Mineral chemistry: modern techniques and applications to exploration

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It is likely that undiscovered ore reserves are currently buried under recently deposited sedimentary cover. As such, our capacity to see through the complexities of this cover and to perceive the nature of the underlying bedrock ore environment has become a fundamental aspect of modern mineral exploration and ore deposit science. To date, the recognition of buried mineral deposits has been aided by our ability to (1) predict indicator minerals in bedrock sources, (2) identify and separate indicator minerals from sedimentary cover, and (3) measure the unique chemical and isotopic composition of these indicator minerals.

A substantial amount of research has been devoted to chemical and physical dispersal of minerals and elements at the Earth's surface in the development of bedrock weathering and erosional footprints. The aerial and spatial extent of these footprint models has been partially limited by our incomplete understanding of the processes involved in mineral and chemical dispersal, but moreover, by the technological challenges of identifying and measuring subtle mineral and chemical changes in these footprint sediments. Within mineral deposit footprints, the examination of the physical dispersion of relatively large (>63 micron) and heavy (>2.85 g/cm^3) mineral concentrates (HMC) from bedrock sources during glaciation has met with great successes in the exploration for kimberlite (Thorleifson 1993; Ward *et al.* 1996; McClenaghan & Kjarsgaard 2001; McClenaghan 2002; McClenaghan *et al.* 2002), base metals (Sarala & Peuraniemi 2007; Kelley *et al.* 2010; Averill 2011; Eppinger *et al.* 2011; McClenaghan *et al.* 2011; McClenaghan *et al.* 2012a,c; McClenaghan & Peter 2013), and gold (Averill & Zimmerman 1984; Sauerbrei *et al.* 1987; Craw *et al.* 1999; Averill 2013) deposits. By using HMC and the mineral chemistry of these indicator minerals, which have been separated from sediments using complex and expensive techniques (e.g. sieved, tabling, heavy liquids, magnetic separation, and hand-picking), the recognition of the spatial extent of the mineral deposit footprint has increased from 100s of metres to 1000s of metres.

In this paper, we present an overview of the current methods and the applications of mineral chemistry using indicator minerals recovered from sedimentary cover. We also discuss new methods and instrumental developments, highlight current research on mineral chemistry, indicator minerals, and mineral exploration, and consider future research directions.

MINERAL IDENTIFICATION AND MINERAL CHEMISTRY

Indicator minerals, by definition, are minerals that have a physical or chemical characteristics that allow them to be readily recovered from stream, alluvial, glacial, or aeolian sediments or soils samples (McClenaghan *et al.* 2000; McClenaghan & Kjarsgaard 2001). Traditionally, the identification and separation of indicator minerals rely on the characteristics largely related to the minerals' chemistry, i.e., visual distinctiveness and moderate to high density.

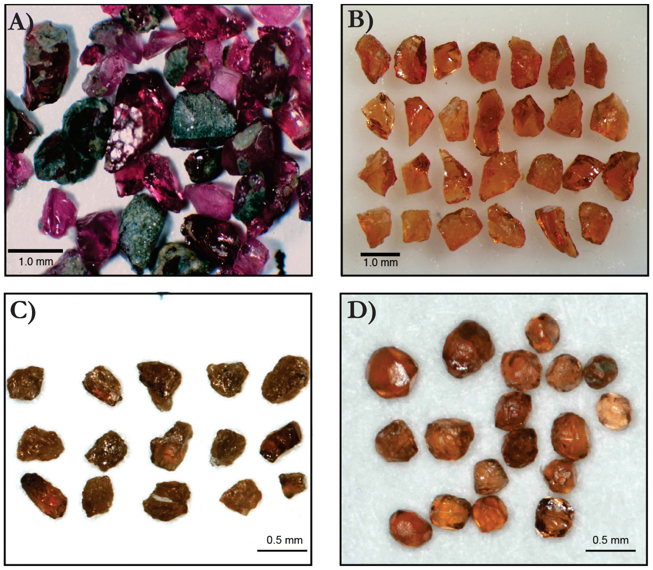

Fig. 1. Examples of colour and habit variation in indicator minerals using optical techniques (modified after McClenaghan & Kjarsgaard 2007; Hicken 2012). **A)** Purple -pyrope, some retaining kelyphite (dark). **B)** Orange eclogitic pyrope-almandine garnets. **C)** Staurolite in sample 09-MPB-006, 0.25–0.5 mm. **D)** Spessartine with deltoidal icositetrahedron habit in sample 09-MPB-031, 0.25–0.5 mm

Optical techniques

Indicator minerals are traditionally selected from samples after the samples have undergone heavy mineral separation (see McClenaghan *et al.* 2000b; McMartin & McClenaghan 2001; McClenaghan 2005). Indicator minerals are "picked" from concentrates during an optical examination under a stereoscopic microscope, a process that may require up to 3 hours per sample. A few tens to several thousand grains may be separated into vials based on colour (Fig. 1A,B) and mineral habit (Fig. 1C,D). The success of a laboratory to produce high-quality mineral concentrates and subsequent mineral picking using experienced technicians is the first critical step in any indicator mineral chemical study.

Electron-based techniques

Once indicator minerals have been recovered, they are commonly epoxy-mounted, polished, and carbon-coated for exam-

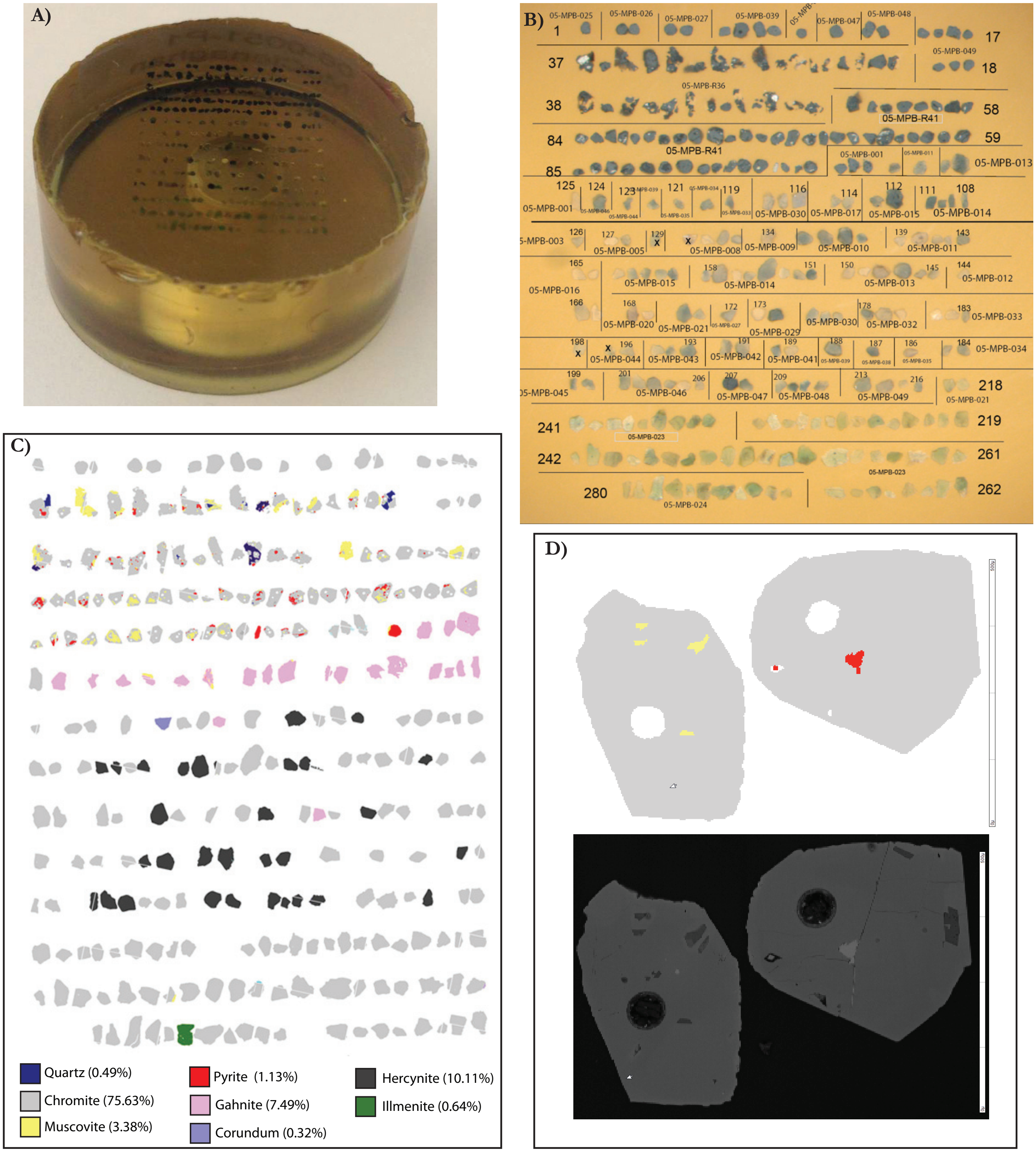

Fig. 2. Example of indicator mineral chemistry workflow from epoxy mount to laser ablation. **A)** Epoxy-mounted mineral grains after mineral separation. **B)** Optical stereo binocular photomicrograph. **C)** False colour processed Mineral Liberation Analysis (MLA) image. **D)** MLA image of chromite (upper) and corresponding BSE image (lower). Note the circular 50 micron laser ablations spots in each grain.

ination using micro-analytical techniques (Fig. 2A). Most mineral chemical investigation methods examine these indicator mineral mounts using an electron-based instrument. Traditionally, a scanning electron microscope (SEM) is used to examine the spatial distribution of backscatter secondary electrons (BSE), which is a reflection of differences in the average atomic number of an area of a grain. This is done in combination with energy dispersive spectrometry (EDS) in order to identify relative element concentrations within mineral phases and mineralogy.

The goals of using an SEM are to (1) confirm of mineralogy that has determined through mineral picking, (2) document mineral associations, (3) document mineral textures and morphology (shape, rounding, size, etc.), and (4) identify opti-

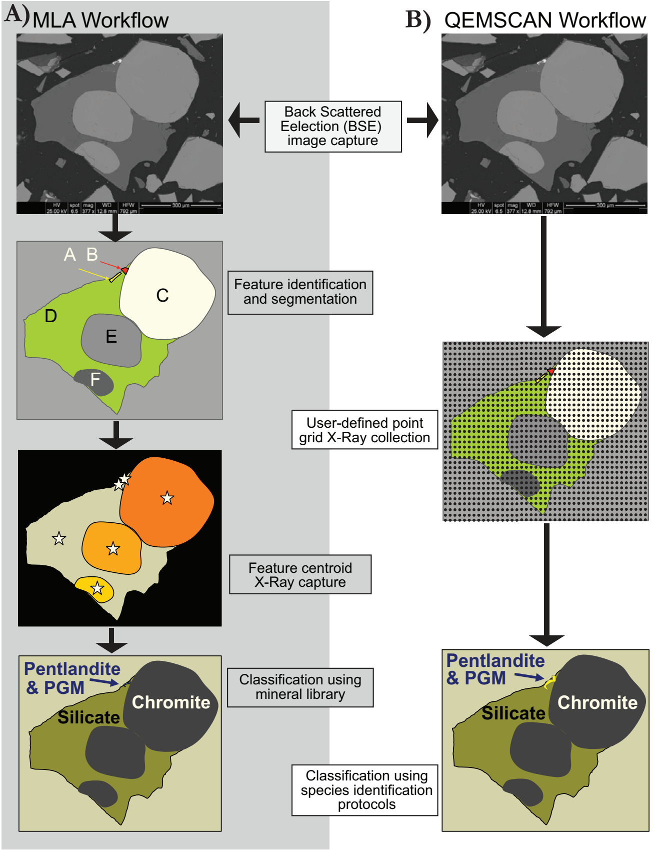

Fig. 3. Comparison of sample work-flow for automated mineralogy for **(A)** mineral liberation analysis and **(B)** QEMSCAN®.

mal mineral grains for further, more costly, mineral chemical characterization. The full characterization of a single epoxy mount with 200 to 500 grains can take 6 to 12 hours on a traditional SEM. Recent advances in automated scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (EDS) are transforming the analysis of mineral grain mounts. Time-consuming and qualitative mineral descriptions are now been replaced with fast, quantitative, and repeatable SEM analysis. These automated SEM methods provide confirmation of mineralogy, quantification of mineral textures and morphology, and reduces grain mount analysis time to 1 to 2 hours.

The most popular automated SEM supplier is FEI™; the company currently offers a tungsten-based or a field emission gun-based hardware that can be coupled with either Quantitative Evaluation of Minerals by SCANning electron microscopy (QEMSCAN®) or Mineral Liberation Analysis (MLA™) software. Mineral Liberation Analysis was initially developed for the mining industry by the University of Queensland, Australia (JKTech) (Burrows & Gu 2006; Gu *et al.* 2012); QEMSCAN® was developed for the mining industry by CSIRO, Australia (Butcher *et al.* 2000; Gottlieb *et al.* 2000; Pirrie *et al.* 2004; Pirrie & Rollinson 2009). However, both software packages are currently licensed and sold through FEI™ and their regional supply companies (e.g. Systems for Research, Canada).

MLA automated mineralogy is based on high-resolution BSE images, image analyses, and elemental chemistry from EDS. Collections of BSE images are combined to create a mosaic image of an epoxy grain mount (Fig. 3). Each BSE image is used to remove epoxy from the image, and centroid image analysis segments grains and minerals into individual particles. The MLA software then collects a full X-Ray spectrum (EDS) at the centre of each particle (Fig. 3). In post-collection processing, the full X-Ray spectrum is compared with a user-defined mineral EDS library and the BSE image to create a coherent data set, which includes a false-colour mineral map, modal mineralogy, grain size, mineral associations (occurrence and interlocking), particle properties (roundness, area, shape), and mineral liberation.

QEMSCAN® automated mineralogy is fundamentally different than MLA, in that is based on fast mineral identification using point analysis on a finely spaced grid. Similar to MLA, QEMSCAN® collects BSE images to create a mosaic image of an epoxy grain mount; however, during automated measurement, the system collects EDS spectra along a pre-defined grid (similar to modal counting using a petrographic microscope). QEMSCAN® uses the EDS spectra in combination with the BSE image data to determine areas of epoxy and areas of mineral, minimizing the collection of background data. On mineral phases, a low-count EDS spectrum is collected that allows for ultra-fast discrimination of most minerals. QEMSCAN® also differs from MLA in the way that mineralogy is determined. In MLA, minerals are identified through comparison of unknown EDS with a user-defined EDS database of known minerals. QEMSCAN® uses a built-in library of 72 elemental reference spectra are used to build a composite elemental spectra that is then used in conjunction with user-defined Species Identification Protocols (SIP) to identify discrete minerals. In addition to output data similar to MLA, QEMSCAN® produces elemental maps in addition to mineral maps.

MLA- or QEMSCAN®-generated BSE and false-colour images of a mineral concentrate have many advantages over traditional optical microscopy (Hartner *et al.* 2011; Gu *et al.* 2012; Sylvester 2012): 1) measurement of compositional data, 2) measurement of thousands of points per sample mount, 3) repeatable and quantitative measurements, 4) fully automated work-folk, 5) faster processing time, 6) less training required, 7) modal mineralogy calculated assay data, 8) micron-scale resolution, and 9) better determination of analysis points for texturally difficult (i.e. polymineralic) grains and for choosing grains for in situ chemical or isotopic analyses.

The occurrence and modal quantification of distinct HMC in till is of great importance in the definition of till dispersion trains in many ore exploration programs (i.e. gold); however, many HMC mounts are further characterized for individual mineral chemistry. Many HMC studies ((McClenaghan 2002b; Morris *et al.* 2002; Lehtonen *et al.* 2005 and references therein) have used the occurrence of HMC in bedrock sources coupled with the major and minor element chemistry to identify the provenance and fertility of the HMC.

The quantification of major elements can be obtained quickly for many elements from EDS software using a SEM with detection limits between 2000 and 10,000 ppm (Z>4). However, because EDS requires that individual X-Ray spectra be separated from other X-Ray spectra in a mineral analysis, some X-Ray energies cannot be separated from background radiation (high detection limit) or from X-Ray spectra of other elements (i.e. peak overlap). Most modern EDS detectors have an energy resolution of 130 to 160 eV (Full Width Half Max). For example, the quantitative analysis of molybdenite (MoS_2)

by EDS is not possible because the Mo L alpha line is at 2.2930 keV and overlaps with the S K alpha line at 2.3070 keV.

More commonly, indicator minerals are analyzed for major and minor elements using electron probe microanalyzer (EPMA). In principle, a EPMA is very similar to a SEM, as the electron source and focusing column are nearly identical. However, an EPMA and SEM collect X-Ray data differently. Both instruments collect chemical spectra using an EDS detector, but on a EPMA, spectra are also collected using wavelength dispersive spectroscopy (WDS). During the collection of WDS, spectra are separated by the mechanical diffraction of X-Rays into wavelengths that are individually measured by a detector. Most modern EPMA have up to 5 wavelength dispersive spectrometers, which allows the simultaneous measurement of five elements. EDS and WDS each have advantages and disadvantages. EDS can quickly collect a full X-Ray spectrum in 10s of seconds; whereas WDS is time consuming, requiring the movement of a diffraction crystal to measure each individual element. Much of the spectral interference encountered during EDS can be eliminated by the high-energy resolution of WDS (~10 eV). The biggest disadvantage of both EDS and WDS systems are the detection limits (~0.1 and 0.01%, respectively) for most elements in the characterization of mineral chemistry.

Mass spectrometry-based techniques

The use of laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) for characterization of mineral chemistry has grown since its first application to geological media (Hale *et al.* 1984; Jackson *et al.* 1992). Conceptually the application of laser ablation for mineral chemical and isotopic analyses is a straightforward, albeit destructive, technique. A short-pulsed (femto- to nanosecond) laser ablates a small volume (~8000 um^3) of a mineral sample over a period of 10s of seconds. During ablation the mineral is converted into vapour and aerosol components. This material is then continually transferred in an Ar or He carrier gas to be ionized in an inductively coupled plasma and mass analyzed in either a quadrupole or magnetic-sector mass spectrometer.

There are several instrument parameters that must be optimized to measure element and isotopic compositions of a mineral by LA-ICP-MS (Arevalo *et al.* 2010; Rogers *et al.* 2010; Koch & Gunther 2011); these include (1) laser pit size, (2) laser wavelength, (3) laser pulse-rate, (4) mass spectrometer, (5) matrix-match standards, and (6) curve calibration. Most laser ablation instruments are capable of adjusting the laser beam size from 1–2 to 300 microns, however, most analyses are completed at ~30 microns. If a laser pit is too small then not enough material is ablated to create a suitable signal in the mass spectrometer. If a laser pit is too large, the mass spectrometer detector may become saturated or go beyond the element calibration curve.

Numerous studies have examined the analyses of geological media using variable laser wavelengths (Motelica-Hieno & Donard 2001; Guillong *et al.* 2005; Jochum *et al.* 2007; Gaboardi & Humayun 2009) and laser pulse-rates (Poitrasson *et al.* 2003; Gonzalez *et al.* 2007; Horn 2008; Saetveit *et al.* 2008; Glaus *et al.* 2010), and collectively using similar laser energies. There is consensus that shorter wavelengths and higher laser pulse rates produce superior data that require fewer corrections for elemental and isotopic bias. In mineral analysis, a shorter wavelength laser (i.e. 193 nm vs 213 nm) produces a flat-bottomed and sharp-walled ablation pit. The higher pulse rate (i.e. femtosecond vs nanosecond) of the mineral, the less thermal heating occurs with a lower abundance of secondary condensates (Gunther & Heinrich 1999; Gunther *et al.* 2000; Poitrasson *et al.* 2003; Hirata *et al.* 2004).

Ultimately, the ability of LA-ICP-MS to measure low-concentration elemental and isotopic data is a function of the mass spectrometer paired with the laser ablation system. There are three options for inductively coupled plasma mass spectrometers for use in laser ablation: 1) quadrapole, 2) high-resolution single collector, and 3) high-resolution multi-collector.

By far the most common mass spectrometer used in laser ablation studies of mineral chemistry is the quadrapole mass analyzer. These instruments filter ions created in the plasma by mass and charge (m/z) as they travel to the detector using variable DC voltages on four parallel stainless steel rods. By adjusting the DC voltage on the quadrupoles, the transient ions created in laser ablation can be filtered and analyzed for most of the periodic table in milliseconds (Hill 2007).

In high-resolution mass spectrometers, ions created in laser ablation and in the inductively coupled plasma are passed along a curved flight path through magnetic and electrical fields to disperse ions according to their momentum and translational energy (Willard 1988). By adjusting the magnetic and electrostatic fields, the transient ions arriving at the detector(s) can be varied on the basis of mass. Because of this geometry, the mass resolution of these instruments is superior to that of quadrupole instruments (e.g. ~10,000 versus ~600, respectively). As such, fractions of mass unit can be effectively separated during analysis, allowing for separation of polyatomic interferences (Hill 2007).

For effective ion transmission through both the magnetic and electrical sectors, ions are accelerated at much higher energies than in quadrapole instruments (e.g. 10 kV versus 10 eV, respectively). As such, less ion scattering is created and lower detection limits are observed using high-resolution instruments. For many mineral chemical applications, a high-resolution mass spectrometer commonly has only one detector. However, in applications where isotopic ratios are measured, high-resolution instruments commonly have several detectors (known as multi-collector). These instruments can measure individual isotopes (i.e. ^{204}Pb, ^{206}Pb, ^{207}Pb, ^{208}Pb) simultaneously, without adjustment of the magnetic or electric sectors, which yields superior isotopic ratios.

Quadrapole and high-resolution mass spectrometers each have advantages and disadvantages in mineral chemical analyses using laser ablation. In quadrapole instruments, a wide range of elements (i.e. m/z) can be analyzed very quickly, compared to magnetic and electrical field sector instruments. In high-resolution instruments, the magnetic sector must be adjusted and allowed to stabilize before analyzing of the next mass range (Giessmann & Greb 1994; Jakubowski *et al.* 1998). Given the transient nature of laser ablation analysis, a quadrapole instrument is much better suited for mineral analyses with varied element mass (i.e. rare earth elements, U, Pb). When there are narrow mass differences (<30%), very small laser ablation pits (<10 microns) or isotopic ratios are needed, for which high-resolution mass spectrometers offer vastly superior precision and detection limits.

Multi-element trace element analysis by LA-ICP-MS has not been universally adopted for mineral analysis because there is a

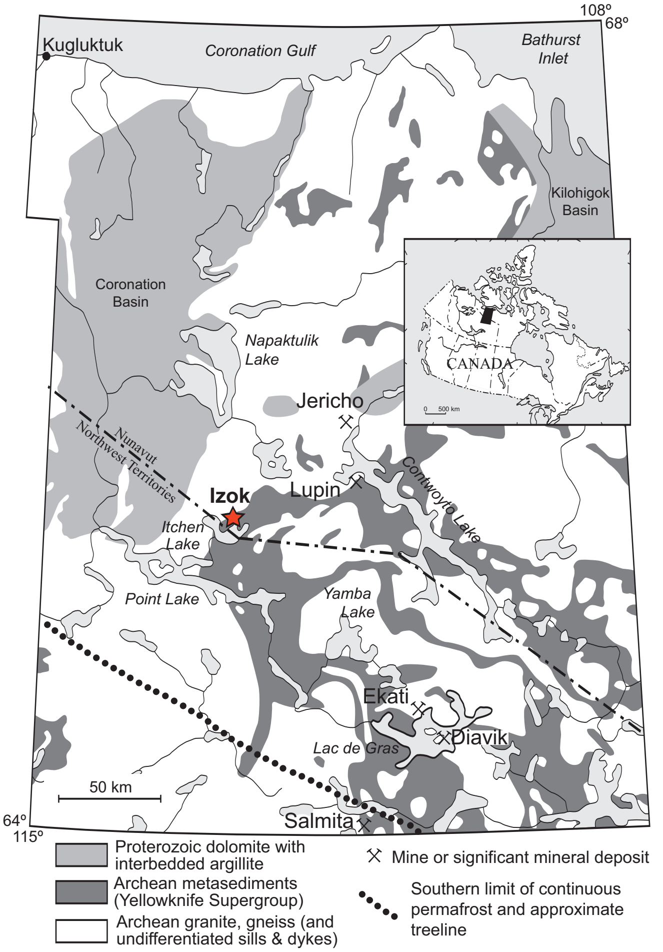

Fig. 4. Location map of the Izok Lake mineralization, Nunavut, Canada (modified after (Dredge *et al.* 1999; Hicken 2012; Hicken *et al.* 2013).

lack of suitable reference materials with similar matrix compositions. Furthermore, there has been a limited effort to find or create matrix-matched standards with variable concentrations of trace elements (i.e. 10, 100, 500 ppm), which is necessary to create standard calibration curves and element quantification. Recently there have been several geological glasses that have been created from rock powder standards (Jochum *et al.* 2000, 2006, 2012; Jochum & Nohl 2008) or by the doping of rock powder standards at variable concentrations (Guillong *et al.* 2005; Jochum *et al.* 2005; Kaiyun *et al.* 2013). The use of these standards in conjunction with EPMA data now allows the reliable quantification of many trace elements in minerals using LA-ICP-MS.

APPLICATIONS IN INDICATOR MINERAL STUDIES

During this workshop, several recent examples will outline the use of mineral chemistry in indicator mineral studies illustrating the methods described above. Due to brevity of an extended abstract, only one case study will be presented.

In exploration for volcanogenic massive sulphide (VMS) deposits in northern Canada, an indicator mineral survey was completed around the Izok Lake mineralization (Fig. 4) occurrence in Nunavut, Canada (McClenaghan *et al.* 2012b,c; McClenaghan *et al.* 2012c; McClenaghan 2013; Paulen *et al.* 2013). Ice-flow mapping in this area shows that glacial trajectories have undergone clockwise rotation from southwest to northwest, in a series of discrete ice-flow phases rather than as a continuous ice-flow change (Kerr *et al.* 1995; Dredge *et al.* 2003; Paulen *et al.* 2013). An early southwest ice-flow was followed by strong west- to west-northwest-trending flow. Surface morphology and ice-flow indicators (e.g. striations) within the Izok Lake area reflect this dominant northwest phase (Paulen *et al.* 2013).

Field documentation of ice-flow in the Izok Lake area, led to till sampling up- and down-ice (Fig. 5). Both bedrock and till

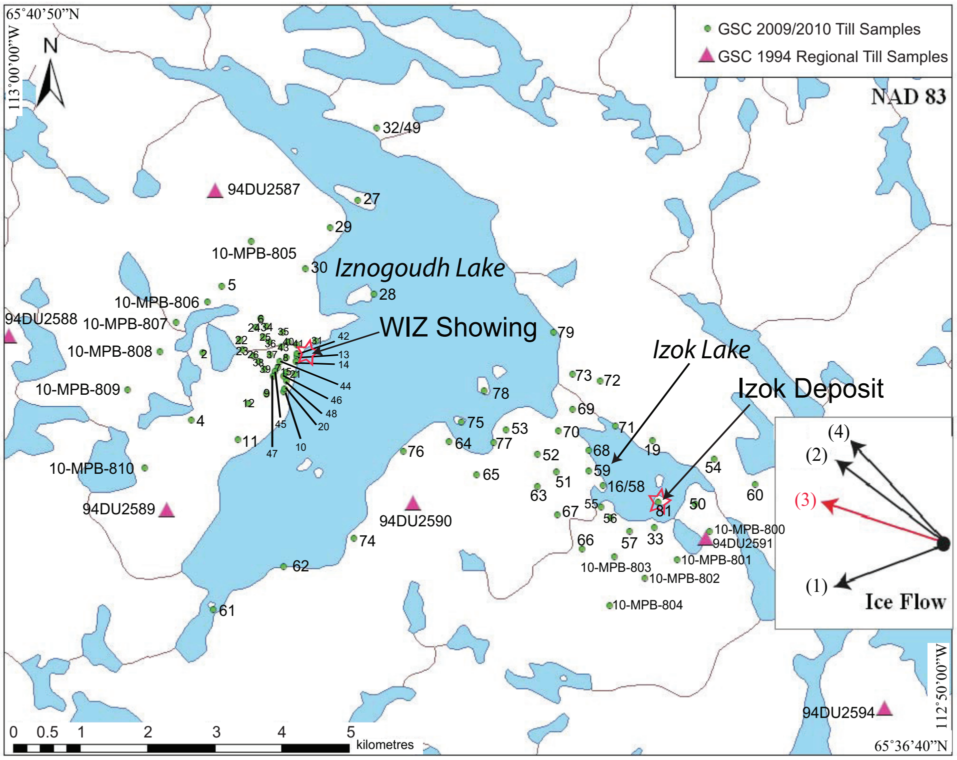

Fig. 5. Locations of till samples (green dots) 1994 Geological Survey of Canada regional samples (pink triangle) and bedrock mineralization (red star) near the Izok Lake deposit (Hicken 2012; Hicken *et al.* 2013).

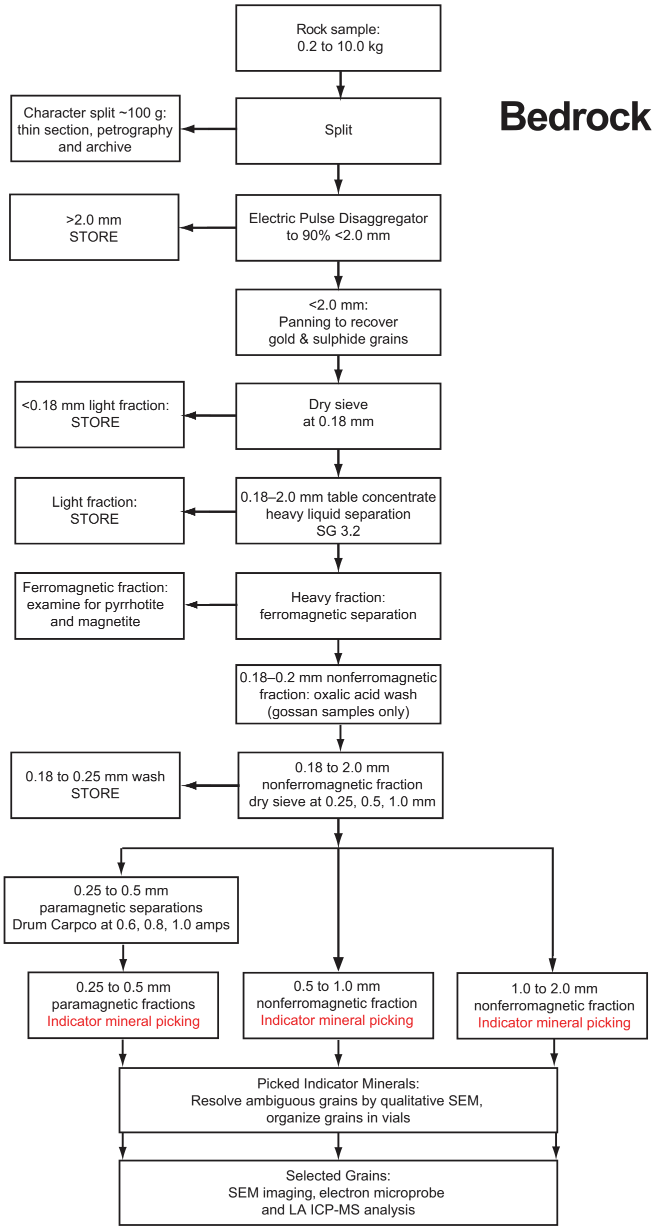

Fig. 6. Flow-sheet outlining the sample processing and picking procedure for bedrock samples processed from the Izok Lake deposit area (Hicken 2012).

Table 1. Comparison of sizes (mm) of key indicator minerals observed in polished thin sections, heavy mineral concentrates, and pan concentrates.

Mineral	**Size Range in Polished Thin Section** (mm)	**Size Range in Heavy Mineral Concentrate** (mm)	**Size Range in Pan Concentrate** (µm)
Pyrite	0.1-6	0.25-1.0	25-200
Chalcopyrite	0.1-5	0.25-1.0	15-200
Sphalerite	0.2-5	0.25-1.0	15-100
Galena	0.01-0.6	0.25-0.50	15-100
Gahnite	0.2-3.0	0.25-1.0	n/a
Staurolite	0.2-1.3	0.25-0.50	n/a
Axinite	0.4-2.0	0.25-0.50	n/a

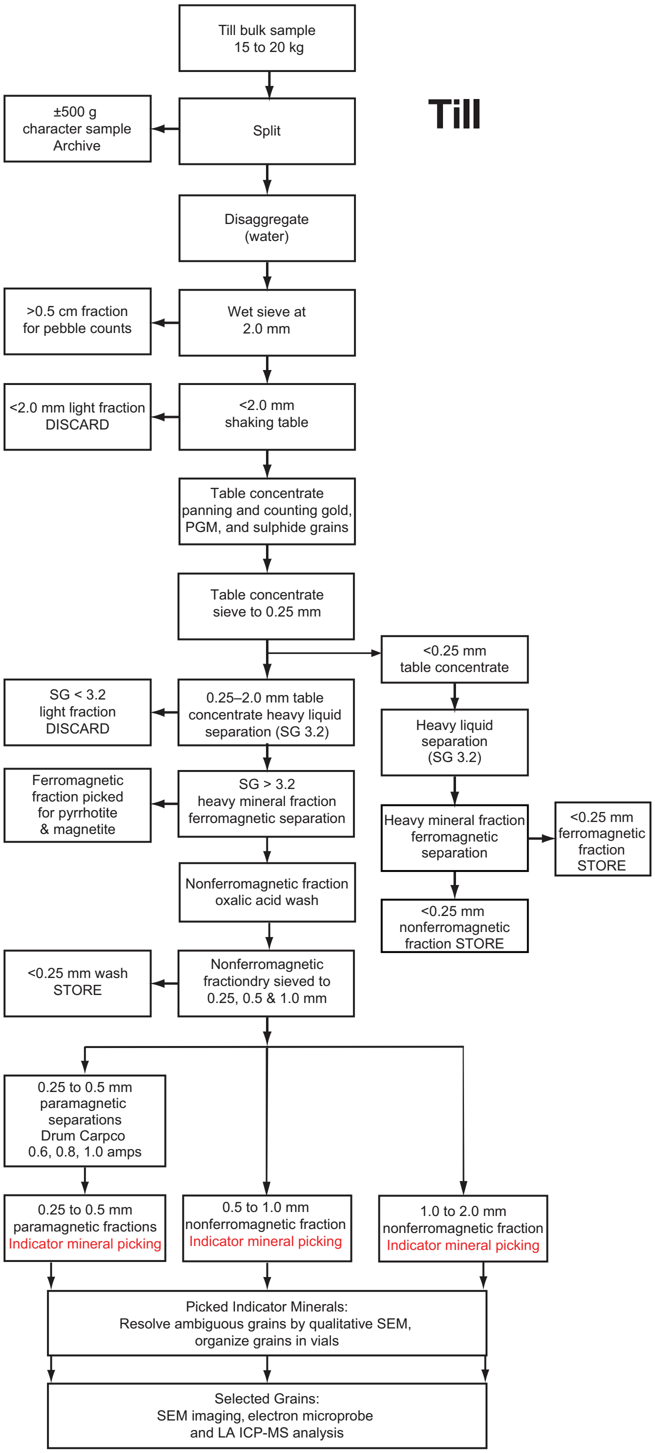

Fig. 7. Flow-sheet outlining the sample processing and picking procedure for till samples processed from the Izok Lake deposit area (Hicken 2012).

samples were processed for geochemistry, HMC mineral counts, and HMC mineral chemistry (Figs. 6, 7). The 0.25–0.5, 0.5–1.0, and 1.0–2.0 mm non-ferromagnetic fractions of the bedrock and till samples were examined using optical techniques (Fig. 8). Representative thin sections were made, in addition to mineral grain mounts based on indicator minerals counted/selected during optical examination (Table 1). Thin sections and grain mounts were examined using MLA-ESEM (Figs. 9, 10) to quantify modal mineralogy, mineral associations,

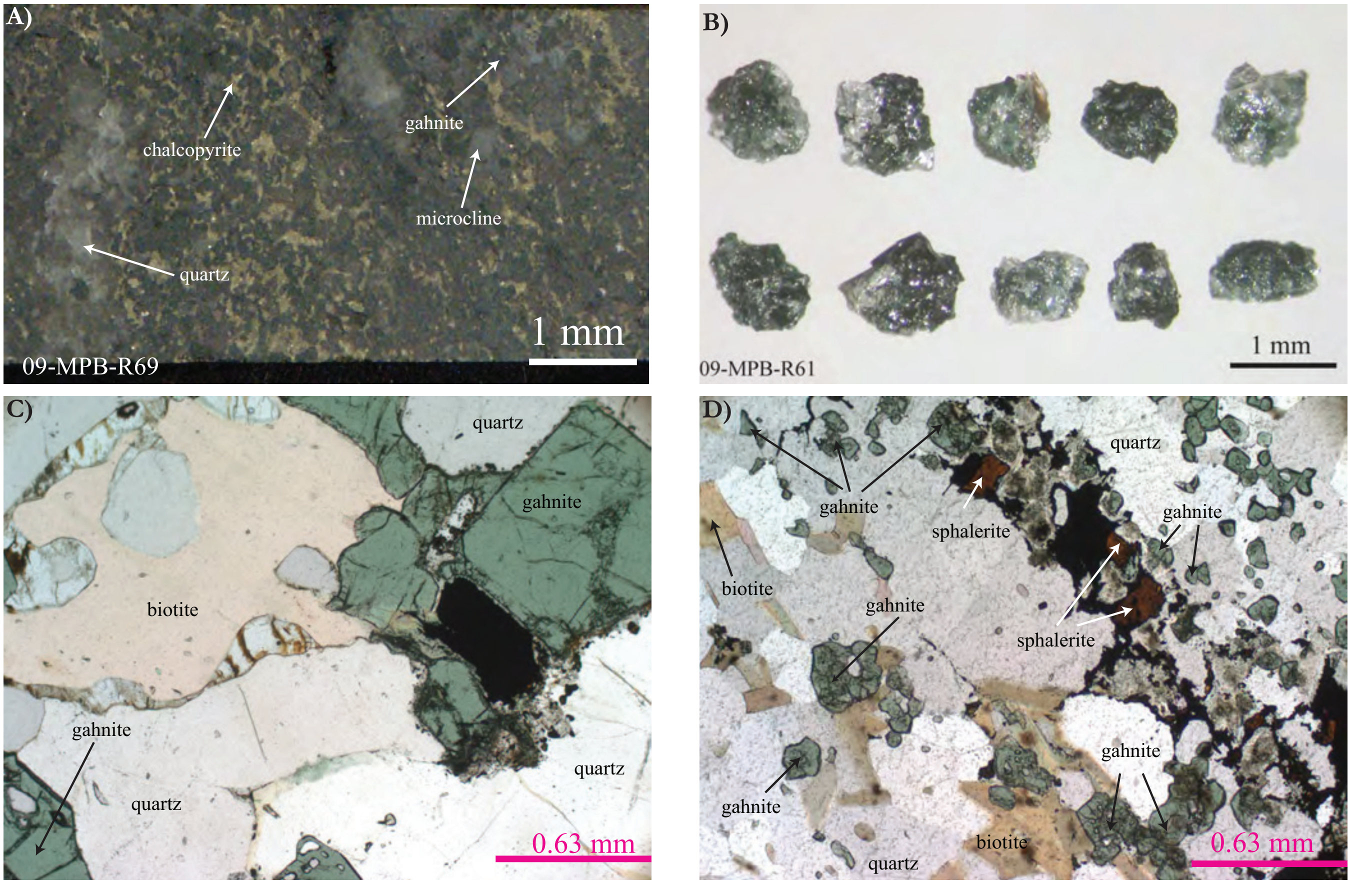

Fig. 8. Gahnite in **(A)** polished slab of drill core (sample 09-MPB-R69); **(B)** grains from a heavy mineral concentrate (sample 09-MPB-R61); **(C)** polished thin section (sample 09-MPB-R37); and **(D)** polished thin section (sample 09-MPB-R41B).

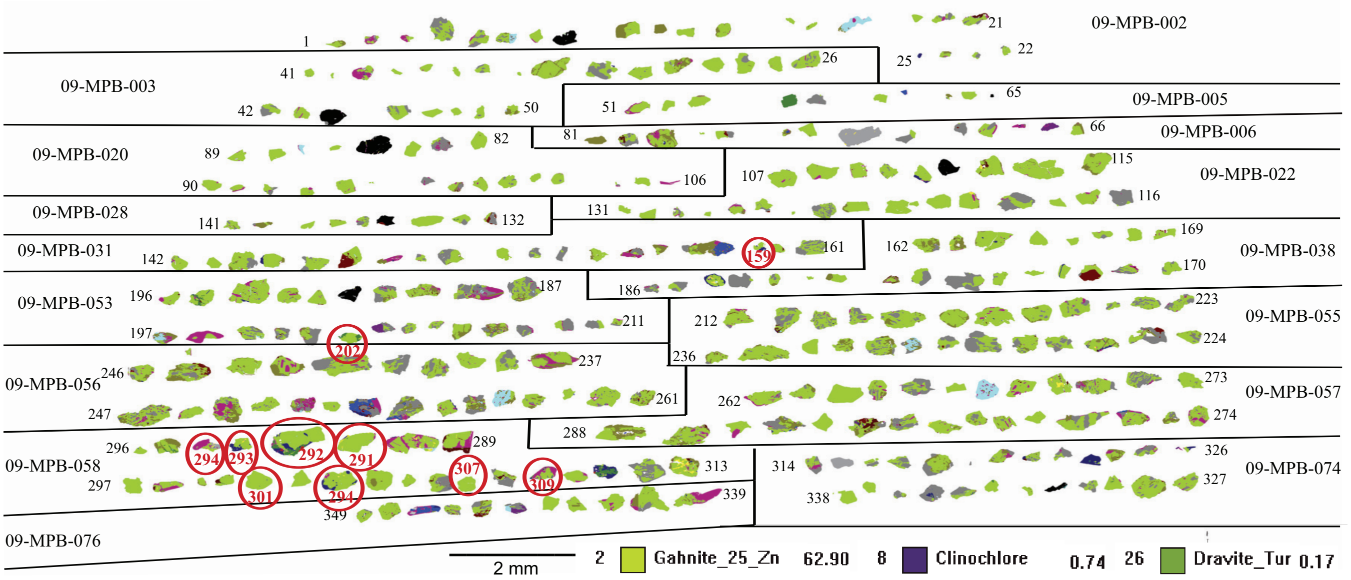

Fig. 9. MLA-SEM image of gahnite grain mount 10-0269-P01 from Izok Lake samples. Adhering gangue mineral compositions are indicated with various colours outlined in the legend. Till sample numbers are listed on the outer sides of the image and grain numbers are listed at the end of each row. Red circles indicate those grains for which the LA-ICP-MS/EPMA mineral chemistry is anomalous (Hicken 2012; Hicken *et al.* 2013).

2	■	Gahnite_25_Zn	62.90	8	■	Clinochlore	0.74	26	■	Dravite_Tur	0.17
14	■	Quartz	15.67	1	■	Gahnite_35_Zn	0.72	29	■	Unknown	0.06
13	■	Muscovite	6.82	20	■	Ripidolite	0.56	15	■	Apatite	0.03
12	■	Biotite	5.52	9	■	Epidote	0.52	4	■	Spess_Alm	0.02
7	■	Ca_Amphibole	2.01	5	■	Sillimanite	0.33	18	□	Monazite	0.02
3	■	Gahnite_Crackle	1.46	21	■	Albite	0.32	17	■	Ilmenite	0.02
19	■	Spinel_loFe_tr_Zı	0.98	6	■	Corundum	0.28	28	■	Xenotime	0.01
11	■	Microcline	0.81								

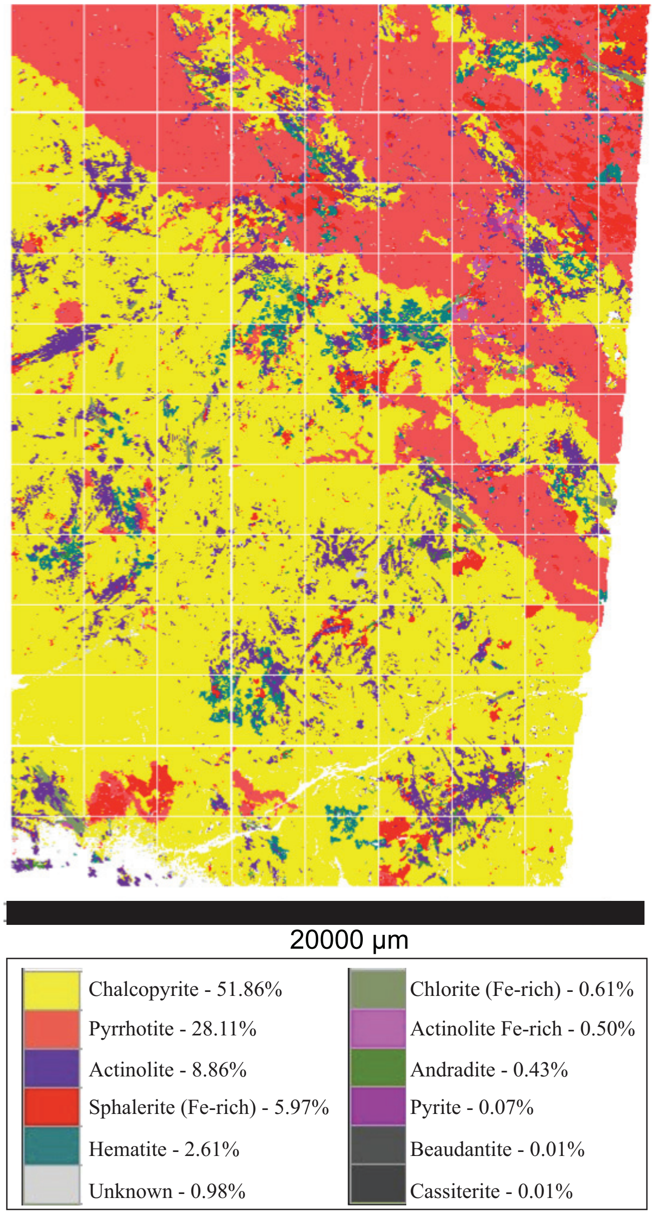

Fig. 10. MLA image of 09-MPB-R60 (massive sulphide) from Izok Lake showing percentages of chalcopyrite, pyrrhotite, actinolite, sphalerite, hematite/magnetite, and trace minerals (Hicken 2012).

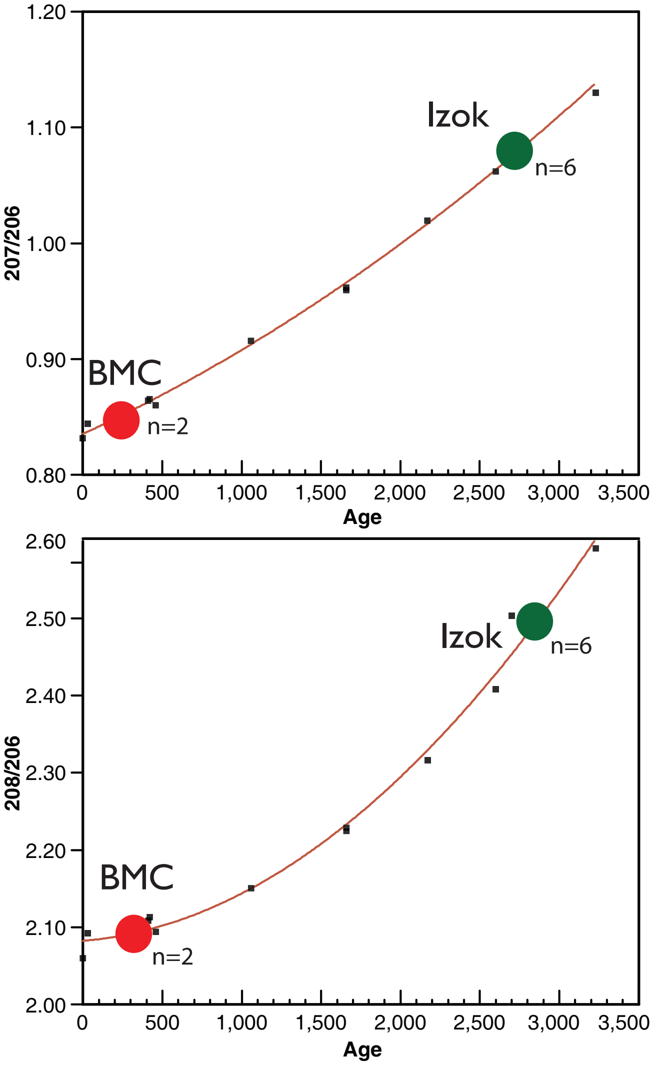

Fig. 11. LA-ICP-MS quadrupole Pb isotopic ratios for gahnite. **A)** ^{207}Pb/^{206}Pb age relations for Izok Lake (green circles) and Halfmile Lake (Bathurst Mining Camp, New Brunswick: red circles); **B)** ^{208}Pb/^{206}Pb age relations for Izok Lake (green circles) and Halfmile Lake (Bathurst Mining Camp, New Brunswick: red circles). Red line is an approximation of terrestrial lead isotopic evolution (Stacey & Kramers 1975). High-precision U/Pb ages for Halfmile Lake is 465 Ma (van Staal *et al.* 2003), for is Izok Lake is 2623 ± 20 Ma (Mortensen *et al.* 1988), and for Izok Lake is 2680.5 +7/-3 Ma (J. Gebert, unpub. 1995).

grain shape, and grain size. EPMA was completed on a selection of indicator minerals and LA-ICP-MS was conducted on a subset of gahnite grains (>50 microns) for trace element and Pb/Pb dating (Fig. 11).

FUTURE DIRECTIONS IN MINERAL CHEMISTRY

Need for novel methods

The identification of discrete indicator minerals in till has greatly influenced mineral exploration. There are well established methods for separation and identification of minerals in HMC. Indicator mineral chemistry has been used to identify bedrock sources and assess their fertility. The question then becomes, "Why do we need new techniques in the application of mineral chemistry to HMC?"

Successful mineral exploration using sediments and HMC requires a high degree of specialization. This type of work requires a person with not only a background in bedrock geology and ore deposits, but also a person with training in sample collection and preparation, mineralogy, analytical chemistry, and quaternary geology. Current exploration models use a team approach, where each individual contributes their own area of expertise. At present, mineral separation methods have been well established for size-fractions larger than 0.063 mm, but these methods are slow, expensive, and require a highly qualified mineralogist.

New HMC and mineral chemical methods are currently being developed to include a greater number of deposit types (e.g. volcanogenic massive sulphides, uranium, Ni-Cu-PGE, rare earth elements), to utilize the smaller size (i.e. <0.063 mm) and less dense fractions (i.e. <2.85 g/cm^3) of samples, and incorporate new, faster, and more accessible analytical instruments (i.e. hyperspectral, MLA express). Development of these new methods will decrease the need for extensive specialized training, decrease the time and cost of HMC characterization, extend the spatial footprint of dispersion trains (i.e. smaller and farther), and ultimately lead to the identification of new indicator minerals in uncharacterized mineralized systems.

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