

USING LEAD ISOTOPES AND ELEMENTAL ABUNDANCES IN TILL FOR MINERAL EXPLORATION IN CORDILLERA **Alexei S. Rukhlov and Travis Ferbey**

ABSTRACT

Elemental abundances and Pb isotopic ratios for 2.5N HCI leachates from Chehalis valley basal till samples (<0.063 mm fraction) highlight down-ice glacial dispersal for volcanogenic massive sulphide (VMS) occurrences. In spite of the relatively young age of the VMS deposit and surrounding volcanic-arc rocks (middle Jurassic), the Pb isotopic ratios show 3-9% difference between the ore and the background crustal samples. This is 2-3 orders of magnitude above the analytical uncertainties of the state-of-the-art results by multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) after Pb purification by ion-exchange separation. The simplified method, measuring Pb isotopic ratios directly in bulk 2.5N HCI leachate solution by high-resolution inductively coupled plasma mass spectrometry (HR-ICP-MS), also has acceptable analytical uncertainties (0.4-0.6%) for the ²⁰⁶Pb/²⁰⁴Pb and ²⁰⁷Pb/²⁰⁶Pb, tracing down-ice dispersal, consistent with the MC-ICP-MS results. For the direct-leachate analyses using guadrupole ICP-MS, the analytical uncertainties of the uncorrected for mass bias Pb isotopic ICP-MS and 200-300 times those of MC-ICP-MS) may be too large for the applications requiring <10% resolution. Although Pb, Zn, Cu, and Ba abundances are enriched in the Seneca VMS deposit (10-1000 times) typical crustal values), they show inconsistent down-ice till anomalies. In contrast, Pb isotopic ratios for leachates from <0.063 mm fraction of the tills appear to be robust indicators of down-ice glacial dispersal for the VMS mineralization. The Pb abundances and isotopic compositions are consistent with the model that Chehalis valley tills are derived from the isotopically heterogeneous local bedrock sources and have variable proportions of lead from the VMS mineralization. The latter has low ²⁰⁶Pb/²⁰⁴Pb, ²⁰⁷Pb/²⁰⁴Pb, and ²⁰⁸Pb/²⁰⁴Pb, and high ²⁰⁷Pb/²⁰⁶Pb and ²⁰⁸Pb/²⁰⁶Pb ratios that are similar to those of galena from the Seneca deposit (Godwin, 1988). The slope of the 207 Pb/ 204 Pb vs. 206 Pb/ 204 Pb near-linear array defined by Chehalis till and rock samples (n = 13, excluding diorite from At. Jasper pluton) corresponds to a secondary isochron age of 2131±180 Ma, with the lower intercept of the Stacev and Kramers (1975) growth curve at 2271 Ma. This is much older than the emplacement age of the Seneca VMS deposit and the surrounding volcanic-arc rocks but falls within the range of the Paleoproterozoic ages of the major crust-forming events worldwide. If the near-linear array had a geochronological significance, it would imply that both the Seneca VMS deposit and the surrounding volcanic rocks shared the same, closed-system Paleoproterozoi source, such as a sub-continental lithosphere.



show boundaries of the morphogeological belts after Gabrielse et al. (1991).

INTRODUCTION

Basal till is a primary bedrock-derived sediment, with little or no reworking by water, transported and re-deposited at the base of a glacier by nearlinear, and often valley-parallel, ice flow during one or more episodes of Quaternary glaciation (Levson, 2001). Lithological, mineralogical and geochemical anomalies within this sediment, resulting from the erosion and down-ice glacial transport of compositionally distinct bedrock, have been widely used as indicators of glacial dispersal for mineral exploration (e.g., Shilts, 1976, DiLabio, 1990). Previous studies have shown that Pb isotopic ratios from 2.5N HCI leachates from <0.063 mm fraction of basal ill can be the effective indicators of glacial dispersal for Paleoproterozoic and early Paleozoic VMS deposits (Bell and Franklin, 1993; Bell and Murton, 1995; Simonetti et al., 1996). We have analyzed 26 till samples (<0.063 mm fraction) and 11 bedrock samples from Chehalis valley, southwestern British Columbia (Fig. 1), for Pb isotopic ratios and elemental abundances to test: (1) the effectiveness of Pb isotopes for tracing glacial dispersal from as young as the middle Jurassic VMS deposits, and (2) the suitability of different instrumentation for the Pb isotopic analysis of 2.5N HCI leachates from tills.







and Mahoney et al. (1995).

darker till with less abundant clasts (unit 2). Boxes indicate locations of Figures 3b and c. b) Close-up of unit 1 in Fig. 3a, showing weakly oxidized, dense till with silty sand matrix and about 35% clasts. c) Close-up of unit 2 in Fig. 3a, showing more oxidized, less dense till with sandy matrix and about 30% clasts. d) Close-up of till with sand- to granule-size oxidized sulphides, directly above the southeast wall of the Seneca pit.

GEOLOGY

Most of the Chehalis valley study area is underlain by intermediate and felsic volcanic-arc rocks of the Early to Middle Jurassic Harrison Lake Formation of the Harrison terrane in the Coast Belt of the southern Canadian Cordillera (Fig. 1; Monger, 1970; Arthur et al., 1993; Monger and Journeay, 1994; Mahoney et al., 1995). The volcanic rocks host several Kuroko-style massive sulphide occurrences, including the Seneca Zn-Cu-Pb deposit (McKinley et al., 1995). The Harrison terrane is intruded by Middle Jurassic porphyry stocks and plutons, made up of diorite, quartz diorite, granodiorite and tonalite, of the Coast Plutonic Complex to the west (Fig. 2).

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Figure 8. Pb-Pb isotopic plots showing high-resolution inductively-coupled plasma mass spectrometry results for leachates from Chehalis valley till <0.063 mm-fraction and whole-rock samples. Uncertainty bars show average relative difference from till <0.063 mm-fraction duplicates. Literature galena analyses from the Seneca deposit and the present-day Pb isotopic compositions for depleted mid-ocean ridge basalt (MORB) mantle end-member, uppe crustal, and "orogene" (mixed upper crust and mantle) reservoirs are shown for comparison. a) 207 Pb/ 204 Pb vs. 206 Pb/ 204 Pb; b) 208 Pb/ 206 Pb vs. 206 Pb/ 204 Pb; c) 208 Pb/ 204 Pb vs. 206 Pb/ 204 Pb; d) 207 Pb/ 206 Pb vs. 208 Pb/ 206 Pb; e) 207 Pb/ 206 Pb

1.95 2.00 2.05 2.10

18.0 18.5 19.0 19.5 20.0

²⁰⁶Pb/²⁰⁴Pb

esent-day "orogene" (mixed

* Present-day upper crustal Pb isotopic

composition (Zartman and Doe, 1981)

composition (Zartman and Doe, 1981)

crustal and mantle) Pb isotopic

Figure 9. Pb-Pb isotopic plots showing quadrupole inductively-coupled plasma mass spectrometry results for leachates from Chehalis valley till <0.063 mm-fraction and whole-rock samples. Uncertainty bars show average relative difference from till <0.063 mm-fraction duplicates. Literature galena analyses from the Seneca deposit and the present-day Pb isotopic compositions for depleted mid-ocean ridge basalt (MORB) mantle end-member, upper crustal, and "orogene" (mixed upper crust and mantle) reservoirs are shown for comparison. a) 207 Pb/ 204 Pb $vs.^{206}Pb/^{204}Pb;b) \frac{1}{208}Pb/^{206}Pb vs.^{206}Pb/^{204}Pb;c) \frac{1}{208}Pb/^{204}Pb vs.^{206}Pb/^{204}Pb;d) \frac{1}{207}Pb/^{206}Pb vs.^{208}Pb/^{206}Pb;e) \frac{1}{207}Pb/^{206}Pb;e) \frac{1}{207}Pb/^$ vs. 206 Pb/ 204 Pb.

²⁰⁸Pb/²⁰⁶Pb

1.9 2.0 2.1

18 19 20 21

crustal and mantle) Pb isotopi

composition (Zartman and Doe, 1981)



valley till < 0.063 mm-fraction and whole-rock samples showing binary mixing valley till < 0.063 mm-fraction and whole-rock samples showing binary mixing < 0.063 mm-fraction and whole-rock samples showing binary mixing models (after Langmuir et al., 1978). Ticks on the model curves mark 10% models (after Langmuir et al., 1978). Ticks on the model curves mark 10% (after Langmuir et al., 1978). Ticks on the model curves mark 10% (after Langmuir et al., 1978). (ppm) vs. 206 Pb/ 204 Pb; b) Pb (ppm) vs. 207 Pb/ 204 Pb; c) Pb (ppm) vs. 208 Pb/ 204 Pb; d) difference from till <0.063 mm-fraction duplicates. Average relative difference $Pb (ppm) vs. {}^{207}Pb/{}^{206}Pb; e) Pb (ppm) vs. {}^{208}Pb/{}^{206}Pb.$



BINARY MIXING MODELS

Figure 11. Plots of Pb isotopic ratios by high-resolution inductively-coupled asma mass spectrometry vs. Pb concentrations for leachates from Chehalis plasma mass spectrometry vs. Pb concentrations for leachates from Chehalis mass spectrometry vs. Pb concentrations for leachates from Chehalis va increments. Pb concentrations are by aqua regia-inductively coupled plasma for Pb concentrations in the duplicates is smaller than the size of the symbols. for Pb concentrations in the duplicates is smaller than the size of the a) Pb (ppm) vs. 206 Pb/ 204 Pb; b) Pb (ppm) vs. 207 Pb/ 204 Pb; c) Pb (ppm) vs. 208 Pb/ 204 Pb; d) Pb (ppm) vs. 207 Pb/ 206 Pb; e) Pb (ppm) vs. 208 Pb/ 206 Pb.



Pb concentrations are by aqua regia-inductively coupled plasma mas difference from till <0.063 mm-fraction duplicates. Average relative d a) Pb (ppm) vs. 206 Pb/ 204 Pb; b) Pb (ppm) vs. 207 Pb/ 204 Pb; c) Pb (ppm) vs. 208 Pb/ 204 Pb; d) Pb (ppm) vs. 207 Pb/ 206 Pb; e) Pb (ppm) vs. 208 Pb/ 206 Pb.



upled plasma mass spectrometry from <0.063 mm fraction of till samples, Chehalis valley. Rock legend and ot symbols as in Figure 2. a) Pb (ppm); b) Zn (ppm); c) Cu (ppm); d) Ba (ppm).



Figure 15. δ values and percentiles (by coupled plasma mass spectrometry for leachates from <0.063 mm fraction of till samples, Chehalis valley. The δ values coupled plasma mass spectrometry for leachates from <0.063 mm fraction of till samples, Chehalis valley. The δ values are obtained by normalizing the isotopic ratios of sample to the least radiogenic ratio of whole-rock analyses from the are obtained by normalizing the isotopic ratios of sample to the least radiogenic ratio of whole-rock analyses from the Seneca VMS deposit (see text for detail). Rock legend and other symbols as in Figure 2. a) δ^{206} Pb/ 204 Pb; b) δ^{208} Pb/ 204 Pb; c) Seneca VMS deposit (see text for detail). Rock legend and other symbols as in Figure 2. a) δ^{206} Pb/ 204 Pb; b) δ^{208} Pb/ 204 Pb; c) Seneca VMS deposit (see text for detail). Rock legend and other symbols as in Figure 2. a) δ^{206} Pb/ 204 Pb; b) δ^{208} Pb/ 204 Pb; c) Seneca VMS deposit (see text for detail). Rock legend and other symbols as in Figure 2. a) δ^{206} Pb/ 204 Pb; c) δ^{208} Pb/ 204 Pb; c) δ^{208} Pb/ 204 Pb; c) δ^{208} Pb/ 204 Pb; c) δ^{208} Pb/ 204 Pb/ 204 Pb; c) δ^{208} Pb/ 204 Pb/ 204 Pb; c) δ^{208} Pb/ 204 Pb/ 204 Pb; c) δ^{208} Pb/ 208 Pb/ 204 Pb/ δ^{207} Pb/ 206 Pb; d) δ^{208} Pb/ 206 Pb.





are obtained by normalizing the isotopic ratios of sample to the least radiogenic ratio of whole-rock analyses from the Seneca VMS deposit (see text for detail). Rock legend and other symbols as in Figure 2. a) δ^{206} Pb/ 204 Pb; b) δ^{208} Pb/ 204 Pb; c) δ^{207} Pb/ 206 Pb; d) δ^{208} Pb/ 206 Pb.



symbol colour and diameter) of Pb isotopic results by high-resolution inductively Figure 16. δ values and percentiles (by symbol colour and diameter) of Pb isotopic results by quadrupole inductivel δ^{207} Pb/ 206 Pb; d) δ^{208} Pb/ 206 Pb.

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SUMMARY AND CONCLUSIONS

The Pb isotopic results for 2.5N HCI leachates from Chehalis valley tills (<0.063 mm fraction), and VMS mineralization and the surrounding volcanic-arc rocks (Figs. 4 and 5) show 3-9% difference. This is 2-3 orders of magnitude above the uncertainties of the state-of-the-art MC-ICP-MS analyses on leachate Pb purified by ionexchange separation (Figs. 6 and 7), and 8-20 times the uncertainties of the HR-ICP-MS analyses directly on bulk Fig. 8). The large Pb isotopic contrast between Chehalis valley VMS mineralization and the background inties of the Pb isotopic results makes Pb isotopes from till leachates suitable for tracing of down-ice glacial dispersal for as young as the Mesozoic deposits in Cordillera. For the direct-leachate Pb sults using more widely available quad instrumentation, the analytical uncertainties of the raw Pb isotopic for mass bias, are 2-9 times those of the HR-ICP-MS and 140-340 times those of the MC-ICP-

Data arrays shown in the Pb abundance vs. Pb isotopic ratio diagrams by MC-ICP-MS are consistent with mixing (after Langmuir et al., 1978) of two distinct end-member compositions (Fig. 10). One of the end members, having the lowest ²⁰⁶Pb/²⁰⁴Pb, ²⁰⁷Pb/²⁰⁴Pb, and ²⁰⁸Pb/²⁰⁴Pb ratios, and the highest ²⁰⁷Pb/²⁰⁶Pb and ²⁰⁸Pb/²⁰⁶Pb ratios, and Pb content, is similar to the isotopic composition of galena from the Seneca deposit (Godwin, 1988) and represents the VMS mineralization. The second end member, having the highest ²⁰⁶Pb/²⁰⁴Pb, ²⁰⁷Pb/²⁰⁴Pb, and ²⁰⁸Pb/²⁰⁴Pb ratios, and the lowest ²⁰⁷Pb/²⁰⁶Pb and ²⁰⁸Pb/²⁰⁶Pb ratios, and Pb content, is the background crust. The Pb isotopic results by HR-ICP-MS and quadrupole ICP-MS show more scattered isotopic ratios from tills and rocks with decreasing Pb concentration, indicating isotopically heterogeneous background crustal materials (Figs. 11 and 12). The larger datasets by these methods are consistent with the model that Chehalis valley tills are derived from the local bedrock sources and have variable proportions of Pb derived from the isotopically distinct VMS mineralization.

Near-linear arrays of till and rock analyses by MC-ICP-MS shown in the Pb-Pb isotopic ratio diagrams (Fig. are consistent with binary mixing of isotopically heterogeneous materials. If interpreted as a secondary isochror the slope of the linear array (n = 13; excluding diorite analysis from Mt. Jasper pluton) shown in the ²⁰⁷Pb/²⁰⁴Pb ²⁰⁶Pb/²⁰⁴Pb diagram (Fig. 7a) corresponds to an age of 2131±180 Ma (95% confidence), with the lower intercept of the Stacey and Kramers (1975) growth curve at 2271 Ma. The mean square of the weighted deviates (MSWD) of 28 indicates that not all of the data points fit a straight line within the estimated uncertainties. This age is much older than the age of the Seneca VMS deposit and the surrounding volcanic-arc rocks (middle Jurassic) but falls within the range of the Paleoproterozoic ages of the major crust-forming events worldwide. If the linear array had a geochronological significance, it would imply that both the Seneca VMS deposit and the background volcanic-arc rocks shared the same, closed-system Paleoproterozoic source, such as a sub-continental lithosphere. However, the Pb-Pb isotopic results by HR-ICP-MS from more till and rock samples are more scattered, suggesting a mixture of leads in the tills derived from the VMS ores and isotopically heterogeneous crustal sources (Fig. 8).

Elemental abundances and Pb isotopic ratios for 2.5N HCI leachates from Chehalis valley < 0.063 mm fraction of basal till highlight down-ice glacial dispersal from the known VMS occurrences. Although Pb, Zn, Cu, and Ba abundances are enriched in the Seneca VMS deposit 10-1000 times typical crustal values (Fig. 5b and c), they show inconsistent till anomalies (Fig. 13). In contrast, Pb isotopic ratios appear to be effective indicators of the glacial dispersal for the VMS deposits (Fig. 14). For the direct analyses of bulk leachates by HR-ICP-MS, the ²⁰⁷Pb/²⁰⁶Pb ratios are consistent with the state-of-the-art MC-ICP-MS results and car glacial dispersal indicators for the VMS deposits (Fig. 15). In the case of the quad o results, the analytical uncertainties may be too large for tracing <10% isotopic contrast (Fig. 16).

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