

Newsletter for the Association of Applied Geochemists



Overview of Indicator Mineral Research at the Geological Survey of Canada - An Update

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INTRODUCTION

This article provides an update on indicator mineral methods research conducted by the Geological Survey of Canada (GSC) since the last report in EXPLORE (McClenaghan et al. 2008). In the glaciated terrain of Canada, indicator mineral methods have been successfully applied to gold and diamond exploration for more than 30 years. The GSC's ongoing indicator mineral research program is focussed on other deposit types: porphyry Cu, magmatic Ni-Cu-PGE, intrusion hosted Sn and W, volcanogenic massive sulphides, Mississippi Valley-Type Pb-Zn, basement-hosted U, and rare metals. This research has been funded by the GSC's Targeted Geoscience Initiative (TGI) 3 Program (2005-2010) in partnership with Canadian Mining Industry Research Organization (CAMIRO, 2005-2008) and the British Columbia Mountain Pine Beetle Project (2007-2009), the TGI-4 Program (2010-2015), and the Geo-mapping for Energy and Minerals (GEM) Program (Phase 1 in 2008-2013; Phase 2 in 2013-2020). All GSC

Figure 1. Location of GSC indicator mineral test sites across Canada that are discussed in this article (base map modified from Potter & Wright 2015).



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METHODS

GSC's indicator mineral research has focused on both surficial (till, stream) sediments and bedrock samples collected around known mineral deposits. For the surficial studies, ore and host rocks (~ 1 kg) and till and stream sediment samples (15 kg) at varying distances up- and down-ice of known deposits were collected at various test sites across Canada (Fig. 1). Samples were processed at a commercial heavy mineral laboratory (Overburden Drilling Management Ltd.) in Ottawa to recover heavy (specific gravity >3.2), and in some cases mid-density (specific gravity 2.8-3.2), mineral concentrates for the identification, counting and analysis of potential indicator minerals. Concentrates were prepared using a combination of tabling and heavy liquids (Averill & Huneault 2006; McClenaghan 2011). Selected grains were photographed, examined using a scanning electron microscope (SEM) and Mineral Liberation Analysis (MLA), and analyzed by electron microprobe (EMP) to confirm the visual identifications and document their major and trace element signatures. In some cases, grains were further analyzed by laser ablation-ICP-MS to characterize their trace element signatures.

Protocols for the collection of till samples and for the processing of unconsolidated sediments for the recovery of indicator minerals were developed at the GSC to ensure quality assurance and quality control on all reported indicator mineral data (McClenaghan et al. 2013a; Plouffe et al. 2013a). These protocols include the use of field duplicate samples, blank samples (e.g. pure quartz) and base material (background till) spiked with known numbers, morphologies, species, and sizes of indicator minerals. Field duplicate samples are used to estimate sediment heterogeneity and/or variability at sampling site. Blank samples serve to detect potential carry-over contamination.

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Spiked samples are used to monitor the accuracy of the sample processing and mineral identification methods for recovering specific minerals. See Plouffe et al. (2013a) for additional details.

TEST SITES

Porphyry Cu-Mo-Au Deposits

Orientation surveys were completed in British Columbia around two calc-alkaline Cu-Mo porphyry deposits (Gibraltar and Highland Valley Cu mines), one alkalic Cu-Au porphyry deposit (Mount Polley Mine) and one mixed calc-alkaline and alkaline Cu-Mo-Au porphyry prospect (Woodjam). The primary objective of these surveys was to define the mineralogical and geochemical signatures of Cu porphyry mineralization in till. These case studies were a collaborative effort between the GSC and the British Columbia Geological Survey, in cooperation with Taseko Mines Limited (Gibraltar), Imperial Metals Corporation (Mount Polley), Teck Resources Limited (Highland Valley Copper), and Gold Fields Limited with Consolidated Woodjam Copper Corporation (Woodjam).

Porphyry Cu indicator minerals in till at these study sites include the ore minerals chalcopyrite and gold, as well as alteration minerals epidote group (Fig. 2), andradite garnet, and apatite. Jarosite, a sulphate mineral typically associated to supergene alteration (Averill 2011; Kelley et al. 2011), was identified in till in the Mount Polley region (Hashmi et al. 2015). Their distributions in till define glacial dispersal trains that extend up to several kilometres (i.e. > 2 km) down ice from mineralized bedrock. In some cases, dispersal trains extend in more than one direction and were formed by multiple phases of ice flow. Preliminary interpretations of the indicator mineral results are presented in Plouffe et al. (2013b; 2015) and Plouffe & Ferbey (2015a). Plouffe & Ferbey (2015b) provide a more detailed overview of the project highlights.

As part of this project, research on indicator mineral composition was completed for: magnetite (Grondahl, 2014; Piziak et al. 2015; Canil et al. 2016), tourmaline (Chapman et al. 2015a, b), and apatite (Rukhlov et al. 2016). Detailed study of epidote group minerals, titanite, and rutile is ongoing by C. Kobylinski at the University of Ottawa under the supervision of K. Hattori.

Intrusion-hosted Sn-W Deposits

Indicator minerals methods for Sn and W intrusionhosted deposits were tested at the Sisson W-Mo and Mount Pleasant Sn-W-Mo-Bi-In deposits in eastern Canada. These case studies were a collaborative effort between the GSC, the New Brunswick Department of Energy and Mines, and the holders of the Sisson (Northcliff Resources Limited, Hunter Dickinson Inc.) and the Mount Pleasant (Adex Mining Inc.) deposits, and Laurentian University.

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Figure 2. Colour photograph of the 0.25-0.5 mm non-ferromagnetic heavy mineral (>3.2 SG) fraction of a till sample from the Woodjam occurrence in western Canada. Epidote group minerals make up about 80% of this concentrate (modal, +/- 10%). The width of view is 5 mm.



Indicator minerals of the Sisson deposit identified in mineralized bedrock, till, and stream sediments include scheelite (Fig. 3), wolframite, molybdenite, chalcopyrite, Bi minerals (joseite, native Bi, bismutite, bismuthinite), galena, sphalerite, arsenopyrite, spessartine, pyrrhotite, and pyrite. Indicator minerals of the Mount Pleasant deposit identified in mineralized bedrock and till include cassiterite, wolframite, molybdenite, topaz, fluorite, galena, sphalerite, chalcopyrite, galena, arsenopyrite, pyrite, and loellingite. Figure 3. Colour photographs of scheelite grains recovered from till overlying the Sisson W-Mo deposit in eastern Canada: a) visible light; b) short wave ultraviolet light. Photographs by Michael Bainbridge.



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Rare secondary indicator minerals in till include beudantite, anglesite, and plumbogummite which formed by oxidation and weathering of the galena. The extensive suites of indicator minerals for each deposit reflect their polymetallic natures and the ability of modern indicator mineral methods to recover these minerals. Detailed results of the Sisson study are reported in McClenaghan et al. (2013b,c; 2014a; 2015a,b) and Thorne et al. (2014) and the Mount Pleasant study in McClenaghan et al. (2014b,c; 2015a,c,d) as well as the TGI-4 Intrusion-hosted Deposits summary volume (Rogers 2015).

The relationship between scheelite mineral chemistry and its cathode luminescence (CL) response was investigated to develop criteria for discriminating scheelite from different deposit types (e.g. porphyry related greisens, skarn, orogenic Au, VMS). These criteria can help identify potential bedrock sources of scheelite grains that are recovered as part of standard stream sediment and till indicator mineral surveys. Results will be reported by Poulin et al. (in press).

Volcanogenic Massive Sulphide Deposits

Indicator minerals methods were tested at the Izok Lake Zn-Cu-Pb-Ag volcanogenic massive sulphide (VMS) deposit, one of the largest undeveloped Zn-Cu VMS resources in North America. This case study was a collaborative effort between the GSC, Queen's University, Université Laval, the property holder, MMG, and Overburden Drilling Management Ltd. At the same time, GSC research continued on indicator mineral signatures of the Halfmile Lake VMS deposit in the Bathurst Mining Camp of New Brunswick.

Till samples down ice of the Izok Lake deposit contain chalcopyrite, sphalerite, galena, and pyrite as well as gahnite $(ZnAl_2O_4)$. Gahnite is an ideal VMS indicator mineral in till because of its occurrence in highly metamorphosed VMS deposits such as Izok Lake. It has a visually distinctive bluish green colour (Fig. 4), a high specific gravity (4-4.6) (ideal for recovery using density-based separation methods), moderate hardness (physical durability during glacial transport), and chemical stability in oxidizing surficial environments (resistance to post glacial weathering). Glacial dispersal of gahnite can be traced at least 40 km down ice of the deposit. Detailed results of the Izok Lake study are reported in McClenaghan et al. (2012a; 2013d; 2014d; 2015e), Hicken et al. (2013a,b) and Paulen et al. (2013).

Till down ice of the Halfmile Lake VMS deposit contains chalcopyrite, pyrite, gold, cinnabar and gahnite. The presence of a preglacial gossan overlying the deposit is reflected in the recovery of secondary minerals in the till down ice: beudantite, jarosite, and goethite, (Budulan et al. 2015; McClenaghan et al. 2012b).

The GSC also contributed to the investigation of magnetite chemistry in VMS deposits and in till down ice. The study focused on bedrock and till samples from the Izok Lake and Halfmile Lake deposits. Results are reported in Makvandi et al. (2015, 2016) and highlight the different chemical compositions of magnetite in massive sulphide ore, alteration zones, and pre-glacial gossans.

The application of laser-ablation ICP-MS analyses was tested as a potential vectoring tool, using pyrite from metalliferous black shales of the Kidd-Munro assemblage proximal and distal to the 2.7 Ga Kidd Creek VMS deposit (Chapman et al. 2009, 2010, 2011) under the GSC's TGI-3 Program. Multiple generations of this pyrite range from syn-ore through diagenetic to metamorphic. Trace elements of hydrothermal origin (as determined by LA-ICP-MS) in the syn-ore pyrite are Ag, Au, As, Bi, Cu, Pb, Sb, Sn, Tl, and Zn; these element enrichments are generally greater than in the diagenetic and metamorphic pyrites. The element enrichment suite Co, Ni, Mo, Se, Pt, and Te is attributed to seawater (hydrogenous). Hydrothermal element enrichments as determined by LA-ICP-MS provide much more localized, specific exploration targets than whole-rock analyses of drill core or portable XRF analyses of ≈ 1 cm diameter pyrite grains or aggregate grains. The much more precise LA-ICP-MS analyses target syn-ore pyrite and thus avoid the diagenetic and metamorphic pyrite that generally has lower trace element contents which dilute the wholerock and portable XRF analyses.

Figure 4. Colour photograph of gahnite grains recovered from the 0.25-0.5 mm non ferromagnetic heavy mineral fraction of till samples down ice of the Izok Lake VMS deposit, northern Canada. Photograph by Michael Bainbridge.



Mississippi Valley-Type Deposits

The Pine Point Pb-Zn Mining District in northern Canada was used to test indicator minerals methods for Mississippi Valley-Type Pb-Zn deposits. This research was a collaborative effort between the GSC, University of Alberta, Teck Resources Ltd., Tamerlane Ventures Ltd., and Overburden Drilling Management Ltd.

Till derived from these deposits has a carbonaterich matrix that buffers the till while it oxidizes and allows the ore minerals galena and sphalerite (Fig. 5) to survive post glacial weathering. Lead isotopic studies of individual galena and sphalerite grains in bedrock and till demonstrated that isotopic analyses can help identify the up ice presence of a buried MVT deposit. Detailed results of this study are reported in McClenaghan et al. (2012c) and Oviatt et al. (2013; 2015).

Figure 5. Honey sphalerite (top row) and black cubic galena grains (bottom row) recovered from till down ice of the N-41 deposit in the Pine Point Mining District, northern Canada. Photograph by Overburden Drilling Management Ltd.



Uranium deposits

The Kiggavik U deposits beside the late Paleoproterozoic Thelon Basin of northern Canada were the focus of a study on indicator mineral and till geochemistry of basement-hosted U deposits in the Canadian Arctic. This research was a collaborative effort between the GSC, Queen's University, AREVA Resources Canada and Overburden Drilling Management Limited. Uraninite is the main ore mineral at Kiggavik, along with less abundant U minerals such as coffinite and uranophane.

GSC results show that uraninite is poorly suited to be an indicator mineral in till for the Kiggavik style of unconformity U deposits because it is too easily oxidized and too fine grained (>250 μ m) to be recovered by traditional heavy mineral processing methods (Robinson et al. 2014, 2016). The discovery of Pb+U-rich fluorapatite (Fig. 6) in the Kiggavik Main Zone however, is intriguing because it has not previously been reported as a component of basement-hosted unconformity-related U deposits. Such fluorapatite has significant potential for improving geochronological constraints on the timing of U mineralization; it may be unique to such deposits and, as a stable, durable, moderately heavy mineral, it could be used as an indicator mineral in till derived from the highly altered, weakly mineralized bedrock halo around basementhosted unconformity-associated U deposits. Challenges for using the Pb+U-rich fluorapatite as an indicator mineral are mainly its small (silt) size and its density, which is the usual density threshold for routine heavy liquid separation (SG 3.2) (McClenaghan 2011).

Figure 6. X-ray map of a single composite fluorapatite grain in bedrock illustrating two euhedral cores that are connected by overgrowths into a single larger euhedral crystal with compositional zonation of (a) Pb, (b) U, and (c) Ca. The sharply-defined outer portions of the grain correspond to the fibrous textured zones rich in Pb and U, and are depleted in Ca. The cores show subtle Ca zonation and an absence of Pb and U (from Robinson et al., 2016).



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Ni-Cu-PGE-Chromium Ore Systems

A decade ago, the GSC initiated numerous studies to characterize indicator mineral signatures in surficial sediments for several types of mineral deposits including magmatic Ni-Cu-PGE deposits in the Thompson Ni Belt (McClenaghan et al. 2012e, 2013d; Dupuis et al. 2012) and Sudbury (Ames et al. 2013; McClenaghan & Ames 2013). These studies identified several suites of indicator minerals in surficial sediments that are useful exploration tools.

In the course of the recently completed TGI-4 Program, new exploration techniques to detect fertility of mafic and ultramafic systems using advanced microanalytical mineral chemistry techniques were developed for oxide phases (chromite, magnetite, ilmenite) in barren and fertile intrusions through examination of Canada's well known Ni-Cu-PGE districts (Sudbury Igneous Complex, Ontario; Voisey's Bay, Labrador and Newfoundland) and Archean komatiite (Alexo, Abitibi-Ontario; McFaulds Lake-"Ring of Fire", Ontario). Oxide phases are quite common in mafic and ultramafic systems, host almost all Ni-Cu-PGE deposits, are extremely resistant and survive post-magmatic processes. For example, Pagé et al. (2015) have proposed binary diagrams such Ni/Mn versus Ni/Cr ratios of the chromite composition that can be used to discriminate processes such as sulphide segregation prior to chromite crystallization vs. superimposed alteration (Fig. 7A).

A large chromite anomaly identified in stream sediments of the McFaulds Lake region («Ring of Fire») of northern Ontario (Crabtree, 2003) reflects heavy mineral contributions from large mafic intrusive complexes. More recently, the re-investigation of these chromite compositions by Burnham et al. (2012) led them to suggest at least nine compositional groups that show spatial associations with the bedrock geology. These chromite compositional associations could better identify fertile mafic and ultramafic intrusions and improve targeting for Cr, Ni-Cu-PGE, and V exploration. Magnetite and ilmenite can also record sulphide saturation through Ni and Cu depletion in Fe-oxides (magnetite, ilmenite), thus distinguishing fertile from barren intrusions (Dare et al. 2015) (Fig. 8). Also, new research highlights apatite, biotite, and epidote-actinolite and their distinctive trace element compositions that can assist with vectoring toward buried Ni-Cu-PGE and Cu-PGE deposits in magmatic mafic and ultramafic systems (i.e. apatite: Shahabi Far et al. 2015; biotite: Hanley et al. 2015; Warren et. al. 2015; chlorite: Brzozowski et al. 2015; epidote-actinolite: Ames & Tuba 2015). More exhaustive results on these studies are summarized in a TGI-4 project synthesis volume (Ames & Houlé 2015).

Figure 7. Plot of Ni/Mn versus Ni/Cr for chromite from komatiite near the Alexo Mine and the Hart deposit (from Pagé et al., 2015). Abbreviations: Oc = olivine cumulate; OPc = olivine + pyroxene cumulate; O spinifex = olivine spinifex; diss sulph = disseminated sulphide; P spinifex = pyroxene spinifex; sulph = sulphide.



Figure 8. N i versus Cr in magnetite from the supposedly barren Newark Island intrusion (from Dare et al. 2015). The barren field is based on mafic igneous complexes that lack significant Ni sulphide concentrations whereas the fertile field is from the Sudbury Igneous Complex.



Rare Metal deposits

The Strange Lake rare earth element (REE) deposit in northeastern Canada is the current focus of GSC GEM-2 indicator mineral studies to further develop methods for REE exploration in northern Quebec and Labrador. This research is collaborative between the GSC, and Laurentian

University in collaboration with Quest Rare Minerals Ltd. GSC collected till samples along the length of the deposit's known 40 km glacial dispersal train defined by Batterson (1989). These samples are currently being examined to determine the indicator mineral suite in till that best reflects the deposit.

Analytical Method Developments

The Inorganic Geochemistry Research Laboratory at the GSC has developed a variety of in situ elemental and isotopic measurement techniques for common resistate indicator minerals using laser ablation (LA) sampling coupled with ICP-MS and MC-ICP-MS detection. Development and application projects have included apatite, chromite, epidote (Tuba & Ames 2015), gahnite (O'Brien et al. 2015a,b), garnet (Riches et al. in press), magnetite, pyrite (Jackson et al. 2013; Gao et al. 2015), tourmaline (Chapman et al. 2015a,b) and zircon (Jackson & Chapman 2012; Chapman et al. 2012; Shen et al. 2015). Particular emphasis has been placed on development of procedures for, and applications of, process-sensitive minerals (e.g., zircon), elements (e.g., REE), isotopes (e.g., Fe in magnetite) and other parameters (magma oxidation state and emplacement age). Unique, high-resolution, quantitative 2-D element mapping techniques have also been developed that provide a wealth of information on complex geochemical histories of the target minerals (e.g., Jackson et al. 2012, 2013; Gao et al. 2015).

An excellent example of the power of combining analytical approaches (elemental, isotopic and 2-D mapping) in indicator mineral analysis is provided by a recent study of the potential of zircon trace element data to determine the Ce⁴⁺/Ce³⁺ ratio of zircon. Zircon Ce⁴⁺/ Ce³⁺ ratio is a proxy for the oxidation state of the host magma, which in turn controls its prospectivity for porphyry Cu deposits. Techniques for in situ trace determination and 2-D mapping of trace element, U-Pb age and Ce^{4+/} Ce³⁺ ratios in zircon were developed (Jackson & Chapman 2012; Chapman et al. 2012) and applied to a number of Cretaceous and Jurassic intrusions in the southwest Yukon. These studies demonstrated that zircon Ce4+/Ce3+ ratios successfully fingerprint the mineralised intrusion that hosts the Cretaceous Casino deposit, clearly distinguishing it from barren intrusions in the same area. The application of Ce⁴⁺/Ce³⁺ ratios to the exploration of Jurassic plutons is more complicated. However, element mapping has revealed a strong sector zoning control of REE substitution in zircon, which affects the calculated Ce4+/Ce3+ ratio and demonstrates that ubiquitously high Ce4+/Ce3+ ratios are apparently related to an early magma oxidation event.

ACKNOWLEDGEMENTS

This article benefited from critical review by C.W. Jefferson (GSC).

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