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Pb isotopic ratios and elemental abundances for selective leachates from near-surface till: implications for mineral exploration

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Abstract—Pb isotope ratios obtained from fine-grained fractions (<63 and <2 µm) from near-surface (<1 m depth) till surrounding ore deposits show isotopic overprinting from the underlying sulfide mineralization, and provide a new approach to mineral exploration for massive sulfide deposits (VMS) in glaciated terrains.

In this study, Pb isotopic measurements, and selective leaching of 6 near-surface till samples down-ice from the Chisel Lake (Manitoba) and Manitowadge (Ontario) VMS deposits were carried out in order to determine the location and nature of the Pb within till. Elemental abundances from selective leachates for all 6 samples display similar patterns and show that chalcophile elements (Cu, Ni, Pb and Zn), derived predominantly from the underlying VMS deposits, occur as (i) adsorbed/exchangeable metals; (ii) associated with oxyhydrous Fe and Mn; (iii) crystalline Fe oxides, and/or (iv) silicate. Despite the relative proximity of some of the till samples to the VMS deposits, only a very small component of the chalcophile elements is present as sulfide. This result is consistent with those from studies of weathered (oxidized) tills, which show that labile minerals such as sulfides have been completely destroyed and their chemical constituents reprecipitated or scavenged locally by clay-sized phyllosilicates and secondary oxides/hydroxides.

Pb isotopic ratios for selective leachates from till samples with VMS-like (anomalous) signatures are similar to those from ore (galena) within the proximal VMS deposits. This indicates that the Pb is of a secondary nature and was probably scavenged and deposited after destruction of original sulfide minerals during till formation. The lack of a predominant sulfide-held Pb component within the selective leachates supports this interpretation. In contrast, Pb isotopic ratios for the same selective leachates from "background" samples are significantly higher and show that the Pb is not derived from proximal VMS deposits but from a more radiogenic source.

Till samples were also leached using 2.5 M HCl ("conventional" leaching). The Pb isotope ratios from the conventional leachates are similar to those obtained from the selective leachates, and show a large difference in Pb isotopic ratios between anomalous and background samples. We propose, therefore, that the conventional leaching rather than selective leaching or complete dissolution of a particular grain-size fraction be adopted for mineral exploration purposes using glacial sediments.

The results from this study support the effective use of Pb isotope ratios from near-surface till as an exploration tool despite the weathered nature of the latter. We feel that this represents a more cost-effective technique over traditional geochemical prospecting methods, if used in conjunction with Pb abundance data. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

Mineral exploration for ore deposits in glaciated terrains is complicated by glacial dispersal of mineralized bedrock and burial of ore beneath glacial sediment. Pb isotopic analysis of overburden, such as gossans, soils, stream sediments, and weathered bedrock, however, has been used as an effective exploration tool for concealed mineralization (e.g. Gulson,

1986 and references within; Gulson *et al.*, 1992). The application of Pb isotopes in mineral exploration for base and precious metal deposits using surficial sediments has been successful because: 1) Pb isotope ratios are not altered in the transition from the ore body to the secondary weathering environment (Gulson, 1986); 2) the isotope signature of some VMS deposits can be quite different to those of the country rock; and 3) Pb isotopic ratios are quantitatively and objectively measured.

Recently, Pb isotope ratios from glacial sediments overlying several known volcanogenic massive sulfide deposits (VMS) in Canada, such as Chisel Lake

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(Manitoba: Bell and Franklin, 1993), Buchans (Newfoundland: Bell and Murton, 1995), and Manitowadge (Ontario: Bell and Card, in prep.) clearly indicate an overprint from the adjacent ore deposits and may provide a new method for detecting buried ore bodies. Pb isotopic ratios from the <63 and <2 μm fractions of till from Buchans (Bell and Murton, 1995), and Chisel Lake (Bell and Franklin, 1993) show a large variation; in general, till samples with overprinted Pb isotopic ratios usually contain higher abundances of Pb, and are close to the ore deposit (<1 km). On the basis of their Pb abundances, Pb isotopic ratios, and down-ice location with respect to ore deposits (Figs 1 and 2), 6 till samples (<63 μm fraction), 4 from Chisel Lake (Manitoba) and 2 from Manitowadge (Ontario), have been selected for this study. The samples from both deposits include those with lower, "ore-like" Pb isotopic ratios ($^{206}\text{Pb}/^{204}\text{Pb} < 18.00$), here referred to as "anomalous" samples, whereas those with higher, more radiogenic (crust-like) isotopic ratios are referred to as "background" samples. Although studies have shown the important use of Pb isotopes in glacial geology (Bell and Murton, 1995) and mineral exploration

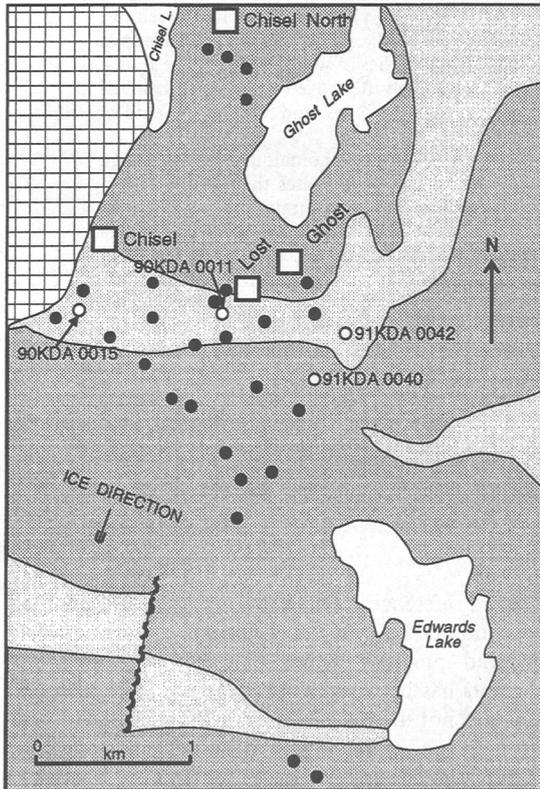


Fig. 1. Simplified geological map of the Chisel Lake area showing location of till samples (solid dots). Samples used in this study are indicated by labelled circles. Grid pattern—Chisel Lake gabbro; light shading—felsic flows, wackes, and breccias; dark shading—mafic flows, wackes, and breccias; Squares—massive sulfide deposits (modified after Bell and Franklin, 1993).

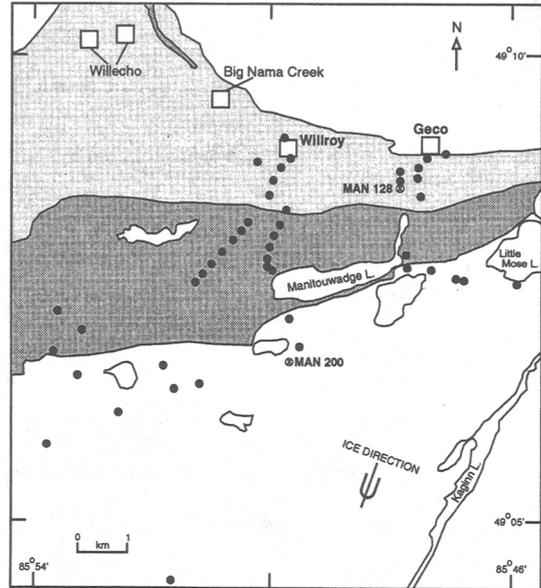


Fig. 2. Simplified geological map of the Manitowadge area showing till sample locations (solid dots, Bell and Card, in prep.). Samples used in this study are indicated as labelled circles. Lighter shading ("Grey Gneiss Group")—is composed of both metasedimentary and minor felsic volcanic rocks; Darker shading ("Hornblende Schist Group") consists of highly deformed mafic, pillowed metavolcanic rocks (Williams *et al.*, 1990); Squares—massive sulfide deposits.

(Bell and Franklin, 1993), the exact location and nature of the Pb being held within glacial sediments is still unknown. Identification of the main binding sites for trace metals is important, providing both insight concerning the geochemical processes during and after till formation, and discrimination between trace-metal sources.

Ore and pathfinder elements are transported by various mechanisms from the source to the surficial environment, where they are held in relatively labile forms associated with different reaction sites (Hall *et al.*, 1993, in press). Organic matter and hydrous coatings of Fe and Mn are the most important surface-active phases ("scavengers"), which are widely distributed in subaerial and subaqueous environments, and have long provided an exploration tool (e.g. Hawkes and Webb, 1962; Levinson, 1980). Formation of Fe and Mn oxides and their metal capture is dependent on the Eh and pH of aqueous solutions, and the activities of many heavy metals are at a minimum in equilibrium with their hydroxides (Jenne, 1962). Selective extraction methods, therefore, have been used in exploration geochemistry to examine only those metals adsorbed on, or included in, specific mineral phases. A summary of the theory, analytical procedures and applications of selective leaches can be found in Chao (1984). Recently, a sequential leaching technique has been developed by the Analytical Method Development section of the Geological Survey of Canada (Hall *et al.*, 1993, in

press). The technique was designed to mimic the action of 2 Soviet selective leaching methods — “MPF” and “TMGM” (e.g. Antropova *et al.*, 1992). The “MPF” method is based on the extraction of metal-organic complexes, whereas the “TMGM” technique is intended to extract elements adsorbed by amorphous forms of Fe and Mn oxyhydroxides (Hall *et al.*, 1993, in press).

Selective leaching was conducted on the <63 µm size fraction from 6 till samples because this grain size fraction is widely used in mineral exploration, and it is much cheaper to extract than other finer-grained size fractions (e.g. <2 µm). The aims of this study are to determine the concentration of Pb and other trace metals in selective leachates and measure the Pb isotopic ratio of each Pb-bearing leachate in an attempt to assess its source — i.e. crustal or VMS-derived. The applied objective is to identify the leaching method (selective vs conventional) which best serves for VMS exploration in glaciated terrains, using Pb isotopes.

GEOLOGY

Two locations were chosen for this study, one in Manitoba and the other in Ontario. Both are associated with Precambrian VMS deposits associated with greenstone belts. Sampling of both areas was carried out during an evaluation programme of the use of Pb isotopes for mineral exploration in glacial sediments.

Chisel Lake

Sampling of the Quaternary cover that overlies the Zn–Cu sulfide deposits at Chisel Lake, near Snow Lake, northern Manitoba (Fig. 1) was completed in 1991 by the Geological Survey of Canada, and material was supplied for Pb isotope analyses. Four sulfide deposits, the Chisel Lake, Chisel Lake North, Lost and Ghost deposits, are present in the bimodal volcanic suite of the early Proterozoic-age Amisk Group (Fig. 1 of Bailes and Galley, 1989; Galley *et al.*, 1990). The deposits and country rocks have been dated at 1889 Ma (U/Pb data; Bailes, 1992). The ore bodies are composed of at least 7.4 million tonnes (t) with an average grade of 10.9% Zn, 1.4% Pb and 0.5% Cu. They contain pyrite, sphalerite, chalcopyrite and galena, as well as trace amounts of arsenopyrite, tetrahedrite and native gold. The deposits are immediately above and adjacent to rhyolite domes and below dacitic ash and breccia. Extensive metamorphosed alteration pipes consisting of muscovite, staurolite, chlorite, gedrite, garnet and pyrite underlie the deposits. Lateral to and slightly below the deposits are zones of garnet–chlorite–muscovite–staurolite and for several hundred meters below the ore horizon the rocks are silicified and albitized. Lower in the

succession thick mafic flows are intercalated with felsic ash and flow sequences. The country rocks are part of the juvenile core of the Trans-Hudson orogen, an arc-related sequence that formed between 1950 and 1835 Ma ago and which was tectonized during the Hudsonian collisional event. All of the rocks are metamorphosed to middle amphibolite grade. Till samples were collected (Fig. 1) from sites <4 km down-ice of the deposits. On the basis of pebble content (C. Kaszycki, 1993, personal commun.), the till (<3 m thick) is considered to be of local provenance and forms a single unit of material derived from Proterozoic rocks of the Snow Lake area. The ice direction is roughly 190 to 210°. The 4 samples from Chisel Lake (90KDA 0011, 0015; 91KDA 0040, 0042) are from the C-horizon, which varies in depth from 0.30 to 0.80 meters.

Manitouwadge

Till samples were collected during a 1992 field excursion, primarily to the south and immediately down-ice from the Willroy and Geco VMS deposits (Fig. 2) Both deposits are hosted by the highly deformed (refolded synform), Archean Manitowadge greenstone belt, which consists of a wide variety of rock types including metavolcanic, metasedimentary and metamorphosed Fe formation, and lies within the Wawa subprovince of the Archean Superior Province (Peterson and Zaleski, 1994; Zaleski and Peterson, 1993; Williams and Breaks, 1990; Zaleski *et al.*, 1994). The Geco Cu mine and several other previously-worked deposits lie south of the main belt of synvolcanic alteration and in most areas are associated with Fe formations. Intrusive rocks within the greenstone belt include foliated diorites to granites, gabbro, K-feldspar-megacrystic granodiorite and strongly foliated to massive pegmatites (Zaleski and Peterson, 1993; Zaleski *et al.*, 1994). Host rocks surrounding the Manitowadge greenstone belt consist of granites and granite gneisses. The greenstone belt is host to 4 known VMS deposits, the largest of which is the Geco Cu–Zn–Ag deposit (Friesen *et al.*, 1982) and contains an ore grading of 1.9% Cu, 3.8% Zn, 1.7 ounces of Ag/ton, and minor amounts of Au, Cd, Bi and Pb (0.30%) (Williams *et al.*, 1990). Mineralization consists of deformed massive sulfides, predominantly pyrite–pyrrhotite–sphalerite–chalcopyrite which is spatially associated with banded ironstone horizons (Williams *et al.*, 1990; Williams and Breaks, 1989).

Glacial sediments in the Manitowadge area are thought to have been deposited during the Late Wisconsinian, with striae measurements indicating that the predominant ice flow direction was toward 210–220° (Kristjansson and Geddes, 1985; Geddes and Bajc, 1985; Barnett *et al.*, 1991; Kettles, 1993a, 1993b). The till commonly forms a thin, discontinuous veneer (up to 1.5 m thick), but can exceed 10 m

thickness in some places (Kristjansson and Geddes, 1985; Geddes and Bajc, 1985). Geochemical analysis of 286 till samples (Kettles and Murton, 1994) indicates the presence of local Precambrian lithologies and/or a large component of Paleozoic carbonate debris, transported more than 100 km from the Hudson and James Bay lowlands. In addition, high concentrations of Cu, Pb and Zn occur within the <63 and <2 µm fractions of till located near the main Manitouwadge VMS deposits (Kettles and Murton, 1994). MAN 128 is from the B/C horizon located at a depth of ~0.4 to 0.5 meters which contains some rusty brown mottles (Fe oxides) indicative of weathering. MAN 200 is a sample of olive-grey, C-horizon till taken at a depth of 0.60 to 0.65 meters.

ANALYTICAL METHODS

Approximately 1 g of till from the <63 µm fraction was sequentially leached according to the method briefly outlined in Table 1 (see Hall *et al.*, 1993, in press for details). Leachate solutions were subsequently evaporated to dryness and conditioned with 3 to 4 ml of 1N HBr acid. Lead was separated in HBr and HCl using a two-column (0.5 and 0.2 ml) extraction procedure (see Simonetti *et al.*, 1995 for details). Samples for Pb isotopic analyses were run on a single Re filament with silica gel and phosphoric acid using a Finnigan-MAT 261 solid-source mass spectrometer in the static mode. Blank levels for Pb in selective extraction reagents (Table 1) range from 0.001 to 0.004 ppm, whereas the total procedural Pb blank varies from 0.2 to 1.5 ng.

RESULTS

Distribution of Pb and other chalcophile elements

Elemental concentrations, obtained using atomic absorption spectrometry (AAS) at the Geological Survey of Canada, for all selective leachates are shown in Table 2, and abundances for various base metals (Cu, Ni, Pb and Zn), are plotted against their respective leachates (A to H) in Figs 3 and 4. Table 2 and Figs 3 and 4 show that the Pb contained within the 6 till samples occurs predominantly in 4 different forms: (1) water-soluble and exchangeable metal (adsorbed); (2) hydrous oxide of Fe or Mn (FeOH-

MnOH); (3) crystalline FeO; (4) silicate and/or residual oxide. An extremely important finding is that *negligible* Pb is held in the sulfide form (leachates G, Table 2). Figure 3 shows that the till sample with the highest Pb concentration (88 ppm), 90KDA 0011 from Chisel Lake, has more than 50% of the Pb held as either an adsorbed metal (leachates A, B) or as an FeOH-MnOH (leachates C, D). In addition, "anomalous" samples 90KDA 0011 and 0015 from Chisel Lake and MAN 128 from Manitouwadge display a similar Pb distribution pattern to those for some "background" samples from the same deposit (Figs 3 and 4), although the latter plot at lower concentrations.

The distribution of the chalcophile elements Cu, Ni and Zn, typically abundant within VMS deposits, for the selective leachates are also shown in Figs 3 and 4. The distribution of these elements is similar to that of Pb, since they occur predominantly as either adsorbed metals, hydrous oxides of Fe and Mn, crystalline FeO, or silicates. A small proportion of the Cu, Ni and Zn occur as sulfides (Figs 3 and 4), which may suggest that sulfide minerals, such as chalcopyrite, and pyrrhotite, are present in trace amounts. A duplicate analysis of Chisel Lake sample 90KDA 0011 (Table 2) shows a mean reproducibility of approximately 2% for the quoted concentrations. In addition, shown in Table 3 are the mean and standard deviation values for various elements in control samples TILL-2 and LKSD-4 (from Hall *et al.*, in press). Abundances for control sample TILL-2, obtained during the course of this study, fall within the accepted standard deviations (Table 3).

Pb isotopic overprinting of some of the till samples (90KDA 0011, 90KDA 0015 and MAN 128) by the underlying ore deposit has been shown by Bell and Franklin (1993) and this occurs despite the lack of Pb in the sulfide form (Table 2). This indicates that a large component of the Pb which occurs as either an adsorbed metal (leachates A, B), hydrous oxide of Fe or Mn (leachates C, D), or crystalline FeO (leachates E, F) must have been derived from the ore deposit. It is highly probable that the dominant Pb-sulfide mineral associated with VMS deposits, galena (PbS), was

Table 1. Sequential extraction scheme (Hall *et al.*, 1993)

Extractant	Phases dissolved	Leachate symbol used
1 M NaOAc.HOAc 1 g sample/20 ml 2 × 6 hr constant shaking	Adsorbed metals, exchangeable, carbonates and some phosphates	A, B
0.25 M NH ₂ OH.HCl in 0.25 M HCl 20 ml reagent, at 60°C; first leach for 2 hr, second for 0.5 hr	Amorphous oxyhydrides of Fe and Mn	C, D
1 M NH ₂ OH.HCl in 25% HOAc 30 ml reagent, at 90°C; first leach for 3 hr, second leach for 1.5 hr	Crystalline Fe oxides (e.g., hematite, goethite, magnetite, maghemite, lepidocrocite)	E, F
KClO ₃ /HCl, 15 ml, for 0.5 hr with mixing; followed by 4M HNO ₃ (10 ml) at 90°C	Sulphides and "less soluble" organic matter	G
HF-HClO ₄ -HNO ₃ -HCl, 10 ml, to dryness	Silicates, residual crystalline fraction (refractory minerals could remain in a final residue)	H

Table 2. Elemental concentrations of selective extraction leachates from < 63 µm fraction of till samples

	Leachates								Total
	A	B	C	D	E	F	G	H	
Pb (ppm):									
90KDA 0011	37	5	24	1	6	-	-	15	88 (79)
90KDA 0011 Dup.	37	5	23	1	8	1	-	14	89
90KDA 0015	2	1	11	1	-	1	-	12	28 (26)
91KDA 0040	-	-	1	-	-	-	-	11	12 (11)
91KDA 0042	-	-	-	-	-	-	-	10	10 (12)
MAN 128	4	1	7	1	4	-	1	10	28 (29)
MAN 200	1	1	4	-	1	-	-	8	15 (11)
Blank*	-	-	0.5	-	1	-	-	-	1.5
Cu (ppm):									
90KDA 0011	8	2	84	11	47	5	14	31	202
90KDA 0011 Dup.	9	2	83	10	48	5	14	31	202
90KDA 0015	2	-	22	2	14	-	5	4	49
91KDA 0040	1	-	11	2	8	-	4	3	29
91KDA 0042	2	-	29	7	17	1	4	5	65
MAN 128	1	1	11	4	15	1	4	4	41
MAN 200	-	-	4	1	8	-	4	2	19
Blank*	-	-	-	-	-	-	1	-	1
Zn (ppm):									
90KDA 0011	2	1	189	37	130	10	30	64	463
90KDA 0011 Dup.	2	-	186	36	135	10	29	64	462
90KDA 0015	2	-	114	10	56	6	19	30	237
91KDA 0040	-	-	17	3	16	3	9	19	67
91KDA 0042	-	-	16	2	8	1	8	23	58
MAN 128	4	1	87	32	135	9	15	35	318
MAN 200	-	-	9	3	14	2	9	16	53
Blank*	-	-	-	-	-	-	4	-	4
Ni (ppm):									
90KDA 0011	-	-	8	1	8	-	4	9	30
90KDA 0011 Dup.	-	-	8	-	8	1	7	9	33
90KDA 0015	-	-	10	1	10	1	5	13	40
91KDA 0040	-	-	7	1	8	1	5	10	32
91KDA 0042	-	-	9	1	6	-	3	10	29
MAN 128	-	-	2	-	8	1	3	8	22
MAN 200	1	-	5	2	14	1	5	12	40
Blank*	1	-	-	-	-	-	1	1	3
Mn (ppm):									
90KDA 0011	2	-	35	4	29	5	11	191	277
90KDA 0011 Dup.	2	-	35	4	29	5	11	188	274
90KDA 0015	6	1	80	4	29	5	14	187	326
91KDA 0040	8	6	89	5	34	6	17	211	376
91KDA 0042	1	-	30	4	19	4	9	316	383
MAN 128	-	-	8	3	28	5	9	138	191
MAN 200	17	13	88	12	55	9	20	158	372
Blank*	-	-	-	-	-	-	-	-	-
Fe (ppm):									
90KDA 0011	48	28	5858	828	6925	1070	2975	16560	34292
90KDA 0011 Dup.	47	26	5865	780	6950	1140	2938	16940	34686
90KDA 0015	53	27	8400	1062	8300	985	2925	14160	35912
91KDA 0040	40	32	5588	885	7400	1070	3013	14460	32488
91KDA 0042	98	38	7005	1314	6750	805	2175	19800	37985
MAN 128	247	135	2258	477	4788	660	1475	7800	17840
MAN 200	106	63	5610	1143	7700	885	2413	10540	28460
Blank*	-	-	-	1	2.5	-	-	2.5	6
Co (ppm):									
90KDA 0011	-	-	3	-	1	-	-	4	8
90KDA 0011 Dup.	-	-	2	-	1	-	-	4	7
90KDA 0015	-	-	4	-	1	-	-	4	9
91KDA 0040	-	-	3	-	3	-	-	4	10
91KDA 0042	-	-	4	-	-	-	-	6	10
MAN 128	-	-	1	-	1	-	-	3	5
MAN 200	-	-	2	-	3	-	1	4	10
Blank*	-	-	-	-	-	-	0.5	-	0.5

Leachates: A—1st leachate for adsorbed/exchangeable metal; B—2nd leachate for adsorbed and exchangeable metal; C—1st leachate for hydrous oxides of Fe and Mn (FeOH-MnOH); D—2nd leachate for hydrous oxides of Fe and Mn (FeOH-MnOH); E—1st leachate for crystalline FeO; F—2nd leachate for crystalline FeO; G—sulphides; H—silicates and residual oxides. Value in bracket for Pb concentrations obtained by ICP analysis, and uncertainty is $\pm 10\%$ of quoted value. Dup. = duplicate analysis; (-) = not detected; * = average values for two runs.

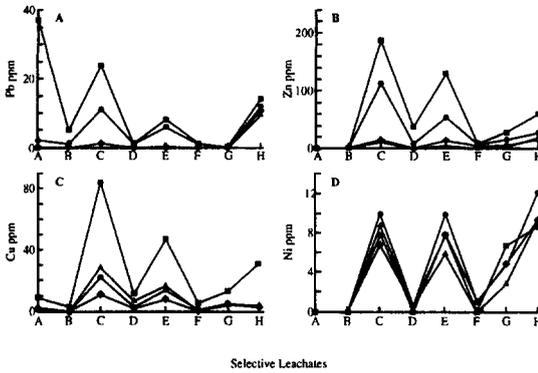


Fig. 3. Plots of elemental abundances vs selective leachates for till samples from Chisel Lake. Letters correspond to the following leachates: A—1st leachate for adsorbed and exchangeable metal; B—2nd leachate for adsorbed and exchangeable metal; C—1st leachate for hydrous oxides of Fe and Mn (FeOH–MnOH); D—2nd leachate for hydrous oxides of Fe and Mn (FeOH–MnOH); E—1st leachate for crystalline FeO; F—2nd leachate for crystalline FeO; G—sulfide leachate; H—silicate and/or residual oxide leachate. Solid square—90KDA 0011; Solid circle—90KDA 0015; Solid diamond—91KDA 0040; Solid triangle—91KDA 0042. A) Pb (ppm); B) Zn (ppm); C) Cu (ppm); D) Ni (ppm).

completely destroyed by glacial processes associated with till formation. The Pb isotopic ratios for the different Pb-bearing selective leachates will certainly provide much needed insight into the source of the Pb.

Pb isotopic ratios—Chisel Lake

Pb isotopic measurements for Pb-bearing selective leachates from Chisel Lake are listed in Table 4 and shown in Figs 5 and 6. Selective leachates A through F from anomalous samples 90KDA 0011 and 0015 contain relatively constant Pb isotopic ratios similar to those from the galena within the Chisel Lake VMS deposits (Fig. 5). In contrast, the silicate leachates (H) from both of these samples contain Pb isotopic ratios

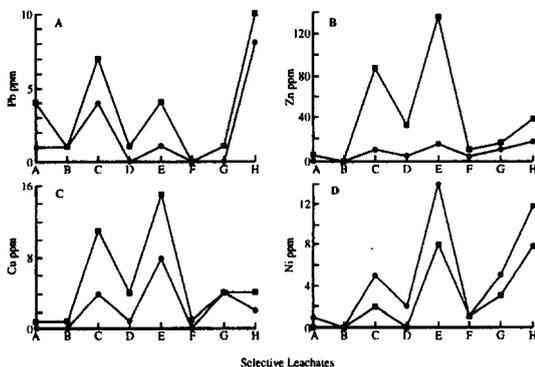


Fig. 4. Plots of elemental abundances vs selective leachates for Manitowadge till samples. Letters representing selective leachates are as in Fig. 3 and Table 1. Solid square—MAN 128; Solid circle—MAN 200. A) Pb (ppm); B) Zn (ppm); C) Cu (ppm); D) Ni (ppm).

that are higher than those from the earlier leachates. The Pb isotopic ratios from total dissolution of the $< 63 \mu\text{m}$ fraction for both 90KDA 0011 and 0015 are intermediate between those obtained for the early leachates (adsorbed metal through to FeOH–MnOH, A to D), and those from the crystalline FeO (E) and silicate (H) leachates (Table 4). The Pb isotopic ratios for selective leachates from a separate, duplicate sequential leaching of 90KDA 0011 show excellent reproducibility, and, with one exception (silicate leachate-H), the duplicate analyses are the same order as duplicates on till (0.1%, 2σ level, Table 4).

In contrast, the Pb isotopic composition for selective leachates from the 2 background till samples from Chisel Lake (91KDA 0040, 0042) differ from those obtained from the anomalous samples. Firstly, sample 91KDA 0042 contains Pb that is restricted mainly to the silicate minerals, whereas 91KDA 0040 contains Pb in both the first FeOH–MnOH (C) and silicate (H) leachates. All of these 3 leachates give Pb isotopic ratios that are much higher than the signature of the Chisel Lake galena. The highly radiogenic Pb isotopic composition ($^{206}\text{Pb}/^{204}\text{Pb} > 23.00$) for the FeOH–MnOH leachate (C) from sample 91KDA 0040 clearly shows that this Pb is derived from a different source to that found in the anomalous samples ($^{206}\text{Pb}/^{204}\text{Pb}$ range = 15.88 to 16.79). Pb in sample 91KDA 0040, was probably derived from the breakdown of rocks with much higher U/Pb ratios than VMS deposits such as those of the associated Proterozoic sequences. Another interesting feature is that the Pb isotopic ratios for the silicate leachates from both background samples approach the isotopic composition of the silicate leachates from the two anomalous samples (Fig. 5).

The $^{207}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ isotopic plot shown in Fig. 6A shows that analyses from the $< 63 \mu\text{m}$ fraction (84 in total) of till from Chisel Lake taken from Bell and Franklin (1993) form a linear array, with a slope of 0.122 ± 0.003 (MSWD = 9.3; corresponding to a date of about 2000 Ma), where the lower end is close to the isotopic signature of the ore deposit. Also shown for reference in Fig. 6 is the Stacey and Kramers (1975) growth curve which reflects the variation of Pb isotopic ratios throughout geologic time in the source region that generated most massive sulfide deposits. The Pb isotopic data from the Chisel Lake ores are close to the 2000 Ma point on the Stacey–Kramers growth curve (Bell and Franklin, 1993). The Pb isotopic ratios determined for selective leachates from the Chisel Lake samples also lie along this same linear array (Fig. 6A). The selective leachates from one of the background samples, 91KDA 0040, show a variation in Pb isotopic ratios that covers much of the range displayed by the 84 analyses of $< 63 \mu\text{m}$ fraction of till samples from Chisel Lake. Figures 5 and 6 show that the Pb isotopic ratios for the FeOH–MnOH leachate (C) from background sample 91KDA 0040 are the most radiogenic recorded in any of the size fractions (both < 63 and

Table 3. Mean and standard deviation values in ppm for various elements in control samples TILL-2 and LKSD-4 (from Hall *et al.*, in press)

Sample	PHASE					Total	Recommended [†]
	AEC (Leach. A + B)	Am Fe ox (Leach. C + D)	Cry Fe ox (Leach. E + F)	Sulphides (Leach. G)	Silicates (Leach. H)		
Pb:							
TILL-2 this study	5	10	4	-	10	29	
TILL-2 [‡]	4.8±0.8	10.2±0.4	<1	<1	8.0±0.7	22.8±1.4	31±3
LKSD-4*	4.6±0.8	16.0±1.2	<1	<1	6.2±3.3	84±10	91±6
Cu:							
TILL-2 this study	13	53	54	11	24	155	
TILL-2	12.2±0.9	56.1±1.9	46.6±1.3	8.3±2.2	22.4±2.0	146±3	150±10
LKSD-4	<1	6.8±0.4	4.6±0.9	11.4±3.0	2±0.4	32.2±2.4	31±4
Zn:							
TILL-2 this study	3	31	52	17	24	127	
TILL-2	3.0±0.3	34.1±1.0	44.9±1.4	13.8±2.0	24.0±2.0	120±3	130±8
LKSD-4	9.8±1.8	64.4±5.1	16.2±1.5	9.6±0.5	14.8±3.5	191±10	194±19
Ni:							
TILL-2 this study	-	9	20	6	11	46	
TILL-2	<1	3.1±1.0	14.6±1.6	5.8±2.1	8.5±0.9	33.3±2.5	32±3
LKSD-4	<1	10.2±0.8	4.0±1.0	4.8±0.4	5.2±1.3	30.6±1.5	31±5
Mn:							
TILL-2 this study	80	252	144	41	140	657	
TILL-2	86.8±8.3	292±11	125±8	43.8±4.0	145±21	693±40	780±28
LKSD-4	16.0±2.0	56.0±6.0	42.2±3.3	11.2±1.7	83.4±1.9	460±39	500±30
Fe:							
TILL-2 this study	339	8447	15890	4425	6240	35341	
TILL-2	403±52	10190±403	14866±600	4131±457	5821±585	35403±1036	37700±1300
LKSD-4	126±20	4610±580	7591±620	5397±278	4963±354	26182±142	28000±200
Co:							
TILL-2 this study	1	4	4	1	2	12	
TILL-2	1±1	4.8±0.5	4.8±1.7	1±1	3±1	14.5±1.4	15±2

[†]: Recommended values for LKSD-4 from Lynch (1990) and for TILL-2 from Hall *et al.* (in press).

[‡]: Average value for 8 analyses.

*: Average value for 5 analyses. In addition, pyrophosphate extraction had been carried out on LKSD-4 prior to the sequential leach of Hall *et al.* (in press).

The total value includes this portion.

<2 µm) of till samples from Chisel Lake analyzed to date.

Pb isotopic ratios—Manitouwadge

Pb isotopic results for Pb-bearing selective leachates from anomalous sample MAN 128 and background sample MAN 200 are shown in Table 5 and Figs 7 and 8. The data exhibit the following features: (1) Pb isotope ratios for selective leachates A through to E from the anomalous sample, MAN 128, are constant and similar to the ratios obtained from the galena associated with the Manitouwadge VMS deposits (Fig. 7); (2) the Pb isotopic composition for the sulfide leachate (G) from sample MAN 128 is the most radiogenic of all its leachates, and is clearly quite different to that of the associated ore deposit (Fig. 7); (3) the selective leachates A, C and E from background sample MAN 200 contain Pb isotopic ratios that are relatively constant but significantly higher than those from MAN 128 (Fig. 7); (4) the silicate leachate (H) from MAN 200 contains an isotopic composition equivalent to that for the silicate leachate from MAN 128 (Fig. 7).

²⁰⁶Pb/²⁰⁴Pb versus ²⁰⁷Pb/²⁰⁴Pb isotopic plot (Fig. 8A), shows that all the analyses from the <63 µm fraction of the Manitouwadge tills plot along a linear array with a slope equivalent to a secondary isochron age of 2700 Ma (Bell and Card, in prep.), consistent with the ca. 2700 Ma age of the Geco and Willroy deposits. With the exception of the ²⁰⁸Pb/²⁰⁴Pb isotope ratio for sulfide leachate (G) from MAN 128, Pb isotope ratios from the selective leachates also plot along the same trends (Fig. 8). Figure 8 shows that most of the selective leachates (A to E) from anomalous sample MAN 128 fall closest to the analyses from the Manitouwadge ore (Bell and Card, in prep.), whereas all but one of those from background sample MAN 200 fall at the other end of the array, with very radiogenic Pb isotope ratios (²⁰⁶Pb/²⁰⁴Pb ~ 24.00).

Conventional leachates

During the development of the exploration technique using Pb isotopes as indicators of mineralization in glacial till, Bell and co-workers used an extraction technique that involved leaching of the till samples for

Table 4. Pb isotopic ratios for ore and selective Pb-bearing leachates for tills from Chisel Lake

Ore*	Measured†		
	$^{206}\text{Pb}/^{204}\text{Pb}$ 15.42-15.46	$^{207}\text{Pb}/^{204}\text{Pb}$ 15.16-15.22	$^{208}\text{Pb}/^{204}\text{Pb}$ 35.00-35.17
90KDA 0011:			
< 63 μm fraction*	16.13	15.23	36.65
A	15.88	15.24	35.37
A-duplicate	15.90	15.26	35.44
B	15.89	15.24	35.34
B-duplicate	15.89	15.22	35.35
C	15.94	15.24	35.40
C-duplicate	15.96	15.26	35.48
D	16.01	15.24	35.44
D-duplicate	16.02	15.28	35.57
E	16.05	15.26	35.52
E-duplicate	16.04	15.26	35.52
F	no signal		
F-duplicate	16.21	15.27	35.67
H	17.44	15.41	37.46
H-duplicate	17.22	15.40	37.35
90KDA 0015:			
< 63 μm fraction*	17.16	15.39	36.90
A	16.70	15.33	35.85
B	16.75	15.32	35.82
C	16.79	15.37	35.94
D	16.79	15.32	35.90
F	17.53	15.40	36.65
H	17.39	15.40	37.61
91KDA 0040:			
< 63 μm fraction*	18.59	15.56	38.03
C	23.03	16.08	40.37
H	17.65	15.46	38.22
91KDA 0042:			
< 63 μm fraction*	20.31	15.77	40.24
H	19.02	15.65	39.82

*: Fractionation corrected ratios using a factor of $0.12\% \pm 0.02$ a.m.u. based on replicate analyses of NBS 982 Pb standard. †: Pb isotope ratios for ore and < 63 μm fraction taken from Bell and Franklin (1993).

about 2 h using 2.5N HCl. The results from the Pb isotope ratios of the leached Pb successfully delimited the mineralized areas, which were spatially similar to those that were found using complete dissolution of the samples with HF and HNO₃.

Conventional leaching experiments were conducted on all 6 till samples in order to measure their Pb isotopic composition and compare the results with those obtained from the selective leachates. 300 milligrams of till from the < 63 μm fraction were immersed in approximately 5 ml of cold, double-distilled 2.5 M HCl for roughly 2 h, and occasionally shaken. The leachate solution was decanted, centrifuged, evaporated to dryness, and then conditioned with 1 N HBr. The residue sample was subsequently dissolved using a multi-acid procedure (HF-HNO₃ mixture and then 6 M HCl). A similar leaching technique was used by Gulson *et al.* (1992) to dissolve

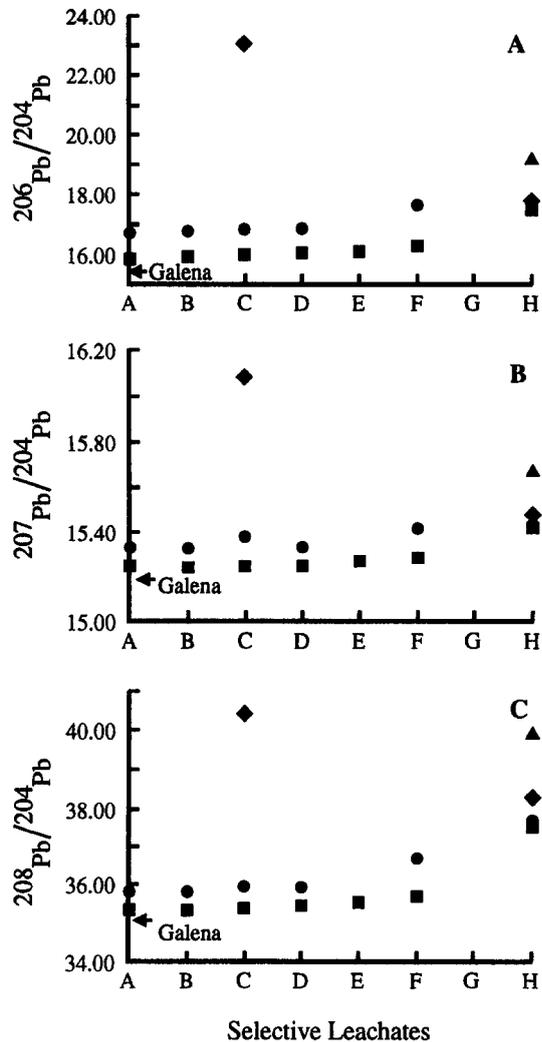


Fig. 5. Diagram showing Pb isotopic ratios for Pb-bearing selective leachates from Chisel Lake samples. Leachate letters and symbols as in Fig. 3. Pb isotopic ratios for galena taken from Bell and Franklin (1993). A) $^{206}\text{Pb}/^{204}\text{Pb}$ vs leachate; B) $^{207}\text{Pb}/^{204}\text{Pb}$ vs leachate; C) $^{208}\text{Pb}/^{204}\text{Pb}$ vs leachate.

Fe and Mn coatings of stream pebbles, from the Mount Emmons area (Colorado), for Pb isotopic analysis in order to determine their feasibility as a guide to concealed mineralization.

Pb isotope ratios for the conventional leachates and residues are shown in Table 6. Figures 9 and 10 show that of the analyses from the total dissolution of the < 63 μm fraction of tills from Chisel Lake (Bell and Franklin, 1993) and Manitouwadge (Bell and Card, in prep.) all but one plot between those obtained from their respective conventional leachate and residue. Anomalous samples 90KDA 0011, 0015, and MAN 128, have conventional leachates with Pb isotope ratios that are less radiogenic (i.e. more "ore-like") than the isotopic signature of the < 63 μm fractions (Figs 9 and 10), and give Pb isotopic ratios similar to those obtained from the earlier selective leachates-adsorbed metal (A,B), FeOH-MnOH

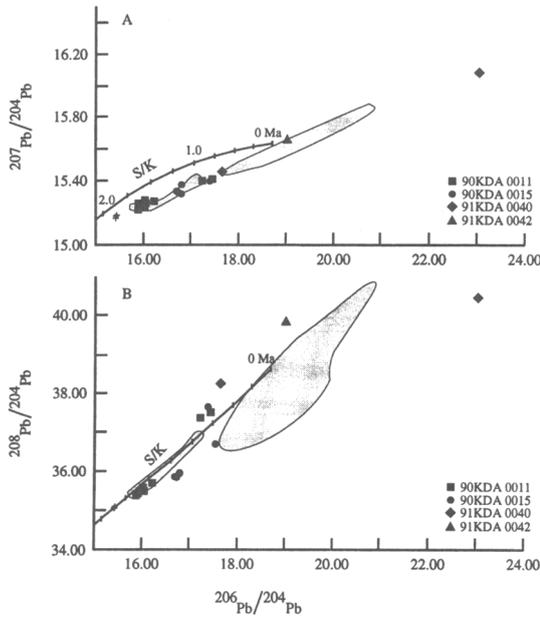


Fig. 6. Pb-Pb isotopic plots showing results for selective leachates from Chisel Lake samples. S/K = Stacey and Kramers (1975) Pb evolution curve; thicks along curve are at 0.25 Ga interval. Fields represent isotopic data from <63 μm fraction analyses (Bell and Franklin, 1993). + = galena analyses. A) ²⁰⁶Pb/²⁰⁴Pb vs ²⁰⁷Pb/²⁰⁴Pb; B) ²⁰⁶Pb/²⁰⁴Pb vs ²⁰⁸Pb/²⁰⁴Pb.

(C,D), or crystalline FeO leachates (E,F). The Pb isotopic composition for the residues from anomalous samples tend to approximate the ratios obtained from the silicate leachates for the same sample (Tables 4-6).

Similarly, the Pb isotopic composition for the

Table 5. Pb isotopic ratios for ore and selective Pb-bearing leachates for tills from Manitouwadge

Ore*	Measured†		
	²⁰⁶ Pb/ ²⁰⁴ Pb	²⁰⁷ Pb/ ²⁰⁴ Pb	²⁰⁸ Pb/ ²⁰⁴ Pb
	13.21-14.03	14.40-14.62	33.08-33.96
MAN 128:			
<63 μm fraction*	14.99	14.84	34.94
" duplicate	14.87	14.79	34.76
A	14.58	14.68	34.44
B	14.60	14.68	34.44
C	14.51	14.68	34.40
D	14.36	14.63	34.20
E	14.44	14.64	34.26
G	16.50	15.03	39.35
H	15.91	15.13	35.87
MAN 200:			
<63 μm fraction*	20.05	15.82	39.69
" duplicate	19.97	15.79	39.57
A	23.84	16.49	43.06
C	24.89	16.69	44.02
E	24.02	16.52	43.59
H	16.57	15.20	36.28

†: see Table 4 caption. *: Pb isotope ratios for ore and <63 μm fraction are taken from Bell and Card (in prep., unpublished data)

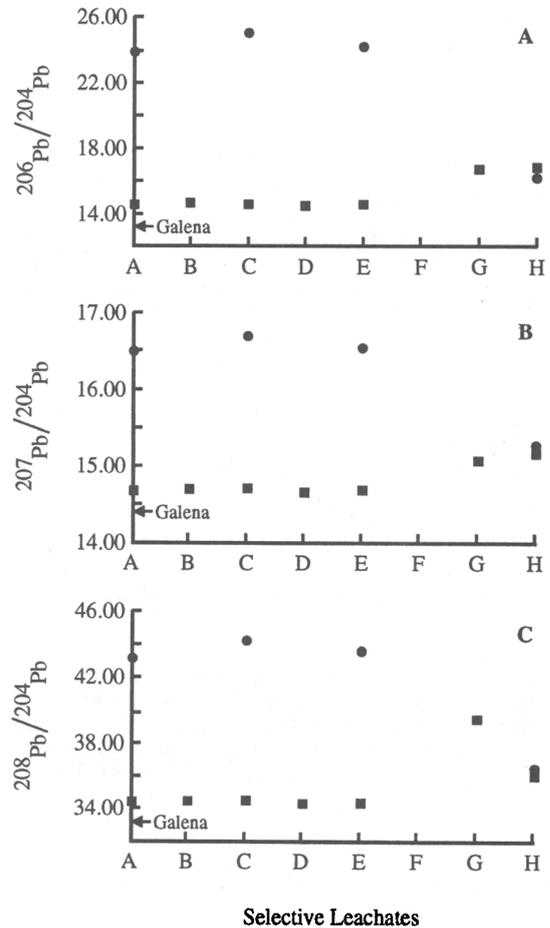


Fig. 7. Diagram showing Pb isotopic ratios for Pb-bearing selective leachates from Manitouwadge till samples. Leachate letters as in Fig. 3, and symbols as in Fig. 4. Pb isotopic ratios for galena taken from (Bell and Card, unpublished data). (A) ²⁰⁶Pb/²⁰⁴Pb vs leachate; (B) ²⁰⁷Pb/²⁰⁴Pb vs leachate; (C) ²⁰⁸Pb/²⁰⁴Pb.

conventional leachates from background samples (91KDA 0040, 0042, MAN 200) are also similar to those obtained from the early selective leachates (adsorbed metal, FeOH-MnOH, or crystalline oxide) from the same samples. The Pb isotopic ratios for the conventional leachates from the background samples, however, are much more radiogenic than values obtained from complete dissolution of the <63 μm fraction (Tables 4-6). Most of the Pb isotope ratios from the selective and conventional leachates seem to plot in the same fields defined by the results from completely digested <63 μm fraction from both deposits (Bell and Franklin, 1993; Bell and Card, in prep.).

DISCUSSION

Selective leachates—weathering of till

Postglacial weathering of till typically occurs within the zone of oxidation above the groundwater or

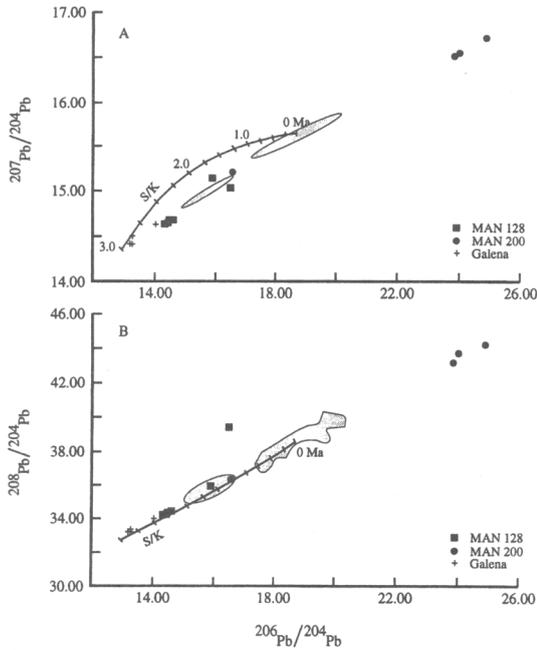


Fig. 8. Pb–Pb isotopic plot showing results for selective leachates of till samples from Manitowadge. Fields represent data from <63 μm fraction analyses (Bell and Card, unpublished data). Other symbols as in Fig. 6. (A) $^{207}\text{Pb}/^{204}\text{Pb}$ vs $^{206}\text{Pb}/^{204}\text{Pb}$; (B) $^{208}\text{Pb}/^{204}\text{Pb}$ vs $^{206}\text{Pb}/^{204}\text{Pb}$.

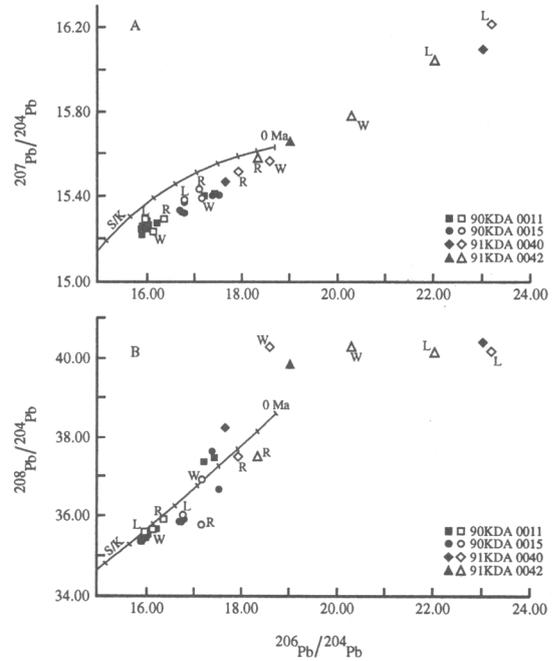


Fig. 9. Pb–Pb isotopic plot showing conventional leachate-residue (*open symbols*) results from Chisel Lake till samples. L—leachate; W—<63 μm fraction analyses (Bell and Franklin, 1993); R—residue. Corresponding filled symbols are selective leachate results from same sample. Other symbols as in Fig. 6. (A) $^{207}\text{Pb}/^{204}\text{Pb}$ vs $^{206}\text{Pb}/^{204}\text{Pb}$; (B) $^{208}\text{Pb}/^{204}\text{Pb}$ vs $^{206}\text{Pb}/^{204}\text{Pb}$.

permafrost table, and this process can alter drift geochemistry to considerable depth below the surface (Rencz and Shilts, 1980; Shilts, 1976, 1984; Peuraniemi, 1984; Shilts and Kettles, 1990). The depth of

Table 6. Pb isotopic results from conventional leaching of Chisel Lake and Manitowadge tills

	Measured [†]		
	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$
Chisel Lake			
90KDA 0011:			
Leachate	15.96	15.29	35.58
Residue	16.36	15.29	35.91
90KDA 0015:			
Leachate	16.80	15.38	36.01
Residue	17.11	15.43	35.76
91KDA 0040:			
Leachate	23.21	16.20	40.83
Residue	17.94	15.51	37.74
91KDA 0042:			
Leachate	22.05	16.03	40.12
Residue	18.34	15.57	37.49
Manitowadge			
MAN 128:			
Leachate	14.53	14.70	34.49
Residue	15.17	14.89	34.75
MAN 200:			
Leachate	24.67	16.62	43.80
Residue	17.77	15.40	36.67

[†]: see Table 4 caption.

leaching and oxidation in till, however, is dependent on the original abundance of pyrite and other sulfides present in the oxidized zone (Levinson, 1980). Sulfide grains in till found within the zone of oxidation, in particular pyrite, are usually completely or partly altered to limonite (Shilts and Kettles, 1990), goethite (Nikkarinen *et al.*, 1984) or other secondary form of sulfide (Peuraniemi, 1984). Shilts and Kettles (1990) show that the upper 2 m of weathered till near Thetford Mines, Québec, is enriched (by a factor of 2 over the deeper sections of till) in goethite, leucoxene and other secondary minerals formed as a result of alteration and destruction of sulfide minerals, suggesting that they were created by weathering. Breakdown of the sulphide minerals can have taken place either prior to glaciation during weathering of the bedrock, during glaciation, or during post-glacial weathering of till. The effects of pre-glaciation weathering of sulfide minerals is difficult to evaluate due to the later superimposition of complex glacial processes and their correlated effects. Compared to sulfide minerals, pre-glacial, finer-grained(?) secondary minerals are less likely to have remained intact and preserve the Pb isotopic signature of the VMS deposit during till formation, assuming they were imparted with the isotopic signature of the ore deposit. Unfortunately, this scenario cannot be evaluated. Despite the alteration and weathering that occurs within the oxidized zones of till, geochemical profiles for the <63 μm

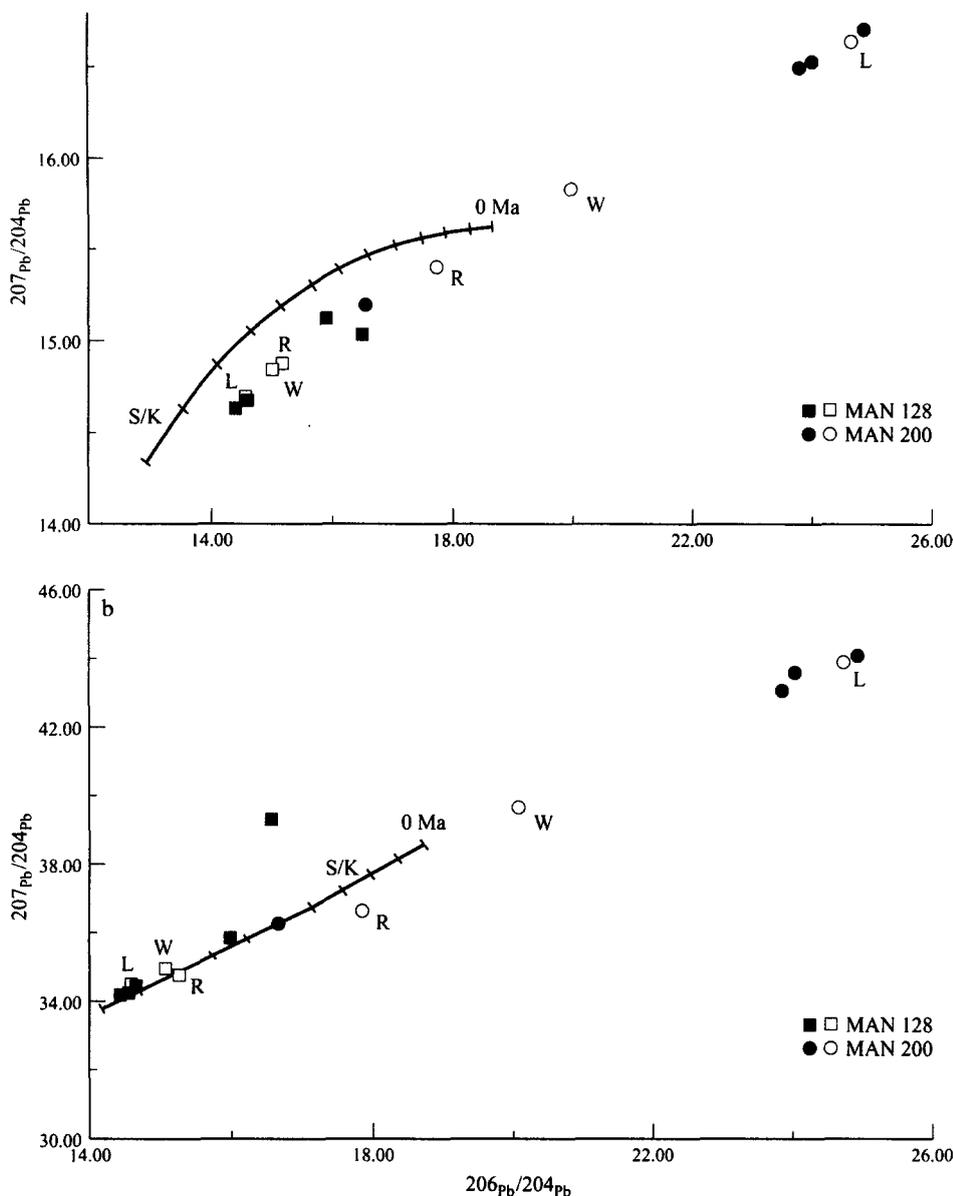


Fig. 10. Diagram showing Pb-Pb isotopic results from conventional leachate-residue (*open symbols*) from Manitouwadge till samples. L—leachate; W— $<63\ \mu\text{m}$ fraction analyses (Bell and Card, unpublished data); R—residue. Corresponding filled symbols are selective leachate results from same sample. Other symbols as in Fig. 6. (A) $^{206}\text{Pb}/^{204}\text{Pb}$ vs $^{207}\text{Pb}/^{204}\text{Pb}$; (B) $^{208}\text{Pb}/^{204}\text{Pb}$ vs $^{206}\text{Pb}/^{204}\text{Pb}$.

grain size fraction show that the concentration of base metals is constant with depth (e.g. Shilts and Kettles, 1990), indicating that the trace metals are effectively scavenged and retained proximal to their site of destruction. Most of the Pb found in the 3 anomalous samples has to have been derived from the breakdown of the sulphide minerals along with the release of Pb into the natural system.

In the anomalous samples, Pb which occurs as crystalline FeO leachate (E, F) may represent Pb isotopic analysis of primary, more resistant FeO phases with low U/Pb (i.e. magnetite and hematite), usually associated with VMS deposits. The Pb abundances of magnetite and hematite, however, are

much lower than those found in galena, which would mean that it would take large amounts of Fe oxides to swamp the isotopic signature of the galena. In addition, the crystalline FeO (E,F) and FeOH-MnOH leachates (C,D) contain high levels of Cu, Ni and Zn (Figs 3 and 4) suggesting sulfide minerals rather than magnetite and hematite which are not known to contain a large quantity of such elements. Although the Pb isotopic ratios for the selective leachates A to E from the anomalous samples are similar to the isotopic signature of the ore, they are not identical which indicates that a minor component of the Pb contained within these leachates was derived from a slightly more radiogenic source, possibly the

surrounding volcanic rocks found within the host greenstone belt.

The sulfide leachate (G) from anomalous sample MAN 128 contains Pb isotope ratios that are quite different to those obtained from ore associated with the Manitouwadge VMS deposits (Fig. 7). The presence of sulfide-held Pb in selective leachates, therefore, should not automatically be attributed to glacial dispersal of sulfide minerals from proximal VMS deposits. One possible explanation for the origin of the sulfide-held Pb in sample MAN 128 is that it may represent a mixture of Pb from more than one source, and which is now contained in sulfide. Several Pb isotopic studies of sulfide minerals associated with VMS deposits (e.g. Red Lake, Gulson *et al.*, 1993; Beardmore-Geraldton, Simonetti, unpublished data), however, clearly show that sulfide minerals associated with VMS deposits, such as pyrite, chalcopyrite and pyrrhotite, have not evolved with the same, low time-integrated μ ($^{238}\text{U}/^{204}\text{Pb}$) value which characterizes galena ($\mu \sim 0$) and as a result contain more variable and higher Pb isotopic ratios. The linear arrays in Pb–Pb isotope diagrams shown by the data from all of the selective leachates simply reflects the various Pb isotope ratios that are the result of differing μ (μ) values in the rocks that make up the host greenstone belt. Compared to silicate and other sulfide minerals, however, galena contains the mass balance of Pb within VMS deposits, and it is this feature which has guaranteed the successful application of Pb isotope ratios to till.

Pb concentrations and isotope composition for the selective leachates from the 3 background samples (91KDA 0040 and 0042, and MAN 200) show the following consistent features (Figs 5–10): (1) most of their Pb occurs in either silicates or residual oxides (leachate H); (2) the Pb isotopic composition for the silicate leachate is similar to that of the anomalous samples from the same deposit; (3) if present, the Pb isotopic signature for the adsorbed metal (A, B), FeOH–MnOH (C, D), or crystalline FeO (E, F) leachates are much more radiogenic than the same leachates from the anomalous samples. The highly radiogenic nature of these analyses (Figs 5 and 7) show that the background samples do not contain any Pb derived from the nearby VMS deposits as the result of glacial erosion and down ice sediment transport. Figures 1 and 2 confirm that samples 91KDA 0040 and 0042 and MAN 200 are either not directly down-ice from known ore deposits, or are too distal from them (>4 km), which may explain their lack of a VMS-like Pb isotopic signature. The Pb isotopic ratios for the silicate leachates (H) from both anomalous and background samples are similar and are less radiogenic than the average value for present-day continental crust (0 Ma point of Stacey and Kramers (1975) Pb evolution curve). Compared to the Pb isotope ratios of sulfides (e.g. galena) from the associated VMS deposits, the silicate leachates from both groups of till contain more radiogenic Pb isotope

values, therefore, these leachates incorporate Pb from minerals with much higher time-integrated U/Pb ratios (μ values). Unlike the sulfide minerals, which have a higher specific gravity and are less-resistant to weathering, silicate components of the VMS terrains can be found at greater distances down-ice from the ore deposits.

All but one of the Pb isotopic measurements from the selective leachates ($n = 33$) plot along the linear arrays (Figs 6 and 8) defined by the analyses of the <63 μm fraction of till from both Chisel Lake and Manitouwadge. This feature further supports the mixing model proposed for till formation at Chisel Lake (Bell and Franklin, 1993) involving end-members with differing U/Pb, and is consistent with the interpretation of the Pb–Pb arrays as relict secondary isochrons (Bell and Franklin, 1993). Additional support for this interpretation is provided by the Pb isotope ratios from the conventional leachates and residues which also plot along the same linear arrays (Figs 9 and 10).

Conventional leachates—new exploration tool

Pb isotopic ratios for the conventional leachates from anomalous till samples are less radiogenic (i.e. more “ore-like”) than analyses from the complete dissolution of the <63 μm fraction, whereas conventional leachates from background samples give Pb isotopic ratios that are more radiogenic, less “ore-like” than the <63 μm fraction. In addition, conventional leachates for all samples contain Pb isotopic ratios (Table 6) that are similar to those obtained from the earlier selective leachates (adsorbed metal to FeOH–MnOH, A to C); whereas Pb isotopic ratios from the residues give isotopic ratios that are closer to those obtained from the silicate leachates (Tables 4–6). The difference in Pb isotopic ratios shown by the conventional leachate and residue for an individual sample, however, is not as large as that obtained from the selective leachates. With the exception of Fig. 9B, the Pb isotopic ratios for the conventional leachates and residues plot on the linear arrays defined by those from the selective leachates. One possible explanation for the scatter of the data points in Fig. 9B is sample heterogeneity since isotope results from conventional leaching (and residue), and whole rock analyses (Bell and Franklin, 1993; Bell and Card, in prep.) were obtained from separate aliquots of the same sample powder. Alternatively, the scatter may be attributed, in part, to a real variation in Th/U ratio in the Chisel Lake deposit and associated volcanic rocks, a feature that is supported by the large variation in $^{208}\text{Pb}/^{204}\text{Pb}$ ratio for a given $^{206}\text{Pb}/^{204}\text{Pb}$ value (Fig. 6B). However, since the Pb isotopic results from the conventional leachates approximate those obtained from the selective leachates, the former could be used as a first-order approximation to sequential leaching. A conventional leaching approach instead of total dissolution of a

particular grain size fraction of till would have resulted in a bimodal distribution of points rather than linear arrays in Pb–Pb isotopic plots (Figs 6 and 8). Conventional leachates from anomalous till samples would give “ore-like” Pb isotopic ratios, whereas those from background samples would give higher isotope ratios than the former (Figs 9 and 10), providing greater resolution between target areas. This greater difference in the Pb isotopic composition for conventional leachates between anomalous and background till samples would greatly facilitate selection of potential sites for further mineral exploration. The conventional leaching method, however, must be tested on additional till deposits surrounding VMS deposits.

CONCLUSIONS

Selective leachates for tills from Chisel Lake and Manitouwadge show similar results in that chalcophile elements such as Cu, Ni, Pb, and Zn (typically concentrated in VMS deposits), are bound as either adsorbed/exchangeable metals, hydroxides of Fe or Mn, crystalline Fe oxides, or silicates. Despite the proximity of some of the till samples to VMS deposits, a very small proportion of these chalcophile elements are held in the sulfide form. Lead isotopic ratios for Pb-bearing selective leachates from anomalous till samples suggest that the Pb and other chalcophile elements held as either an adsorbed/exchangeable metal, hydrous oxide of Fe or Mn, or crystalline Fe oxide were most probably derived from the breakdown of original sulfide minerals during glaciation. In contrast, Pb within the same leachates from background samples give isotopic compositions that are significantly more radiogenic than those from anomalous samples, which clearly suggests that this Pb does not originate from the associated VMS deposits. It is also interesting to note that Pb from natural sources can be relatively mobile, and that such Pb can be scavenged from solution in the natural environment and concentrated. In addition, only Pb isotopic ratios from till can accurately provide interpretations into the origin of the Pb (and other chalcophile elements), and that the latter can be at odds with interpretations based solely on elemental distribution patterns obtained from selective leachates.

We propose that conventional leaching rather than total dissolution of a particular grain size of till samples be conducted for mineral exploration purposes, since the former can be done more quickly and cheaply and the latter type of analysis tends to mask or reduce the “ore-like” Pb isotopic component within anomalous samples.

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REFERENCES

- Antropova L. V., Goldberg I. S., Voroshilov N. A. and Ryss Ju. S. (1992) New methods of regional exploration for blind mineralization: application in the USSR. *J. Geochem. Explor.* **43**, 157–166.
- Bailes A. H. (1992) Wekusko Lake (North) Project (MTS 63J/13SW), *Manitoba Energy and Mines, Mineral Division, Report of Activities*, pp. 56–64.
- Bailes A. H. and Galley A. G. (1989) Geological setting of and hydrothermal alteration below the Chisel Lake massive Zn–Cu sulphide deposit, *Manitoba Energy and Mines, Minerals Division, Report of Field Activities*, pp. 31–45.
- Barnett P. J., Henry A. P. and Babuin D. (1991) Quaternary geology of Ontario, east-central sheet, *Ontario Geol. Surv.*, Map 2555.
- Bell K. and Franklin J. M. (1993) Application of lead isotopes to mineral exploration in glaciated terrains. *Geology* **21**, 1143–1146.
- Bell K. and Murton J. B. (1995) A new indicator of glacial dispersal: lead isotopes. *Quaternary Science Reviews* **14**, 275–287.
- Chao T. T. (1984) Use of partial dissolution techniques in geochemical exploration. *J. Geochem. Explor.* **20**, 101–135.
- Friesen R. G., Pierce G. A. and Weeks R. M. (1982) Geology of the Geco base metal deposit. *Geol. Assoc. of Canada Special Paper* **25**, 343–363.
- Galley A. G., Bailes A. H., Syme E. C., Bleeker W., Mackek J. J. and Gordon T. M. (1990) Geology and mineral deposits of the Flin Flon and Thompson belts, Manitoba (8th International Association for the Genesis of Ore deposits Symposium field trip guidebook no. 10). *Geol. Surv. Canada, Open file* **2165**, 136.
- Geddes R. S. and Bajc A. F. (1985) Quaternary geology of the White Lake (Hemlo area), District of Thunder Bay, *Ontario Geol. Survey, Map, P. 2849*.
- Gulson B. L. (1986) Lead isotopes in mineral exploration. *Developments in Economic Geology* **23**, 245.
- Gulson B. L., Church S. E., Mizon K. J. and Meier A. L. (1992) Lead isotopes in iron and manganese oxide coatings and their use as an exploration guide for concealed mineralization. *Applied Geochemistry* **7**, 495–511.
- Gulson B. L., Mizon K. J. and Atkinson B. T. (1993) Source and timing of gold and other mineralization in the Red Lake area, northwestern Ontario, based on lead-isotope investigations. *Can. J. Earth Sci.* **30**, 2366–2379.
- Hall G. E. M., Vaive J. E., Beer R. and Hoashi M. Selective leaches revisited, with emphasis on the amorphous Fe oxyhydroxide phase extraction, *J. Geochem. Explor.*, (in press).
- Hall G. E. M., Vaive J. E. and Kaszycki C. (1993) The diagnostic capabilities of selective leaching. *Explore* **80**, 3–9.
- Hawkes H. E. and Webb J. S. (1962) *Geochemistry in Mineral Exploration*, Harper and Row.

- Jenne E. A. (1962) Controls on Mn, Fe, Co, Ni and Zn concentrations in soils and water: the significant role of hydrous Mn and Fe oxides. *Advances in Chemistry Series, Am. Chem. Soc.* **73**, 337–388.
- Kettles I. M. (1993a) Reconnaissance geochemical data for till samples from the Manitowadge area. Ontario. *Geol. Surv. Canada, Open file* **2616**, 197.
- Kettles I. M. (1993b) Till geochemistry in the Manitowadge area. Ontario. *Current Research, Geol. Surv. Canada, Paper* **93-1E**, 165–173.
- Kettles I. M. and Murton J. B. (1994) Till composition in the vicinity of the Manitowadge greenstone belt, Ontario. *Geol. Surv. Canada, Curr. Res.* **1994-C**, 249–257.
- Kristjansson F. J. and Geddes R. S. (1985) Quaternary geology of the Manitowadge area, Ontario. *Curr. Res. Geol. Surv. Canada* **93-1E**, 165–173.
- Levinson A. A. (1980) *Introduction to Exploration Geochemistry*. 2nd edition, Applied Publishing, Wilmette, Illinois, p. 924.
- Lynch J. J. (1990) Provisional elemental values for eight new geochemical lake sediment and stream sediment reference materials LKSD-1, LKSD-2, LKSD-3, LKSD-4, STSD-1, STSD-2, STSD-3 and STSD-4. *Geostand. Newsl.* **14**, 153–167.
- Nikkarinen M., Kallio E., Lestinen P. and Ayras M. (1984) Mode of occurrence of Cu and Zn in till over three mineralized areas in Finland. *J. Geochem. Explor.* **21**, 239–247.
- Peterson V. L. and Zaleski E. (1994) Structure and tectonics of the Manitowadge greenstone belt and Wawa-Quetico subprovince boundary, Superior Province, northwestern Ontario. *Current Research, Geol. Surv. Canada* **1994-C**, 237–247.
- Peuraniemi V. (1984) Weathering of sulfide minerals in till in some mineralized areas in Finland, In: *Prospecting in Areas of Glaciated Terrain, Inst. Min. Metall.*, pp. 127–135, London.
- Rencz A. N. and Shilts W. W. (1980) Nickel in soils and vegetation of glaciated terrains, In *Nickel in the Environment*, (ed. Nriagu, J. O.), John Wiley and Sons, Inc., pp. 151–188.
- Shilts W. W. (1976) Glacial till and mineral exploration. In *Glacial Till*, (ed. Legett, R. F.), Special Publication 12, Royal Society of Canada, pp. 205–233.
- Shilts W. W. (1984) Till geochemistry in Finland and Canada. *J. Geochem. Explor.* **21**, 95–117.
- Shilts W. W. and Kettles I. M. (1990) Geochemical/mineralogical profiles through fresh and weathered till. In *Handbook of Glacial Indicator Tracing*, (eds Kujansuu, R. and Saarnisto, M.), pp. 187–216, Balkema, Rotterdam.
- Simonetti A., Bell K. and Viladkar S. G. (1995) Isotopic data from the Amba Dongar carbonatite complex, west-central India: Evidence for an enriched mantle source. *Chem. Geol.* **122**, 185–198.
- Stacey J. S. and Kramers J. D. (1975) Approximation of terrestrial lead isotope evolution by a two-stage model. *Earth Planet. Sci. Lett.* **26**, 207–221.
- Williams H. R. and Breaks F. W. (1989) Geological studies in the Manitowadge-Hornpayne area. *Ontario Geol. Surv. Misc. Paper* **146**, 79–91.
- Williams H. R. and Breaks F. W. (1990) Geology of the Manitowadge-Hornpayne area; *Ontario Geol. Surv. Open file*, Map **142**.
- Williams H. R., Breaks F. W., Schnieders B. R., Smyk M. C., Charlton S. G. and Lockwood H. C. (1990) Field Guide to the Manitowadge area, In *Mineral Deposits in the western Superior Province, Ontario*, Open file 2164, pp. 7–25, Geol. Surv. Canada.
- Zaleski E. and Peterson V. L. (1993) Lithotectonic setting of mineralization in the Manitowadge greenstone belt, Ontario: preliminary results. *Curr. Res. Geol. Surv. Canada* **93-1C**, 307–317.
- Zaleski E., Peterson V. L. and van Breemen O. (1994) Geological, geochemical and age constraints on base metal mineralization in the Manitowadge greenstone belt, northwestern Ontario, *Current Research, Geol. Surv. Canada*, **1994-C**.