature for each group. The number of samples in each group appears in parentheses beside the group number. The root mean squared appears at the top of each bar. (from Hamilton, 1990, Fig. 5.2).

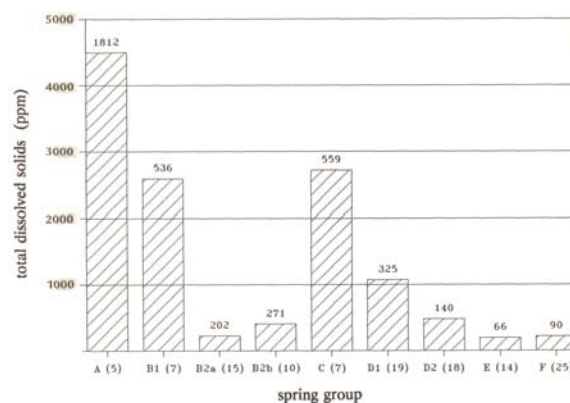


Figure 5.10 Mean total dissolved solids concentration, calculated from major ion data. The root mean squared is at the top of each bar. (from Hamilton, 1990, Fig. 5.3)

Group	Sample		Group	Sample		Group	Sample	
Kraus Hot Springs (at Clausen Creek)			C	055		Thermal springs related to quartz monzonite		
			C	056				
			C	057				
A	063		C	058		(E	011)	
A	064	*	C	058	*	E	018	
(A	122)		High TDS springs carbonate terrane			E	019	
A	123					E	018A	*
Acidic, high SO ₄ ²⁻ - metalliferous springs Meilleur River			hot, fault-local.			E	018B	
						D1a	001	
			D1a	021		E	033	
B1	072A		D1a	027		E	033	*
B1	072B		D1a	027	*	(E	034)	
B1	072B	*	D1a	029		E	038	
B1	073A		D1a	030		E	052	
B1	073B		D1a	040		E	053	
B1	073C		D1a	041		E	053	*
B1	112		D1a	043		E	060	
Acidic, high SO ₄ ²⁻ - Ragged Ranges shale near intrusions			D1a	082		E	060	*
			D1a	082A		E	116	
			D1a	082B	*	Low TDS springs and surface waters		
B2a	012		High TDS springs carbonate terrane					
B2a	012A	*				Various other		
(B2a	012B)		F	004				
B2a	012C		D1b	010		F	009	
(B2a	015)		D1b	059		F	013	
B2a	025		D1b	067		F	028	
(B2a	035)		D1b	074		F	044	
B2a	036		D1b	083		F	045	
(B2a	037)		D1b	110		F	048	
B2a	042		D1b	111		F	050	
B2a	049		D1b	127		F	051	
(B2a	054)		Moderate TDS springs in carbonate terrane			F	065	
B2a	100					F	066	
B2a	103					F	068	
(B2a	105)		D2	006		F	075	
Acidic, high SO ₄ ²⁻ - Mattson Formation sandstone & shale			D2	007		F	076	
			D2	022		F	077	
			D2	023		F	101	
B2b	062		D2	024		F	104	
B2b	069		D2	026		F	106	
B2b	070		D2	031		F	107	
B2b	071		D2	032		F	117	
(B2b	078)		D2	046		F	118	
(B2b	079)		D2	047		F	119	
B2b	080		D2	061		F	120	
B2b	108		D2	081		F	124	
(B2b	109)		D2	102		F	128	
B2b	121		D2	113				
High pCO ₂ Flat River valley			D2	114				
			D2	115				
C	017		D2	125				
C	017	*	D2	126				

Table 5.5 (left). Final Classification of spring waters in the three South Nahanni River study areas. Samples in parentheses were placed in the group subsequent to cluster analysis; repeat samples are marked with an asterisk.

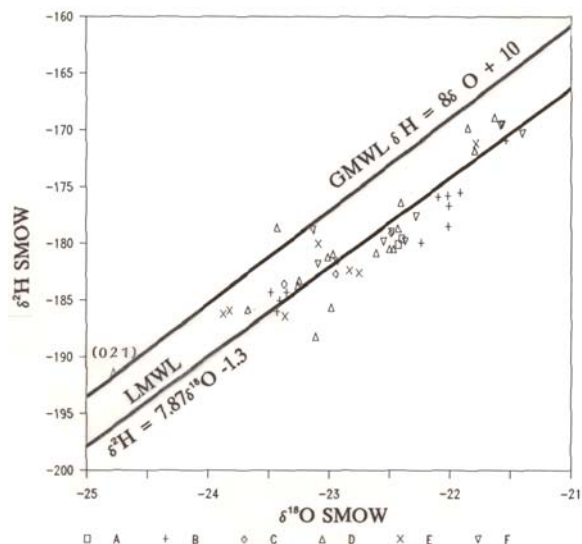


Figure 5.11 $\delta^{18}\text{O}$ and 2H plot of spring waters in the study areas. Data are listed in Table A-4.2(iv) in Appendix A-4.2. (from Hamilton, 1990, Fig. 5.4).

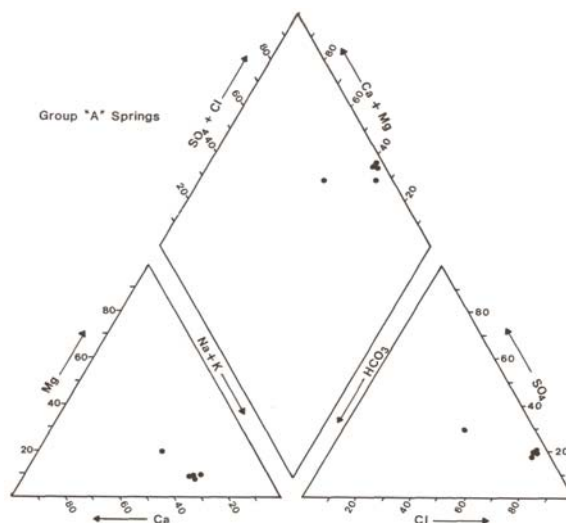


Figure 5.12 Piper diagram showing major ion chemistry for Group A. Concentrations are high (Appendix 4-b) (from Hamilton, 1990, Fig. 5.5)

Normally, marine sulphates contain $\delta^{18}\text{O}$ values greater than zero. However, a large portion of the sulphur in the waters at Clausen Creek is interpreted

Table 5.6 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) = HCO_3^- , determined by titration in the laboratory and corrected by charge balance techniques; AA = atomic absorption; D = DIONEX ion chromatography; n/a = not applicable or not analyzed. K^+ in 1987 was measured by 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 4.1 for field data and Appendix 4.2 for a complete listing of analyses and sources.

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	0.2	0.2	0.2	0.05	2	20/5	10/2	5	2	0.1	0.1	1	0.3	0.04
Units	(°C)	n/a	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppb	ppb	ppb	ppb	ppb	ppb	ppt	ppb	ppm
method	n/a	field	ICP	ICP	ICP	ICP	T(c)	D	D	ICP	AA	AA	AA	AA	ICP	ICP	AA	AA	S
86-063	38.5	6.62	610	114	1168	88.1	194.6	853	2347	30	852	75	30	4	0.2	0.4	n/a	7.2	0.83
86-064	37.5	6.62	617	116	1118	84.4	224.8	860	2333	30	129	57	13	<2	<1	0.3	n/a	1.4	0.82
87-064	36	6.61	502	92	1252	(345)	264.8	829	2368	23	163	85	13	<2	0.7	0.5	<1.0	0.3	n/a
87-122	22.5	7.02	157	42	183	(22)	300.9	243	278	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	22	123	230	8	<2	0.3	0.4	1.5	<3	n/a

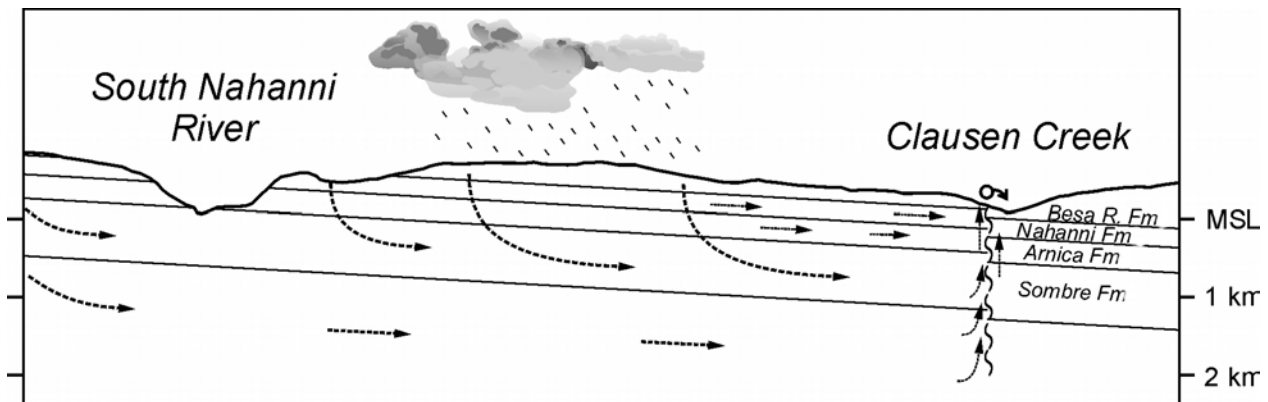


Figure 5.13 Schematic explanation for the localization and chemistry of the springs in Group A. Recharge is in the First Canyon Plateau to the west. Waters travel along easterly gradients in marine carbonate units and encounter unknown evaporites. Upon encountering a fault in the Clausen Creek area, waters move rapidly up from depth and discharge. (from Hamilton, 1990, Fig. 5.6).

to have been transported in a reduced form (such as HS^-) and is being re-oxidized to sulphate during mixing with shallow, meteoric waters. A component of the oxygen in the resulting SO_4^{2-} is interpreted to be 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.

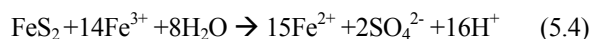
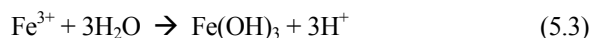
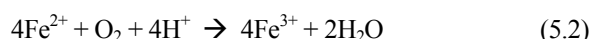
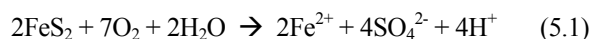
Figure 5.13 explains the location and chemistry of the springs. A regionally high hydraulic head would be maintained due to recharge in the First

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, giving it a high porosity. When groundwaters encounter the inferred fault, they would move rapidly up from depth and discharge. Assuming the global average of $30^\circ\text{C}/\text{km}$ 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).

5.5.3. Group B - Acidic, high SO_4^{2-} springs

The geochemistry of Group B is thought to be influenced by oxidation of sulphides. Most of the springs in this group have associated iron hydroxide precipitates at the vent. This group is very important to the resource assessment. As the waters in this group are so diverse, they 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 to have 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. The oxidation of sulphides increases the concentration 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 requires free oxygen. 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, also requiring free oxygen (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).

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

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

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, whereas Fe and other metals are commonly present in concentrations ranging from just detectable to very high. Fe and Mn tend to vary together (Fig. 5.14), although the abundance of Mn is generally much lower than that of Fe.

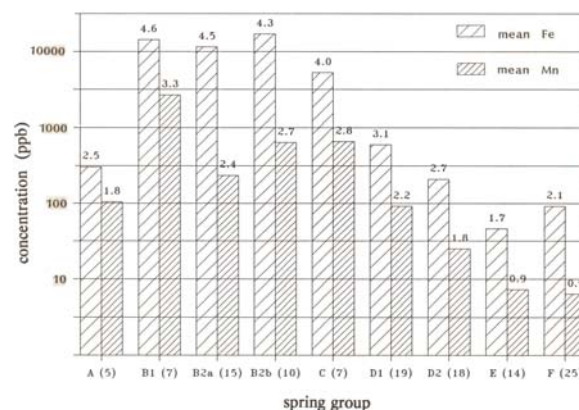


Figure 5.14. Mean of Fe and Mn for each group, as listed in Table 5.5. The sample size is in brackets beside the group number and the log of the root mean squared (RMS) is shown at the top of each bar. The correlation of the mean with the RMS allows no rigorous statistical conclusions to be made from this graph – it is simply a qualitative display (from Hamilton, 1990, Fig. 5.7).

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 together with high concentrations of trace metals such as Zn, Ni, Cd, Co or Cu. Subgroups B2a and B2b also contain a number of waters with neutral pH and high Fe, Mn, SO_4^{2-} and in some cases detectable HCO_3^- concentrations, but these waters characteristically have low trace metal contents. Figure 5.15 shows the average Zn and Ni concentrations for the various groups, including the three subgroups of Group B, within which differences are important.

The 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 5.16) shows ferrous iron to be the dominant species and the ferric ion to be insoluble at

pH > 4.0. Ni and Co tend to be stable under similar conditions as Fe^{2+} and co-precipitate with it (Hem, 1986). It is 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. Therefore, if waters are acidic and Fe is the only metal present at elevated concentrations, then sulphides other than pyrite are generally not abundant in the source mineralization. Mean Zn and Ni concentrations are graphed in Fig. 5.15 for all groups.

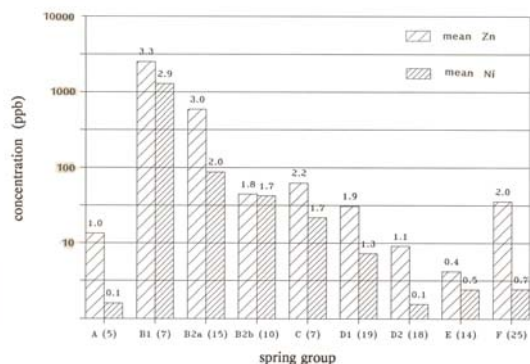


Figure 5.15 Mean Zn and Ni concentrations for each group as listed in Table 5.5; numbers are explained in the caption to Fig. 5.14 (from Hamilton, 1990, Fig. 5.8).

During routine charge-balance calculations, 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 and 121). This may result from the presence of neutral sulphate species, particularly FeSO_4^0 . 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 due to sulphur anion complexes, which have a valence of -1 as opposed to -2 for sulphate.

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 5.16 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^- .

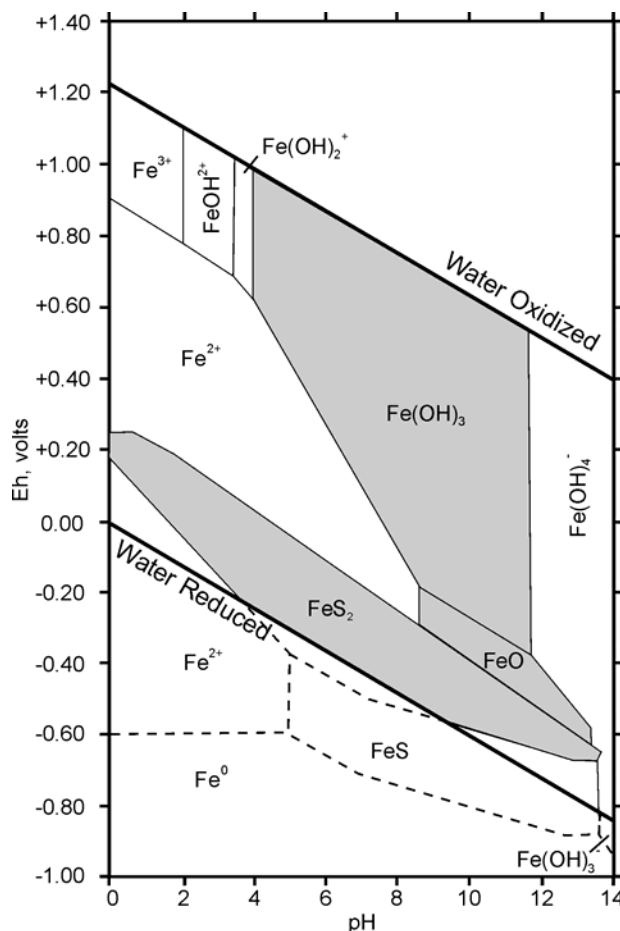


Figure 5.16 Stability field for iron in solution (from Hem, 1985). The shaded areas represent solid phases. (from Hamilton, 1990, Fig. 5.9).

Subgroup B1 - Metalliferous springs in the Meilleur River area

Subgroup B1 is composed essentially of 2 spring locations, 112 and 072; the latter has at least 5 vents, which includes 073. The two spring groups may have many chemical similarities (Fig. 5.17, Table 5.7), 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 these groundwaters coincide

with stream sediment (silt) Zn anomalies in the region (Chapter 4; Spirito *et al.*, 1988).

Spring 072 is located at the base of a ridge formed by the eastward dipping South Headless Thrust Fault mapped by Morrow and Cook (1987), just north of the Meilleur River. 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 group of vents is located downhill along the edge of the riverbank and appears to represent re-emergent waters that drained from the 072 pond above and travelled only through shallow overburden in their short passage. A white sulphate precipitate covers the bottom of the 072 pond and rims 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 of the B group springs (Fig. 5.18).

This assemblage of elements is similar to that of pore waters in the Howards Pass Pb-Zn deposits (Goodfellow, 1989). Zn in waters from springs 072 and 073 in the Meilleur River area is higher than the average values at Howards Pass. 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 Howards Pass.

The total primary flow from the springs is about 15 L/s. Considering the concentrations of metals in the water, the amount of Zn metal 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 equivalent, for example) is being dissolved in the subsurface each year.

The ^{18}O and ^2H data (Fig. 5.13) indicate that the water is unaltered from precipitation under modern climatic conditions. Tritium in the primary vent water 072B indicates relatively young water. Mixing is unlikely because some of the metals are very unstable under oxidizing conditions and would have precipitated at the point of mixing. Thus the overall length of the flow path must be relatively short. These results strongly indicate a large base-metal sulphide body dominated by zinc and lacking in iron sulphides, underlying this site.

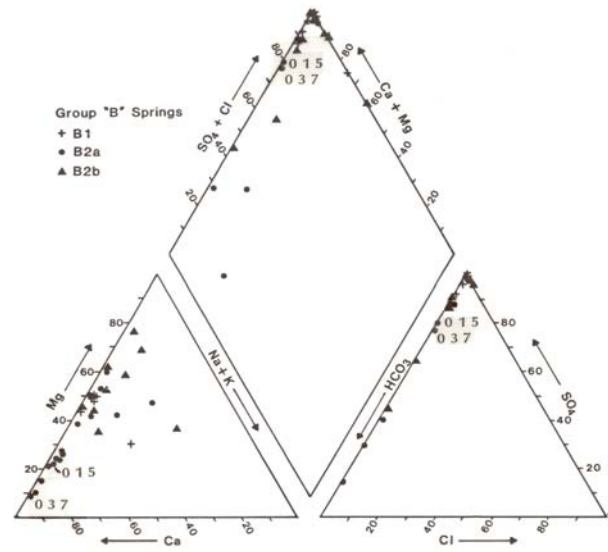


Figure 5.17 Piper plot showing the major ion chemistry of springs from the Meilleur River area (B1), the Ragged Ranges area (B2a) and discharging from the Mattson Formation (B2b). (from Hamilton, 1990, Fig. 5.10)

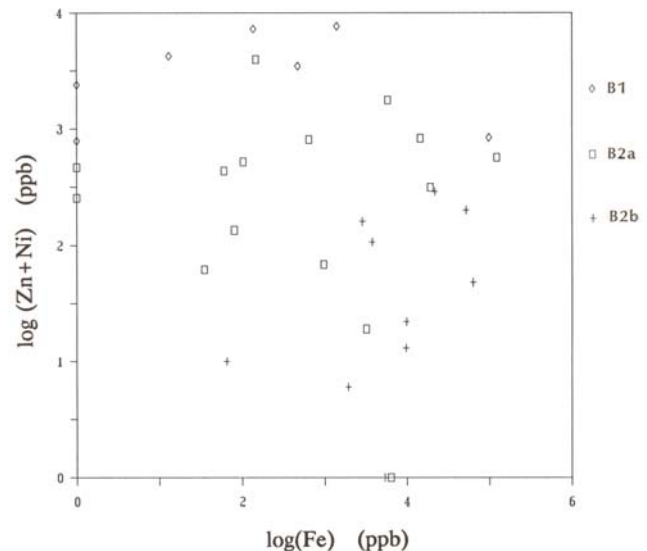


Figure 5.18 Scatter plot of $\log(\text{Zn}+\text{Ni})$ vs. $\log(\text{Fe})$ for the three subgroups from Group B (from Hamilton, 1990, Fig. 5.11)

Several origins are possible for the 072-073 spring waters. They 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 would 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 5.17, Table 5.7) indicates contact with dolomite as opposed to limestone.

Another possibility is that the mineralization 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 deposit types and the presence of Ni and Co could be explained by preferential dissolution. This is a stronger possibility because the relative lack of cation-exchanged Na^+ in the water negates interaction with 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, found in 1987, is also metalliferous. 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 overlie the Arnica Formation. The stratigraphy (including age) of the shale units in this area is poorly understood. Descriptions of each formation are not available as they were mapped as undifferentiated shales, which may include some or all of a number of shale units.

The ^{18}O and ^2H data (Fig. 5.11) indicate local meteoric water. Tritium was found to be below detection level. 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 5.16). 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 were 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 ion exchange by clay minerals. The high Ca^{2+} and Mg^{2+} concentrations and relatively high pH indicate that they also have encountered carbonates (probably dolomite) at some point. The most likely scenario is that the groundwater first encountered 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 and re-precipitating some of the Fe.

A significant quantity of sulphides, other than pyrite, was probably not encountered by the spring waters in their passage through 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 therefore indicates the presence of an iron-sulphide occurrence, probably within shale.

Subgroup B2a - Metalliferous springs in Ragged Ranges Study Area

The Ragged Ranges study area contains 12 springs of Subgroup B2a, located mostly in metamorphosed Road River shales (hornfels) adjacent to plutons within high upland areas. Pyrite is abundant in the hornfelsed shales of the Ragged Ranges and imparts a rusty colour to the rocks. The trace element composition of half the waters in this subgroup (spring samples 015, 035, 037, 054, 103 and 105) appears to be controlled by pyrite mineralization within the hornfels. These springs have very high Fe and Mn and low to moderate concentrations of other trace metals. They have neutral to acidic pH and high SO_4^{2-} . Major ion chemistry is shown in Figure 5.17 and Table 5.7.

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 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 contain significant quantities of Ca^{2+} and HCO_3^- , and very

Table 5.7. Major ion and selected trace element concentrations for Group B springs. See caption to Table 5.6 for details; Appendix 4.1 for field data and Appendix 4.2 for a complete listing of laboratory analyses.

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 ⁺ 0.2 ppm ICP	HCO ₃ ⁻ 0.2 ppm T(c)	SO ₄ ²⁻ 0.2 ppm D	Cl ⁻ 0.05 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 ppt AA	As 0.3 Ppb AA	F 0.04 ppm S
Subgroup	B1																			
86-072A		5	6.29	613	310	18	2.5	115	2403.8	16.83	12	136	2824	4977	2318	<.1	0.2	n/a	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	n/a	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	n/a	1.3
87-073A		4	6.93	363	212	20	(3)	190.9	1609.7	1.09	7	10	15	1613	768	0.4	0.2	n/a	<.3	1.32
87-073B		11.5	5.24	299	175	20	(3)	<0.2	1489.7	1	10	13	3818	2713	1513	0.4	0.6	n/a	<.3	2.18
87-073C		3	7.23	354	206	18	(3)	275.1	1507.7	1	6	<5	18	155	633	0.3	0.2	n/a	<.3	1.36
87-112		3	6.09	397	160	254	(7)	31.9	2122	14.9	5	98100	3098	538	303	0.2	0.2	<1.0	n/a	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	n/a	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	0.1	<1.0	<.3	0.05
87-012B		1	6.95	26	3	<1	<1	12.6	62.9	0.1	11	<5	3	220	35	3	0.2	n/a	<.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	n/a	<.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	n/a	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	n/a	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	<.1	n/a	0.5	0.13
86-036		n/a	4.29	18	1	<1	0.2	<0.2	181	0.1	7	645	534	640	168	<.1	0.2	n/a	n/a	0.1
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	n/a	2.2	0.4
86-042		4	4.92	33	9	<1	0.8	<0.2	140.2	0.19	13	5816	225	1488	273	<.1	<.1	n/a	0.6	0.08
86-049		5.5	4.88	122	26	2	1	<0.2	562.4	0.16	22	122307	856	331	233	<.1	<.1	n/a	<.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	n/a	4	0.19
87-100		0	4.74	8	6	<1	0	<0.2	56.1	0.19	8	80	108	98	38	<.1	<.1	n/a	<.3	0.04
87-103		4	5.8	40	39	38	(11)	365.4	44.6	1.07	11	6363	305	3	<2	0.1	0.1	n/a	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	n/a	<.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	n/a	<.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	n/a	<.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	n/a	0.2	0.15
86-071		7	3.86	92	71	11	0.9	<0.2	611.3	0.6	16	21517	1047	187	103	<.1	<.1	n/a	1.3	0.34
86-078		1.5	7	96	64	<1	2.8	64.9	405	0.29	7	63347	1180	15	34	<.1	0.2	n/a	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	n/a	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	n/a	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	n/a	<.3	0.04
87-109		0	6.63	25	45	12	(4)	122.5	168.4	1.7	12	5373	250	3	<2	<.1	<.1	n/a	0.3	0.36
87-121		4	3.76	17	16	<1	0	<0.2	211	0.24	15	3763	313	58	50	<.1	<.1	1.2	<.3	0.11

high SO₄²⁻, 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 the accompanying carbonate, would cause increasing concentrations of Ca²⁺, Mg²⁺, SO₄²⁻ and Fe as seen in springs 015 and 037. The relatively high pH is due to

dissolution of carbonate. The Road River Group and overlying Carboniferous unit are calcareous in places.

It is unlikely that the above-described springs in Subgroup B2a have been in contact with significant quantities of base metal sulphides. However, the other half of the waters in Subgroup B2a (springs 012, 025, 036, 042, 049 and 100) have compositions that record dissolution of pyrite and trace metals. Those waters with very high zinc (springs 25 and 42) may have come into contact with significant amounts of lead-zinc sulphides; nevertheless these together with those containing moderate amounts of zinc could mainly be a

product of preferential hydromorphic adsorption of zinc at surface by the iron and manganese which act as geochemical “sponges”.

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 Spring 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 is 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 was 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 Spring 036 was sampled drains an extensive 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 Spring 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 Subgroup 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, near the “MB” tungsten mineral showing, 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-} also is elevated relative to the other major ions and the pH is low. The presence of a mineral deposit in this location previously was known. However this demonstrates that waters with low TDS contents can detect nearby base metal sulphides.

Because all the springs and surface waters in Group B2a probably are 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.

Subgroup B2b - Metalliferous 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, and 121) and are discharging from or near 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, while 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 outcrop areas of the formation. This is the only example in the study area where the

location of springs shows obvious stratigraphic control. The springs have a floccular Fe-hydroxide precipitate near the vent. Some also have a cemented, tufa-like precipitate probably composed of Fe-hydroxides.

Waters from the Mattson Formation, particularly from the Tlogotsho Plateau area, have low pH, high SO_4^{2-} and high to very high Fe concentrations. Also, for unknown reasons, Mg^{2+} is unusually high in most of these springs, as indicated in Figure 5.17. 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 (Fig. 5.18) 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 metallic mineral deposits within the Mattson Formation.

5.5.4. 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 and extend almost to the park boundary. Five springs were sampled in this group (017, 055, 056, 057 and 058). Three more were 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. The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values (Figure 5.11) plot very close to the local meteoric water line (LMWL), 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) was emitted at each vent. The major ion chemistry (Figure 5.19, 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 5.8). 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 sharply with increasing distance from the vent due to exsolution of CO_2 . The

$p\text{CO}_2$ values at the vents are very high, with values above 1 bar (Figure 5.20).

All of the unusual chemical characteristics of these springs result directly or indirectly from the

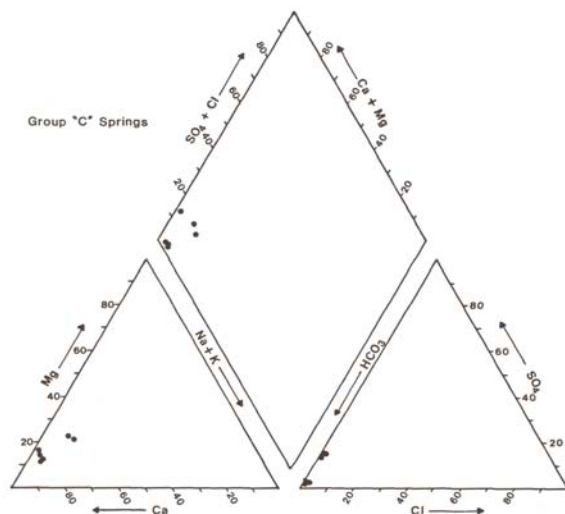


Figure 5.19 Piper plot of the major ion chemistry of waters in Group C. Concentrations of the dominant ions are very high (Appendix 4.2). (from Hamilton, 1990, Fig. 5.12).

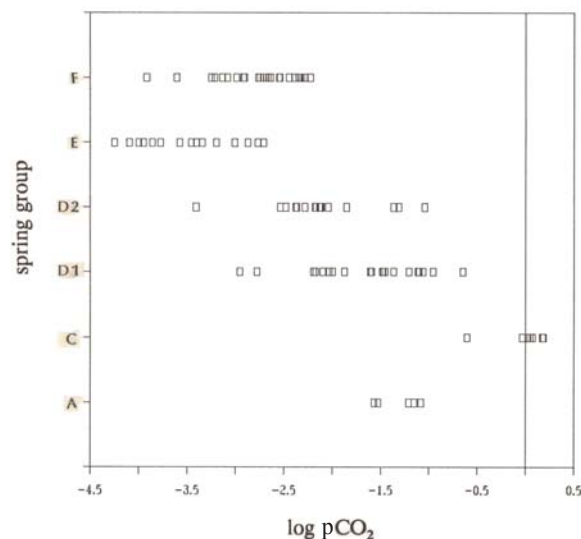
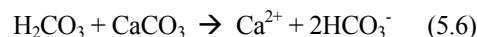
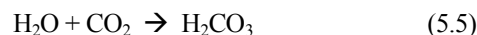


Figure 5.20. Calculated partial pressure of CO_2 for all samples in the non-acidic groups (i.e., Group B is omitted). Calculations are based on concentrations of carbonate species and pH at the time of sampling. (from Hamilton, 1990, Fig. 5.13).

presence of excess CO_2 . The dissolution of limestone is aided by CO_2 according to the reactions:



The exsolution of CO₂ at the surface causes these reactions to reverse and CaCO₃ to be 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 5.21 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) 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.

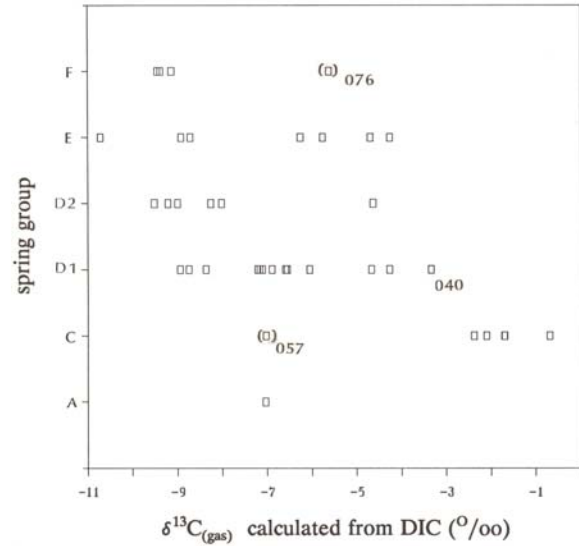


Figure 5.21 $\delta^{13}\text{C}_{(\text{gas})}$ calculated from $\delta^{13}\text{C}_{(\text{DIC})}$ for springs in various groups. (from Hamilton, 1990, Fig. 5.14)

Table 5.8. Major ion and selected trace element concentrations for Group C springs. See caption to Table 5.6 for details; Appendix 4.1 for field data and Appendix 4.2 for a complete listing of laboratory analyses.

Element DL(ppm)	Temp. N/a	pH n/a	Ca ²⁺ 1	Mg ²⁺ 1	Na ⁺ 1	K ⁺ 0.2	HCO ₃ ⁻ 0.2	SO ₄ ²⁻ 0.2	Cl ⁻ 0.05	SiO ₂ 2	Fe 20 / 5	Mn 10 / 2	Zn 5	Ni 2	Mo 0.1	W 0.1	Au 1	As 0.3	F 0.04
units	(°C)	n/a	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppb	ppb	ppb	Ppb	ppb	ppb	ppt	ppb	ppm
method	n/a	(field)	ICP	ICP	ICP	ICP	T(c)	D	D	ICP	AA	AA	AA	AA	ICP	ICP	AA	AA	S
86-017	5.5	6.27	791	68	60	8.1	2428	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	6.1	782	138	119	38	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	6.2	647	66	32	5.6	1918	38	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	3.1	13	<5	275	8	<2	0.2	0.3		<3	0.38

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 authors consider the range of mantle-derived CO₂ to be -8 to -4 ‰ and that values above this indicate a metamorphic source. Thermal metamorphism of carbonates produces CO₂ 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 CO₂.

"Soda springs", such as those in Group C, are known elsewhere in Canada and the world. Global compilations of known CO₂ discharges by Barnes *et al.* (1978,1984) indicate that CO₂ discharge occurs 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 CO₂ 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 CO₂, 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 metamorphic CO₂ appears to

be mixing with volcanogenic CO₂. $\delta^{13}\text{C}_{(\text{gas})}$ 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. There is no evidence that water-rock interaction has occurred (Fig. 5.20). If they had, 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. This suggests that a separate CO₂-rich (low in water) metamorphic fluid is travelling upward from depth and mixing with shallow meteoric water.

Figure 5.22 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 forming a linear pattern is to have a large fault acting as a conduit. Barnes *et al.* (1984) noted such localization of CO₂ discharges along major faults in California, including segments of the San Andreas Fault. Although no fault was recognized in the valley during the GSC reconnaissance scale mapping of the mid 1960's, evidence for one was found during a follow-up B.Sc. study (Timlin, 1991; Hamilton *et al.*, 1991).

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 could 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, Mine. 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 take place, releasing large quantities of metamorphic CO₂. For 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. Heat transfer would likely be conductive rather than convective as the flux of present-day fluids is 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 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.

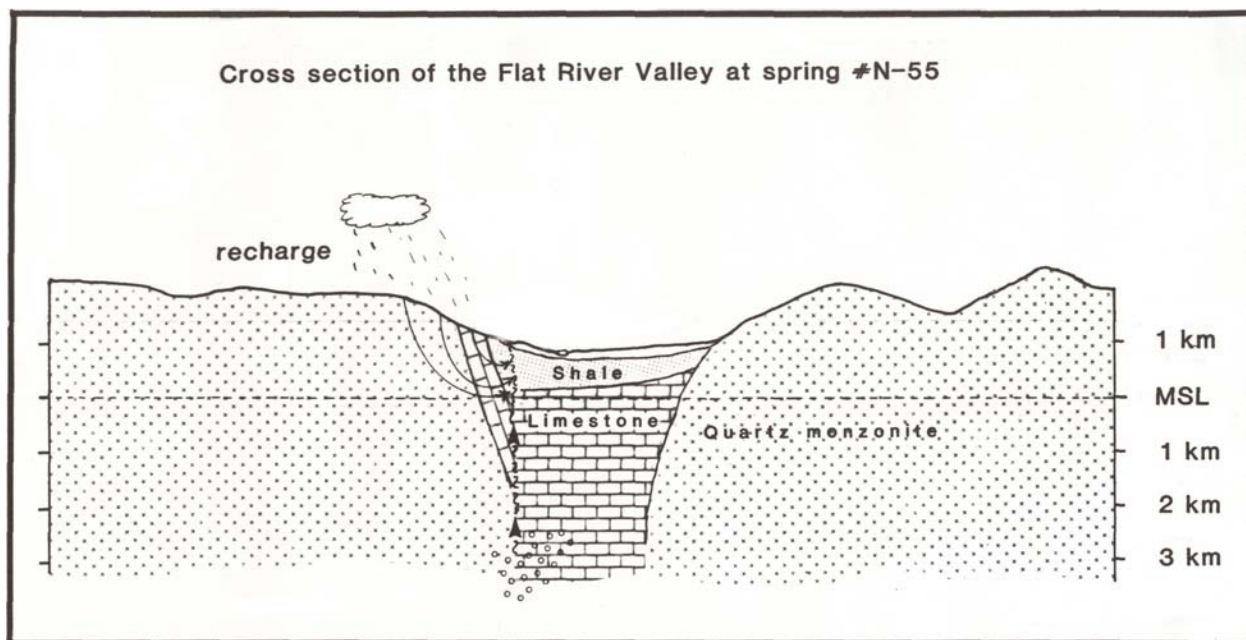


Figure 5.22 Cross section of the Flat River valley showing the possible model for the origin of CO₂ rich fluids. CO₂ is produced in the shallow crust by metamorphism of carbonates in contact with Cretaceous plutons. The CO₂ travels upward along an inferred fault and mixes with shallow meteoric water. The waters dissolve large quantities of carbonates which are re-precipitated on surface upon discharge. (from Hamilton, 1990, Fig. 5.15).

5.5.5. Group D - High TDS springs in carbonate terrane

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. Group D1 contains a number of thermal, fault-controlled waters and a group of non-thermal waters. The two groups will be dealt with as Subgroups D1a and D1b.

The major ion chemistry for all D1 waters is shown in Figure 5.23. The waters generally exhibit elevated concentrations of major ions (Table 5.9). 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, including Fe, are usually very low. The pH is generally below neutral but rises, in all cases, after the waters leave the vent.

The pCO₂ values are consistently lower in this group than in Group C (Figure 5.20), however; spring 040 has a considerably higher pCO₂ than the other springs in Group D1. The δ¹³C values are also

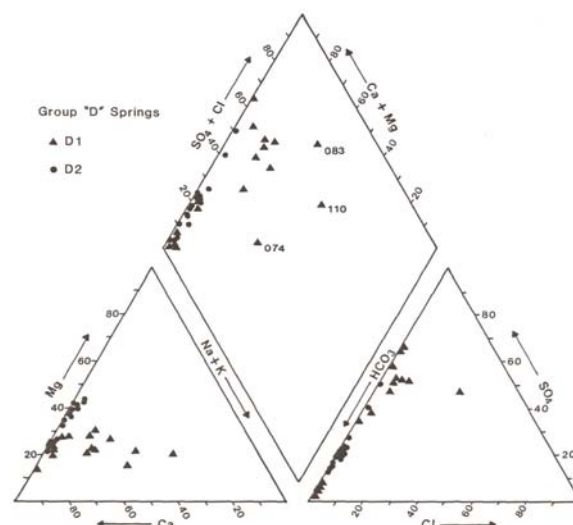


Figure 5.23 Piper plot of major ion chemistry of Subgroups D1 and D2. Concentrations of the major ions are moderate to high. (from Hamilton, 1990, Fig. 5.16).

uniformly lower in this group than in Group C and Spring 040(=041) is, again, anomalously higher. The lower pCO₂ and δ¹³C values for D1 waters indicate a smaller input of CO₂ and that this CO₂ is less likely to be metamorphically derived.

The ^{18}O and ^2H data show no evidence of water-rock isotope exchange and the waters plot on the LMWL (Fig. 5.11). This indicates that the waters have not experienced very high temperatures. Sample 021 plots close to the LMWL but is considerably more depleted in both ^{18}O and ^2H than any of the other samples in the study area.

Subgroup D1a, fault localized thermal springs

The springs in Subgroup D1a (001, 021, 027, 029, 030, 040, 041, 043, and 82) range in temperature from 14 to 49°C and precipitate large deposits of tufa. The only, arguably, 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), and spring 001 was the subject of the M.Sc. study by Gulley (1993).

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 precipitate large deposits of tufa.

Table. 5.9 Major ions and selected trace element concentrations for Group D springs. See Appendix 4.1 for field data and 4.2 for a complete listing of laboratory analyses.

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		0.3	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	0.4	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	0.8	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	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	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	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	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	0.1	2.6	<3	0.4
Subgroup D1b																			
86-010	22	8.15	114	19	1	0.2	227	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	1.17	6	337	92	61877	65	0.6	<1		49.6	0.49
86-074	16	7.4	179	57	146	8.8	672.6	301.1	0.51	15	465	653	58	16	0.8	<1		0.8	0.06
86-083	3.5	8.1*	228	45	184	4.6	254.6	451	212.65	17	5179	437	15	<2	3	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	<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	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	0.1
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	0.2		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	0.4		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	0.21
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	93	29	2	3.8	254	81.7	0.91	51	460	23	<5	<2	1.4	0.2		2.4	0.42
86-046	8	7.8	71	33	2	1.4	239	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	2.47	13	72	<10	13	<2	3	0.2		0.6	0.23
86-061	8	7.37	56	27	2	0.6	207.8	31.3	0.5	6	1817	123	<5	3	0.6	0.1		0.5	0.2
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	0.66	4	<5	<2	<2	<2	0.6	<1		<3	0.09
87-113	8	7.96	79	24	<1	0	304.6	32	0.49	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	87.2	0.32	8	<5	<2	58	<2	15.3	<1	<1.0	<3	0.21
87-126	6	7.4	49	15	<1	0	199.5	15.8	0.8	5	523	10	10	<2	2.8	<1		0.3	0.16

Tritium was measured in Springs 001 and 040. It was detected in 001 (34 +/- 8 T.U.), possibly due to mixing with younger waters in the shallow subsurface. Spring 040 had undetectable tritium and the highest temperature recorded in this group (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 an 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 pCO₂ and δ¹³C values of Sample 040 suggests possible input of metamorphic or mantle CO₂, 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 structure. The anomalously low δ¹⁸O and δ²H concentrations reported above suggest possible recharge during a cooler climatic period or preferentially from a high altitude snow pack. Tritium is barely above the detection limit (11 +/- 8 T.U.). Its presence may be due to contamination from rainwater that had fallen just prior to sampling or could reflect a relatively young age.

Spring 043 and a number of unsampled thermal springs are located in an area of complex structure near Grizzly Bear Lake and are probably fault-controlled. Springs 027 and 029 of Group D1a and Spring 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 (37°C) was discovered during the 1986 field season and re-visited during 1987. It has since been visited by NNPR personnel who have tentatively named it the "White Aster Hot Spring". It is described here in more detail because it has not been reported previously in published literature and it has important implications for 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, though 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 of non-decomposed plant matter (leaves and moss) and wood with a modern ¹⁴C 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. The Ca²⁺, Mg²⁺, HCO₃⁻ and SO₄²⁻ 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 H₂S odour suggests it is fairly low in the immediate subsurface.

In addition to the buff coloured tufa being precipitated at Spring 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 that settles around the vents to form a thick mud which has completely filled the uppermost of the three large vents.

The 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 listed in Appendix 4.2, Table A-4.2(v). Hamilton's (1990) review of them indicates that the 082 trace metal results are far higher than any of the others, including 082y, which is the travertine from the same spring.

Although much 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. 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 (>1 km) 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 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 member of Subgroup D1a and differs from all the others in that the waters are not thermal (7°C). It is located several kilometres south of Spring 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 Spring 082, probably because of the lower temperature. The high SO_4^{2-} concentrations are nearly identical with Spring 082, but Na^+ and Cl^- are virtually absent. The zinc and nickel concentrations in waters from Spring 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. Lead values also are elevated in the tufa, while uranium values are elevated in the water (Appendix 4.2).

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 Spring 082 and the waters 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.

Subgroup 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. Numerous 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 D1b and Spring 116 of Group E have had their chemistry altered by cation exchange within shales. Springs 074 and 110 discharge directly from shales, whereas Spring 116 is an apparently spring-fed pond in shale terrane. Waters at Spring 074 precipitate unidentified (highly soluble) salts on the bedrock and those at Spring 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 chalcopryrite. 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 with Group D1.

Subgroup D2 - Moderate TDS springs in carbonate terrane

Subgroup D2 is made up mostly of Ca-HCO₃⁻ dominated springs, some of which are thermal and some of which are fault-controlled. The major difference between Groups D2 and D1 is the lower concentration of major ions, which results in part from lower pCO₂ (Figure 5.20).

The Ca²⁺ and HCO₃⁻ 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 SO₄²⁻ and Na⁺ are lower (Figure 5.23, Table 5.9). Some of these springs discharge from overburden (007, 022, 024, 061, 081 and 102). The elevated TDS levels probably result from dissolution of carbonates by soil CO₂ 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 5.5.7.

5.5.6. Group E - Thermal springs related to quartz monzonite

The physical features associated with Group E are given in Appendix A-4.1.3. Six are classified as hot springs (018, 033, 038, 052, 053 and 060) with temperatures ranging from 42°C to 65°C and all have been previously reported (Crandall and Sadler-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 Spring 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 that are also thermal. The flow rates of these springs vary considerably. Total flow from "CanTung West" (018) exceeds 25 l/s while the flow from "CanTung East" (060) in 1986 was 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 5.24 and Table 5.10 show the major ion chemistry for the group. The waters are Na-HCO₃ dominated, with the exception of Spring 019 which has a higher proportion of Ca²⁺ than Na⁺ and high SO₄²⁻. Sample 019 comes from a drill hole in the mine, which intersects a large fault zone.

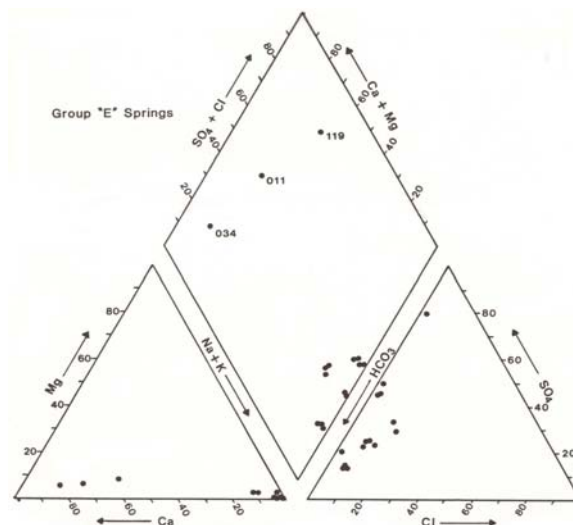
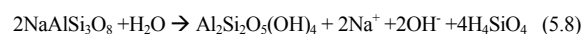


Figure 5.24 Piper plot showing major ion chemistry for springs in Group E. Concentrations are relatively low. (from Hamilton, 1990, Fig. 5.17).

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. Tungsten (W) is very high in concentration.

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 dissolution 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 the other spring groups, ¹⁸O and ²H data (Figure 5.11) in Group E indicate that groundwaters are meteoric, and that there is no evidence of water-rock exchange. Tritium was analyzed for Samples 018, 033, 053 and 060. It was undetected in Samples 033 and 060 (<6 T.U.), Sample 018 had 7 +/- 8 T.U. and Sample 053 had significant tritium (15 +/- 8). This may indicate that the water discharging from Spring 053 is less than 35 years old, but more likely indicates mixing with shallow meteoric water.

The mechanism for heating the water is simple, provided a high heat flow can be assumed within the intrusions. 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 eventually discharges in an adjacent valley.

Using the same assumption for heat flow as for Group C, 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 air temperature ($< 0^{\circ}\text{C}$), the estimated average groundwater temperature of $< 7^{\circ}\text{C}$ and a mine water temperature (CanTung mine) of 16°C . The mine adit is only a few hundred meters below the surface of the mountain.

Elements such as Mo and W in the thermal spring waters suggest that the host plutons are associated with scheelite- / molybdenum-bearing skarns. 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. Spring 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 are all elevated and As is above detection, despite the low TDS content of the sample. The waters also have elevated Na^+ , although Ca^{2+} dominates. These characteristics strongly indicate that the waters from Spring 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 plutons, they spatially superimposed various data sets. They analyzed Landsat images for associated faults and fractures. Stream sediment data indicated increased concentrations of associated elements (similar to the element assemblage in the hot springs), and stream water geochemistry provided evidence of hornfelsed slates (increased metals and decreased pH).

A more direct economic potential of these hot springs is as a geothermal resource. Some of the springs produce large quantities of water, some of which may discharge through the overburden in the shallow subsurface. Any new communities, perhaps related to the mining industry, could tap these resources. Using modern heat-pump technology the larger springs could help to heat communities and thereby greatly reduce the use of fossil fuel. Significant savings and reduced pollution could also be realized in the mining plant operations.

Table. 5.10. Major ion and selected trace element concentrations for Group E springs. See Appendix 4.1 for field data and 4.2 for a complete listing of laboratory analyses.

Element DL(ppm)	temp. n/a	pH n/a	Ca^{2+} 1	Mg^{2+} 1	Na^+ 1	K^+ 0.2	HCO_3^- 0.2	SO_4^{2-} 0.2	Cl ⁻ 0.05	SiO_2 2	Fe 20/5	Mn 10/2	Zn 5	Ni 2	Mo 0.1	W 0.1	Au 1	As 0.3	F 0.04
Units method	($^{\circ}\text{C}$) n/a	(field) n/a	ppm ICP	ppm ICP	ppm ICP	ppm ICP	ppm T(c)	Ppm D	ppm D	ppm ICP	ppb AA	ppb AA	ppb AA	ppb AA	ppb ICP	ppb ICP	ppt AA	ppb AA	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		0.5	1.33
86-018	41	8.17	8	<1	60	1	105.3	26	6.48	47	<20	<10	<5	<2	8	59.6		1.8	4.09
87-018	41	8.6	6	<1	50	<1	100.8	25	6.59	39	<5	3	<2	<2	9.1	75.1		1.9	4.27
87-018B	43.7	8.6	7	<1	55	<1	109.4	28.3	7.48	43					9.9	83	7.8	1.8	4.71
86-019	16	8.38	36	4	22	0.3	28.2	92	2.09	26	199	37	<5	<2	8.1	21		5.2	1.1
86-020	16	8.48	4	3	115	0.9	144.1	60.2	25.17	38	65	<10	<5	<2	1.1	169		<2	9.31
86-033	58	9.05	2	<1	80	1	103.9	69.3	1.44	63	36	<10	<5	11	19	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	5	0.3	2.94
87-034	5	8.2	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	224		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	14.9		23.7	2.62
86-053	47.5	7.86	1	<1	31	0.5	63	8.7	2.18	70	72	<10	8	4	21	17.6		25.5	2.77
87-053	46	9.13	1	<1	28	<1	50.7	6.6	1.9	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	121		0.5	6.53
87-060	46	9.3	2	<1	67	(2)	7	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	3.8	<2	105	<2	5	<2	0.4	<1		0.4	0.91

5.5.7. Group F - Low TDS spring 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 5.25, Table 5.11) and are situated in carbonate terranes. Eleven of the 25 samples are known or suspected to be surface water (009, 050, 068, 077, 101, 104, 117, 118, 120, 124 and 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 anomalous 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 in the region.

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.

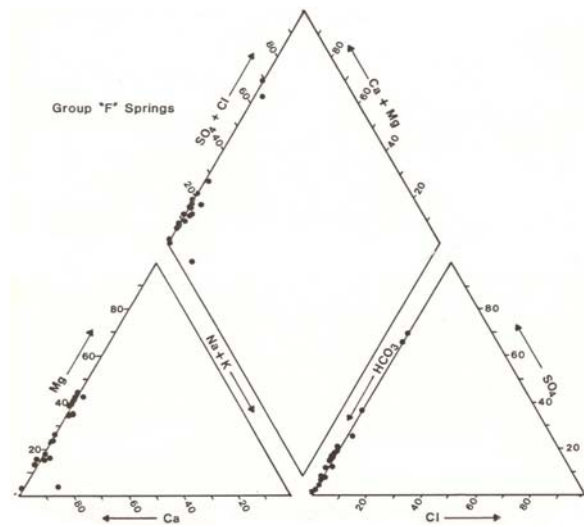


Figure 5.25 Piper plot of the very low TDS waters of Group F. (from Hamilton, 1990, Fig. 5.18).

Table 5.11. Major ion and selected trace element concentrations for Group F springs. See Appendix 4.1 for field data and 4.2 for a complete listing of laboratory analyses.

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	0.2	0.2	0.2	0.05	2	20 / 5	10 / 2	5	2	0.1	0.1	1	0.3	0.04
units	(°C)	n/a	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppb	ppb	ppb	ppb	ppb	ppb	ppt	ppb	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	8.3	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	7.6	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	0.64	4	<20	<10	<5	<2	1	0.2		32.9	0.14
86-028	10	7.6	63	13	<1	0.7	206	12.9	0.34	6	<20	<10	<5	<2	2	0.2		0.2	0.12
86-044	32	7.75	35	19	<1	0.8	132	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	0.09
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	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	0.1
86-068	3.3	8.03	33	18	<1	<0.2	132	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	1.6	<2	337	<10	36	<2	0.3	0.1		0.3	0.1
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	7.5	30	14	1	-1	130.3	23.2	0.28	8	<5	<2	<2	<2	0.3	<1	1	0.3	0.12
87-107	4	7.5	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		0.1	
87-118	3.5	8.2	31	14	<1	0	138.4	19.1	0.27	<2	<5	<2	10	<2	1	<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	0.4	0.1
87-120	2	7.79	49	21	1	-1	215.1	31.8	0.3	3	<5	<2	5	<2	1.4	<1	1	<3	0.12
87-124	18	8.2	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

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 host gas and Mississippi Valley type Pb-Zn occurrences (Morrow et al. 1990).

Extensive karst topography has developed in the carbonates and was described by Brook (1976). Five springs (065, 066, 075, 076 and 119) and a number of surface waters were sampled in the Nahanni Karst area. Four of these springs (except 119) are thought to be related to karstic flow systems.

Two of the springs sampled have very high flow rates, resembling large streams or small rivers. 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. Dead drainage areas are widespread on the Ram Plateau further to the north. Surface and subsurface karst is being developed. A conservative estimate of carbonate removed from the area yearly by these two springs alone is 53,000 tonnes.

The waters in this area are Ca-HCO₃-dominated, however, detectable Zn, Cu, Co and Ni are found in all five of the springs sampled. 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, located in the Nahanni Formation carbonates, 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 are located within Manitou Facies dolomites.

Three springs from Group D2 (114, 115, and 125) also discharge in the Nahanni Karst area. Sample 125 discharges near "first polje" and was mentioned by Brook (1976). It has slightly elevated zinc levels 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 that 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. All three have high Ca²⁺, Mg²⁺ and HCO₃⁻ concentrations. Spring 115 also has high SO₄²⁻ and detectable Na⁺ and Cl⁻ concentrations.

Springs 114 and 115 are of particular interest because they occur very near stream-sediment gold anomalies. Spirito et al. (1988) and Jefferson and Paré (1991) suggested nearby fault or fracture associated lode gold as a possible source. On the other hand, we now consider glacial transport from the Great Slave Lake area as a more likely source for the placer gold. Nevertheless, the chemistry of the waters suggests probable fault-control, which is unusual in this area of mostly karstic flow systems. Elevated gold was found in one water sample from Spring 114 (3.7 ppt). The five other springs and surface waters (115, 119, 120, 125 and 128) in the karst area, which were analyzed for gold had concentrations at, or below detection levels (1.0 ppt). The significance of these results is unclear due to the small quantity of Au data.

5.6. Hydrogeological Conclusions

5.6.1. Classification of springs

The three study areas 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 employed, of which cluster analysis was found to be the most suitable. Cluster analysis produced groups based on similar characteristics to those produced by the other two methods, but some springs were assigned differently. The classification has six major groundwater types. Each group of waters records different flow histories or different hydrogeochemical processes in the subsurface, summarized as follows (see also Table 5.5).

- A** brackish, high sulphate waters of the Clausen Creek area (Kraus Hot Springs).
- B** Waters that encountered iron and base-metal sulphides which, upon oxidation, have produced low pH (acidic), high iron and high sulphate waters. Three sub-groups in B are:
 - B1 metalliferous springs in the Meilleur River area,
 - B2a metalliferous springs associated with hornfelsed shales of the Ragged Ranges,
 - B2b metalliferous springs associated with pyrite-rich sandstones of the Mattson Formation.

- C Very distinct, high $p\text{CO}_2$, high alkalinity springs in the upper Flat River Valley, interpreted as being influenced by an external input of metamorphic CO_2 in the subsurface.
- D Fault-localized hot springs and other tufa-precipitating springs that have characteristically high TDS contents, but low trace metal concentrations.
- E Thermal springs spatially and geochemically associated with Cretaceous quartz monzonite intrusions in the Ragged Ranges study area.
- F Waters of low TDS values, generally Ca^{2+} and HCO_3^- dominated; includes most surface waters and springs with karstic flow systems.

5.6.2. Details of Final Spring Water Classification (see also Table 5.5)

The most distinct group identified by all three methods comprises the Clausen Creek samples, Group A (equivalent to P4, T7 and C1). It contains 5 samples, all of which have elevated NaCl. Sample 122 has been added to this group. It is located directly across the river from 063 and 064, and has a similar suspended sulphate precipitate in the water, and 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).

Sub-groups B1 and B2 contain waters from C2 and C4, respectively, and 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. B1 waters are akin to B2 but distinguished by very high metal concentrations.

The final sub-groups B1 and B2 include a number of samples that were assigned to other groups by Field, Tree and/or Cluster methods. Spring 012B was in Group C8 but is here included because it is similar in character to waters from 012A and 012C except for recording dilution 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 relatively high trace metals, Fe and is acidic.

Waters of Group C are consistent with the C3 group and comprise the high $p\text{CO}_2$, high alkalinity

springs of the upper Flat River Valley. Seven samples from 5 different springs were part of 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 much greater. They are not included as a more extreme example of Group D because they are genetically different.

Group D1 comprises waters that are supersaturated with respect to calcite (they precipitate tufa) and are mostly thermal. The group originates from Group C5. Group D2 comprises waters that appear to be similar to Group D1, but with only moderately high Ca^{2+} and HCO_3^- concentrations that are slightly above or below saturation with respect to calcite. Group D2 was initially defined by cluster analysis (C7) and is roughly equivalent to the "trees" group T2.

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 that probably cannot be further subdivided. It includes all surface water samples except for acidic streams.

5.6.3. Anomalous springs and areas of special interest (Table 5.12)

In the Ragged Ranges study area, four B2-type springs are high in trace metals such as Zn and Ni. Springs 012, 025 and 100 have Zn-dominated trace metal anomalies and Spring 049 is Fe dominated. Spring 100 is associated with the "MB" skarn W (tungsten) showing (base metals are typically associated with tungsten skarns). Springs 012 and 025 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 along the groundwater flow path, although it is probably pyrite dominated.

Group E hot springs are restricted to the Ragged Ranges study area and are related to the quartz monzonite intrusions. The major and trace element composition of this group of waters is highly distinctive. 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.

Thermal waters at this latitude are a potential geothermal resource. These low-temperature hot springs can be used to heat buildings utilizing modern heat-pump technology.

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. These are located within a belt of eastward and westward dipping thrust faults, the South Headless Fault forming the eastern boundary of the Meilleur geologic domain.

Springs are situated in several different formations and comprise several different types but three show high to very high concentrations of metals. 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.

Spring 112 is the other B1 representative. 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 shallow, pyrite-dominated, sulphide-rich body is located along the flow path of Spring 112 waters. 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.

In addition to the metalliferous springs of the Meilleur Domain, a large, world-class hot spring (082) was located during the 1986 field season in this region. This spring, informally named "White Aster Hot Spring" by park personnel, is a resource in itself because of its beauty and unspoiled nature, and it has a 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 have been 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 CaCO_3 tufa that is precipitated 50-100 m from the main vents toward the Meilleur River, 700 m north. The distal precipitate contains almost no metals, but the proximal precipitate has the highest metal values of any precipitates in the region, especially zinc, 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. Its waters and tufa also contain elevated concentrations of Zn and other metals (Appendix 4.2, Table A-4.2(v)).

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. Based on spring data alone, the Arnica Formation in the Meilleur River area (which as mapped, may include the Sombre Formation) has a high potential for base-metal sulphides, possibly of the Mississippi Valley and Sedex deposit types. The parallel stream silt survey conducted during this project also shows this region to be anomalous in Zn (Spirito *et al.*, 1988; Chapter 4, section 4.7 of this report).

The Nahanni Karst study area produced few highly elevated trace metal concentrations. The zinc and nickel concentrations are higher in Group F waters in this area than elsewhere in the study areas, for example Spring 66 with 40 ppb Zn which, given its high volume and limited transit time, may indicate 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 that were sampled in the karst area are from springs 114, 115 and 125. Samples 114 and 115 were collected on "Wretched Creek" in an area dominated by normal faulted (near vertical fault planes) 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, gold anomalies in heavy mineral concentrates from stream sediments may be derived from unknown fault- and fracture- related lode gold deposits nearby. Gold in the water of Spring 114 is higher than background but the significance of this is unclear because of insufficient data.

East of the Nahanni Karst study area, at Nahanni Butte, a significant Zn anomaly in Group F waters of Spring 107 is close to the Nahanni Butte vein Zn-Cu occurrence (Appendix 1), suggesting that this type of mineralization extends down into the flow path of the spring waters.

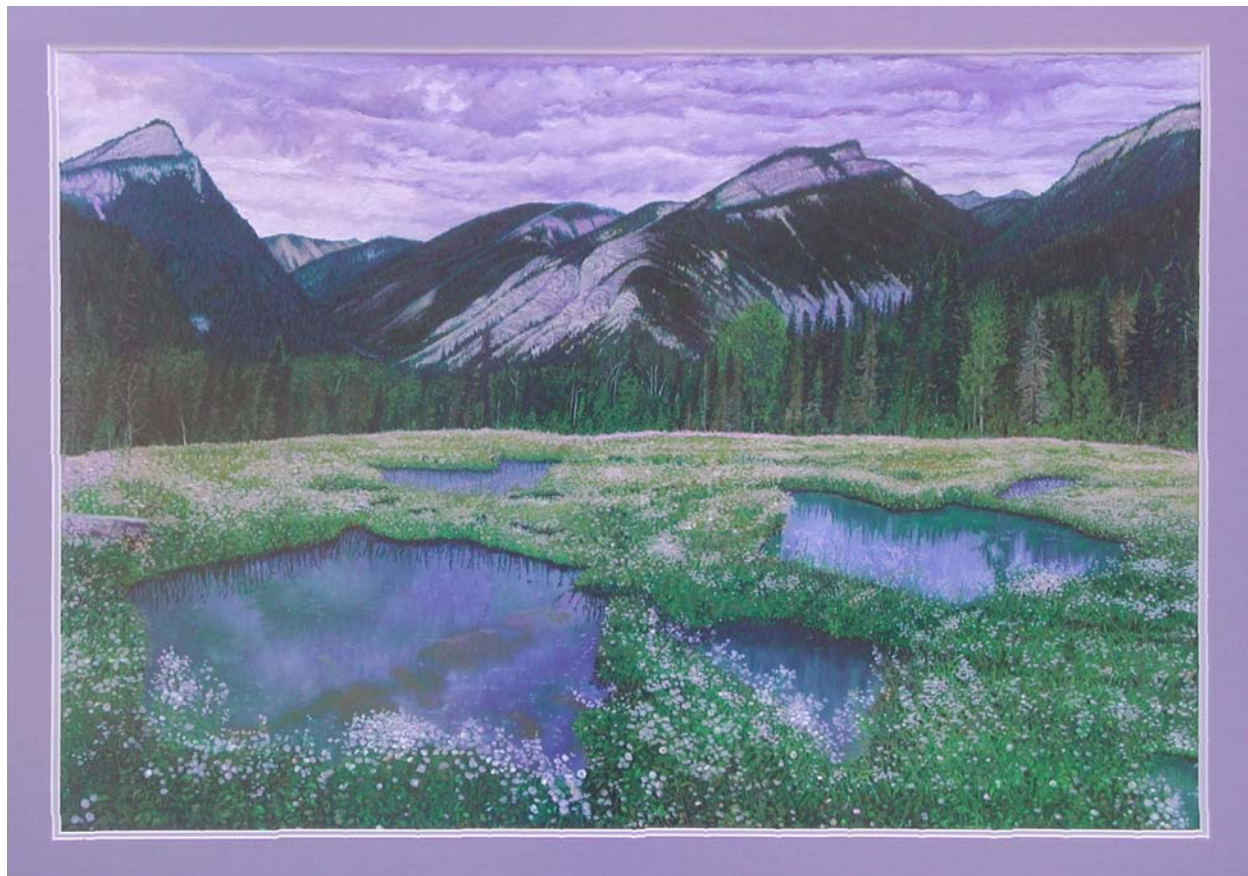


Figure 5.26. View looking north over “White Aster hot spring” (#082), the largest of the thermal and hot springs discovered during the 1986 and 1987 field seasons (Hamilton et al., 1985). This is reproduced with permission of the painter, Chuck Blyth, Park Warden of NNPR, and was purchased by Charlie Jefferson. This spring complex is located in a remote area near the Meilleur River, west of Headless Range.

Table 5.12. Summary of interesting and/or geochemically anomalous ground waters in the South Nahanni River Region. All but four (Nahanni Butte well water, Prairie Creek Mine water and 2 CanTung Mine waters) are from natural surface springs. **Classifications** (*): P: Physical, Field ; T: Kleiner-Hartigan "trees"; C: Cluster analysis; **Final: see text, Section 5.5**. Special attributes of waters (Sp**) are: >20° = hot (hs), 7-20° = thermal (t), <7° = cold (c), high Total Dissolved Solids (TDS) = (hi), low TDS = (lo), high iron = (Fe), CO₂ bubbles = (c), fault-related = (f), well water = (w), mine water = (m). Primary data are in Appendix 4; selected geochemical data are in Tables 5.6 to 5.11 inclusive for each of the final classification groups A through F.

Spring = Sample #	Longitude	Latitude	Classifications*	Geological	MERA	T	Anomalous / High Metals	Strong (some) Park Attribute or
#Name	° min Sec	° min sec	P T C Final	Sp** Host Rock	Domain	°C	Decreasing Abundance →	Mineral Deposit Type Signature
001 Rabbitkettle	127 11 23	61 56 30	P1 T2 C5 D1	hs,f shaley carbonate	Broken	21.0		Tufa travertine - scenic beauty
010 unnamed	127 39 27	62 21 20	P6 T9 C7 D1	hs shaley carbonate	Broken	22.0	U, Mo, Ni	Tufa travertine mounds (skarn / Sedex)
011 unnamed	127 47 31	62 11 00	P3 T6 C6 E	t qtz monzonite	Ragged	14.7	Zn, Mo, U, W, F	(very weak tungsten skarn)
012 unnamed	127 50 24	62 07 54	P2 T5 C4 B2	Fe shale	Ragged	1.1	Zn, Ni , Co, Cu, Cd, U	Sedex lead-zinc-silver
013 unnamed	127 41 22	62 03 41	P6 T1 C8 F	lo qtz monz / shale	Ragged	2.1	As	(vein gold?)
015 Glacier Lake	127 35 26	62 05 30	P2 T4 C8 B2	Fe shale	Ragged	3.5	Fe, Zn , Mn, Ni, Co	Sedex lead-zinc-silver
018 CanTung West	128 13 20	61 56 58	P3 T6 C6 E	hs qtz monzonite	Ragged	41.0	W, Mo, F , As, Au	tungsten skarn
019 CanTung Mine	128 15 09	61 57 44	P3 T6 C6 E	t,m qtz monzonite	Ragged	16.0	W, Mo, As , F, Ag	tungsten skarn
020 CanTung Mine	128 15 09	61 57 44	P3 T6 C6 E	t,m qtz monzonite	Ragged	16.0	W, F, Mo , Ag	tungsten skarn
021 unnamed	127 51 21	62 13 12	P1 T3 C5 D1	t shaley carbonate	Broken	17.0	Fe, Mn, As , U	(?vein gold?)
025 NW Glacier L	127 34 53	62 07 36	P2 T5 C4 B2	Fe Shale	Ragged	5.0	Zn , Mn, Fe	Sedex lead-zinc-silver
027 Wild Mint	126 34 36	61 25 29	P1 T2 C5 D1	hs,f shaely carbonate	Ragged	25.0		scenic tufa hot spring
028 Old Pot	126 29 28	61 31 55	P1 T1 C8 F	hs shaley carbonate	Ragged	28.0		scenic tufa hot spring
032 Moore's	128 09 16	62 20 10	P6 T2 C7 D2	hs,f shaley carbonate	Broken	54.0	Fe	scenic tufa hot spring – "Honeymoon"
033 unnamed	128 40 59	62 22 17	P3 T6 C6 E	hs qtz monzonite	Ragged	58.0	Mo, W, Cu	(tungsten skarn)
034 unnamed	128 40 59	62 22 17	P3 T6 C6 E	t qtz monzonite	Ragged	5.0	U, Mo	weak molybdenum skarn?
035 unnamed	128 48 17	62 41 51	P2 T5 C8 B2	Fe shale	Ragged	4.4	Fe, Ni, Co, Cu	red-orange iron spring (Sedex?)
036 unnamed	128 48 17	62 41 51	P2 T9 C4 B2	Fe shale	Ragged	?	Fe, Zn, Mn, Ni, Co	red iron spring (Sedex lead-zinc-silver)
037 unnamed	128 00 48	62 44 56	P2 T4 C5 B2	Fe shale	Ragged	4.2	Fe, Mn, Zn, Ni	red iron spring (Sedex lead-zinc-silver)
038 unnamed	128 50 35	62 48 35	P3 T6 C6 E	hs qtz monzonite	Broken	63.5	W, As, Mo , F	tungsten skarn
040 Broken Skull	128 08 33	62 45 19	P1 T3 C5 D1	hs,f carbonate	Broken	49.0		scenic tufa hot spring
041 Broken Skull	128 08 33	62 45 13	P1 T3 C5 D1	hs,f carbonate	Broken	30.5	Fe	scenic tufa hot spring
042 unnamed	128 09 57	62 45 45	P2 T5 C4 B2	Fe shale	Broken	4.0	Fe, Zn, Ni , Mn, Cd, Cu, Co	red iron spring (Sedex lead-zinc-silver)
043 Grizzly Bear	127 53 28	62 40 15	P1 T3 C5 D1	hs,f carbonate	Broken	44.0		scenic tufa hot spring
044 CanTung N	128 24 56	62 06 43	P6 T2 C8 F	hs,f qtz monzonite	Ragged	32.0		hot spring spa
049 unnamed	127 34 11	62 02 38	P2 T5 C4 B2	Fe shale	Ragged	5.5	Fe, Mn, Zn, Ni, Co	red iron spring (Sedex lead-zinc-silver)
050 unnamed	127 34 11	62 02 38	P6 T2 C8 F	lo shale	Ragged	3.0	Zn, Fe, Ni	(Sedex lead-zinc-silver)
052 Hole-in-the	127 19 08	61 46 35	P3 T6 C6 E	hs qtz monzonite	Ragged	40.5	As, W, Mo	(scenic hot seep; tungsten skarn)
053 Hole-in-the	127 19 08	61 46 35	P3 T6 C6 E	hs qtz monzonite	Ragged	47.5	As, Mo, W	(scenic hot seep; tungsten skarn)
054 unnamed	127 14 12	61 47 13	P2 T4 C8 B2	t,Fe shale	Ragged	10.0	Fe	red-orange thermal iron spring
055 unnamed	127 Xx Xx	61 Xx Xx	P2 T3 C3 C	Fe shale	Ragged	1.6	Fe, Mn, Zn, Ni, Co	red-orange iron spring, possible Sedex

058	Flat Fruit	127	36	34	61	40	44	P1	T3	C3	C	t,c	shaley carbonate	Ragged	8.9		tufa travertine mounds
060	CanTung East	128	11	21	62	02	47	P3	T6	C6	E	hs	qtz monzonite	Ragged	46.0	W, Mo, F, Au	weak tungsten skarn
062	unnamed	124	45	19	60	58	44	P2	T4	C4	B2	Fe	sandstone	Mattson	3.0	Fe, Mn	red-orange iron spring
063	Kraus	124	04	05	61	15	19	P4	T7	C1	A	hs	shale	McDonald	38.5		hot spring spa
064	Kraus	124	04	05	61	15	19	P4	T7	C1	A	hs	shale	McDonald	37.5		hot spring spa
065	White Spray	124	08	40	61	18	15	P5	T1	C8	F	lo	karst	McDonald	4.3		scenic high volume fountain spray
066	unnamed	124	12	37	61	33	44	P5	T1	C8	F	t,lo	karst	McDonald	8.2	Fe, Zn, Cu	weak base metal (MVT lead-zinc)
067	Prairie Ck.	124	47	50	61	33	20	P6	T9	C5	D1	hs,f	karst	Meilleur	3.0	Zn, Cu, Cd, Sb, Ni, Co	Vein silver-lead-zinc - mine water
069	Twisted Mtn	123	38	43	61	11	14	P2	T5	C4	B2	t,Fe	sandstone	Mattson	11.5	Fe, Mn, Ni	red-orange thermal iron spring
071	unnamed	124	28	14	61	10	18	P2	T5	C4	B2	t,Fe	sandstone	Mattson	7.0	Fe, Mn, Ni	red-orange thermal iron spring
072	Meilleur River	124	46	02	61	11	14	P2	T5	C2	B1	Fe	shale	Meilleur	5.0	Mn, Zn, Ni, Fe, Co, Cd, Cu,	Sedex lead-zinc-silver
073	unnamed	124	46	02	61	11	14	P2	T5	C2	B1	t,Fe	shale	Meilleur	11.5	Mn, Zn, Ni, Co, Cd, Au	Sedex lead-zinc-silver
075	unnamed	124	23	52	61	35	24	P5	T1	C8	F	lo	karst	McDonald	5.0	Zn, Cu	weak MVT
076	Bubbling	124	07	51	61	36	08	P5	T2	C8	F	c	karst	McDonald	4.0		<i>Interesting CO₂ bubbling cold spring</i>
078	unnamed	124	22	42	60	53	40	P2	T9	C5	B2	Fe	shale/sandstone	Horn/Mattson	1.5	Fe, Mn	Etanda Dome: red Fe-Mn gossan
080	unnamed	123	49	49	61	08	45	P2	T5	C4	B2	t,Fe	sandstone	Mattson	12.0	Fe	thermal, red Fe-Mn gossan, minor others
082	White Aster	124	07	37	61	07	37	P1	T3	C5	D1	hs,f	shale / carbonate	Meilleur	38.5	Zn, As, Mo, W	Fragile Scenic Travertine – Frontispiece & Figure 5.26 Sedex / MVT lead-zinc-silver
100	unnamed	127	48	49	61	25	46	P2	T5	C4	B2	Fe	shale hornfels	Ragged	0.0	Mn, Zn, Fe, Ni	(skarn zinc) - at MB Showing
103	unnamed	127	08	41	61	42	27	P2	T4	C4	B2	Fe	shale hornfels	Ragged	4.0	Fe	red Fe-Mn gossan, minor other metals
105	unnamed	127	48	14	59	27	50	P5	T5	C8	B2	Fe	shale hornfels	Ragged	4.5		red gossan; large karst spring nearby
107	unnamed	123	19	41	61	04	27	P6	T2	C7	F	lo	shaley carbonate	Horn	4.0	Zn	Near Tetrahedrite veins at Nahanni Butte
109	unnamed	124	50	15	60	59	32	P2	T4	C8	B2	Fe	shaley carbonate	Meilleur/Mattson	0.0	Fe	red Fe-Mn gossan, minor other metals
111	Amica Fm	124	54	00	61	06	32	P1	T2	C5	D1	t	shaley carbonate	Meilleur	7.0	Zn, Ni, Mo, U	Sedex lead-zinc-silver
112	unnamed	124	51	19	61	06	28	P2	T5	C2	B1	Fe	calc. shale	Meilleur	3.0	Fe, Mn, Zn, Ni, Co, As	Sedex lead-zinc-silver
114	unnamed	123	55	33	61	25	53	P1	T9	C7	D2	Fe	karst	McDonald	3.5	Mo	tufa travertine
115	unnamed	123	55	53	61	26	06	P1	T9	C7	D2	Fe	karst	McDonald	3.0	Mo	tufa travertine
121	unnamed	124	21	21	61	08	42	P2	T5	C4	B2	Fe	sandstone	Mattson	4.0	Fe, Mn, Zn, Ni	red Fe-Mn gossan, minor other metals
125	unnamed	124	03	41	61	33	35	P1	T9	C7	D2	lo	karst	McDonald	1.0	Zn, Mo	Sedex lead-zinc-silver
127	Nahanni Butte	123	21	00	61	03	00	P6	T2	C5	D1	w	shale & carbonate	Horn	3.5		potable well water