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Differentiating sources of dissolved lead in mine waters using lead isotope techniques, Sullivan Mine, British Columbia

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[1] This study investigates the use of Pb isotopes in acid rock drainage studies and outlines a protocol for sampling and analysis of dissolved Pb in mine waters. Groundwaters and surface waters were sampled at the Sullivan Mine, British Columbia, to quantify Pb isotope ratios and to identify possible sources of Pb in mine effluent and back groundwaters, respectively. The Sullivan Deposit is a sediment-hosted Fe-Pb-Zn massive sulphide deposit with a well-defined homogeneous Pb isotopic composition, which provided a suitable end-member for the isotopic study. The Pb isotopic compositions of water samples define a mixing line between the homogeneous Pb isotopic signature of the Sullivan Ore and at least one other more radiogenic end-member. This end-member may correspond to Pb in the host rocks (Aldridge Formation), Pb from aerosols that have infiltrated the local surficial deposits with recharge, or Pb from the surficial deposits themselves. Further study is needed to more completely characterize the composition of potential isotopic end-members in the study area. The study demonstrates that different source regions for Pb have distinct and measurable isotopic compositions, which enable "fingerprinting" sources of Pb contamination that result from ore deposits or from other sources. *INDEX TERMS:* 1040 Geochemistry: Isotopic composition/chemistry; 1065 Geochemistry: Trace elements (3670); 1094 Geochemistry: Instruments and techniques; 1803 Hydrology: Anthropogenic effects; 1831 Hydrology: Groundwater quality; *KEYWORDS:* dissolved lead, lead isotopes, acid mine drainage, hydrogeology

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1. Introduction

[2] The variability of isotope ratios has proved valuable when studying a wide variety of geological and environmental problems. There are two possible mechanisms by which the isotopic abundance of elements may vary including: (1) variations due to the radioactive decay of naturally occurring unstable elements (such as uranium (U) and thorium (Th) which decay to Pb); and (2) variations due to isotopic fractionation during physical, chemical or biological processes (which are generally limited to the lighter elements). For the heavier elements, isotopic fractionation is negligible because the differences in mass between the various isotopes are small, and one isotope is not preferentially selected over another during mass-dependent processes [*Russell and Farquhar*, 1960]. Therefore variations in Pb isotope abundance result from only the first mechanism described above. For this reason, Pb isotopes are used routinely as a tool during geological investigations. For example, Pb isotopes have been used for determining the age of the Earth [*Russell and Farquhar*, 1960] and the age of mineral deposits [*Godwin and Sinclair*, 1982]; for interpreting the genesis of mineral deposits [*Doe*, 1970]; for assisting in the exploration for mineral deposits [*Godwin et al.*, 1988; *Gulson*, 1986]; and for understanding the evolution of Pb in the crust and mantle [i.e., *Beaudoin*, 1997; *Doe*, 1967; *Gariepy and Dupre*, 1991; *Godwin and Sinclair*, 1982].

[3] More recently, the study of Pb isotopes has been applied to environmental problems, such as determining the source(s) and extent of anthropogenic Pb contamination in the geosphere [*Abraham*, 1994; *Shirahata et al.*, 1980], the atmosphere [*Chow and Johnstone*, 1965; *Hopper et al.*, 1991; *Sturges and Barrie*, 1987], the biosphere [*Shen and Boyle*, 1987; *Tommasini et al.*, 2000] and the hydrosphere [*Erel and Patterson*, 1994], including oceans [*Patterson et al.*, 1976; *Sanudo-Wilhelmy and Flegal*, 1994; *Veron et al.*, 1994; *Wu and Boyle*, 1997], rivers [*Elbaz-Poulichet et al.*, 1986], lakes [*Flegal et al.*, 1989; *Ritson et al.*, 1994], snow and ice [*Chisholm et al.*, 1995; *Rosman et al.*, 2000] and groundwater [*Beck*, 1997; *Erel et al.*, 1990]. Some studies have taken an integrated approach and have analyzed samples from several environmental media [i.e., *Ault et al.*, 1970; *Murozumi et al.*, 1996]. Only limited work has been done using Pb isotopes to trace contamination from large-scale mining operations. In this respect, most of the work has been completed on sediment samples [e.g., *Abra-*

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ham, 1994; *Church*, 1994]. Lead isotopes in groundwater have been used to investigate seepage from a uranium tailings pond [e.g., *Gulson et al.*, 1989].

[4] This paper summarizes the results of a study undertaken at the Sullivan Mine (Pb-Zn deposit) in British Columbia, Canada to identify the source(s) of dissolved Pb in surface water and groundwater potentially contaminated by acid rock drainage (ARD). The primary research objectives were to test a protocol for sampling and analysis of Pb isotopes in water, and to differentiate possible sources and pathways for Pb contamination at the mine site. In this paper, the results for a portion of the mine site (the number 1 shaft area) are presented. *Lepitre* [2001] reports the results for the entire site.

2. Pb Isotopes

[5] There are four naturally occurring stable isotopes of Pb: ^{204}Pb (1.36%), ^{206}Pb (25.42%), ^{207}Pb (21.11%), and ^{208}Pb (52.10%); where indicated percentages represent present-day relative abundance in average crustal rocks. The first isotope, ^{204}Pb, is nonradiogenic, therefore its abundance does not change through time. The other three isotopes (^{206}Pb, ^{207}Pb, and ^{208}Pb) are the daughter products of ^{238}U, ^{235}U and ^{232}Th, respectively, and thus are radiogenic and accumulate through time [*Faure*, 1986]. Pb isotopes are measured as ratios, and ^{204}Pb is the stable, nonradiogenic reference isotope against which the other isotopes are typically compared [*Russell and Farquhar*, 1960].

[6] Naturally occurring Pb in various geological materials comprises both Pb that was incorporated at the time the material formed and radiogenic Pb generated by radioactive decay since that time. Most geological materials incorporate at least minor amounts of U and/or Th; thus their Pb isotopic composition will evolve (become more radiogenic) with time, as the radiogenic component accumulates. Relatively Pb-rich and U- and Th-poor minerals such as Pb-rich sulphides or feldspars, however, incorporate negligible amounts of U and Th during formation, and therefore their Pb isotopic compositions will remain unchanged with time.

[7] Lead-bearing ore deposits have distinct Pb isotopic signatures (because of different geological environments and ages of ore deposits) that can enable the "fingerprinting" of sources of anthropogenic Pb contamination [e.g., *Church*, 1994; *Rabinowitz and Wetherill*, 1972]. Similarly, because ore deposits generally have a nonradiogenic isotopic signature relative to that of the host rocks, the Pb isotopic signature of a particular ore deposit could be used to trace transportation pathways of dissolved Pb contamination in both surface waters and groundwater down-gradient of the deposit. However, the isotopic composition of Pb contamination in a particular water sample may be the result of mixing between multiple sources of Pb contamination, such as Pb from the ore deposit of interest, Pb from other nearby natural Pb reservoirs (i.e., host rocks or local surficial deposits), or Pb from aerosols deposited due to atmospheric Pb pollution.

[8] In cases where multiple sources are present, their respective Pb isotopic compositions must first be measured or estimated. Water that dissolves Pb sequentially as it passes through different geological materials, or alternatively, waters from different source regions that mix in the flow system, will vary in their isotopic composition along the flow path. Samples collected at various locations along a flow path are expected to be composites of the sources, and should plot on mixing lines between the various sources in Pb isotopic space (e.g., on a plot of ^{207}Pb/^{204}Pb versus ^{206}Pb/^{204}Pb). The amount of Pb derived from each source could be determined assuming simple mixing. Therefore measuring Pb isotopic ratios in water can be a useful tool for: (1) distinguishing between multiple sources of Pb contamination by measuring the Pb isotopic composition of potential sources of Pb contamination, and (2) estimating the relative amounts of dissolved Pb originating from different sources based on simple mixing.

[9] In order to use Pb effectively as a "fingerprinting" tool, certain criteria must be met including: (1) the Pb isotope composition of the main source of Pb must be relatively homogeneous, and (2) the Pb isotope compositions of other potential Pb sources in the area must be defined. The Sullivan Pb-Zn deposit provides a very useful end-member for mixing models because the Pb isotopic composition of the Sullivan deposit is homogeneous [*Hamilton et al.*, 1982] and defines a distinct tight linear array on Pb isotope ratio plots [*Beaudoin*, 2001]. The Pb isotopic composition of the ore is also found to be significantly different from that of the host rocks (Aldridge Formation) [*LeCouteur*, 1973]. These rocks are estimated to have a present-day composition, which corresponds to approximately 0 Ga on the "shale curve" (corresponding to isotopic ratios ^{208}Pb/^{206}Pb of approximately 2.0389 and ^{207}Pb/^{206}Pb of 0.8053). The "shale curve" is a model curve that depicts the Pb isotopic evolution of rock units within the eastern portion of the Canadian Cordillera through time [*Godwin and Sinclair*, 1982].

[10] The Sullivan deposit is anticipated to be the source of most dissolved Pb in waters near the mine site. However, there are several other potential sources of Pb at the site. Two smaller Pb-bearing deposits are located to the south of the Sullivan deposit (the Stemwinder and North Star deposits), and may offer potential sources of Pb in isolated parts of the mine area. Other potential sources for Pb at low concentrations include both the local bedrock (host rocks) and the overlying glacial overburden. These glacial sediments have likely been transported a significant distance, and therefore their Pb isotopic composition may be considerably different from that of the local bedrock. Also, Pb may originate from aerosols that enter the local hydrologic system through precipitation.

3. Site Description

[11] The Sullivan Mine is located in Kimberley, in southeastern British Columbia (Figure 1). Cominco Ltd. (currently Teck Cominco Limited) operated the mine from the early 1900s until its recent closure in December 2001. There are three areas where waste rock was dumped at the mine site during operation. The number 1 shaft waste rock dump was the active waste rock dump until closure and is the focus of the current study (Figure 1).

3.1. Bedrock Geology and Ore Deposits

[12] Most of the bedrock in the Kimberley area belongs to the Lower and Middle divisions of the Aldridge Formation, including gabbroic intrusions of the Moyie Sills [*Hamilton*

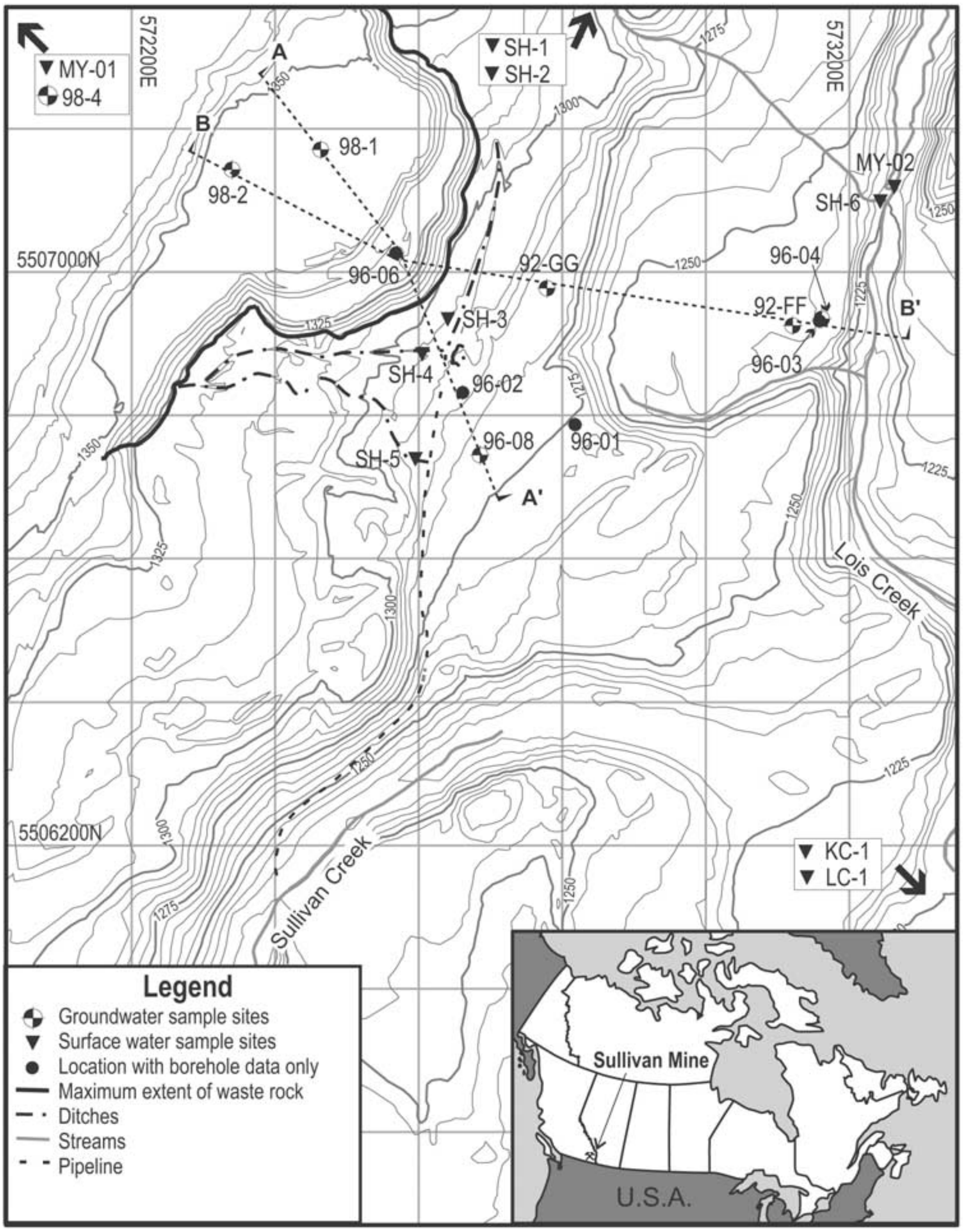

Figure 1. Groundwater and surface water sample sites in the vicinity of the number 1 shaft waste rock dump, Sullivan Mine. Lines of cross sections for Figure 2 are shown. Mine process water and seepage from the waste rock dump are diverted by ditches to a pipeline that discharges into Sullivan Creek. Sullivan Creek is collected and sent to the Drinking Water Treatment Plant. Inset map shows the location of the Sullivan Mine in southeastern British Columbia, Canada.

et al., 1982]. Locally, the Aldridge Formation consists of a 4000-m thick sequence of mainly quartzite, argillite and wacke. The Sullivan Deposit is a world-class, sediment-hosted, stratiform Fe-Pb-Zn massive sulphide (SEDEX) deposit that is hosted by the clastic sedimentary rocks of the upper part of the Lower Aldridge Formation. The orebody is roughly semi-circular in plan, with maximum dimensions of 2 km (north–south) by 1.6 km (east–west). The deposit reaches a maximum thickness of about 100 m near its geographic center, thins outward in all directions, and underlies much of the mine site at depth. Mineralization consists primarily of pyrrhotite, sphalerite and galena, with minor pyrite.

[13] The Stemwinder and North Star deposits are mineralogically similar to the Sullivan deposit [*Turner et al.*, 2001], but are considerably smaller (some tens of meters in width) and probably only of very local significance in terms of their contribution to Pb-Zn contamination.

3.2. Hydrogeology

[14] Glacial deposits consisting primarily of sands, gravels and till overlie bedrock over much of the site. These deposits are of variable thickness, but are commonly several tens of meters thick. Figure 2 shows two geologic cross sections through the number 1 shaft area (the locations of the sections are shown in Figure 1). Geologic data were

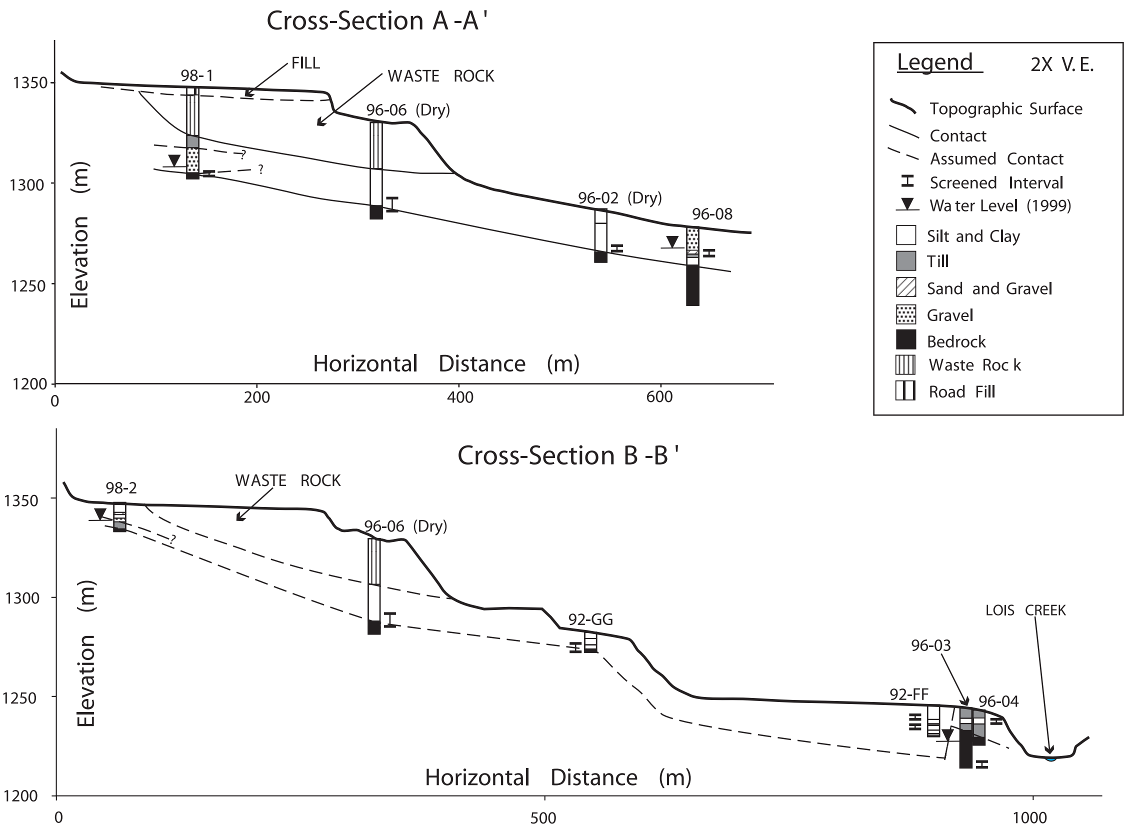

Figure 2. Geological cross sections (a) A-A′ and (b) B-B′ showing hydrostratigraphic units and representative water table elevations. (Section locations are shown in Figure 1).

obtained from borehole lithology logs and were divided into hydrostratigraphic units primarily on the basis of lithology. Available hydraulic conductivity data for the various units also helped to constrain the hydrostratigraphy. Table 1 lists for each piezometer: ground surface elevation, depth of completion, depth of the screened interval, description of lithology over the screened interval, depth to water and water elevation.

[15] On both sections, bedrock is observed to slope relatively smoothly toward Lois Creek, although there are some discontinuities that may be related to faulting (as shown). The average hydraulic conductivity (log K) of the

Table 1. Piezometer Completion Details Showing Lithology and 1999 Water Levels at the Sullivan Mine Site[a]

Piezometer	Ground Elevation, m above sea level	Depth, m bgs	Top of Screen, m bgs	Bottom of Screen, m bgs	Lithology over Screened Interval	Depth to Groundwater, m bgs	Groundwater Elevation, m
92-FF1	1246	15.24	10.36	11.89	clayey sandy gravel		
92-FF2	1246	15.24	5.49	7.01	silty gravel; clayey fine gravel		
92-GG1	1295	8.84	5.79	8.84	gravelly sandy silt; silty sandy gravel		
92-GG2[b]	1295	8.84	1.52	3.05	silty gravel		
96-01	1273	50.29	26.21	28.96	silty sand and gravel (till)	16.83	1256.17
96-02[b]	1286.77	25.91	17.98	20.73	clayey-silty sand and gravel; bedrock	dry	
96-03	1243.21	28.96	26.21	28.96	bedrock	13.78	1229.43
96-04A[b]	1243.24	16.76	12.65	15.54	silt and sand (till); weathered bedrock	dry	
96-04B	1243.24	16.76	5.18	6.40	silty sand	4.24	1239.00
96-06A[b]	1330.26	47.55	38.1	43.2	silty sand and gravel; bedrock	dry	
96-06B[b]	1330.26	47.55	21.34	24.08	waste rock; silty sand and gravel	dry	
96-08A[b]	1277.50	38.40	29.26	38.25	bedrock	dry	
96-08B	1277.50	38.40	10.97	14.02	sand, gravel and cobbles; sand; clay, silt, sand and gravel	9.83	1267.67
98-1D	1347.12	44.50	42.10	43.60	gravel; bedrock	42.40	1304.72
98-1S[b]	1347.12	44.50	26.20	27.80	silt till	dry	
98-2D	1348.36	12.80	11.50	12.20	silt till; bedrock	9.18	1339.18
98-2S	1348.36	12.80	8.60	10.30	silt till	6.91	1341.45
98-4	1565.02	23.20	21.40	22.85	silt till; bedrock	8.71	1556.31

[a] See *Klohn-Crippen* [2000]. Depths referenced in meters below ground surface (m bgs).

[b] Not sampled for Pb isotopes.

bedrock is −7.12 ± 1.47 m/s, based on slug test data acquired in 4 piezometers completed over this unit throughout the mine site. The dominant lithology of the surficial deposits in the number 1 shaft is silt with some clay. The average log K of this unit is −5.94 ± 0.43 m/s (data from 4 piezometers). The gravel unit, present only as isolated lenses, has an average log K of −2.58 ± 0.25 m/s (data from 5 piezometers). Where present, the gravel will be the dominant hydrostratigraphic unit through which groundwater flows. However, because the gravels are discontinuous, and the difference in K between bedrock and the silt unit is only slightly greater than 1.5 orders of magnitude, groundwater will probably flow through both of these units.

[16] The number 1 shaft waste rock dump is situated to the west and up-gradient of Lois Creek (see cross sections). Above the waste rock dump, the ground becomes level, and accommodates several mine buildings and the main mine portal (Figure 1). Piezometers 98-1 and 98-2 are situated amongst these buildings. The ground increases in elevation to the northwest toward piezometer 98-4 and surface pond MY-01. Groundwater originating at these higher elevations is expected to discharge in the main valley containing Lois Creek. Similarly, surface drainage (unless diverted by ditches) will flow naturally down the topographic gradient toward Lois Creek. Water table elevations are included on each cross section and indicate a lateral hydraulic gradient of 0.08 to 0.12. As several of the piezometers used to construct these cross sections were dry, the gradient is only a rough estimate based on limited information.

[17] The piezometers are completed at various depths within both the surficial deposits and the bedrock. Screened intervals are shown on the cross sections. A downward gradient of approximately 0.95 was measured between 98-2S and 98-2D by considering the change in hydraulic head over the interval between the center of the screens. Using an estimated K of 3.6×10^{-7} m/s for till (present between the screens), the flux is roughly 2.9 cm/day. Upward gradients are present near Lois Creek. The vertical hydraulic gradient measured between adjacent piezometers 96-03 and 96-04B is roughly 0.133. Using an average K of 7.6×10^{-8} m/s estimated for the bedrock (both piezometers are completed in bedrock), the upward flux is 0.1 cm/day.

[18] Mine seepage, originating from the number 1 shaft waste rock dump, was detected in Lois Creek. Consequently, Cominco Ltd. installed a series of interceptor ditches to collect drainage from the waste rock and direct it (via pipeline) into Sullivan Creek (see Figure 1). The entire flow of Sullivan Creek is collected and piped to the Drainage Water Treatment Plant (DWTP) further downstream. Although the ditches redirect a significant portion of the drainage from the number 1 shaft waste rock dump into Sullivan Creek, some drainage reaches Lois Creek possibly via deeper groundwater flow paths through the surficial sediments and/or the bedrock. This is evidenced by the levels of contamination in several piezometers, and by the results of surface electromagnetic (EM) surveying conducted throughout the area (EM data not shown).

4. Methodology

[19] Cominco Ltd. currently carries out a water-quality monitoring program at the mine site that is supported by a large network of multilevel piezometers and surface sampling sites. Waters are sampled twice yearly for full chemical analysis (once during spring freshet in late May and once during low flow in September). The dissolved Pb concentrations for each sampling site were compared over several consecutive sampling periods. If the Pb concentrations were notably different, then Pb concentration was reanalyzed from a sample collected during our sampling period (early June). For those Pb concentrations that were used as part of this research, the sampling protocol, as reported in the 1999 Water Quality Monitoring Report [*Klohn-Crippen*, 2000], was the same as that employed in our study. This protocol included the use of acid washed bottles, purged piezometers, and samples that were filtered and acidified in the analytical lab. Samples were analyzed by ICP-MS. Duplicate samples for 10% of the groundwater samples and 10% of the surface water samples were submitted for analysis, and the analytical results were verified for acceptable (<5%) charge balance error.

[20] For the Pb isotopic sampling program, bottle preparation, filtration, evaporation and isotopic analysis of Pb was carried out in the Geochronology Laboratory at the University of British Columbia (UBC), using clean laboratory facilities and high purity reagents as per the methodology outlined below. All procedures were carried out in clean air, in a laminar-flow, HEPA-filtered hood. Reagents used (e.g., acids, water, resin, etc.) were ultra-pure to minimize the introduction of blank Pb during laboratory processing.

4.1. Preparation of Pb Isotope Sample Bottles

[21] Bottles (500 ml) made of high-density polypropylene (HDPE) were used for collecting water for Pb isotopic analysis. The Pb isotope sample bottles were washed in a concentrated laboratory cleaning solution (Contrad®, a similar clean-rinsing laboratory cleaning solution could be substituted) and ultra-pure water (MQ water with a resistance of 18 mega-ohms from a Millipore® purifying system). The sample bottles were then fluxed on a hot plate for a minimum of three full days in order to leach any Pb from the interior bottle walls; this was done by adding approximately 10–20 ml of quartz-distilled, high purity 6N hydrochloric acid (HCl). Finally, the sample bottles were rinsed with MQ water, recapped, and stored in individual, sealed plastic bags (to minimize contamination from particulate matter) for transportation to the field.

[22] Bottles used to collect samples for dissolved Pb concentration (250 ml) had been previously acid washed by the analytical lab, but were further cleaned with Contrad® and MQ water before use.

4.2. Field Sampling

[23] The water-sampling program was completed over two field seasons. The majority of the samples were collected during June of 1999; however, due to an unusually dry winter (i.e., low snowpack, and therefore low spring meltwater runoff) some of the piezometers in the study area were dry. The remaining samples were collected on a second trip in June 2000. Groundwater and surface water samples were collected both up-gradient and down-gradient of the waste rock dumps in the number 1 shaft area (Figure 1).

[24] Groundwater was sampled from existing piezometers by means of dedicated pumps. Each piezometer was purged

prior to sample collection by removing approximately 3 borehole volumes. Approximately half of the surface water samples were collected at sampling stations designated as part of Cominco Ltd.'s water quality monitoring program, and the balance at groundwater seeps both up-gradient and down-gradient of the number 1 shaft waste rock dump. Flowing surface water samples were collected by immersing the sample bottles in the source water.

[25] All samples were collected with minimal handling to prevent possible contamination of sample bottles by particulate matter (both surface and atmospheric). The sample bottles were sealed in plastic bags for transport to the laboratory. Samples submitted for dissolved Pb analysis were filtered (using 45 μm filter papers) and acidified at the analytical laboratory (CanTest Laboratories, Burnaby, BC) in order to avoid any unnecessary contamination from particulate matter in the field. The samples were analyzed using Graphite Furnace Atomic Absorption Spectrophotometry (GF-AAS). Samples collected for isotope analysis were filtered and acidified in the clean lab facilities at UBC (see section 4.3).

[26] Samples of local till from near the Sullivan deposit and sulphide mineralization at the two nearby, smaller sulphide deposits (galena from the North Star deposit and pyrrhotite from the Stemwinder deposit) were collected to determine the Pb isotopic composition of other possible sources of Pb.

4.3. Filtration of Pb Isotope Samples

[27] Water samples for Pb isotopic analysis were filtered in clean air using 45μm filter papers. The filtration apparatus was washed three times with MQ water after each use to avoid cross contamination between samples. As an extra precaution, samples were filtered in an order of increasing Pb concentration to reduce the possibility of a sample with low Pb concentration being contaminated by a previously filtered sample with high Pb concentration. Following filtration, each sample was preserved by acidifying with high-purity concentrated 14 N nitric acid (HNO_3).

4.4. Evaporation of Pb Isotope Samples

[28] A 50 nanogram sample of Pb is optimal for isotopic ratio analysis. The required water volume was calculated from Pb concentration data for each sample. This volume of water was decanted into a clean (acid-fluxed) beaker and evaporated on a hotplate inside a laminar flow hood. After evaporation was complete, the precipitate was dissolved overnight in dilute 2N HNO_3 in covered beakers. Solutions were then dried down and the dissolution process repeated. Residues that did not dissolve were treated with concentrated (48%) hydrofluoric acid (HF) and 8N HNO_3. After drying down the second time, approximately 1 ml of 2 N HCl was added to each sample, and they were dried to a damp crystal mush. One to two milliliters of 1N hydrobromic acid (HBr) were added, and the samples were capped and left on the hotplate for at least three days. When the Pb concentration was reported as less than detection (<0.001 mg/l), an estimate of half the detection limit was used for determining the required volume. If insufficient sample was obtained, more liquid was evaporated.

[29] A laboratory blank was prepared with each batch of samples by adding an aliquot of ^{205}Pb tracer to a new clean beaker. The laboratory blank was treated the same as the samples, therefore it represents the contribution of Pb from all laboratory procedures, including storage in clean beakers and all reagents used during sample dissolution, column chemistry and mass spectrometry.

[30] Separation and purification of Pb was completed using Bio-Rad® columns loaded with 1 ml of precleaned Dow 100–200 mesh anionic resin. Samples were loaded onto the columns in 1 N HBr solution. After washing the loaded column with 4 ml of 1N HBr, the Pb was eluted into a clean beaker using 2 ml of 6N HCl. Finally, 2–3 drops of 0.3N phosphoric acid (H_3PO_4) were added to each sample and the samples were dried down on the hotplate.

4.5. Analysis of Pb

[31] Samples, comprising approximately 50 nanograms of Pb in chloride form, were loaded onto single rhenium filaments using the phosphoric acid-silica gel technique. The Pb isotopic ratios were measured using a Faraday detector on a modified VG-54R solid source, thermal ionization mass spectrometer (TIMS). The measured ratios were corrected for instrumental mass fractionation of 0.12%/amu (Faraday detector) or 0.43%/amu (Daly detector) based on repeated measurements of the National Bureau of Standards (NBS) SRM 981 Standard Isotopic Reference Material and the values recommended by *Todt et al.* [1996]. Errors were numerically propagated including all mass fractionation and analytical errors, using the technique of *Roddick* [1987], and are reported at the 2σ level. The average total procedural blank on the trace lead chemistry was 110 ± 10 picograms, measured on the laboratory blanks by isotope dilution mass spectrometry. Several samples were reanalyzed due to low precision in initial analyses. These repeat analyses are labeled as "rerun" in all figures.

4.6. Analysis of Sulphide and Till Samples

[32] Samples of galena and other sulphides were processed as described by *Marshall et al.* [2000]. Lead was extracted from two till samples by a partial leach in 2 N HNO_3.

4.7. Field Blank Samples

[33] Prior to each field season, MQ water was dispensed into two acid-fluxed Pb isotope sample bottles (total of four field blanks). Three of these blank samples underwent all of the same processes as the samples collected in the field. Therefore these blank samples represent all of the processes that may potentially contribute Pb other than the sample itself. The fourth blank sample was not filtered but otherwise underwent all of the same processes as the previous three blank samples.

[34] The first three blank samples were used to assess the effectiveness of cleaning the filtration apparatus between samples. One blank sample was filtered after approximately every twenty samples. The fourth blank sample was used to obtain an estimate of the Pb contributed by sample storage in the acid fluxed HDPE sample bottles. This estimate was obtained by subtracting the concentration of Pb in a blank sample that contains Pb contributed by all processes except filtration (647 ± 10 picograms) from the concentration of Pb in a blank sample that contains Pb contributed by all processes (including sample bottle storage, filtration, evap-

oration, dissolution, separation and purification of Pb and mass spectrometry (933 ± 10 picograms)). The difference (approximately 286 ± 20 picograms) is an estimate of the Pb concentration contributed from the HDPE sample bottles. An estimate of the Pb contributed as a result of the filtration process alone is approximately 537 ± 20 picograms. This estimate was determined based on the difference between the Pb concentration of the unfiltered field blank sample (647 ± 10 picograms) and the Pb concentration of the laboratory blank sample (110 ± 10 picograms).

4.8. Replicate Samples

[35] One or more replicate samples, comprising separate aliquots taken from the same sample bottle and evaporated in a different beaker, were run for approximately half of the Pb isotope samples and for one of the field blanks to assess the reproducibility of the analyses and to determine whether the sample concentration was a factor in the reproducibility. Replicate samples were labeled with the suffix REP or REP2. Samples selected for replicate analysis spanned the entire range of Pb concentrations from below the detection limit (<0.001 mg/L) to the higher concentrations.

5. Results

[36] Dissolved Pb concentrations in water samples range from below the detection limit (<0.001 mg/L) up to 0.28 mg/L in the number 1 shaft area. The maximum Pb concentration across the entire site is 1.04 mg/L [*Klohn-Crippen*, 2000].

[37] The Pb isotopic results for groundwater samples and surface water samples collected from the number 1 shaft area are listed in Table 2. The Pb isotopic results are compared on plots of ^{208}Pb/^{206}Pb versus ^{207}Pb/^{206}Pb (Figures 3a and 3b for groundwater and surface water samples, respectively). Lead isotopic compositions are commonly presented in ^{208}Pb/^{204}Pb versus ^{206}Pb/^{204}Pb or in ^{207}Pb/^{204}Pb versus ^{206}Pb/^{204}Pb plots. However, because the ^{204}Pb peak is relatively weak, ratios involving this isotope are less precisely determined (as shown later). This may be avoided by employing the less commonly used ^{208}Pb/^{206}Pb versus ^{207}Pb/^{206}Pb plot, which has the added advantage of making it possible to evaluate variations in all three isotopes (thorogenic, i.e., 208, and uranogenic, i.e., 207 and 206) simultaneously on a single plot.

[38] Lead isotopic ratios for the various potential Pb sources in the region are also included on the plots. These include: (1) the Sullivan ore [*Beaudoin*, 2001], (2) the North Star and Stemwinder deposits, (3) two till samples collected near the number 1 shaft area, (4) two Pb-Zn deposits (the Red Dog and Pine Point mines) that were smelted at the nearby Cominco smelter in Trail, BC, and may have been distributed as aerosols, and (5) the estimated present-day isotopic of Proterozoic rocks of the Aldridge Formation. Results from the field blank samples are also included on the graphs.

[39] Lead isotopic ratios for groundwater samples range from 2.035 to 2.191 for the ^{208}Pb/^{206}Pb ratio and from 0.828 to 0.936 for the ^{207}Pb/^{206}Pb ratio. A narrower range of Pb isotopic ratios is observed in the surface water samples, with the ^{208}Pb/^{206}Pb ratio ranging from 2.138 to 2.187 and the ^{207}Pb/^{206}Pb ratio ranging from 0.867 to 0.934. The surface water samples cluster near the values of the Sullivan ore, which is characterized by a Pb isotopic composition of 2.183 to 2.194 for the ^{208}Pb/^{206}Pb ratio and 0.935 to 0.938 for ^{207}Pb/^{206}Pb ratio. The range in the Pb isotope ratios of the Sullivan alteration spans a slightly larger range, with the ^{208}Pb/^{206}Pb varying from 2.167 to 2.209 and the ^{207}Pb/^{206}Pb varying from 0.923 to 0.945.

[40] Analytical results for replicate samples (identified with REP in Figures 3a and 3b) indicate some variation in Pb isotopic composition for the same water sample. For each replicate analysis, a separate precipitate (containing Pb) was obtained by evaporating an aliquot of water from the water sample. Lead was then separated from the precipitate and loaded onto a filament. Because each replicate Pb sample was obtained from a different precipitate, the isotopic compositions may vary. Also, due to their low concentrations, several samples were analyzed with the Daly detector, which has a tendency to produce results that are not as reliable.

[41] The Pb isotopic results from samples of the sulphide mineralization obtained from the Stemwinder and North Star deposits plot close to that of Sullivan ore (Figures 3a and 3b), and therefore are essentially indistinguishable from Sullivan Pb. The two till samples have Pb isotopic compositions distinct from the Sullivan ore and from each other, suggesting a heterogeneous Pb isotope composition for the surficial deposits.

[42] Field blank samples were also analyzed for Pb isotopic composition (Table 2). The Pb isotopic composition of the field blanks ranges from 2.056 to 2.178 for the ^{208}Pb/^{206}Pb ratio, and from 0.907 to 0.961 for the ^{207}Pb/^{206}Pb ratio. Some of the isotopic ratios obtained for the field blank samples are completely different from any of the potential sources of Pb discussed. A few filtered field blank samples seem to be "taking on" a Sullivan-type isotopic composition as they plot near the isotopic composition of the Sullivan ore. This indicates a potential problem (memory effect) with the filtration processes; however, the concentration of Pb in the field blank samples was several orders of magnitude below any of the other samples. Also, several water samples with low Pb concentrations have Pb isotopic compositions that are quite different from the Sullivan signature.

[43] It is worthwhile noting that the same mixing line and scatter is observed in the Pb isotopes on the ^{207}Pb/^{204}Pb versus ^{206}Pb/^{204}Pb graph (Figure 4). Surface water samples plot as a cluster in the vicinity of the Sullivan end-member. However, as there are much larger errors due to the low abundance of ^{204}Pb, there does not appear to be an advantage of using the ^{204}Pb data over the other Pb isotopes for this type of study.

[44] The ^{208}Pb/^{206}Pb ratio versus Pb concentration shows a variable Pb isotopic ratio (the ^{208}Pb/^{206}Pb ratio varies from 2.035 to 2.176) for samples with low Pb concentrations (Figure 5). For samples with elevated Pb concentrations, the Pb isotopic composition is relatively constant (the ^{208}Pb/^{206}Pb ratio only varies from 2.179 to 2.186), and falls within the range of the Sullivan ore and the Sullivan alteration. Samples with Pb concentrations below the detection limit of 0.001 mg/L were assigned a value of half of the detection limit for plotting purposes. This practice allows

Table 2. pH, Pb Concentrations and Pb Isotope Results for Water from the Number 1 Shaft Waste Rock Dump Area, and Pb Isotope Results for Till Samples, Sulphide Samples, and Field Blank Samples

Sample Number	pH (Field)	Pb, mg/L	^{206}Pb/^{204}Pb	^{206}Pb/^{204}Pb Absolute Error	^{207}Pb/^{204}Pb	^{207}Pb/^{204}Pb Absolute Error	^{208}Pb/^{204}Pb	^{208}Pb/^{204}Pb Absolute Error	^{207}Pb/^{206}Pb	^{207}Pb/^{206}Pb Absolute Error	^{208}Pb/^{206}Pb	^{208}Pb/^{206}Pb Absolute Error
Groundwater												
92-FF1 rerun	7.1	<0.001	18.5758	0.0566	15.6140	0.0412	38.3314	0.1288	0.8406	0.00128	2.0636	0.00292
92-FF2	7.4	<0.001	18.3834	0.0059	15.6457	0.0048	38.3392	0.0130	0.8511	0.00007	2.0857	0.00024
92-FF2 REP rerun			18.4552	0.0059	15.6542	0.0046	38.4469	0.0130	0.8482	0.00011	2.0834	0.00023
92-GG	7.0	<0.001	19.2360	0.0197	15.9185	0.0148	39.1386	0.0439	0.8276	0.00036	2.0348	0.00091
96-04B[a]	6.9	<0.001	17.3443	0.0162	15.4646	0.0137	36.9481	0.0354	0.8916	0.00027	2.1304	0.00045
96-08[a]	6.8	<0.001	18.2363	0.0070	15.6321	0.0058	38.0462	0.0152	0.8572	0.00008	2.0864	0.00024
96-08 REP			18.2126	0.0569	15.6758	0.0487	38.0255	0.1192	0.8607	0.00029	2.0879	0.00047
98-01D	2.3	0.28	16.6531	0.0167	15.5173	0.0152	36.3952	0.0372	0.9318	0.00019	2.1856	0.00043
98-02D	7.4	0.002	16.5479	0.0036	15.4776	0.0033	36.2094	0.0082	0.9353	0.00004	2.1882	0.00011
98-02D REP			16.5628	0.0021	15.5053	0.0012	36.2825	0.0056	0.9362	0.00009	2.1906	0.00019
98-02S	7.3	0.001	16.6046	0.0199	15.4622	0.0177	36.1846	0.0440	0.9312	0.00032	2.1793	0.00049
98-4	6.8	<0.001	17.8535	0.0310	15.4533	0.0262	37.2553	0.0667	0.8656	0.00033	2.0867	0.00092
98-4 REP2[a]			17.9951	0.0075	15.4938	0.0024	37.7550	0.0192	0.8610	0.00033	2.0982	0.00061
98-4 REP[a]			18.0431	0.0090	15.5543	0.0074	37.8539	0.0205	0.8621	0.00013	2.0981	0.00043
Surface Water												
KC-1	7.6	0.0003[b]	17.0029	0.0462	15.5039	0.0419	36.7627	0.1002	0.9118	0.00025	2.1622	0.00049
LC-1	7.5	0.0003[b]	17.2403	0.0115	15.5235	0.0098	36.9402	0.0250	0.9004	0.00018	2.1427	0.00028
MY-01	6.6	<0.001	17.8058	0.0544	15.4490	0.0461	38.0801	0.1172	0.8676	0.00056	2.1386	0.00081
MY-01 REP2	6.6	<0.001	17.9282	0.0119	15.5461	0.0100	38.3199	0.0266	0.8672	0.00012	2.1375	0.00045
MY-02	7.3	0.0004[2]	17.0318	0.0152	15.4792	0.0136	36.7172	0.0328	0.9088	0.00014	2.1558	0.00010
SH-1	6.9	<0.001	17.3681	0.0045	15.5372	0.0034	37.2678	0.0101	0.8946	0.00013	2.1458	0.00016
SH-1 REP2			16.8934	0.0101	15.4838	0.0074	36.7166	0.0236	0.9166	0.00033	2.1734	0.00051
SH-2	7.0	<0.001	16.6114	0.0738	15.3945	0.0682	36.1518	0.1614	0.9267	0.00029	2.1763	0.00095
SH-2 REP2[a]			16.8822	0.0113	15.4252	0.0092	36.2447	0.0266	0.9137	0.00028	2.1470	0.00063
SH-3	2.9	0.21	16.7634	0.0223	15.5252	0.0197	36.6079	0.0782	0.9261	0.00038	2.1838	0.00365
SH-3 REP			16.7402	0.0025	15.4737	0.0014	36.4720	0.0057	0.9243	0.00011	2.1787	0.00011
SH-3 REP2			16.6989	0.0053	15.4331	0.0040	36.3881	0.0123	0.9242	0.00017	2.1791	0.00025
Surface												
SH-4	3.7	0.21	16.7008	0.0050	15.4773	0.0045	36.3608	0.0112	0.9267	0.00006	2.1772	0.00014
SH-4 REP			16.6770	0.0023	15.4611	0.0019	36.3345	0.0055	0.9271	0.00006	2.1787	0.00014
SH-5[a]	7.5	0.003	16.5397	0.0135	15.4528	0.0113	36.1744	0.0310	0.9343	0.00034	2.1872	0.00056
SH-6[a]	7.4	<0.001	16.7326	0.0149	15.3973	0.0122	36.3323	0.0346	0.9202	0.00038	2.1715	0.00073
SH-6 REP[a]			16.7551	0.0168	15.3715	0.0150	36.3409	0.0393	0.9174	0.00023	2.1691	0.00088
Sulphides												
North Star			16.4289	0.0017	15.4314	0.0010	36.0422	0.0038	0.9393	0.00008	2.1938	0.00004
Stemwinder			16.4424	0.0080	15.4687	0.0062	36.1510	0.0189	0.9408	0.00026	2.1987	0.00041
Tills												
Till1			18.2761	0.0015	15.6141	0.0012	38.6342	0.0033	0.8543	0.00002	2.1139	0.00004
Till2			16.8937	0.0159	15.5780	0.0131	37.1027	0.0386	0.9221	0.00039	2.1963	0.00099
Blanks												
Blank 1[a]			16.6714	0.0041	15.4497	0.0033	36.3105	0.0093	0.9267	0.00011	2.1781	0.00016
Blank 1 REP[a]			16.3946	0.0242	15.3298	0.0207	35.6943	0.0553	0.9351	0.00056	2.1773	0.00103
Blank 2			16.6895	0.0231	15.4025	0.0210	36.2800	0.0505	0.9229	0.00020	2.1738	0.00034
Blank 3			15.3670	0.1410	14.7720	0.1320	31.5960	0.3090	0.9613		2.0561	
Blank 4			16.9040	0.3540	15.3400	0.3120	35.3770	0.7680	0.9075		2.0928	

[a] Pb isotope ratios were measured using the Daly collector, all others were measured using the Faraday collector.

[b] Concentrations of total Pb rather than dissolved Pb.

samples that have a measured Pb concentration of 0.001 mg/L to be differentiated from samples with a measured Pb concentration below the detection limit.

6. Discussion

[45] As part of mine closure Cominco Ltd. is required to ensure that all mine effluent has been accounted for and that all potential sources of contamination in the natural environment are identified. However, to establish the level satisfactory for cleanup, it is necessary to determine the background concentration of Pb. At the outset of this project, there was question as to whether all of the Pb found dissolved in waters can be specifically related to mining activities. Pb isotopes were anticipated to possibly identify different sources of Pb within the mine area, and by association, determine the level of background Pb at the site.

[46] Water samples with elevated Pb concentrations were found to have Pb isotopic compositions indistinguishable

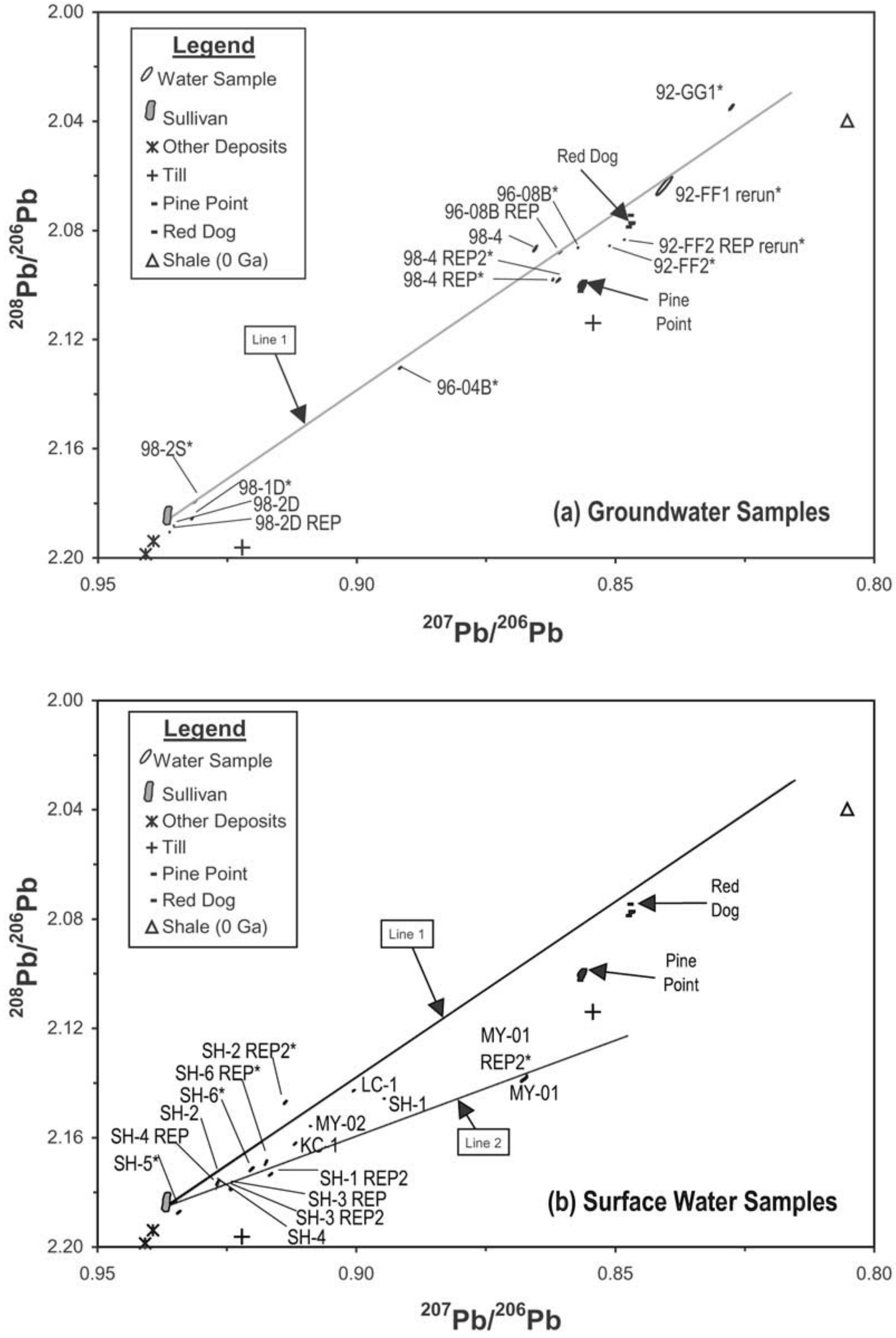

Figure 3. Pb isotope ratios for samples from the number 1 shaft waste dump area: (a) groundwater samples and (b) surface water samples. All error ellipses for water samples are plotted at the 2σ level. Also shown on both graphs are isotopic compositions of (1) the Sullivan ore [*Beaudoin*, 2001], (2) sulphide samples from two other nearby mineral deposits, (3) till samples, (4) field blank samples, (5) the host rocks based on a 0 Ga composition on the shale curve [*Godwin and Sinclair*, 1982], and (6) ore deposits smelted at the Trail, BC smelter.

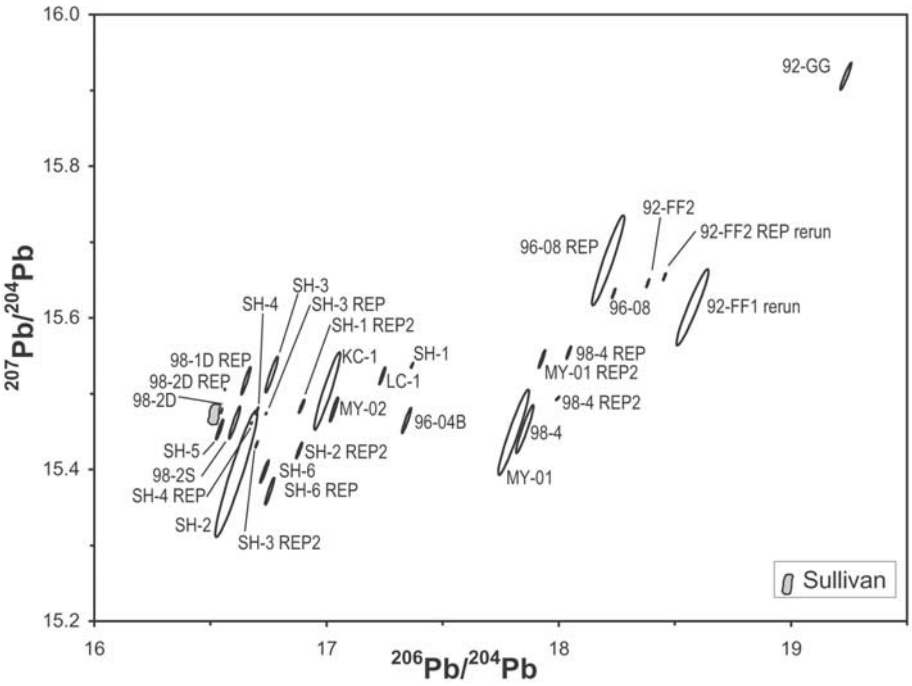

Figure 4. ^{207}Pb/^{204}Pb versus ^{206}Pb/^{204}Pb for samples from the number 1 shaft waste dump area. The 2σ error ellipses are much larger than on the other graph due to the large ^{204}Pb error.

from the Sullivan ore and alteration (Figure 5), whereas water samples with low Pb concentrations display a range in Pb isotopic composition. The large range in Pb isotopic composition of the water samples with low Pb concentrations cannot be explained by the Sullivan ore as a source, rather there must be at least one other source of more radiogenic Pb that is contributing to the observed Pb isotopic compositions. Therefore not all the waters collected in the study area originate from Sullivan ore or mining operations as previously thought.

[47] Filtration was not done in the field because of concern about potential cross sample contamination due to the lack of adequate facilities for cleaning the filtration apparatus between samples. Fortunately, the filtration process did not introduce enough blank Pb to influence the results of the Pb isotope analysis. However, it is possible

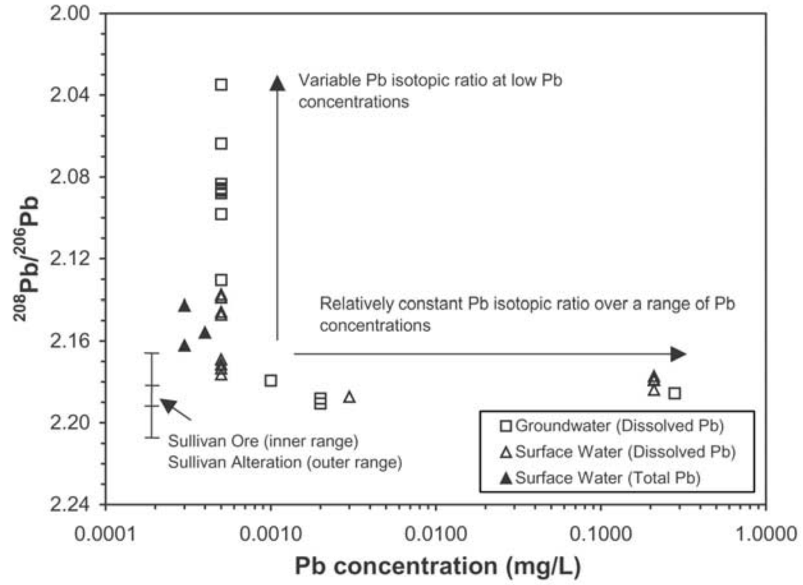

Figure 5. The ^{208}Pb/^{206}Pb ratio plotted against Pb concentration. Samples that are below the detection limit are assigned a value equal to half of the detection limit to differentiate them from samples that are at the detection limit.

that Pb may have precipitated in the sample bottles prior to filtration, acidification and analysis, which were carried out at the lab, thereby reducing the overall concentration of Pb reported in Table 2 and Figure 5. This could have implications for determining the level of background Pb that is not directly associated with mining operations.

[48] Table 2 shows the pH of waters measured in the field. As might be expected, the concentration of Pb is elevated in those samples that are isotopically similar to Sullivan Pb, and which have a low pH (below 4). In contrast, the concentration of Pb is very low in waters that span a broad range in isotopic composition and that have near neutral pH. While some Pb may have precipitated prior to filtration, this does not appear to have influenced the isotopic results. Nevertheless, developing a better filtration process may be more critical for studies needing accurate Pb concentrations or for studies where Pb isotopes are to be measured on and differentiated between samples with much lower Pb concentrations. In-line filters (disposable) may be sufficient for field sampling, but their use should be validated by comparative studies. A further consideration is the possibility of Pb adsorption or desorption from colloidal particles contained within the water sample prior to filtration at the laboratory, which could represent a problem in terms of determining Pb concentrations [*Kimball and Schemel*, 2000].

[49] There is a relatively well-defined spatial distribution for Pb isotopes in water samples collected in the vicinity of the number 1 shaft waste rock dump as shown in the graphs of ^{208}Pb/^{206}Pb versus ^{207}Pb/^{206}Pb (Figures 3a and 3b). Both the deep (D) and shallow (S) groundwater samples taken from piezometers completed in the vicinity of the waste rock dump (98-2S, 98-2D and 98-1D), and surface water samples taken from immediately down-gradient (i.e., SH-5) have Pb isotopic ratios similar to the Sullivan ore. These results suggest that ARD produced by the waste rock is the dominant source for Pb in these waters. The high concentrations of Pb in these waters is most certainly a consequence of their acidity. In contrast, water samples collected up-gradient of the waste rock (i.e., piezometer 98-4 and surface water MY-01) are isotopically distinct both from each other (MY-01 plots slightly below 98-4 on the graph of ^{208}Pb/^{206}Pb versus ^{207}Pb/^{206}Pb) and from the Sullivan ore (both are significantly more radiogenic), suggesting a different source(s) for dissolved Pb. The concentration of Pb in these samples is low, reflecting negligible contamination by ARD as might be expected on the basis of their location up-gradient of the waste rock.

[50] Groundwater samples that were collected down-gradient of the waste rock vary from intermediate Pb isotopic compositions (e.g., piezometer 96-04) to more radiogenic compositions (e.g., piezometers 92-GG and 92-FF1 and 2) as shown in Figure 3a. The tendency toward a more radiogenic composition suggests that these waters represent a varying degree of mixing with groundwaters that might be considered "background" in terms of isotopic composition. The end-member could be isotopically similar to these samples, but could equally be more radiogenic and plot further toward the top-right corner in Figure 3a. In either case, the Pb in these samples is distinct from Sullivan Pb. There are no spatial trends such as those that might be expected (i.e., an increase in "background" radiogenic Pb with increasing distance down-gradient), perhaps due to variations in completion depths and lithology over the screened intervals for these piezometers (see Figure 2). However, it is worthwhile noting that both the bedrock piezometers and those completed in the surficial deposits record similar Pb isotope compositions. This similarity suggests that groundwater flows in both the bedrock and the surficial deposits.

[51] The range in Pb isotopic ratios measured at the site defines a fairly clear mixing line (Line 1 on Figures 3a and 3b) between a well-defined end-member corresponding to the Sullivan ore and a more radiogenic end-member. Line 1 was determined as the best-fit line through the groundwater samples (Figure 3a). If only the surface water samples are considered, the fit is not as good because most of the samples plot near the Sullivan end-member. One sample, MY-01 plots below the others and may lie along a second mixing line (Figure 3b). This second mixing line is speculative based on the fact that it is constrained by one sample. However, if all of the data for the mine site are included (not shown here, but included in the work of *Lepitre* [2001]), the second mixing line is constrained by several samples.

[52] The source of the more radiogenic Pb end-members has not been fully characterized in this study. However, we are able to speculate on potential sources based on the measured ratios in the surficial deposits (i.e., the till samples), other Pb isotopic data for the site (reported by *Lepitre* [2001]), and the range in values of measured Pb isotopic ratios.

[53] Tills (and other surficial deposits) may constitute a Pb end-member because these are generally more radiogenic than the Sullivan ore and associated alteration. However, the tills do not represent the ultimate Pb isotopic end-member because some of the water samples yield even more radiogenic compositions than the till samples. Although it is possible that additional sampling of the surficial deposits may yield isotopic compositions that are more radiogenic, the heterogeneous composition of the till (based on the fact that the two tills analyzed are distinctly different) does not support a conclusion that the surficial deposits constitute the distinct, homogeneous Pb end-member required to produce the observed mixing line.

[54] A second possibility for an end-member is Pb found in the host rocks. Figures 3a and 3b show the isotopic composition corresponding to 0 Ga on the "shale curve", which represents an average isotopic composition for Pb in the host rocks. This point lies to the right (is more radiogenic) than even the most radiogenic of our samples, and therefore could be an end-member for some of the observed isotopic mixing arrays.

[55] A third possibility for an end-member is Pb aerosols. Lead from a different source may enter the hydrologic cycle via precipitation. If aerosols are a source of Pb, then the isotopic composition must be fairly well constrained to generate such a well-defined mixing line. To investigate the possibility, the Pb isotopic composition of two Pb-Zn ores (Red Dog and Pine Point), which have been smelted at the Cominco smelter in Trail, BC (west of the study site), were plotted on Figures 3a and 3b. It is curious that both of these deposits plot very close to the mixing line, with the Red Dog deposit lying almost directly on the mixing line.

Although it is entirely speculative to suggest that Pb at the site may originate from aerosols carried by prevailing winds (westerlies) and enter the groundwater system via precipitation, this idea does introduce a new working hypothesis that may be used to guide future research.

[56] Clearly, the isotopic compositions of the various end-members need to be better constrained, and to do this would require additional sampling. These samples should include all types of surficial deposits (not only tills), local bedrock, and precipitation away from the mine site and to the west toward potential source areas such as the smelter at Trail, BC. Notwithstanding the need for additional data to constrain the other end-members, there is clear evidence that Pb at the Sullivan Mine site originates not only from the mining operations associated with the Sullivan orebody but from other source(s) as well.

[57] One final point for consideration is the water-sampling period, which was during or immediately following the spring freshet. This sampling period may have some important implications with respect to the interpretation of the results. Under high recharge conditions, consistent with the spring freshet, shallow groundwater may be diluted by juvenile recharge water that is typically low in total dissolved solids. In contrast, groundwater sampled during drier periods of the year (late summer and early fall) may be more concentrated in total dissolved solids as a result of lower recharge and higher evaporation. As a consequence of the late spring sampling period for this study, it is anticipated that the water chemistry may reflect a greater contribution from juvenile groundwater. To the advantage of this study however, this sampling bias may accentuate the contribution of background groundwater, thus making it possible to identify sources of Pb that might otherwise be difficult to detect because of their low concentrations. Unfortunately, with the restricted sampling periods, neither short nor long term temporal variations in the isotope geochemistry were investigated.

7. Conclusions

[58] This study successfully used Pb isotopes as a means to fingerprint Pb in groundwaters and surface waters at the Sullivan Mine. Not only was it possible to distinguish different Pb isotopic compositions at the site, but mixing between Sullivan Pb and one or more distinct Pb end-member(s) was clearly observed. Therefore Pb dissolved in waters originates from a variety of sources including mining operations, potentially the ore itself and background sources. Further sampling of local surficial deposits and the waters contained therein (particularly in areas away from the mine site) would be needed to better constrain the composition of other Pb end-members.

[59] The Pb isotopic results also indicate that at high concentrations all of the Pb originates from the Sullivan deposit, whereas at low Pb concentrations there is definitely at least one other source. This finding may be useful for estimating a target concentration of Pb for cleanup operations following mine closure. Better filtration techniques may be needed, however, to produce reliable estimates of Pb at low concentrations.

[60] Lead 204 data do not appear to add to the overall value of the isotopic characterization, and therefore future studies could potentially be undertaken using simpler and less expensive analytical procedures such as inductively coupled plasma mass spectrometry (ICP-MS) to measure only the ^{208}Pb/^{206}Pb and ^{207}Pb/^{206}Pb ratios.

[61] Based on the successful use of Pb isotopes at this study site, we propose that isotopes of other heavy elements may be similarly used for environmental studies. Expansion of the fingerprinting concept to accommodate other potential elements should be investigated.

[62] **Acknowledgments.** Richard Friedman generously assisted with the evaporation of some of the water samples. The authors thank Cominco Ltd. for their generous support in allowing access to the site, and providing digital maps and copies of reports. The project was funded in part by a Graduate Research in Engineering and Technology (GREAT) scholarship from the Science Council of British Columbia.

References

Abraham, J., Impact of mining on the trace element geochemistry and lead isotopic composition of sediments in Coeur d'Alene River, Idaho, M.Sc. thesis, Eastern Wash. Univ., Cheney, 1994.

Ault, W. U., R. G. Senechal, and W. E. Erlebach, Isotopic composition as a natural tracer of lead in the environment, *Environ. Sci. Technol.*, *4*(4), 305–317, 1970.

Beaudoin, G., Proterozoic Pb isotope evolution in the Belt-Purcell Basin: Constraints from syngenetic and epigenetic sulfide deposits, *Econ. Geol.*, *92*, 343–350, 1997.

Beaudoin, G., The lead isotope composition of the Sullivan deposit, in *The Geological Environment of the Sullivan Pb-Zn-Ag Deposit, British Columbia*, edited by J. W. Lydon et al., *Spec. Vol. 1*, pp. 574–581, Min. Dep. Div., Geol. Assoc. Can., Toronto, Ontario, 2001.

Beck, N. G., The applicability of stable lead isotopes to trace groundwater contamination, M.Sc. thesis, Univ. of Calif., Santa Cruz, 1997.

Chisholm, W., K. J. R. Rosman, C. F. Boutron, J. P. Candelone, and S. Hong, Determination of lead isotopic ratios in Greenland and Antarctic snow and ice at picogram per gram concentrations, *Anal. Chim. Acta*, *311*(2), 141–151, 1995.

Chow, T. S., and M. S. Johnstone, Lead isotopes in gasoline and aerosols of Los Angeles basin, California, *Science*, *147*, 502–503, 1965.

Church, S. E., Use of lead isotopes to fingerprint sources of heavy-metal contamination in the environment, in *USGS Research on Mineral Resources, 1994, Part A, Programs and Abstracts*, edited by L. M. H. Carter, M. I. Toth, and W. C. Day, *U.S. Geol. Surv. Circ., C1103-A*, pp. 16–17, 1994.

Doe, B. R., The bearing of lead isotopes on the source of granitic magma, *J. Petrol.*, *8*(1), 51–83, 1967.

Doe, B. R., *Lead Isotopes*, Springer-Verlag, New York, 1970.

Elbaz-Poulichet, F., P. Holliger, J. M. Martin, and D. Petit, Stable lead isotope ratios in major French rivers and estuaries, *Sci. Total Environ.*, *54*, 61–76, 1986.

Erel, Y., and C. C. Patterson, Leakage of industrial lead into the hydrocycle, *Geochim. Cosmochim. Acta*, *58*(15), 3289–3296, 1994.

Erel, Y., C. C. Patterson, M. J. Scott, and J. J. Morgan, Transport of industrial lead in snow through soil to stream water and groundwater, *Chem. Geol.*, *85*, 383–392, 1990.

Faure, G., *Principles of Isotope Geology*, 2nd ed., John Wiley, New York, 1986.

Flegal, A. R., and V. J. Stukas, Accuracy and precision of lead isotopic composition measurements in seawater, *Mar. Chem.*, *22*(2–4), 163–177, 1987.

Flegal, A. R., J. O. Nriagu, S. Niemeyer, and K. H. Coale, Isotopic tracers of lead contamination in the Great Lakes, *Nature*, *339*, 455–457, 1989.

Gariepy, C., and B. Dupre, Pb isotopes and crust-mantle evolution, in *Applications of Radiogenic Isotope Systems to Problems in Geology, Short Course Handbk.*, vol. 19, edited by L. Heaman and J. H. Luggen, pp. 191–224, Mineral. Assoc. of Can., Toronto, Ontario, 1991.

Godwin, C. I., and A. Sinclair, Average lead isotope growth curves for shale-hosted zinc-lead deposits, Canadian Cordillera, *Econ. Geol.*, *77*(3), 675–690, 1982.

Godwin, C. I., J. E. Gabites, and A. Andrew, Leadtable: A galena lead isotope database for the Canadian Cordillera, with a guide to its use by explorationists, *Pap. 1988-4*, Min. Energy, Mines and Petrol. Resour., Toronto, Ontario, Canada, 1988.

Gulson, B. L., *Lead Isotopes in Mineral Exploration*, Elsevier Sci., New York, 1986.

Gulson, B. L., K. J. Mizon, M. J. Korsch, and B. N. Noller, Lead isotopes as seepage indicators around a uranium tailings dam, *Environ. Sci. Technol.*, *23*(3), 290–294, 1989.

Hamilton, J. M., D. T. Bishop, H. C. Morris, and O. E. Owens, Geology of the Sullivan Orebody, Kimberley, BC, Canada, in *Precambrian Sulphide Deposits, H.S. Robinson Memorial Volume*, edited by R. W. Hutchinson, C. D. Spence, and J. M. Franklin, *Geol. Assoc. Can. Spec. Pap.*, *25*, 597–665, 1982.

Hopper, J. F., H. B. Ross, W. T. Sturges, and L. A. Barrie, Regional source discrimination of atmospheric aerosols in Europe using the isotopic composition of lead, *Tellus, Ser. B*, *43*, 45–60, 1991.

Kimball, B. A., and L. E. Schemel, Metal colloids in stream water affected by acid mine drainage, *in Eos Trans. AGU*, *81*(40), Fall Meet. Suppl., F479–F480, 2000.

Klohn-Crippen, , The Sullivan Mine 1999 Groundwater and Surface Water Monitoring Program Annual Report, Cominco Ltd., Kimberley, British Columbia, 2000.

LeCouteur, P., A study of lead isotopes from mineral deposits in southeastern British Columbia and from the Anvil Range, Yukon Territory, Ph.D. thesis, Univ. of British Columbia, Victoria, British Columbia, Canada, 1973.

Lepitre, M., An Integrated geochemical, isotopic and hydrogeologic investigation of acid rock drainage, Sullivan Mine, British Columbia, M.Sc. thesis, Dep. of Earth Sci., Simon Fraser Univ., Burnaby, British Columbia, Canada, 2001.

Marshall, L. J., J. K. Mortensen, and J. E. Gabites, Lead isotope data from epigenetic sulphide occurrences in the Purcell Supergroup, southeastern British Columbia, and implications for exploration for sediment-hosted base metal deposits, in *Geological fieldwork 1999*, *Rep. 2000-1*, pp. 185–191, British Columbia Geol. Surv., Victoria, British Columbia, Canada, 2000.

Murozumi, M., S. Nakamura, and C. Patterson, Industrial lead contamination of natural ecosystems in Japan, in *Earth Processes: Reading the Isotopic Code*, *Geophys. Monogr. Ser.*, vol. 95, edited by A. Basu and S. Hart, pp. 409–427, AGU, Washington, D. C., 1996.

Patterson, C., D. Settle, and B. Glover, Analysis of lead in polluted coastal seawater, *Mar. Chem.*, *4*(4), 305–319, 1976.

Rabinowitz, M. B., and G. W. Wetherill, Identifying sources of lead contamination by stable isotope techniques, *Environ. Sci. Technol.*, *6*(8), 705–709, 1972.

Ritson, P. I., B. K. Esser, S. Niemeyer, and A. R. Flegal, Lead isotopic determination of historical sources of lead to Lake Erie, North America, *Geochim. Cosmochim. Acta*, *58*(15), 3297–3305, 1994.

Roddick, J. C., Generalized numerical error analysis with applications to geochronology and thermodynamics, *Geochim. Cosmochim. Acta*, *51*(8), 2129–2135, 1987.

Rosman, K. J. R., C. Ly, K. Van de Velde, and C. F. Boutron, A two century record of lead isotopes in high altitude alpine snow and ice, *Earth Planet. Sci. Lett.*, *176*(3–4), 413–424, 2000.

Russell, R. D., and R. M. Farquhar, *Lead Isotopes in Geology*, Wiley-Interscience, New York, 1960.

Sanudo-Wilhelmy, S. A., and A. R. Flegal, Temporal variations in lead concentrations and isotopic composition in the Southern California Bight, *Geochim. Cosmochim. Acta*, *58*(15), 3315–3320, 1994.

Shen, G. T., and E. A. Boyle, Lead in corals: Reconstruction of historical industrial fluxes to the surface ocean, *Earth Planet. Sci. Lett.*, *82*, 289–304, 1987.

Shirahata, H., R. W. Elias, and C. C. Patterson, Chronological variations in concentrations and isotopic compositions of anthropogenic atmospheric lead in sediments of a remote subalpine pond, *Geochim. Cosmochim. Acta*, *44*(2), 149–162, 1980.

Sturges, W. T., and L. A. Barrie, Lead 206/207 isotope ratios in the atmosphere of North America as tracers of US and Canadian emissions, *Nature*, *329*, 144–146, 1987.

Todt, W., R. A. Cliff, A. Hanser, and A. W. Hofmann, Evaluation of a ^{202}Pb-^{205}Pb double spike for high-precision lead isotope analysis, in *Earth Processes: Reading the Isotopic Code*, *Geophys. Monogr. Ser.*, vol. 95, edited by Asish Basu and Stan Hart, pp. 429–437, AGU, Washington, D. C., 1996.

Tommasini, S., G. R. Davies, and T. Elliott, Lead isotope composition of tree rings as bio-geochemical tracers of heavy metal pollution: A reconnaissance study from Firenze, Italy, *Appl. Geochem.*, *15*, 891–900, 2000.

Turner, R. J. W., C. H. B. Leitch, T. Hoy, P. W. Ransom, A. Hagen, and G. D. Delaney, Sullivan graben system: District-scale setting of the Sullivan deposit, in *The Geological Environment of the Sullivan Pb-Zn-Ag Deposit, British Columbia*, *Spec*. Vol. 1, edited by J. W. Lydon et al., pp. 370–407, Min. Dep. Div., Geol. Assoc. Can., Toronto, Ontario, Canada, 2001.

Veron, A. J., T. M. Church, C. C. Patterson, and A. R. Flegal, Use of stable lead isotopes to characterize the sources of anthropogenic lead in North Atlantic surface waters, *Geochim. Cosmochim. Acta*, *58*(15), 3199–3206, 1994.

Wu, J., and E. A. Boyle, Lead in the western North Atlantic Ocean: Completed response to leaded gasoline phaseout, *Geochim. Cosmochim. Acta*, *61*(15), 3279–3283, 1997.

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