



Review Current Techniques and Applications of Mineral Chemistry to Mineral Exploration; Examples from Glaciated Terrain: A Review

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Abstract: This paper provides a summary of traditional, current, and developing exploration techniques using indicator minerals derived from glacial sediments, with a focus on Canadian case studies. The 0.25 to 2.0 mm fraction of heavy mineral concentrates (HMC) from surficial sediments is typically used for indicator mineral surveys, with the finer (0.25–0.50 mm) fraction used as the default grain size for heavy mineral concentrate studies due to the ease of concentration and separation and subsequent mineralogical identification. Similarly, commonly used indicator minerals (e.g., Kimberlite Indicator Minerals—KIMs) are well known because of ease of optical identification and their ability to survive glacial transport. Herein, we review the last 15 years of the rapidly growing application of Automated Mineralogy (e.g., MLA, QEMSCAN, TIMA, etc) to indicator mineral studies of several ore deposit types, including Ni-Cu-PGE, Volcanogenic Massive Sulfides, and a variety of porphyry systems and glacial sediments down ice of these deposits. These studies have expanded the indicator mineral species that can be applied to mineral exploration and decreased the size of the grains examined down to ~10 microns. Chemical and isotopic fertility indexes developed for bedrock can now be applied to indicator mineral grains in glacial sediments and these methods will influence the next generation of indicator mineral studies.

Keywords: indicator minerals; mineral chemistry; automated mineralogy; MLA; QEMSCAN; laser ablation; mineral exploration; ore deposits

1. Introduction

Most new mineral deposits yet to be discovered are likely concealed underneath cover rocks or unconsolidated sediments. The ability to see through this cover and to detect and understand the nature of the underlying bedrock ore environment has become a fundamental aspect of modern mineral exploration and ore deposit science [1-3]. The detection of buried mineral deposits using a variety of surficial materials has been aided using indicator mineral methods, specifically in our ability to (1) identify minerals that are indicative of specific mineral deposit types; (2) identify and separate these same indicator minerals from sediment samples; and (3) measure the unique chemical and isotopic composition of these indicator minerals [4-7].

The extent of the Last Glacial Maximum (LGM) was likely around 34.5 million km² with the greatest areas impacted in the Northern Hemisphere and covered by the Laurentide and Fennoscandian ice sheets [8]. Over the last 2 million years, most of Canada was glaciated leaving only 10% of its bedrock surface exposed as outcrop [9]. Approximately 80% of Canada is covered primarily by glacial and related sediments varying from <1 to 300 m in thickness. Over the past 30 years, indicator mineral methods in Canada have advanced such that they can now be used to detect a broad spectrum of mineral deposit types that are covered by glacial sediments (Table 1). In this paper, we present an overview of the current methods for, and applications of, indicator mineral chemistry with examples



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). from the glaciated terrain of Canada, and in particular for till—the optimal indicator mineral sample medium in glaciated terrain [5].

Table 1. Common indicator minerals that can be readily recovered from glacial sediment samples derived from different mineral deposit types (modified from McClenaghan et al., 2020) [10].

Deposit Type	Ore Elements	Common Indicator Minerals	Published Reviews and Selected Examples
Kimberlite-hosted diamonds	С	Cr-pyrope, Cr-diopside, eclogitic garnet, Mg-ilmenite, chromite, olivine, diamond	Lehtonen et al. (2005) [11]; McClenaghan and Kjarsgaard (2001, 2007) [12,13]; McClenaghan et al. 2002, 2004, 2012c) [14–16]; Strand et al. (2009) [17]; Stea et al. (2009) [18]; Pell et al. (2013) [19]
Volcanogenic massive sulphide	Cu, Pb, Zn, Ag, Au	chalcopyrite, sphalerite, galena, pyrrhotite, gold, pyrite, gahnite, staurolite, cassiterite, spessartine, sillimanite, andalusite, beudantite, jarosite, barite, tourmaline, hogcomite, nigerite	Lalonde et al. (1994) [20]; Morris et al. (2002) [21]; Averill (2001) [22]; Paulen et al., (2013) [23]; McClenaghan et al. (2015a,b) [24,25]; Makvandi et al., (2016) [26]; Lougheed et al. (2020) [27]
Carbonate-hosted lead-zinc	Ag, Cu, Pb, Zn	chalcopyrite, sphalerite, galena, pyrite, barite, spessartine, smithsonite, anglesite, cerussite	Paulen et al. (2011) [28]; Oviatt et al. (2015) [29]; McClenaghan et al., (2018) [5]
Gold	Au, Ag	gold, scheelite, tourmaline, rutile, sulphides, tellurides, PGM, barite, cinnabar	Averill and Zimmerman (1986) [30]; Averill (2001, 2013, 2017) [22,31,32]; Plouffe (2001) [33]; McClenaghan (2001) [34]; Sarala et al. (2009) [35]; McClenaghan and Cabri (2011) [36]; Sarapää and Sarala (2013) [37]; Manéglia et al. (2018) [38]
Magmatic Ni-Cu-PGE	Ni, Cu, PGE	pentlandite, chalcopyrite, pyrite, millerite, PGM, chromite, Cr-diopside, enstatite, olivine, Cr-andradite	Bajc and Hall (2000) [39]; Barnet and Averill (2010) [40]; McClenaghan and Cabri (2011) [36]; Averill (2011) [41]; McClenaghan et al. (2013; 2020b) [42,43]; Hashmi et al. (2021) [44]; Makvandi et al. (2021) [45]
Rare metals	Rare Metals	pyrochlore, columbite, Ta-minerals, allanite, zircono-silicates, apatite, monazite, fluorite, rhabdophane, arfvedsonite	Lehtonen et al. (2015) [46]; Sarapää and Sarala (2013) [37]; Mao et al. (2016) [47]; Mackay et al. (2016) [48]; McClenaghan et al. (2019) [49]
Porphyry Cu-Au-Mo	Cu, Mo, Au, Ag	chalocopyrite, chalcocite, pyrite, molybdenite, gold, silver, epidote, tourmaline, apatite, andradite, barite, monazite, rutile, titanite, zircon, jarosite, malachite, pyrolusite, magnetite	Averill (2011) [41]; Kelley et al. (2011) [50]; Eppinger et al. (2013) [51]; Hashmi et al. (2015) [52]; Chapman et al. (2015, 2018) [53,54]; Plouffe et al. (2016; 2019) [55,56]; Pisiak et al. (2017) [57]; Plouffe and Ferbey (2017) [58]; McClenaghan et al. (2020c) [59]; Lee et al., 2021 [60]; Beckett-Brown et al. (2021) [61]
Intrusion-hosted Sn-W	Sn, W, Mo	cassiterite, scheelite, wolframite, molybdenite, chalcopyrite, Bi sulphides, sulphides, fluorite, topaz, tourmaline	McClenaghan et al. (2017a, 2017b) [6,7]; Poulin et al. (2018) [7], Lougheed et al., 2021 [62]
Iron oxide- Copper-Gold	Fe, Cu, Au	magnetite, gold, apatite, pyrite, chalcopyrite, pyrrhotite, titanite, epidote	McMartin et al. (2011) [63]; Sappin et al. (2014) [64]; Normandeau et al. (2018a, b) [65,66];
Uranium	U	uraninite (*pitchblende), thorianite, tourmaline, sulphides, monazite, allanite, zircon, baddelyite, niccolite, U-Th anatase, U-Th rutile, brannerite, magnetite	Geddes (1982) [67]; Makvandi et al. (2017, 2019, 2021) [68–70]

PGM = Platinum Group Minerals; PGE = Platinum Group Elements; * pitchblende- brown or black pitchy massive form of uraninite.

2. Mineral Identification and Mineral Chemistry

2.1. Mineral Identification for >0.25 mm (Medium to Very Coarse Sand-Sized) Grains

The separation and visual identification of indicator minerals from glacial sediment samples relies on characteristics largely related to mineral chemistry, i.e., visual distinctiveness and moderate to high density [13,22,41]. Indicator minerals are selected from a >0.25 mm heavy mineral concentrate (HMC) after a sediment sample has undergone concentration and separation using various combinations of sizing, density, and magnetic methods (McClenaghan, 2005, 2011) [4,71]. During an optical examination of an HMC under a stereoscopic microscope, indicator minerals are counted and a selection of grains is "picked", a process that may require up to 3 h per sample. A few grains to several thousand grains may be separated into vials based on colour and mineral habit, such as the well-known kimberlite indicator minerals used for diamond exploration (Figure 1). The production of high-quality HMCs and mineral identification and selection by experienced technicians are vitally important in the first critical step of any indicator mineral chemical study. Selected mineral grains are commonly epoxy-mounted in organized rows (Figure 2A,B), polished, and carbon-coated for examination using microanalytical techniques. Traditional indicator mineral picking of the >0.25 mm HMC of till samples for mineral exploration in glaciated terrain has been used for more than 50 years, mostly for the exploration for gold and diamond deposits [4,12,13,22,43].



Figure 1. Examples of the colour and habit variations in kimberlite indicator minerals that can be observed using optical techniques (modified from McClenaghan and Paulen, 2020): (**a**) purple to pink Cr-pyrope; (**b**) Cr-pyrope with dark green-grey kelyphite rims (k); (**c**) Cr-diopside; (**d**) eclogitic garnet; (**e**) Mg-ilmenite; (**f**) chromite showing resorbed crystal faces; (**g**) forsteritic olivine; (**h**) diamond. Mineral photography by Michael J. Bainbridge. Eclogitic garnet grains provided by Mineral Services; diamond provided by Herb Helmstaedt, Queen's University. Modified from McClenaghan and Paulen (2018) [5].



Figure 2. Example of the indicator mineral chemistry workflow from epoxy mount to laser ablation analysis. (**A**) Epoxy-mounted mineral grains after mineral separation. (**B**) Optical stereo binocular photomicrograph of polished grains in an epoxy mount; most grains 0.25–0.5 mm diameter. (**C**) False-colour processed Mineral Liberation Analysis (MLA) image of mineral grains in an epoxy mount. (**D**) MLA image (upper) of chromite grains (grey) with inclusions (red, yellow) and corresponding backscatter secondary electron image (lower); both images f show circular 50 μm laser ablations spots in each grain. Scale bar is 500 μm. Modified from Layton-Matthews et al., 2014 [72].

2.2. Mineral Identification for <0.25 mm (Silt to Fine Sand-Sized) Grains

The most cost- and time-effective means to identify indicator minerals in a <0.25 mm (medium silt and finer) HMC of a sediment sample is using Automated Mineralogy [27,46,48,73–75]. The mineral grains in this size range are too small and too numerous to visually sort, identify and count. Instead, Automated Mineralogy methods can be used to identify the minerals (10,000–100,000) in this smaller size fraction. A HMC is produced prior to mineral identification. The <0.25 mm fraction of the HMC can be

further sieved into still smaller size fractions (e.g., $185-250 \mu m$, $125-250 \mu m$, or $<64 \mu m$) and then a split ($\sim 0.2-0.4$ g) of a specific size fraction is mounted as a monolayer epoxy mount containing 1000s of grains (Figure 3). Better density and representivity of HMC can be achieved through a two-step mounting procedure [27]. Better physical individual grain separation can be facilitated by thoroughly mixing with powdered fine and high purity graphite as a parting agent ($\sim 1:1$ graphite to sample by mass) [76–79]. This greatly reduces the digital separation needed in the post-analytical workflow. These mounts are then careful polished, carbon-coated and examined using automated mineralogy methods (see below for further details).



Figure 3. Example of mounting schematic of till in two mounting stages. (**A**) Primary grain mount was quartered, and three quarters are reoriented and made into (**B**) second grain mount that was quartered, and three quarters are reoriented and to display one basal surface and two cross-sectional surfaces for analysis. (**C**) MLA false colour output quarter labelled "2" in B. Cross-sectional surfaces are indicated by the black grey bar in A pane of figure. Modified from Lougheed et al., 2020 [27].

2.2.1. Electron-Based Techniques

Most mineral chemical investigations examine the 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 reflects differences in the average atomic number of an area of a grain. This scanning is done in combination with energy dispersive spectrometry (EDS) to identify relative element concentrations within mineral phases (Figure 4) and mineralogy.

The goals of using an SEM are to (1) confirm of mineralogy that has been determined through visual mineral identification; (2) document mineral associations; (3) document mineral textures and morphology (shape, rounding, size, etc.); and (4) identify optimal 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 h on a traditional SEM by an experienced technician. Recent advances in automated scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (EDS) are transforming the analysis of mineral grain mounts [21,25]. Time-consuming and qualitative mineral descriptions have now been replaced with fast, quantitative, and repeatable SEM analyses. These automated SEM methods provide confirmation of mineralogy, quantification of mineral textures and morphology, and reduces grain mount analysis time to 1 to 2 h.



Figure 4. Example of sample workflow for automated mineralogy for (**A**) mineral liberation analysis (MLA) and (**B**) QEMSCANTM. Modified from Layton-Matthews et al., 2014 [72].

The most popular automated SEM supplier was FEI; the company offered tungstenbased or field emission gun-based hardware that can be coupled with either QEM-SCAN[®] [80] or MLA software [81]. Mineral Liberation Analysis (MLA) was initially developed for the mining industry by the University of Queensland, Australia (JKTech) [82,83]; QEMSCAN[®] was developed for the mining industry by CSIRO, Australia [80–86]. However, both software packages are currently licensed and sold through Thermo Fisher and are under new software development under the MAPS software package. With the proliferation of the applications of Automated Mineralogy several additional hardware-software platforms have seen application in surficial media characterization, including TESCAN Integrated Mineral Analyzer (TIMA) [87], ZEISS MinSCAN [88] and Oxford Instruments IncaMineral [89].

MLA-automated mineralogy is based on high-resolution BSE images, image analysis, and elemental chemistry from EDS. There are several different MLA data collection modes

(i.e., XBSE, SPL, XMOD [79,90]), however most rely on the collection of BSE images that are combined to create a mosaic image of an epoxy grain mount or region of interest (Figure 4). An individual grayscale (0–255 range) BSE image is used to remove epoxy from the image using a user defined value (~10), allowing the isolation and centroid image analysis of segmented grains and minerals into individual particles. The MLA software then collects a full X-ray spectrum (EDS) at the centre of each particle (Figure 4) at a user defined dwell time. 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 (Figure 2C), modal mineralogy, grain size, mineral associations (occurrence and interlocking), particle properties (roundness, area, shape), and mineral liberation.

QEMSCAN[®]-automated mineralogy is fundamentally different from MLA, in that is based on fast mineral identification using point analysis on a finely spaced grid. In most routine analysis, 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 scanning of mineral phases, a low-count EDS spectrum is collected that allows for ultrafast 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. In QEMSCAN[®], a built-in library of 72 elemental reference spectra is used to build a composite elemental spectrum 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 and mineral maps [80,85,91].

MLA- or QEMSCAN[®]-generated BSE and false-colour images of a mounted indicator minerals (Figure 2C) have many advantages over traditional optical microscopy [48,83,90,92]: (1) measurement of compositional data; (2) measurement of thousands of points per sample mount; (3) repeatable and quantitative measurements; (4) fully automated workflow; (5) faster processing time; (6) less mineral identification training required; (7) modal mineralogy calculated assay data; (8) micron-scale resolution; (9) ability to measure and compare grain size; and (10) 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 heavy minerals in till is of great importance in the definition of glacial dispersal trains in many ore exploration programs (i.e., gold); however, many HMC grain mounts are further characterized for individual mineral chemistry. Many indicator mineral studies in glaciated terrain (e.g., McClenaghan et al. 2002, 2013; Morris et al. 2002; Lehtonen et al. 2005, and references therein) [11,14,21,42] have demonstrated the use of major and minor element mineral chemistry to identify the bedrock provenance and assess fertility.

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 (MoS₂) by EDS is not easily accomplished because the Mo L alpha line is at 2.2930 keV and overlaps with the S K alpha line at 2.3070 keV [93].

More commonly, indicator minerals are analyzed for major and minor elements using electron probe microanalyzer (EPMA). In principle, an EPMA is very similar to a SEM, as the electron source and focusing column are nearly identical. However, an EPMA and a SEM collect X-ray data differently. Both instruments collect chemical spectra using an

EDS detector, but on an EPMA, spectra are also collected using wave-length 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 that allow 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 and the inability of WDS to quantify light elements such as carbon [94,95]. However, the biggest advantage to EPMA is the small sampling volume and spatial resolution, especially with field emission gun instruments [96,97].

2.2.2. X-ray-Based Techniques

Mineral characterization and analysis by Micro Energy Dispersive X-ray Fluorescence (μ -EDXRF) mapping is becoming a routine non-destructive method for the identification of mineralogy and determination of mineral chemistry [98–100]. These benchtop instruments are similar to synchrotron radiation X-ray micro-beam XRF (SR- μ XRF) [101–103] however, use much lower source energies (e.g., 50 keV vs. >2 GeV) [100,104], are less expensive and are more widely available. Ideally suited for any geological materials, including loose HMC grain mounts, μ -EDXRF gives optimal results on flat, polished mounts because of detrimental topographic shading of the fluorecence [105] on rough surfaces. Advances in capillary optics focus X-rays, producing a small beam (~5–20 μ m) [106,107] which has allowed the development of high spatial resolution, commercial benchtop μ -EDXRF instruments, such as the M4 Tornado (Bruker Nano GmbH, Germany) [98,108]. As with many of these instruments, beam-size, dwell time and atomic mass can greatly affect the detection limits, however in general for most elements >10 ppm limits of detection (LOD) are acheivable in geological media.

The Bruker M4 Tornado µ-EDXRF uses an MLA- and QEMSCAN-like software, the Advanced Mineral Identification and Characterization System (AMICS), and is the latest software package for automated identification and quantification of minerals. The AM-ICS software [109,110] is divided into 3 parts that include: (1) Investigator, a µ-EDXRF instrument control and data acquisition package; (2) AMICSProcess, a data processing and analysis package and; (3) MineralSTDManager, a mineral database management package [108]. Within the Investigator, several parameters can be set, saved and recalled that include spatial resolution, particle grid (Figure 5A), and dwell time, and assign a mineral database for on-the-fly classification. Post analysis allows AMICSProcess to create an X-ray Intensity mosaic (similar to the BSE mosaic imaging in MLA or QEMSCAN) that reflects the average atomic number (Z) of individual image pixels. The false-coloured Particle Grid (Figure 5A) can be sorted by area within each group (Figure 5B), allowing particles to be grouped by mineralogy, calculated for modal mineralogy (wt%, Area %, particle count, etc. Figure 5C) or assay or elemental distribution. Within AMICSProcess sample images can be created to reflect minerals classified (Figure 5D) or can be filtered to highlight and find a specific mineral(s) of interest (Figure 5E). Additionally, AMICSProcess also allows the export of major and trace elemental contents reduced by fundamental parameters [111–114] to be used in data exploration software such as ioGAS (REFLEX, Australia) [115] or through commercial services such as Portable Spectral Services-https://www.portaspecs.com/ (accessed on 23 March 2021)(Figure 5F).

Figure 5. Examples of μ -EDXRF AMICS data exploration. (**A**) False-coloured sample image classified using the M4 Tornado MineralSTDManager software [108]. (**B**) Size and mineralogy (olivine, garnet and plagioclase) sorted Particle Grid [58]. (**C**) Sorted calculation table including wt%, Area%, and Particle Numbers [108]. (**D**) False-coloured sample image of 2.5 cm epoxy mount. (**E**) False-coloured sample image of 2.5 cm epoxy mount filtered for chalcopyrite (olive green). (**F**) Bivariate plot of S (ppm) vs. Cu (ppm) filtered by Cu > 150,000 ppm in ioGASTM [115] to identify chalcopyrite grains of interest. Note images D, E, and F supplied by Portable Spectral Services (PSS) (Pers. Comm., N. Brand 2021).

 μ -EDXRF has several distinct advantages over SEM-based methods. Firstly, the average cost of a μ -EDXRF instrument such as the Bruker M4 Tornado is in the order of \$200k USD, whereas the MLA/QEMSCAN equipped SEM instruments are >\$1 million USD. Second, quanatative μ -EDXRF can be completed on a variety of media and unlike quantitative MLA/QEMSCAN do not require coating with a conductive layer (i.e., carbon or gold), leaving the material available for repeat or alternate instrument analysis. Thirdly, using similar spatial resolution on identical samples with simple textures (i.e., HMC epoxy mounts), an AMICS μ -EDXRF characterization is faster than that of MLA or QEMSCAN, making instruments such as the Bruker M4 Tornado ideal for quick initial characterization. Fourthly, μ -EDXRF can simultaneously provide mineralogical identification and major and trace element contents. SEM-based methods are limited by EDS requiring the additional use of mass spectrometry-based techniques (see Section 2.2.3) for trace element quantification. One of the main detrimental aspects of μ -EDXRF is spatial resolution. Field emission gun MLA instrumentation are capable of submicron analysis, whereas the capillary optics of μ -EDXRF limit the resolution to ~5 μ m.

2.2.3. 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 [116,117]. Its application for characterizing mineral chemistry has grown in the past 15 years to include a broad range of minerals [118–129].

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 (5–8000 μ m³) of a mineral sample over a period of 10 s 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 [130].

There are several instrument parameters that must be optimized to measure element and isotopic compositions of a mineral by LA-ICP-MS [131–133]; 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 (Figure 2D). If a laser pit is too small, 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 [134–137] and laser pulse-rates [138–142] 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 can produce less thermal heating with a lower abundance of secondary condensates [138,143–145].

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) Quadrupole; (2) Time of Flight; (3) High-resolution single collector; and (4) High-resolution multi-collector.

By far the most common mass spectrometer used in laser ablation studies of mineral chemistry is the quadrupole 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 elements on the periodic table in milliseconds [130].

Time-of-flight mass spectrometers have seen less application to laser ablation applications in geological sciences. However, they are ideally suited to capitalize on the extremely fast washout times of new ablation cells and higher laser frequencies [146,147]. These plasma-based instruments use the difference in ballistic travel and kinetic energy of light versus heavy isotope masses through a vacuum and a charge potential to separate mass to charge ratios over short time intervals [148]. Current Time-of-flight mass spectrometers can complete a full mass scan at ~30 μ s allowing 33,000 full mass scans per second [96]. Early Time-of-flight mass spectrometers did not have the sensitivity of quadrupole mass analyzers, however recent research would suggest sensitivities that rival sector field instruments and allow single digit parts per million for single-shot laser pulse from a 10- μ m diameter laser spot [149].

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 [150]. By adjusting the magnetic and electro-static 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 [130].

For effective ion transmission through both the magnetic and electrical sectors, ions are accelerated at much higher energies than in quadrupole instruments (e.g., 10 kV versus 10 eV, respectively). As such, less ion scatter 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., ²⁰⁴Pb, ²⁰⁶Pb, ²⁰⁷Pb, ²⁰⁸Pb) simultaneously, without adjustment of the magnetic or electric sectors, which yields superior isotopic ratios [151].

Quadrupole and high-resolution mass spectrometers each have advantages and disadvantages in mineral chemical analyses using laser ablation. In quadrupole 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 the next mass range [152,153]. Given the transient nature of laser ablation analysis, a quadrupole instrument is much better suited for mineral analyses of samples with varied element mass (i.e., rare earth elements, U, Pb). When there are narrow mass differences (<30%), very small laser ablation pits (<10 μ m) or isotopic ratios are needed, for which high-resolution mass spectrometers offer vastly superior precision and detection limits [154].

Multi-element trace element analysis by LA-ICP-MS requires the use of suitable reference materials with similar matrix compositions [155,156] and calibration using multiple external standards with a wide-range of elements contents [156–158]. Over the past 10 years there has been a limited effort to find or create matrix-matched standards with variable but homogeneous concentrations of trace elements (i.e., 10, 100, 500 ppm), which is necessary to create standard calibration curves and element quantification. Many of these studies have focused on geological glasses that have been created from rock powder standards [159–163] or by the doping of rock powder standards at variable concentrations [163,164]. 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.

3. Indicator Mineral Examples in Glaciated Terrain

Examples of the application of automated mineralogy, EPMA and LA-ICP-MS to characterize indicator minerals used to explore for mineral deposits in the recently (Pleistocene) glaciated terrain of Canada are described below.

3.1. Volcanogenic Massive Sulphide Deposits

To assist exploration for volcanogenic massive sulphide (VMS) deposits in northern Canada, an indicator mineral survey was completed around the Archean Izok Lake Zn-Cu-Pb-Ag volcanogenic massive sulphide (VMS) deposit (Figure 5) in Nunavut, Canada [24,165,166]. During the mid to Late Wisconsinan, southwest ice flow followed by west- to west-northwest-trending ice flow eroded indicator minerals from the mineralized bedrock and transported and deposited them down ice as till [23].

Mineralized bedrock samples as well as till samples were collected up- and down-ice of the Izok Lake deposit (Figure 5) and processed to recover HMCs (>3.2 g/cm³) from which the 0.25–0.5, 0.5–1.0, and 1.0–2.0 mm non-ferromagnetic heavy mineral fractions were examined using optical techniques [165]. Grain mounts for indicator minerals recovered from bedrock samples were examined first using MLA-ESEM to quantify modal mineralogy, mineral associations (Figure 6), grain shape, and grain size to determine the minerals that could be expected in till samples. EPMA was completed on a selection of indicator minerals to confirm visual identification and to characterize trace element compositions.

Indicator minerals identified in mineralized bedrock and till down ice of the deposit include: chalcopyrite, galena, sphalerite, chalcopyrite, and gahnite (Zn-spinel) (Figure 7). The distribution of gahnite in till reflects both phases of ice flow, forming a wide glacial dispersal fan down ice of the deposit (Figure 8). EPMA data were used to identify the compositional range (Mg-rich vs. Fe-rich) of gahnite (Figure 9), showing that most grains in till are Fe-rich and that the rarer Mg-rich grains were sourced from the central zone of the deposit.

Figure 6. MLA-SEM image of gahnite grain mount 10-0269-P01 for 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 position numbers on the mount 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 [165]).

Figure 7. Gahnite grains in bedrock and till samples from Izok Lake: (**A**) polished slab of drill core (sample 09-MPB-R69); (**B**,**C**) polished thin sections (sample 09-MPB-R37 and 09-MPB-R41B, respectively); (**D**) grains from heavy mineral concentrate of till sample 12-MPB-913 (photograph by M.J. Bainbridge Photography). Modified from Hicken (2012) [165].

Figure 8. Fan-shaped glacial dispersal of gahnite abundance in the 0.25–0.5 mm fraction of till (normalized to a 10 kg) down-ice of the Izok Lake volcanogenic massive sulphide deposit in northern Canada. The fan formed by two phases of ice flow towards the southwest (blue polygon) and northwest (yellow polygon). Arrows indicate relative ice-flow chronology (1 = oldest) and vigor (arrow size) of flow events. Blue dots indicate the four till samples for which the <0.25 mm heavy mineral fraction was examined using MLA. Modified from McClenaghan et al. (2015 [24]). Location of mineralization indicated by solid red polygons and additional gahnite-bearing rocks by green stars.

The gahnite found in till at Izok Lake was found to contain elevated contents of transition metals (Co > Ti > Ni > Mo > Cr > Cu > Pb) through LA-ICP-MS. Given the age of the Izok Lake deposit (~2.7 Ga) [167,168] and the possible younger granitic or Helikian-aged Mackenzie Swarm provenance for the gahnite, LA-ICP-MS in Pb contained in the gahnite was completed. The Pb/Pb dating of individual grains allowed the interpretation of gahnite sourcing from metamorphic footwall stringer sulphide zone from the Izok Lake deposit (Figure 10).

The <0.25 mm HMC of 4 till samples ranging from 1 km up-ice to 9 km down-ice of the deposit (Figure 8) was examined using MLA-ESEM to compare abundances and mineral associations to the coarser (>0.25 mm) optically counted indicator minerals. MLA of the finer HMC fraction indicates that the same indicator minerals occur in the <0.25 mm and that these smaller grains can be detected much farther down ice (Lougheed et al., 2020), thus expanding the areal extent of the glacial dispersal fan, and hence the exploration target. For example, sulphide minerals in the coarse (>0.25 mm) HMC are detectable up to 2 km down ice of the deposit and up to 8 km down ice in the fine grained (<0.25 mm) HMC (Figure 11).

Figure 9. Ternary plot of zincian spinel compositional in terms of gahnite, spinel and hercynite end members for: (**A**) bedrock from Izok Lake deposit, and (**B**) till samples down ice of the Izok Lake deposit.

Figure 10. (**A**) Box and Whisker plot of LA-ICP-MS quadrupole trace element data for gahnite from tills from the Izok Lake VMS and the Thompson Ni-Cu PGE deposits areas. (**B**) LA-ICP-MS 207 Pb/ 206 Pb age relations for Izok Lake VMS (green circles) and Halfmile Lake VMS (Bathurst Mining Camp, New Brunswick: red circles). (**C**) LA-ICP-MS 208 Pb/ 206 Pb age relations for Izok Lake VMS (green circles) and Halfmile Lake VMS (Bathurst Mining Camp, New Brunswick: red circles). Red lines are an approximation of terrestrial lead isotopic evolution (Stacey and Kramers 1975) [169]. High-precision U/Pb ages for Halfmile Lake is 465 Ma (van Staal et al. 2003) [170], for is Izok Lake is 2623 ± 20 Ma (Mortensen et al. 1988) [168] and 2680.5 +7/-3 Ma (J. Gebert, unpub. 1995).

Figure 11. Lines plots comparing the abundance of pyrite, galena, and chalcopyrite grains in 5 different size fractions of heavy mineral concentrates (HMC) from till samples up and down ice of the Izok Lake VMS deposit. Location of mineralization is indicated by grey vertical line in each plot. Uppermost plots (250–500 μ m) represent grain abundance/10 kg determined by visual inspection of the HMC. Lower 4 plots (<250 μ m fractions) represent grains abundance/1000 grains determined by MLA. Modified from Lougheed et al. (2020) [27].

3.2. Magmatic Ni-Cu Deposits

Sulphide, oxide and silicate indicator minerals have been recovered from till down ice of known magmatic Ni-Cu-PGE deposits. These minerals include pentlandite, pyrrhotite, chalcopyrite, pyrite, gold, platinum group minerals (PGM), chromite, Cr-diopside, and Cr-andradite [39–43]. However, few studies of magmatic Ni-Cu indicator minerals in glacial sediments have included the use of mineral chemistry. One exception to this is the McClenaghan et al. [42] application EPMA techniques to chromite in mineralized and barren bedrock samples to document the mineralization signature (elevated ZnO) for the Proterozoic Thompson Nickel Belt Ni-Cu deposits (Figure 12-colored symbols). They identified similar mineralization signatures in chromite in till down ice (west and southwest) of the Thompson deposits (Figure 12-black symbols). LA-ICP-MS of chromite further

confirmed the elevated ZnO content and also identified V as an additional discriminator to identify the Thompson Ni-Cu ore signatures in spinels [171].

Figure 12. (a) Cr_2O_3 versus MgO and (b) Cr_2O_3 versus ZnO concentrations in chromian spinels from bedrock and till samples from the Thompson Ni Belt: mineralized bedrock (orange and red symbols), unmineralized bedrock (blue and green symbols), and till samples (black symbols). Dashed vertical line indicates 2 wt % ZnO. Modified from McClenaghan et al. (2013) [42].

The occurrence of the highest metamorphic grade in the belt (at Thompson Mine-South Pit) [172–174] coupled with the highest ZnO and Al₂O₃ contents of spinel group minerals that trend toward the gahnite-hercynite tie line imply a metamorphic/metasomatic origin for these spinels. The correlation of the highest ZnO within spinel group minerals and the highest concentration of sulfide mineralization in the Thompson Nickel Belt implies that this unique spinel group mineral chemistry is indicative of a mineralized ore system at upper amphibolite facies. This study showed that the distinctive mineralization signature in chromite in the belt can be used to further explore the heavy-drift covered region using indicator methods.

3.3. Porphyry Cu Deposits

Common indicator minerals of porphyry Cu deposits that can be readily recovered from glacial sediments include chalcopyrite, pyrite, gold, epidote, tourmaline, jarosite, apatite titanite, and andradite [41,50,58,175,176]. Some case studies around porphyry Cu deposits in the glaciated terrain of western Canada have used EPMA and LA-ICP-MS methods to establish deposit signatures from bedrock samples and identified the same signature in till samples down ice, providing insights into glacial dispersal patterns and demonstrating that mineral chemistry can be used to identify the presence of mineralized bedrock in a region.

One example of the use of mineral chemistry is the study of tourmaline in till down ice of the Woodjam porphyry Cu-Au deposit [177] in western Canada. The distribution of tourmaline in till (Figure 13A) indicates that it is likely an indicator of the mineralization, but the broad tourmaline distribution pattern, including in samples up ice of mineralization, suggest that some tourmaline grains in till may also be derived from unmineralized bedrock. Using a combination of EPMA and LA-ICP-MS chemical (oxy-dravite povondraite trend, high Sr, low Zn and Pb) and physical characteristics (lack of inclusions, grain color), Beckett-Brown et al. (2021) [61] demonstrated that porphyry-derived tourmaline can

be distinguished from background tourmaline in till (Figure 13B). In a second example, Pisiak et al. (2017) [57] used LA-ICP-MS analysis to distinguish between porphyry-derived and background magnetite grains in glacial sediments down ice of the Mount Polley porphyry Cu-Au-Ag deposit (Figure 14). Other porphyry-related indicator mineral studies have identified discrimination criteria for epidote, zircon [178], and apatite [179,180]. These studies demonstrate that mineral chemistry can be an important exploration tool for porphyry Cu mineralization in glaciated terrain.

☆ Woodjam porphyry Cu-Mo-Au mineralized zone

Figure 13. (**A**) Distribution of 0.25–0.5 mm tourmaline in the 2.8–3.2 specific gravity fraction of till samples down ice of the Woodjam porphyry Cu-Au deposits, counts normalized to 10 kg. White dots indicate samples for which the tourmaline grains were analyzed by MLA. (**B**) Percentage of tourmaline grains that were analyzed and that were identified as 'porphyry-derived' based on high concentrations of Sr, low concentrations of Zn and Pb, and their lack of inclusions. Bedrock geology from Logan et al. (2010) [181] and Plouffe and Ferbey (2017) [58]. Modified from Beckett-Brown et al. (2021) [61].

Figure 14. Percentage of magnetite grains that were identified as 'hydrothermal porphyry' based on the Ti-Ni/Cr discrimination diagram of Dare et al. (2014) [118] in 20 till samples around the Mount Polley Cu-Au deposit. Symbol size is proportional to percentage of total number of magnetite grain analyzed. Deposit location indicated by yellow star. Bedrock geology from Logan et al. (2010) and Plouffe and Ferbey (2017) [58]. Modified from Pisiak et al. (2017) [57].

4. Conclusions

This paper presents an overview of the current methods for, and applications of, indicator mineral chemistry to mineral exploration in the glaciated terrain of Canada. Indicator mineral chemistry can now be used to identify potential bedrock sources of the mineral grains and assess bedrock source fertility and help to prioritize targets for further exploration. There will always be a role for traditional heavy mineral concentrate methods, however automated minerology instrumentation can now augment these methods providing a means to identify more that optically distinct minerals (i.e., Cr Diopside, Cr Pyrope, etc.) and provide fertility indexes using mineral chemical of trace elements.

Successful mineral exploration using surficial sediment indicator mineral methods in glaciated terrain 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 shift in training to include surficial 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 and future exploration success will need to incorporate the roles of automated mineralogy and mineral chemistry.

Mineral separation methods are well established for size fractions larger than 0.25 mm, and these methods require a highly qualified mineralogist to visually identify minerals. Indicator mineral identification chemical characterization that utilizes the smaller grain size (i.e., <0.25 mm) and less dense fractions (i.e., <2.85 g/cm³) of sediments, and methods that incorporate new, faster, and more accessible analytical instruments (i.e., hyperspectral) are becoming more widely available and are currently used in the mineral exploration industry by the combination of SEM, EDS, WDS and LA-ICP-MS methods. Ongoing developments of these methods will decrease the need for extensive specialized mineral identification training, decrease the time and cost of HMC characterization, extend the spatial footprint of

glacial dispersal trains, and ultimately lead to the identification of new indicator minerals in uncharacterized mineralized systems.

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