

APPLICATION OF SPRING-WATER CHEMISTRY TO EXPLORATION IN THE DRIFTPILE CREEK AREA, NORTHEASTERN B.C. (94K/4, 94L/1)

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INTRODUCTION

In the Kechika Trough of northeastern British Columbia, secondary iron oxide precipitates and ferricrete deposits are commonly associated with springs draining Paleozoic basinal-facies clastic rocks. These rocks host the Stronsay (Cirque), Bear and Driftpile Creek lead-zinc-silver-barite sedex deposits (MacIntyre, 1992). Depending on the pH and Eh of the near-surface environment secondary goethite in gossans can accumulate up to several thousand parts per million of As, Ba, Cu, Pb and Zn (Hassen and Bourezg, 1990). Carne (1983) also found that limonite spring deposits in an area immediately north of the Driftpile Creek deposit typically contain over 1% Zn and up to 463 ppm Pb, 200 ppm As and 158 ppm Mo. High (>0.5) Co/Ni ratios, detected in a number of the limonite precipitates, were explained by a possible massive sulphide source for the cobalt. Carne observed that the metals were most concentrated in the spring deposits where the discharging ground water was close to neutral. Fletcher and Doyle (1974) found high Co, Cu, Mn, Ni and Zn levels in acid stream-waters draining Paleozoic shales in Macmillan Pass, Yukon Territory. The shales are similar to those in the Kechika Trough. The absence of appreciable metal enrichment by secondary iron oxides in stream sediments was explained by the suppressed absorption of trace metals at low pH.

The enrichment of many metals by secondary iron oxides suggests a close relationship between the oxide mineral chemistry and the ground water chemistry. Previous studies have shown that ground water chemistry alone can be a valuable guide to buried metal sulphides. For example, Hoag and Webber (1976) distinguished between subsurface oxidation, inorganic surface oxidation and bacterial oxidation of sulphides as the processes responsible for liberating SO_4 into ground water. Using geochemical data for drill hole and spring-water samples collected around the Eustice, Quebec massive sulphide deposit, Hoag and Webber determined that sulphate levels below 160 ppm were principally due to non-bacterial oxidation whereas higher sulphate reflected extensive bacterial surface oxidation of sulphides. In the Jilin region, northeast China, Jiang *et*

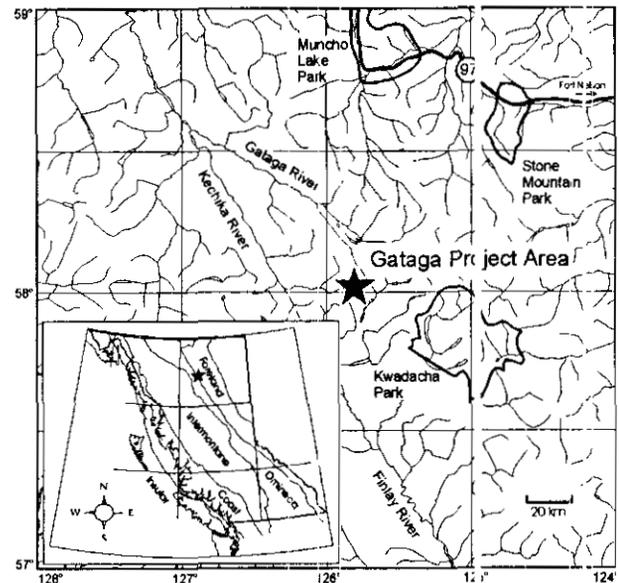


Figure 1. Location map of the Gataga Project.

al. (1994) demonstrated a spatial relationship between SO_4 -Mo enriched spring waters and copper-molybdenum skarn deposits concealed under Cenozoic plateau basalts. Sequential analysis of spring-sediment samples from the area revealed that molybdenum is predominantly present as sulphides and residual minerals, but that over 40% of the lead and zinc is bound to non-crystalline and crystalline iron oxides.

Orientation surveys were carried out in the Driftpile Creek area (Figure 1) during the 1994 field season to investigate the relationship between spring-water and spring-sediment chemistry. The surveys were also designed to study other geochemical exploration problems, typical of the Kechika Trough, such as the effect of high zinc and silver backgrounds in soils and stream sediments. Preliminary geochemical data for the spring-water samples are discussed in this paper.

DESCRIPTION OF STUDY AREAS

LOCATION AND TOPOGRAPHY

Six sites neighboring the Driftpile Creek area were selected for detailed geochemical sampling and study (Figure 2). The region, situated east of the Rocky Mountain Trench in the Muskwa Range of the northern Rocky Mountains is characterized by northwest-trending

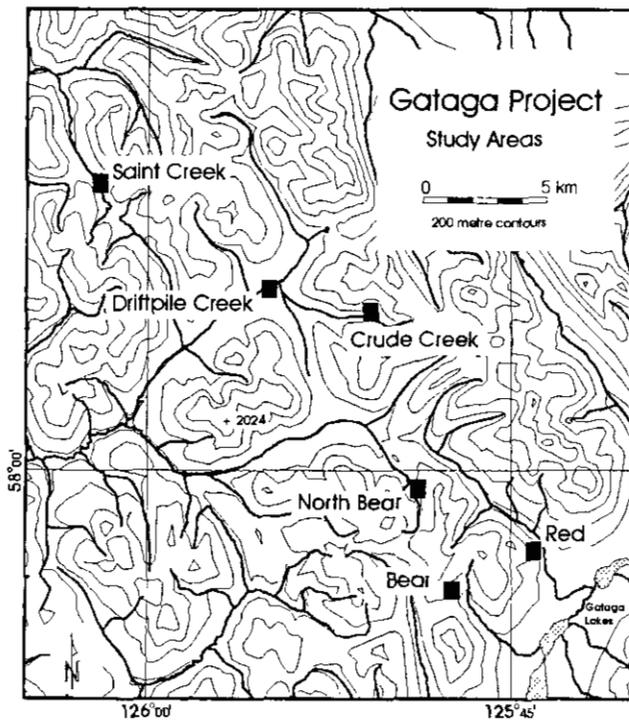


Figure 2. Location map of study areas.

mountain ridges which are 1000 metres to over 2000 metres in elevation. Evidence of glacial erosion and alpine glaciation can be found throughout the area. The rugged topography reflects rapid physical erosion of the Paleozoic sedimentary rocks. Streams flow in a predominantly trellised drainage pattern. Steep sided, narrow northwest-trending valleys are intersected by larger, subsequent, east to west-trending valleys. The tree line reaches up to 1500 metres with mixed woodland and grassland in the valley bottoms and alpine fir, black spruce and alder extending up the valley sides. Surface flora above 1500 metres consists of scattered alpine fir, willow and heather. Irregular patches characterized by an absence of vegetation and surface soil horizons, plus an abundance of ferruginous material are common throughout the area. Many of these vegetation 'kill zones' are associated with springs and seepages; others reflect high levels of elements such as Pb, Ba, Zn and Cd in the near-surface environment.

GEOLOGICAL SETTING

Geology, mineralization and structure of the Driftpile Creek area have been previously described by Carne (1983), McClay and Insley (1985) and MacIntyre, (1992) and currently, geological mapping of the region is being conducted by Ferri *et al.* (1995, this volume) as well as various mining companies. Principal geological elements of the Driftpile Creek area can be summarized as follows:

- A northwest-trending belt of tightly folded, predominately black, fine-grained siliciclastic Paleozoic rocks typical of euxinic basinal sediments filling the Kechika Trough.

- A stratigraphic sequence of Ordovician carbonaceous black argillites, cherts and thin limestone beds succeeded by orange-weathering Silurian dolomitic micaceous siltstone. The siltstone is overlain by Lower Devonian recessive silver-grey weathering black argillite, chert and, locally, crinoidal limestone. Ordovician to Lower Devonian strata form the Road River Group. Above this group is a conformable sequence of laminated siltstone succeeded by recessive, silver-weathering black argillites, cherty argillite, thin-bedded chert and, locally, chert-pebble conglomerate. These Middle to Upper Devonian strata form the lower Earn Group, locally identified as the Gunsteel formation in the Gataga district. The Gunsteel formation is host for several stratiform barite-pyrite-galena-sphalerite deposits such as the Bear and Driftpile Creek.
- Massive to laminated barite, laminated fine-grained pyrite with varying amounts of sphalerite and galena are interbedded with chert and black cherty argillite. Sedimentation and sulphide deposition demonstrate a rhythmic pattern characterized by pyrite-laminated siliceous argillite at the base of the sequence succeeded by laminated pyrite-sphalerite-galena; massive barite and carbonate nodules and blebby barite at the top.
- Geological structure is dominated by northwest-striking, steeply dipping chevron folds and west-dipping thrusts. The Mount Waldemar thrust is a major structure which separates older strata in the west from the lower Earn Group rocks.

SURFICIAL DEPOSITS

Glaciogenic landforms typical of the region around Driftpile Creek include long, U-shaped valleys, hanging tributaries and proglacial lake strandlines. A prominent terrace at the 1350-metre elevation along both sides of Driftpile Creek marks a transition from the steeper valley side to the more subdued upland topography. The terrace is marked by sandy textured deposits containing locally derived pebbles. Sorted, gravel-textured deposits also occur at the 1600-metre elevation on a steep, south-facing hill slope close to the Bear occurrence and these may represent sand deposits of a proglacial lake. Immediately south of Driftpile Creek, at a similar elevation to the 1350-metre strand line along a flat valley floor, is an area of irregular mounds and short ridges which may represent ice-stagnation deposits. Valley floor and lower hill slopes are mantled by an unknown thickness of drift and colluvium. Above tree line, ridge crests and steeper hill slopes are covered with rock talus and felsenmeer. A typical soil catena consists of regosols, alpine dystric brunisols above tree line, orthic dystric brunisols on moderate hill slopes, gleysols and organic soils along the margins of streams.

SPRING-RELATED DEPOSITS

A total of 86 samples were collected from ground water springs and seepages. Most of the sample sites are

surrounded by secondary mineral deposits which have a varying morphology. The most common deposits are:

- Small (10-20 cm high) mounds surrounding the actual spring discharge. The 'cold-spring' mounds consist of laminated red to dark brown iron oxide terracettes.
- Surface crusts of laminated iron oxide which are probably derived from the physical erosion of the cold spring deposits. The surface crusts also consist of variegated, friable ferruginous sinter which can form slabs scattered over the surface of vegetation kill zones. In the Red Gossan area, ferruginous sinter is associated with kill zones of 1 square kilometre in area, with no related ground water discharge.
- Ferricrete deposits consisting of rounded Paleozoic pebbles and cobbles cemented with sandy textured ferruginous material. These deposits may be several metres thick and may extend for several hundred metres along the side of creeks. No active springs are associated with them.
- White, laminated precipitate coating clastic sediment and vegetation debris in stream channels. This type of precipitate is less common than the ferruginous deposits and is most likely to consist of aluminum hydroxide. The precipitate is not generally found surrounding springs, but is most evident in the channel several metres downstream from the discharge. White precipitates occur in streams draining the Bear occurrence and the streams draining into the north Bear valley.
- White, laminated travertine forming the bank of a small pool surrounding a spring in the upper reaches of Crude Creek.

SAMPLING AND FIELD METHODS

At each of the study sites samples of the following media were collected:

- Water samples from seepages, spring and surface streams. At the sample site, water pH and temperature were measured with a Corning Checkmate meter, dissolved solids (conductivity) was measured with a Hanna Model 3ATC meter and dissolved oxygen was measured with a Hanna 8543 oxymeter. Sufficient water was collected to enable preparation of a filtered (0.45 μm), acidified (ultrapure nitric acid to pH 2) sample in the field. The sulphate content and alkalinity were also measured in the field with Hach analytical kits.
- Spring precipitate and ferruginous sinter samples.
- Soil and drift samples from areas surrounding selected spring deposits. Two soil-drift traverses were also sampled across the strike of the Bear sulphide horizon at the 1600 and 1650-metre elevations.
- Rock and ferricrete samples.
- Stream sediment and moss-mat samples.

LABORATORY ANALYSIS

Filtered, acidified water samples were analysed for a suite of 66 elements (Li, Be, Na, Mg, Al, Si, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Rb, Sr, Y, Zr, Nb, Mo, Ru, Pd, Ag, Cd, In, Sn, Sb, Te, I, Cs, Ba, La, Ce, Pt, Nd, Sm, Eu, Gd, Tb, Dy, Er, Tm, Yb, Lu, Hf, Ta, W, Re, Os, Pt, Au, Hg, Tl, Pb, Bi, Th and U) by inductively coupled plasma mass spectroscopy and inductively coupled plasma emission spectroscopy at Activation Laboratories Ltd., Ancaster, Ontario. Results for several of the elements were excluded from the interpretation because of known inter-element interference (Ti), probable significant loss of element during the interval between sampling and analysis (Hg) and absence of any detectable element concentration in the samples (Au, Pt). Quality of the water geochemical data and possible sample contamination were monitored by analysis of filtered, acidified distilled water blanks, blind sample replicates and standards prepared by spiking bulk-filtered water from Crude and Driftpile Creeks with Cu, As, Co, Ni, Zn and Cd. Sulphate and fluoride in water were measured by ion chromatography and specific ion electrode by Chemex Laboratories, Vancouver.

Spring deposit, soil and drift samples were air dried and sieved to -63-micron size and were analysed by Acme Analytical (Vancouver) for 29 elements (Mo, Cr, Pb, Zn, Ag, Ni, Co, Mn, Fe, As, U, Th, Sr, Cd, Sb, Bi, V, Ca, P, La, Cr, Mg, Ba, Ti, B, Al, Na, K and W) by aqua regia digestion and inductively coupled plasma emission spectroscopy. Mercury was analysed by cold vapour atomic absorption spectrometry. Thirty-five additional elements (Au, Ag, As, Ba, Br, Ca, Co, Cr, Cs, Fe, Hf, Hg, Ir, Mo, Na, Ni, Rb, Sb, Sc, Se, Sn, Sr, Ta, Th, U, W, Zn, La, Ce, Nd, Sm, Eu, Tb, Yb and Lu) were determined by thermal neutron activation analysis.

Ferricrete samples were broken up and the sandy matrix sieved to -180 microns. Rock samples were crushed and ground in a tungsten carbide mill to -75 microns. The prepared samples were analysed for the 29-element suite by hydrofluoric-nitric-perchloric-hydrochloric acid digestion and inductively coupled plasma emission spectroscopy. Mercury was analysed by cold vapour atomic absorption spectrometry and the 35-element suite by thermal neutron activation analysis.

RESULTS AND DISCUSSION

Mean concentrations for selected elements in spring-water samples from the study areas are shown in Table 1. A number of the elements originally determined were excluded because most values were below instrumental detection limits. The mean values reveal differences in spring-water chemistry between the areas. Saint and Red spring waters are neutral to weakly alkaline and have

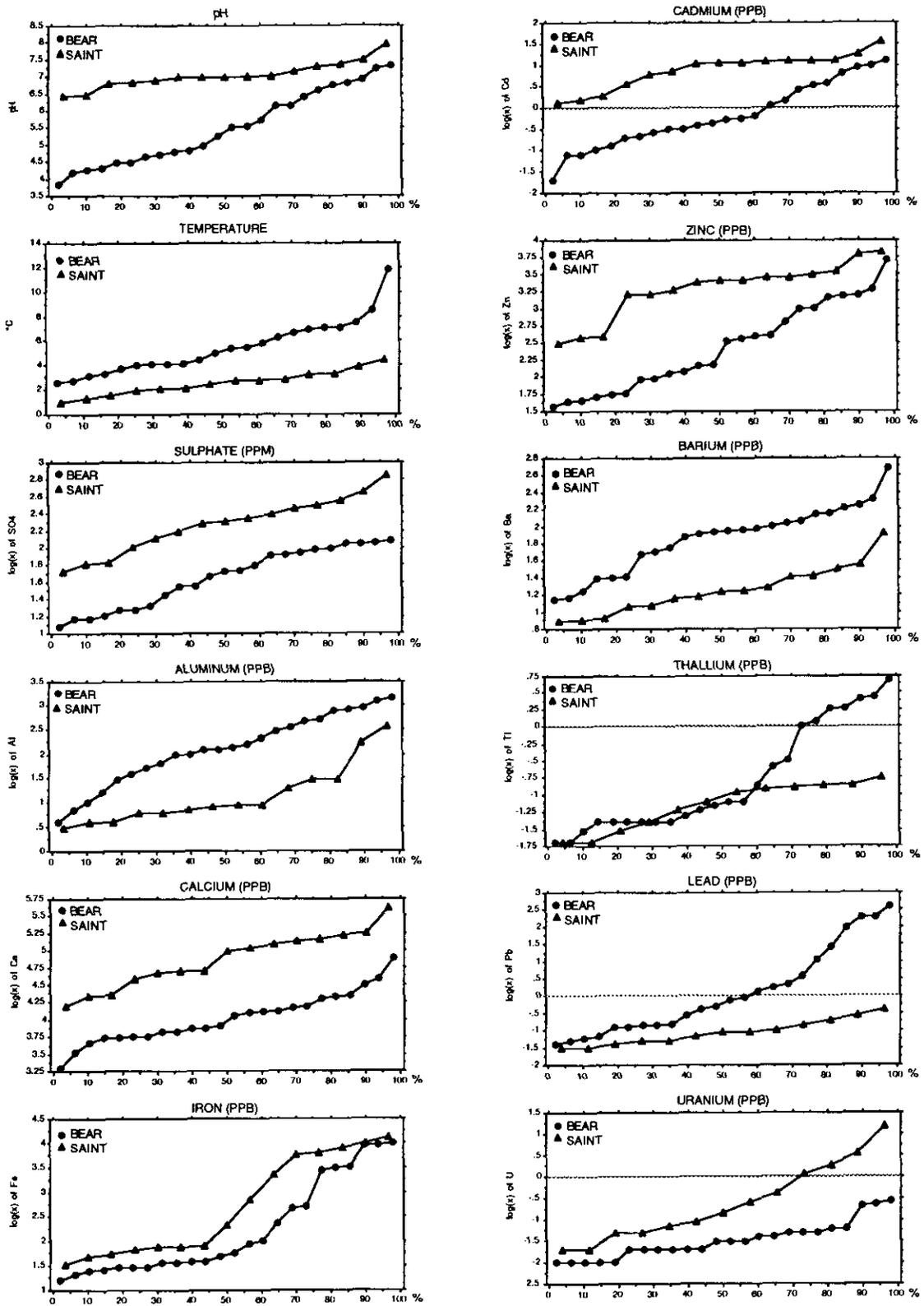


Figure 3. Comparison of Bear and Saint spring-water percentiles for pH, temperature, sulphate, aluminum, calcium, iron, cadmium, zinc, barium, thallium, lead and uranium.

TABLE 1
MEAN CONCENTRATION OF SELECTED ELEMENTS
IN SPRING WATER

Unit	Bear	N.Bear	Drift	Saint	Red	Crude
N	23	21	12	15	9	5
F ppb	242	269	250	482	336	316
SO ₄ ppm	58	174	74	236	264	321
pH	5.5	6.4	7.5	7.0	7.5	7.3
T °C	5.4	4.4	6.7	2.5	4.9	3.7
Con uS	78	225	286	404	436	498
O ₂ ppm	7.00	5.50	9.40	4.67	4.50	5.04
Alk ppm	1.40	2.10	4.36	5.50	10.20	7.60
Li ppb	5.60	24.00	36.00	5.79	8.60	6.56
Na ppb	133	982	9320	1540	799	1971
Mg ppb	2138	11016	6072	15676	15688	21997
Al ppb	321.0	719.0	159.0	44.0	8.7	18.0
Si ppb	3395	3465	4037	3517	4189	5200
K ppb	676	487	594	1067	2379	1133
Ca ppb	14991	48367	41356	107577	149606	122726
Mn ppb	142	848	530	327	174	285
Fe ppb	1651	3578	449	3122	2065	6567
Co ppb	4.25	30.00	2.84	13.94	11.98	16.30
Ni ppb	38	155	48	382	284	225
Cu ppb	2.04	5.50	1.70	1.08	0.80	0.88
Zn ppb	698	560	3470	2610	2057	1262
Ga ppb	0.06	0.15	0.23	0.12	0.07	0.11
Ge ppb	0.04	0.07	0.14	0.09	0.08	0.09
As ppb	0.13	0.56	0.14	0.99	4.50	1.24
Rb ppb	1.69	0.87	1.61	1.90	4.70	1.89
Sr ppb	75	345	270	513	1052	641
Y ppb	0.67	4.55	0.45	0.76	0.60	0.93
Zr ppb	0.94	1.50	1.41	1.53	1.54	1.55
Mo ppb	0.16	0.29	4.94	1.74	2.84	3.52
Cd ppb	2.23	1.57	7.54	10.67	20.09	5.07
Cs ppb	0.21	0.12	1.00	0.24	0.62	0.12
Ba ppb	102	32	141	23	49	22
Tl ppb	0.73	0.06	0.79	0.07	0.38	0.09
Pb ppb	38.52	0.74	0.95	0.12	0.09	0.51
U ppb	0.06	0.17	1.23	1.71	5.87	0.42

greatest SO₄, F, Mg, Ca, Ni, Sr, Cd, and U contents. Bear and North Bear waters are weakly acid and have higher dissolved oxygen, Al, Ba and Pb. The neutral to weakly alkaline Drift spring waters are enhanced in Mo, Zn and Ba, but have lower SO₄ than the other areas. Element associations were identified by correlation coefficients calculated from untransformed data for all of the areas combined. Among the strongest, sympathetic associations (correlation coefficient >+0.9) are Pb with Zn and Cs with Tl. The correlations may reflect a common association of the metals in more mineralized water samples. A strong negative correlation between pH-Pb-Mn can be explained by the greater solubility of Pb and Mn minerals in more acid waters.

Differences between the Bear and Saint spring-water chemistry are highlighted by a comparison of percentile plots for spring-water pH, temperature, SO₄, Al, Ca, Fe,

Cd, Zn, Ba, Tl, Pb and U (Figure 3). The shape of the Ca, Ba and SO₄ plots for the two areas suggests that values are drawn from one population and have a similar source. The higher Ca and SO₄ means for the Saint area may reflect a longer residence time for the ground water in geological structures, enabling a greater contribution of the more soluble elements from bedrock. The Zn, Pb, Tl, pH and U distributions have different moment statistics and, in the case of Pb and Zn for the Bear waters, are bimodal. The higher range of values are clearly related to a second source for these metals which is most probably a weathering sulphide body. The Fe distribution is bimodal and may reflect two distinct sources for the dissolved iron in both areas. Similar Cd and Zn percentile plots can be explained by common mineral association of these metals such as cadmium-rich sphalerite.

Oxidation of pyrite-bearing shales, generation of sulphuric acid and release of metals from the shale into groundwater is a probable source for the higher Fe, Co, Ni, Zn, Cd and U in Saint spring water. Very acid (pH<4) streams draining sulphide-bearing volcanics on northern Vancouver Island have more than 200 ppm SO₄, 23.3 ppm Ca, 0.55 ppm Fe and 15.49 ppm Al (Koyanagi and Panteleyev, 1992). The Saint spring waters have similar Ca, Fe and SO₄ levels, but have very low Al content and are also neutral to weakly alkaline. In situ neutralization of the acid water by carbonate rocks, interbedded with the shale, may explain the neutral pH of surface waters. Subsurface precipitation of Al(OH)₃ in the pH range 6 to 7 may also be the reason for the low Al content of the Saint spring water.

In contrast to the Saint area, the more acid, Bear spring waters have much higher Al, Ba, Pb and Tl, but lower Zn, Cd and SO₄. The Bear spring-water chemistry may reflect shorter residence time for the ground water in geological structures and solution of Pb-Zn-Fe sulphides

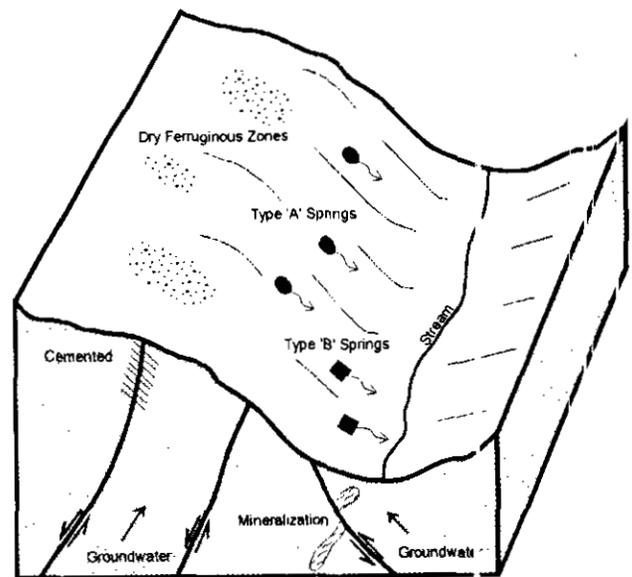


Figure 4. Generalized model for dry ferruginous zones, type 'A' and type 'B' springs.

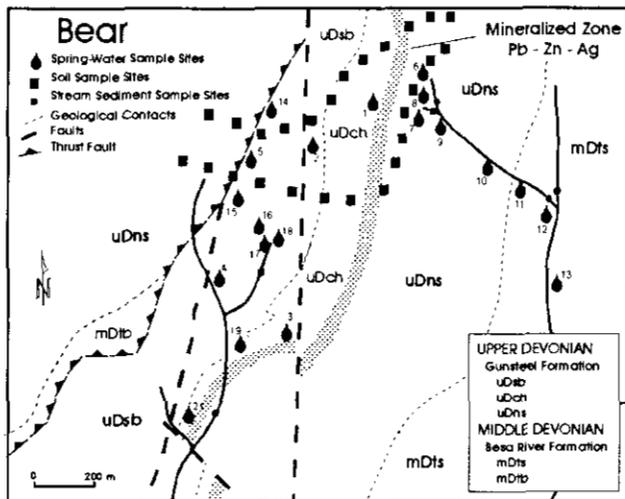


Figure 5. Bear water, soil and stream sediment sample sites.

in contact with the water. The low pH and the higher Al and Ba are characteristic of massive pyrite oxidation, release of sulphuric acid into the groundwater and partial dissolution of baritic shale. Galena and sphalerite will also dissolve in acid groundwater producing high dissolved Pb and Zn. The average Ba content of the Bear spring waters is close to the maximum concentration allowed by the barite solubility product, water temperature and SO₄ content (Steele and Wagner, 1983). As Ba mobility is less susceptible than Pb and Zn to pH changes, higher dissolved Ba levels may persist in the groundwater for a greater distance from the barite-sulphide source. Elevated Tl levels up to 100 ppm have been found in Cu-Pb-Zn massive sulphide ore and in minerals from Pb-Zn veins (Murao and Itoh, 1992). Hence, the association of dissolved Tl with the dissolved Pb can be an especially useful guide for galena mineralization because the thallium ion is stable over a wider pH range than lead (Fergusson 1990).

In summary, there are two distinctive types of spring-water chemistry. Type A waters are neutral to weakly alkaline, low in dissolved O₂, cool (2-4 °C) and have high SO₄, Zn, F, Ca, Mg, Ni, Co Sr, Cd, and U.

Copious secondary iron precipitates surround most springs. Type B waters are acid to neutral, generally have higher dissolved O₂, are warmer (2-8 °C) and commonly have high Ba, Al, Pb, Tl. Secondary iron oxide precipitates are less abundant. Acid springs may have a copious white precipitate.

The different geological structures assumed to channel ground water and to be responsible for the two types of spring water are shown in a conceptual model (Figure 4). Also illustrated in Figure 4 is the spatial relationship between dry, ferruginous surface kill zones and active type A springs. This relationship is most evident in the Red area and can be explained by precipitation of secondary iron oxides around springs, later subsurface cementation of the ground water conduit with calcite or gypsum and subsequent displacement of the vertical ground water flow to other structures, producing a second spring line.

The very high Pb levels and associated Tl, typical of acid spring-waters discharging close to mineralization, are highlighted by the results in Table 2 and Figure 5. High Pb levels with elevated Ag, Co, Ni, Zn and As occur in the secondary iron oxide precipitates and moss-mat sediments at Bear sites 1, 6 and 9. The large enrichment of metals in precipitates associated with almost neutral spring-waters can be explained by the powerful sorption characteristics of iron oxides in the pH range 4 to 8. Analysis is in progress to determine if metals bound to specific minerals in the precipitates from the Bear and other areas can be used to discriminate between different source rocks.

CONCLUSIONS

Preliminary results of spring-water sample analysis reveal:

- Two distinct types of spring water occur. Type A waters, typical of the Saint and Red areas, are neutral to weakly alkaline and have elevated SO₄, Zn, F, Ca, Mg, Ca, Ni, Co Sr, Cd, and U. Type B waters associated with known Pb-Zn-Ag mineralization at the Bear deposit are more acid and have high Ba, Al, Pb, Tl.

TABLE 2.
WATER CHEMISTRY OF SELECTED BEAR SPRING-WATER SITES

Site (Sample ID)	pH	SO ₄ ppm	O ₂ ppm	Al ppb	Ca ppb	Fe ppb	Co ppb	Ni ppb	Zn ppb	Cd ppb	Ba ppb	As ppb	Tl ppb	Pb ppb
Bear 1 (943002)	7.2	80	1.3	4	38633	2700	15.0	75	1452	1.1	25	0.2	0.14	0.8
Bear 6 (943009)	6.1	88	7.4	7	31584	9245	12.7	114	5208	12.5	15	0.1	1.18	0.1
Bear 7 (943014)	6.9	112	7.0	16	21749	29	0.5	36	994	2.6	91	0.1	1.82	192.3
Bear 8 (943015)	4.3	114	7.4	97	15119	36	1.9	42	1551	8.5	77	0.1	2.54	392.1
Bear 9 (943016)	6.8	119	0.7	10	78235	3328	5.1	40	1509	0.1	14	0.2	2.73	1.4
Bear 10 (943017)	4.7	46	7.4	125	11350	58	1.2	23	1028	6.2	93	0.1	1.82	196.1
Bear 11 (943018)	4.7	36	7.2	126	6664	29	1.0	16	641	3.7	87	0.1	1.02	93.8

- The differences in water chemistry reflect the residence time for groundwater in bedrock and geological structures, oxidation of pyrite, weathering of shale, solution of lead-zinc sulphides, and in situ neutralization of acid groundwater.

FUTURE WORK

Further interpretive work involving results from the analysis of spring-waters, secondary iron oxides, soils and stream sediments will include :

- Distinguishing between barren, pyritic shale and lead-zinc sulphides as the potential source for the secondary iron oxide precipitates.
- Distinguishing between high geochemical background in stream sediments and soils due to the influence of metal-rich black shale and the contribution of anomalous metal from oxidizing base metal sulphides.

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