

Advances in ICP-MS Technology and the Application of Multi-Element Geochemistry to Exploration

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ABSTRACT

There have been several advances in inductively coupled plasma mass spectrometer (ICP-MS) analytical technologies in the last decade (2007 to 2017). Collision/reaction cell ICP-MS and triple quadrupole ICP-MS instruments can produce lower detection limits for select elements that experience interferences with a standard quadrupole instrument (i.e., Se and As). Triple quadrupole ICP-MS instruments in particular, can eliminate virtually all polyatomic or isobaric interferences for highly accurate measurements of some element isotopes systematics that are of great interest in mineral exploration, namely Pb/Pb. Laser ablation ICP-MS has become more popular as an effective analytical tool to measure mineral grain trace elements, which could assist in vectoring to mineralization or exploration drill targets. The ablation of a spot on a Li-borate fused glass disk paired with X-Ray fluorescence (XRF) analysis has also gained popularity as an alternative to total whole rock characterization packages that employ several separate digestions and analytical methods. While there have been several advancements in ICP-MS technologies in exploration geochemistry in the last decade, they have not been widely accepted or implemented. This slow adaptation could be due to the extended recession in the mining industry over the last 5 years, which is not currently over. It is also possible that standard ICP-MS data (i.e., no collision/reaction cell) is still fit for purpose. This stands in stark contrast to implementation of ICP-MS in the previous decade (1997 to 2007), which was transformational for the industry.

Consideration of all elements from large multi-element ICP-MS analytical suites for mineral exploration can be an extremely powerful tool in the exploration toolkit. The discovery of the White Gold district, Yukon, is a prime example of how the utilization of soil geochemical data, when plotted spatially, can vector to Au mineralization. The presence of Au+As+Sb soil anomalies were key to delineating mineralization, especially when accompanied by publicly available geological, geographical, and geophysical data. Additionally, elements and element ratios not typically considered in Au exploration including Ni and U were utilized to determine the lithological and structural controls on mineralization. The availability of multi-element ICP-MS data was also useful in the discovery of the Cascadero Copper Taron Cesium deposit. Ore grade Cs was discovered only because Cs was included in the multi-element ICP-MS exploration geochemistry suite. Before the availability of ICP-MS, it is unlikely that this deposit would have been discovered.

INTRODUCTION

History of ICP-MS in Geochemistry

The first inductively coupled plasma mass spectrometer (ICP-MS) instrument was the Perkin Elmer SCIEX Elan 250, introduced commercially in 1983. It was not long before the technology was adopted by the geosciences (Date, 1985; Hall, 1989; Garbe-Schönber, 1993), especially with respect to exploration (Date and Huchison, 1986; Hall, 1993). The draw to this new analytical instrument was the ease and relative low cost in generating trace multi-element data, including the rare earth elements (REE) (Jenner et al. 1990). Heavy investment in ICP-MS technology by commercial laboratories in the early to mid-1990s saw a plethora of new analytical packages based on sample partial extractions, traditional digestions (e.g., aqua regia, 4-acid), and decompositions (e.g., lithium-borate fusion). Exploration geochemistry now had a broader selection of pathfinder elements at effective detection limits significantly lower than previously possible with inductively coupled plasma optical emission spectrometry (ICP-OES), neutron activation, or atomic absorption spectrometry (Longerich et al. 1990; Hall et

al. 1995) with concomitant access to new sample media and/or media substrates. The overall result was the ability to better evaluate or reevaluate greenfields, brownfields, and mine exploration sites.

What is an ICP-MS

An ICP-MS instrument operates where a liquid sample (i.e., water, digested sample) or an ablated sample pass through a nebulizer into a spray chamber with a carrier gas (usually argon). As the spray and argon carrier gas (the aerosol) moves through the high temperature (6,000 to 10,000 K) Ar plasma, the mist is dried, atomized, and ionized (Figure 1). The ion stream then passes into the instrument where the ions are focused using electrostatic lenses, and are separated from the neutral species by bending them into the quadrupole (the mass spectrometer). The quadrupole mass filter is comprised of four rods that are approximately 1 cm in diameter and about 20 cm long. Alternating AC and DC voltages at opposite rod pairs create an electrostatic filter, which allows only ions with one mass to charge ratio through the quadrupole at a time. Changes in voltage occur very quickly and allow different mass to charge ratio ions to pass. Up to 2400 individual atomic mass units

(amu) can pass per second. As the ions pass through the quadrupole they strike a detector plate, and are measured by a computer.

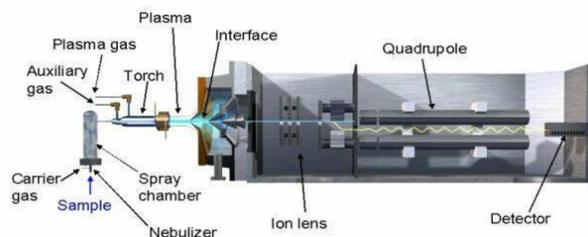


Figure 1: Schematic diagram of a single quadrupole ICP-MS (from <http://ececslabs.seas.wustl.edu/ICP-MS.aspx>).

Collision or reaction cells can be included with the ICP-MS instrument as a primary filter before ions enter the quadrupole. Although the quadrupole is a filter in itself, allowing ions with one mass to charge ratio (m/z) to pass at a time, certain ions can interfere with determination of a desired analyte. Polyatomic interferences occur when ions combine with Ar or other ions common in sample matrices such as O, N, H, Cl, and F to form a mass that is very similar to the desired ion. Isobaric interferences are also common, where the interfering ion is a different element that has the same mass as that of the analyte of interest. Interferences that pass through the quadrupole to the detector translate to poorer detection limits and accuracy of desired analytes. Reaction cells chemically convert ions that may cause spectral interference for certain elements or isotopes into different ion species that do not interfere. The cell uses a highly reactive gas such as NH_3 or CH_4 to react with polyatomic or undesirable ions to reduce or remove isobaric interferences. For example, $^{40}\text{Ar}^{16}\text{O}$ is a polyatomic interference on ^{56}Fe , but the introduction of NH_3 in a reaction cell results in the separation of $^{40}\text{Ar}^{16}\text{O}$ into Ar and O, thereby removing the interference (Figure 2). In another example, the isobaric interference of $^{204}\text{Hg}^+$ on ^{204}Pb is removed, as the NH_3 neutralizes the $^{204}\text{Hg}^+$ to $^{204}\text{Hg}^0$ and results in a different mass to charge ratio (Figure 3). With a collision cell, ions that pass into the cell are introduced to a non-reactive gas such as He and results in the collision of the ions with the gas. The kinetic

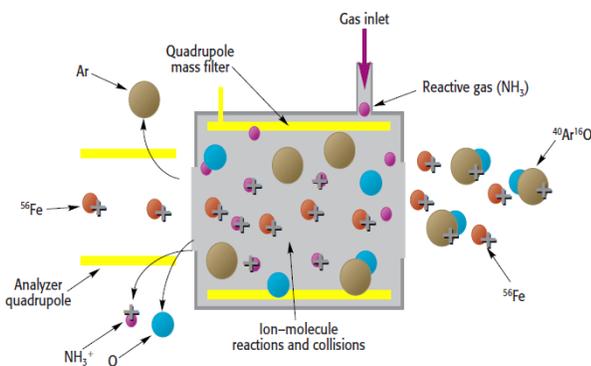


Figure 2: Schematic diagram of a dynamic reaction cell removal of isobaric interference $^{40}\text{Ar}^{16}\text{O}$ on ^{56}Fe (from Thomas, 2002).

process separates and removes larger polyatomic ions that can cause isobaric interferences, while leaving the smaller analyte ions untouched.

A triple quadrupole ICP-MS (TQ-ICP-MS) is similar to a single quadrupole ICP-MS, except that that the TQ-ICP-MS has tandem (quadrupole) units. There is an initial quadrupole (Q1), followed by a reaction/collision cell (Q2), followed by a second quadrupole (Q3) (Figure 3). The first quadrupole is used as a preliminary filter and rejects all off-mass ions. Therefore, the ion stream that enters into Q2 is consistent. The reaction/collision cell can then remove the isobaric interference independent of any potential issues arising from the sample matrix and the presence of other analyte ions. The ions that then enter into the Q3 (the second quadrupole) are virtually free of any interference, and the Q3 is set to reject all off mass ions. The result is highly accurate, low detection measurements. Comparatively, in a typical reaction cell ICP-MS all ions enter the cell and all interferences are removed at one time. Each element is measured at its isotope mass where no other element is present. In a complex matrix, many of these isotopes are overlapped by polyatomic interferences.

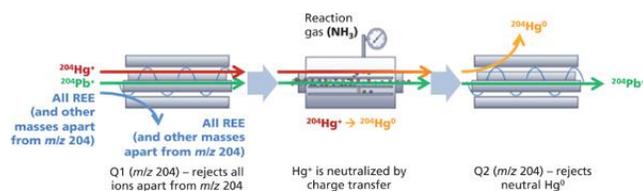


Figure 3: Schematic diagram of a TQ-ICP-MS instrument demonstrating the removal of interferences on ^{204}Pb (from Woods and McCurdy, 2013).

ICP-MS ANALYTICAL ADVANCEMENTS

Previous Advancements

During the previous decade, from 1997 to 2007, mineral exploration saw a marked increase in the number of elements that could be analyzed by ICP-MS, as well as decreases in element detection limits. The number of elements that could be determined to levels well below average crustal abundance after 4-acid digestion of a geological sample increased significantly (Caughlin, 2007). It was also a period where several new instruments became more commonplace including high resolution ICP-MS (HR-ICP-MS), and multi-collector ICP-MS (MC-ICP-MS). These improvements in instrument technology and reductions in detection limits were transformational in mineral exploration, especially where low-level concentrations were required (Hall, 1993). The analyses of weak partial extraction leachates for low level pathfinder elements (i.e., de-ionized water leaches, hydroxylamine leaches, MMI, etc.) (Hall et al. 1996; Gray et al. 1999; Cameron et al. 2004; Mann et al., 2005) would not have been technically feasible without the commercialization of ICP-MS instrumentation. The application of subtle variations in the chemistry of ground and surface water for exploration for diamonds (i.e., Sader et al. 2007; 2011) and sulphide deposits (i.e., Leybourne and Goodfellow, 2003; Phipps et al. 2004; Cameron and Leybourne, 2005; de Caritat et

al. 2005; Eppinger et al. 2012) also would not have been possible.

Advancements in the Last Decade (2007 – 2017)

Collision and Reaction Cells

In comparison to the decade before, this last decade (2007 to 2017) has broadened the ICP-MS instrument capability by pairing quadrupole technology with other instrumentation. Collision and reaction cells are being used more commonly to achieve lower detection limits of some elements and for determination of certain isotopes. Although the technology itself is not new, it is now starting to become more commonly implemented in exploration. Collision and reaction cells can remove mass interferences, typically due to doubly charged rare earth elements (REE^{++}), to achieve lower detection limits for certain elements that commonly experience polyatomic or isobaric interference (Hall and Pelchat, 1997; Hu et al. 2005). Hydride generation dynamic reaction cells (DRC) ICP-MS have been used to determine Se concentrations and isotopes to low levels in volcanogenic hosted massive sulfide (VHMS) deposits (Layton-Matthews et al. 2008, 2013). In this application, the authors suggested that sulphide Se content is directly related to depositional environment. They also showed that at the Kudz Ze Kayah and Wolverine deposits, the presence of high temperature zone refining of chalcopyrite is associated with elevated Se. While low level Se has shown definite application in exploration geochemistry scientific studies, the availability of a standard method from commercial geochemical laboratories has occurred only in the last few years.

Single quadrupole ICP-MS instruments used in conjunction with a reaction cell are capable of determining isotopes of elements including Ca, Fe, Se, and Pb (Becker, 2002). Of these, the isotopes of Pb are particularly useful in mineral exploration. Reaction cells can remove isobaric interferences on ^{204}Pb from ^{204}Hg by using NH_3 in the reaction cell chamber (Woods and McCurdy, 2013). Isotope determination using triple quadrupole ICP-MS (TQ-ICP-MS) technology is also becoming more common in analytical geochemistry. The same high quality data for the isotopes of Pb can now be offered from a TQ-ICP-MS (Woods and McCurdy, 2013). This high precision data was previously only available from HR-ICP-MS or MC-ICP-MS. In addition, TQ-ICP-MS are less expensive to purchase and require substantially less maintenance.

The reaction cell and TQ-ICP-MS technological advancements provide significant benefit to exploration programs where Pb/Pb isotope systematics applied. In these programs, Pb concentration is no longer the most important factor, but rather, the isotopic signature (fingerprint) is. The detection of a signature in surface samples that is the same as the deposit that is being sought can greatly assist in vectoring to mineralization (Holk et al. 2003; de Caritat et al. 2005; Leybourne et al. 2009; van Geffen et al. 2013). Pb isotopes can also help to differentiate between the desired deposit style and those that are not desired in regions with multiple episodes of mineralization (i.e., Godwin and Sinclair, 1982; Godwin et al. 1990).

While a definite advancement in analytical geochemistry, the implementation of single collision/reaction cell quadrupole ICP-MS or TQ-ICP-MS instruments for isotope determination have yet to be widely adopted by the mineral exploration industry. Conversely, collision/reaction cell ICP-MS or TQ-ICP-MS instruments are commonly used in environmental geochemistry or other applications (Wong et al. 2003; Li et al. 2004; De Muynck et al. 2007). The slow adaptation in exploration is likely due to the added set-up and analytical costs compared to a standard ICP-MS instrument. Unlike laboratories that cater to other industries, minerals and geochemistry labs receive highly variable sample matrices and concentration ranges, which make implementation more challenging. There is also an apparent limited demand from a critical mass of mineral exploration groups.

Laser Ablation ICP-MS

Laser ablation ICP-MS (LA-ICP-MS) systems were first designed only shortly after the first commercial ICP-MS was developed (Gray, 1985). In the mid to late 1990s, neodymium-doped yttrium aluminum garnet (Nd-YAG) solid state laser systems were commercialized. These units were commonly coupled with HR or MC ICP-MS instruments for geochronology and in-situ analysis of inclusions in grains mainly by universities and research institutions. By the mid-2000s there were several rapid improvements in capability including the evolution of specific sample cells, for mapping and elemental distribution, and the development of geochemical multi-element methods. The systems were mainly applied to spot analyses (i.e., Jackson et al. 1992). Price and availability were prohibitive for general application in exploration. From the later 2000s to present compact excimer gas lasers became readily available. An excimer laser uses a combination of a noble gas and a halogen reactive gas to create an excimer pseudo-molecule. When this pseudo-molecule is in its excited state it produces laser UV light in pulses in the nano to femtosecond range.

The most common application of current LA-ICP-MS systems involves the ablation of a pre-selected spot on a sample of material using excimer 193 nm or Nd-YAG 213 nm wavelength lasers. As the laser ablates the specific spot, gas and fine particles are drawn into the ICP-MS induction system via a carrier gas to identify the elemental concentrations. The target may be a fused glass bead to determine bulk sample composition, or a specific mineral grain to determine composition and/or trace to ultratrace element impurities. Alternately, the laser may blast a multitude of points in a traverse or grid pattern to produce a one or two dimensional multi-element map of a grain or rock sample. While an electron probe microanalyzer (EPMA) is similar to LA-ICP-MS in the sense that it allows spot geochemical analysis of materials, the LA-ICP-MS has lower detection limits and a greater range of quantifiable elements across the periodic table compared with an EPMA. However, the spot size of a LA-ICP-MS is typically larger than that of an EPMA instrument.

During the last decade, LA-ICP-MS instruments and methods have become more common in exploration applications. These instruments are now being applied in indicator mineral surveys for a variety of deposit types. For example, LA-ICP-MS analysis

of trace element geochemistry in magnetite grains associated with mafic and ultramafic intrusions may be able to predict whether intrusions have been contaminated by a sulphur source, thus having high potential for Ni-sulphide mineralization (Dare et al. 2014). LA-ICP-MS of mineral grains is also gaining significant traction in exploration of hydrothermal deposits, namely porphyry and epithermal systems. Several AMIRA International projects including P765, P765A, and P1060 have investigated how LA-ICP-MS analysis conducted on minerals from the propylitic alteration zone (i.e., epidote, chlorite, and pyrite grains) coupled with whole rock geochemistry and mineralogy could vector to a drill target (Cooke et al. 2015). These studies found that in the pyrite halo of porphyry systems, elements including As, Sb and Pb are scavenged by pyrite. However, in the more distal propylitic zone the sulfides have been exhausted, leaving As, Sb and Pb to substitute into epidote (Cooke et al. 2014). O'Brien et al. (2016) determined that trace element geochemistry of gahnite grains could be used as an indicator of high grade Pb-Zn-Ag deposits in metamorphosed terrains. One major mining company in particular also started implementing laser ablation ICP-MS to the degree that they offered junior mineral exploration companies the opportunity to analyze their samples on a non-confidential basis (International Mining, 2015).

The use of LA-ICP-MS to ablate a spot on a Li-borate fused glass disk for determination of bulk major, minor, trace and ultra-trace element geochemistry has increased in popularity (Figure 4). The application of laser ablation can be paired with X-Ray fluorescence (XRF) analysis of the disk to provide a complete whole rock analysis (Fedorowich et al. 1993; Günther et al. 2001; Eggins, 2003; Kon et al. 2015). The method is gaining popularity and is currently offered as a routine analysis by Bureau Veritas Minerals (BVM). There are several benefits to using LA-ICP-MS on a fused glass bead over more traditional acid digestion ICP-MS methods for total whole rock analysis. As no acids are involved in the digestion, there are fewer concerns with respect to matrix interferences and incomplete or unstable digestions. For example, samples with high Pb and Ba concentrations (i.e., sedimentary hosted Pb/Zn or VHMS deposits) can exhibit low recoveries where the sample is digested via a standard 4-acid method. Isomorphous minerals anglesite (PbSO_4) and barite (BaSO_4) can precipitate as the digestion is brought to dryness. These highly insoluble minerals do not digest well in the aqua regia or HCl back leach.

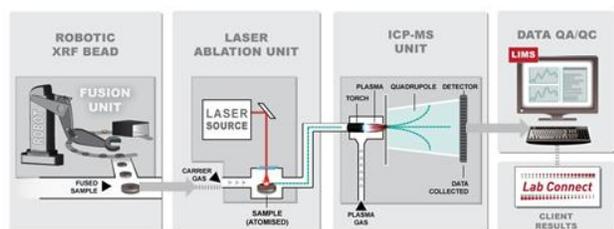


Figure 4: Diagram of LA-ICP-MS analysis on a Li-borate fused glass disk (figure courtesy of BVM).

In terms of analytical benefit, the method represents a total analysis at detection levels that are equivalent to wet chemistry 4-acid or Li-borate fusion and ICP-MS analysis methods. When

LA-ICP-MS is paired with an XRF instrument, the dynamic range can be extended from sub-ppm level to percent level from a single fusion (i.e. no over limit concerns). These dynamic ranges are especially important for determinations of REEs, U and some base metal deposits where detection of LILE and HFSE refractory elements are critical at low level.

Limited Implementation of ICP-MS Advancements in Mineral Exploration

Although stand-alone ICP-MS instruments have likely reached a mature stage of development, there have been several incremental advances over the last decade—especially relating to add-on technology to enhance their capabilities (i.e., the application of collision/reaction cells and LA-ICP-MS). However, the application of these advances applied to mineral exploration has been slow. The routine analysis of geological exploration samples has not changed substantially from 2007, nor have detection limits changed materially either. By comparison, environmental geochemistry has embraced these advances more fully, especially TQ-ICP-MS, and HR-ICP-MS, perhaps due to requirements set out by regulatory bodies.

There are several possible reasons why there have not been more developments or innovations in ICP-MS and trace element geochemistry in mineral exploration. One possibility is that the drivers for innovation are simply not present. Innovation is commonly driven by the consumers of laboratory services (i.e., mining and exploration companies). They define a certain problem, and a laboratory may help to solve that problem. Solutions to these problems could include lower detection limits, larger element suites, and innovative new analytical methods that could be used to find new mineral deposits. However, for approximately 5 of the last 10 years, the minerals and commodities industry has been in a historically long and painful recession. One of the hardest hit sectors was exploration and there has been significantly diminished market pull from the sector.

This recession has also translated into significantly less revenue for commercial laboratories which in turn translates to fewer funds available for internal innovation initiatives. Sample volumes submitted to commercial labs have dropped drastically, especially the number of samples submitted for exploration methods. As an example, BVM method AQ250, an aqua regia ultratrace exploration ICP-MS method, tracks annual non-ferrous exploration spends very closely (Figure 5). In 2012 exploration spending neared USD \$22 billion and BVM analyzed a high volume of samples for AQ250. Not surprisingly, in the years following there was a steep decrease in exploration spending, which tracked very closely with a decrease in AQ250 volumes.

There are other possible reasons as to why ICP-MS advancements have not progressed more. The geochemical knowledge base of how to utilize large multi-element datasets reported from ICP-MS methods may not yet have caught up with the volume of data generated, and the detection limits reported. Several commercial laboratory methods report nearly 60 elements. The general mineral exploration community may still be exploring how to best apply the currently reported data in

order to extract full value. The use of other tried and tested analytical methods including collision/reaction cells or TQ-ICP-MS to achieve ultra-low detection limits may not currently be applicable because the geological systematics they are designed to define are not fully understood. There may be the perception that new analytical methods and potential higher costs do not provide sufficient value. Therefore, the currently available commercial ICP-MS offerings could be still fit for purpose and provide satisfactory value for the end user. This explanation can be summarized by the following equation (Gravel, pers. comm.):

$$\text{Value} = (\text{Quality} \times \text{Information}) / \text{Cost}$$

The end user wants to maximize *Value*, however, it does come at a *Cost*. He or she will accept the *Cost* if both the *Quality* and *Information* is high. If the assumption is made that *Quality* is constant, *Information* becomes key. If the *Information* is fit-for-purpose then there is no need to go to a higher cost analytical method because the incremental increase of *Information* does not substantially improve the user's solution to the problem (i.e., identifying a mineral deposit). In this equation *Cost* includes both *Price* and *Time* hence an analytical method that substantially reduces *Cost* (*Price* and/or *Time*) may represent equal (or better) *Value* to the Client even though *Quality* and/or *Information* are inferior.

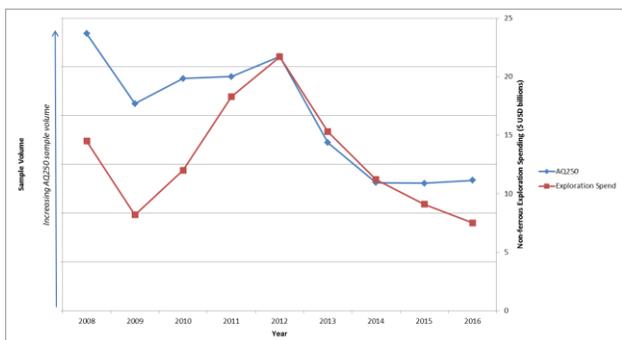


Figure 5: BVM AQ250 ultratrace ICP-MS geochemistry method tracks annual global non-ferrous exploration spending and demonstrates the direct impact it has on laboratories (annual global non-ferrous exploration spending values from S&P Global Market Intelligence).

ICP-MS in the Next Ten Years

The next decade in exploration geochemistry is likely to see greater application and acceptance of collision and reaction cells to achieve lower detection limits for specific elements of interest, and LA-ICP-MS methods for litho-geochemistry. Triple quadrupole ICP-MS instruments will also likely become more commonly employed for isotope determination, especially Pb/Pb systematics. However, with the availability of lower detection limits and greater use of isotopes in exploration endeavors, adjustments to sample collection and handling protocols will be required to mitigate potential sample collection-related contamination issues.

Laser ablation ICP-MS will likely become more integral in exploration. Several studies have already confirmed the value of

trace element chemistry of mineral grains and their capability as vectors to mineralization. LA-ICP-MS coupled with XRF analysis of fused beads may also become common place as a replacement for traditional multi-digestion and multi-instrument analysis for complete whole rock characterization. It may be especially attractive in jurisdictions where OHSE regulations or site logistics inhibit the use of wet chemical digestions and/or disposal of consequent waste.

The implementation of neural networks and machine learning will become more important, as companies consider more efficient ways in which to extract more information from existing or new large multi-element data sets. Deep learning neural networks (including self-organizing maps), utilize a training dataset, which is input into an artificial intelligence machine learning algorithm. The computer learns without being specifically programmed to do so, and the model can be applied to new input data to make exploration predictions. When paired with other geological and geospatial data, these methods can significantly increase success by providing predictions of exploration targets (Singer and Kouda, 1997; Carranza, 2011; Abedi and Norouzi, 2012; Harris et al. 2015; Granek, 2016; Kirkwood, et al. 2016).

ICP-MS ANALYSES APPLIED TO MINERAL EXPLORATION: CASE STUDIES

The White Gold District, Yukon, Canada

Introduction

The White Gold District has had a long history of gold mining and exploration activity, as it includes the Klondike Gold Fields district (Figure 6). The Klondike gold rush was between 1896 and 1899, and was sparked by the discovery of placer gold along Bonanza Creek (near Dawson City). As the gold rush progressed, area river banks were staked and prospectors began mining Au-rich placer deposits. Since that time, several exploration companies, prospectors, and placer gold miners have been searching for the source of the gold without a great deal of success.

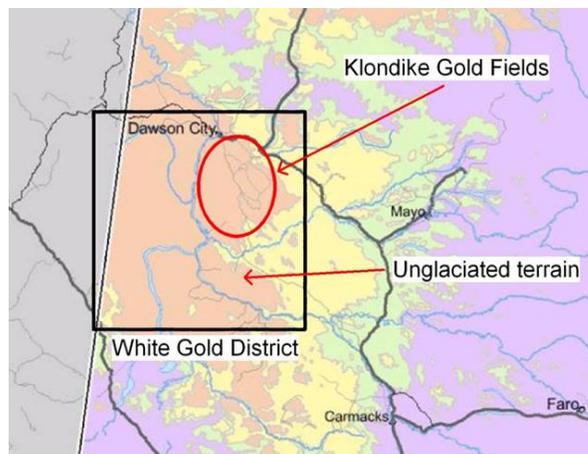


Figure 6: The location of the Klondike placer gold district, and the White Gold District.

Conversely, Ryanwood Exploration has been highly successful. They have discovered and defined several ore deposits within the White Gold District. Their approach was heavily based on surficial geochemical sampling and represents a prime example of how multi-element geochemistry can be utilized for highly effective and efficient exploration. Several hundreds of thousands of soil samples were collected at close (50 x 100 m) spacing. These samples were analyzed over the course of > 10 years and the geochemistry was plotted spatially using simple statistical treatments. Ore and ore pathfinder elements, plus additional elements were plotted to provide clues on the underlying bedrock lithology and structure.

Geology

Deposits of the White Gold District, western Yukon, formed within metamorphic sedimentary and magmatic host rock units of the accreted Yukon-Tanana terrain (Nelson and Colprom, 2007; Bailey 2013; Buitenhuis, 2014) (Figure 7). The collision event and accretion onto the North American Plate occurred during the Middle Jurassic (Nelson and Colprom, 2007). The accreted terrain is comprised of the pre-Devonian siliciclastic Snowcap assemblage and three volcanic island arc sequences (the Finlayson assemblage, Klinkit assemblage, and the Klondike assemblage). The gold mineralization event occurred during the mid-Cretaceous, and has been classified as an epizonal, early-brittle orogenic gold deposit by Buitenhuis (2014). The proximal Golden Saddle deposit has been dated at 163-155 Ma by Re-Os dating (Bailey, 2013).

Unglaciaded Terrain

Historically the prospecting methods employed in the White Gold District involved looking for mineralized float on surface to indicate the presence of an ore body. This exploration strategy may partially explain why no new discoveries had been made since the days of the Klondike gold rush. The White Gold District is one of only a few areas that were not glaciated by the Laurentide Ice Sheet, even during the Wisconsin glacial maximum (Figure 8). The lack of glaciation was largely due to lower temperatures in the western part of Yukon and eastern Alaska, plus low moisture levels (Kaufman and Manley, 2004). Therefore, any potential mineralized float was likely to have long since weathered—not unlike regolith terrains.

While the lack of float (and very little outcropping rock) in these unglaciaded terrain hindered previous exploration groups, it was actually one of the reasons for Ryanwood's exploration success. The soil geochemistry in the region has fewer complexities compared to soils from many other northern regions in Canada, northern US, and northern Europe and Asia, as it was not transported. The unglaciaded terrain allowed Ryanwood Exploration to assume that sampled soils were proximal to their parent rock source and any anomalies were near to mineralization.

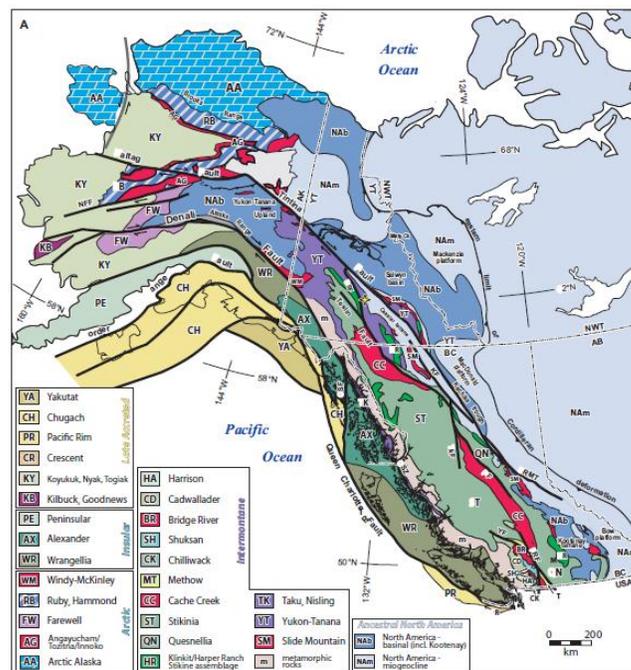


Figure 7: Geology and major faults of the Canadian and Alaskan Cordilleran (modified from Nelson and Colprom, 2007).

Soil Profile Orientation Survey

A second reason for Ryanwood Exploration's success was related to the implementation of orientation surveys to determine optimal sample collection depth. Ryanwood determined that the best geochemical response came from soil samples that were collected deeper, where the soil profile transitions into a saprolite (45 to 80 cm depth), rather than the oxidized upper B horizon. The upper B horizon is commonly the default soil sampling unit due to its oxidizing nature and its ability to adsorb and complex mobile cations to Fe and Mn oxides (Cameron et al. 2004). However, As and Sb pathfinder elements in the White Gold District form oxyanions and do not readily adsorb onto the abundant negatively charged Fe and Mn oxide sites of the upper B horizon. Instead they migrate into the deeper reduced C horizon soil. Gold concentrations were also usually elevated at deeper sampling zones compared to the upper B horizon.

Multi-Element Soil Analysis by ICP-MS

A third and very important reason for Ryanwood's exploration success was the commercial availability of inexpensive, high quality ICP-MS data. The analysis package used in this Yukon case study incorporates a unique modified aqua regia leach using equal parts hydrochloric acid (HCl), nitric acid (HNO₃) and water in a hot water (95°C) bath for 1 hour. It was designed for large sample weights (15 to 30 g). Dean Toye of Acme Analytical Laboratories (AcmeLabs) developed this leach in the late 1980s for wet analysis (versus fire assay) of Au by graphite furnace AA following an MIBK extraction from an aliquot of the sample solution (Gravel, pers. comm.). A second aliquot of the sample solution could then be analyzed using the MAGIC (methyl isobutyl ketone - amine synergistic iodine complex)

extraction for 18 trace elements (Clark and Viets, 1981) by ICP-OES. With the advent of a robust ICP-MS that could provide ultratrace detection limits (e.g. Perkin Elmer Elan 5000), AcmeLabs could report Au plus 52 other elements directly from the aqua regia sample solution without the added precision and accuracy errors associated with the MIBK and MAGIC extractions.

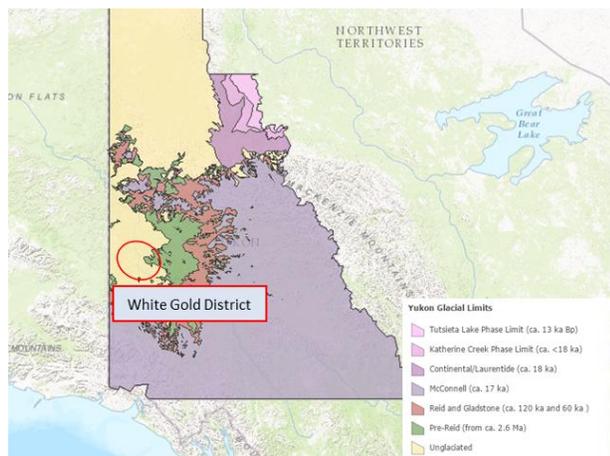


Figure 8: The White Gold District was not glaciated during the Wisconsinian glacial period; therefore soils had not been transported. Quaternary geological map modified from Yukon Geological Survey.

The use of the 15 g 1:1:1 (HCl:HNO₃:H₂O) aqua regia leach was chosen by Ryanwood for several reasons. Firstly, internal laboratory evaluation on hundreds of duplicate sample analyses comparing aqua regia leaching relative to fire assay demonstrated negligible accuracy bias (<5%) (Figure 9). This high degree of accuracy was corroborated by Hall and Oates (2003) in an external study comparing Au and PGE results for 28 reference materials (CRMs) reported by five commercial geochemical laboratories using fire assay methods (NiS and Pb-oxide) relative to AcmeLabs' aqua regia extraction. Secondly, the aqua regia method was highly cost effective. For the cost of a fire assay method, Au plus a suite of useful exploration pathfinder elements were reported. Ryanwood Exploration started from humble beginnings and in the early years of the company they did not have the benefit of investors that could finance exploration programs. The cost of analytical work represented a significant part of their exploration budget.

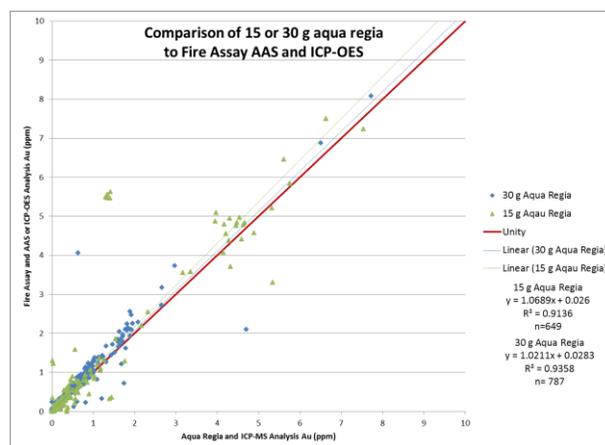
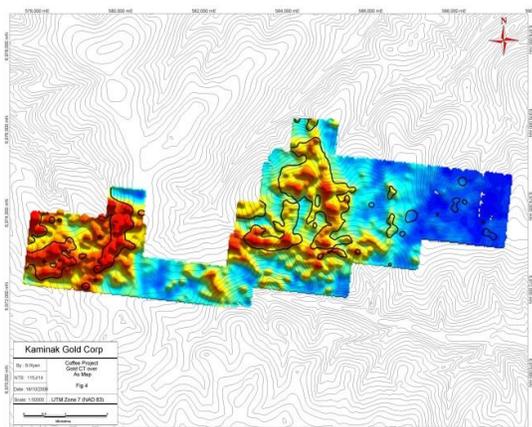


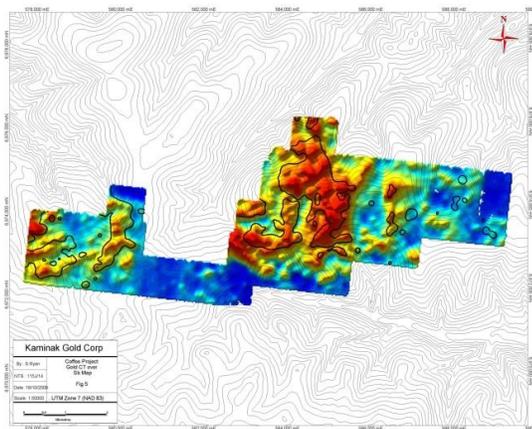
Figure 9: The plot demonstrates that results from larger weight aqua regia analysis (15 or 30 g) vary by less than 5% compared with fire assay AAS, ICP-OES, or ICP-MS analysis for soil samples.

In soils over the Coffee Supremo-Latte Gold deposit (4-5 M oz Au), Au, Sb, and As ICP-MS data spatially correlate very well (Figures 10a, 10b) and provided a valuable regional geochemical fingerprinting tool. Gold in these orogenic systems are typically hosted in arsenian pyrite due to the alteration of mica and availability of iron to form sulphide minerals (Buitenhuis 2014). The correlation between Au and the more mobile Sb and As elements is also a confirmation that significant hydromorphic transport of As and Sb has not occurred and a given soil anomaly is likely in the residual soil (i.e., the mineralization is near the soil anomaly).

In addition to determination of vectors to the actual Coffee ore deposit, soil multi-element geochemistry provided valuable information on host rock lithology and structural controls. The U and Ni soil geochemical maps in Figures 11a and 11b clearly indicate gold anomalies are present across several lithological units and suggest that the gold mineralization is primarily controlled by regional structure rather than by lithology. The high U/low Ni values delineate felsic units, including the Coffee Creek Granite. Conversely, the high Ni/low U values delineate mafic units including the Upper Latte Biotite Schist unit. Moderate Ni and U soil values to the east represent the Augen Gneiss. Ryanwood's assessment of structural controls based on soil geochemistry was confirmed by subsequent investigations by Buitenhuis (2014). His findings suggested that mineralization is controlled by the Coffee Creek fault and structural control is the most important aspect for understanding the ore body.



(a)



(b)

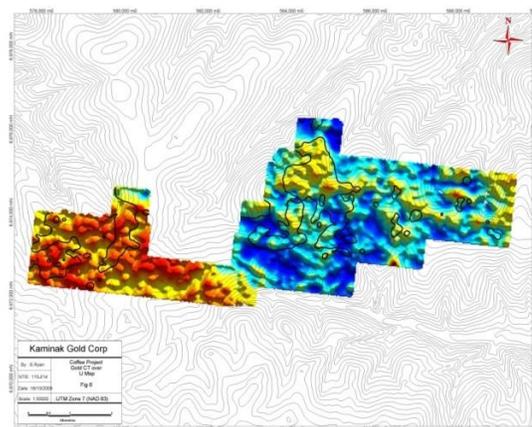
Figure 10: Anomalous gold values in soils (denoted with black outlines) are very closely associated with high As (a) and Sb (b) soil concentrations.

While the main control on mineralization is structure, there are lithological controls too, which can be delineated by soil geochemistry. Gold mineralization is dependent on the sulphidation of mica (Buitenhuis, 2014). Units without mica minerals, such as ultramafic and marble units do not contain mineralization partially for this reason. These units are also barren, as they behaved as aquitards for gold-rich fluids (Buitenhuis, 2014). The identification of these barren ultramafic units can be delineated accurately based on ratios of elements in soils including Mg, Ni, Fe, and Cr. Marble units were delineated by recognizing high ratios of Ca/Mg.

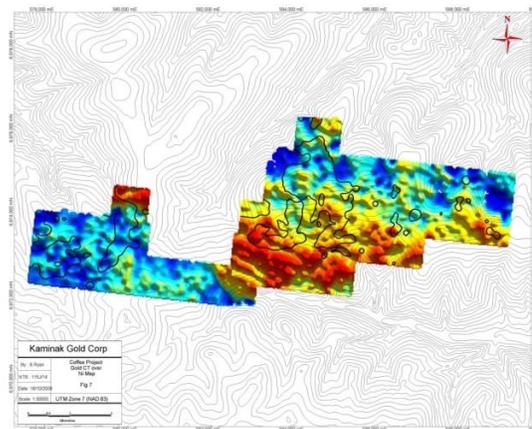
The Taron Cesium Project, Salta Province, Argentina

Introduction

Selecting a broad spectrum multi-element analysis such as ICP-MS in greenfield exploration can have unforeseen fortuitous consequences as seen in the discovery of Taron, the world's first



(a)



(b)

Figure 11: Anomalous gold values in soils (denoted with black outlines) appear to cross lithology. Lithological changes are based on variable concentrations of Ni and U in the soils. The high U/low Ni values delineate felsic units, including the Coffee Creek Granite to the west. The high Ni/low U values delineate mafic units including the Upper Latte Biotite Schist unit in the middle, and moderate Ni and U soil values to the east represent the Augen Gneiss.

primary Cs deposit. Applying ICP-MS analyses in a regional setting known to host multiple deposit types is a proven strategy as seen in GGL Diamond Corp's discovery of magmatic Ni-Cu-PGE during diamondiferous-kimberlite exploration in the Northwest Territories, Canada (Gravel, 2010). However, the Taron Cs discovery was wholly unexpected as it introduced a new deposit type.

Location and Geology

The Taron Cs deposit is located in Salta Province, Argentina approximately 50 km south of the village of Pocitos (Figure 12). The geology of the area as summarized by Trueman et al. (2017) is: basement Precambrian orbicular granites of the Faja Eruptive are overlain by cataclaste/trubiditic anchimetamorphic sedimentary rocks of the Puncoviscana Fm (Aceñolaza and Miller, 1982; Omarini et al. 1999). These units are uncomfortably overlain by olistostrome or melange deposits of late Precambrian to Cambrian age. Mineralization is hosted in

Miocene epithermal geysirite including cryptocrystalline silica, colloids, gels, manganates, arsenates, and oxides (Cascadero Copper, 2017).

Multi-Element Rock Analysis by ICP-MS

Exploration for Cs deposits was not the primary target for Cascadero Copper. Their initial involvement in the region was for copper exploration, as there are several Cu-Au-Mo deposits and showings including the world-class, First Quantum-owned, Taca Taca deposit. In 2004, the field geologist working on the project collected grab samples, as they appeared similar to rocks he had seen elsewhere. Not knowing what the non-descript rocks were and curious as to their composition, he submitted the samples for a multi-element ICP-MS analytical method. Although there was no significant Cu, Mo, or Au, the rock contained ore grade Cs (up to 1.5%), with elevated concentrations of Rb, As, and Mn. Cascadero Copper had stumbled upon what may be one of the largest undeveloped Cs deposits on the planet.

An exploration geologist with a keen sense of inquisitiveness and a strategy of planned serendipity was key to the initial discovery. However, selection of an extensive multi-element ICP-MS analysis package was another major reason for the discovery. Had the exploration program been conducted 10 years prior when ICP-OES packages were the 'go-to' multi-element analytical schemes, Taron would not have been discovered. Then, as now, ICP-OES packages targeted to base-metal exploration do not include Cs in the element offerings.



Figure 12: The Cascadero Taron Cs project is located in northern Argentina in Salta Province near the Chilean boarder. Figure from Cascadero Copper (2017).

CONCLUSION

ICP-MS technology has advanced significantly over the past 10 years and is being applied to exploration geochemistry to solve problems and increase the chances of exploration success. However, these advancements are not yet used routinely in exploration. Instead, the industry appears to be traversing a path from research to application on specific projects to application on a widespread scale. Many of these advancements currently fall into the category of "specific targets" and the overwhelming analytical choices for exploration are the same as those employed 10 years ago. Before several of these technological advancements become routine, the minerals industry must deem that the information gleaned from them is worth the value obtained. Better understanding of how to extract value out of the currently available ICP-MS data may be required before more advanced ICP-MS associated technologies (and associated results) are readily embraced.

The availability of large multi-element, low detection limit ICP-MS analytical packages have contributed to several exploration discoveries. When applied to surface geochemical sampling, the spatial distribution of ore and pathfinder elements can provide valuable information that can be used to vector to mineralization or drill targets. The ICP-MS data can provide other information including controls on mineralization and definition of overburden parent rock.

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