Applied Geochemistry in Mineral Exploration and Mining

Kurt Kyser[1], John Barr[2], and Christian Ihlenfeld[3]

The prosperity of our societies and our standards of living are directly related to our ability to find, exploit, and manage our metal and mineral resources. Metal and mineral deposits are, in fact, geochemical anomalies and, as such, applied geochemistry plays a critical role throughout the mineral resources value chain, from early stage exploration to mine closure. The fundamentals of element mobility (i.e. transport and fixation) in the near-surface environment are used by geochemists to detect mineral deposits at depth, reveal element distributions in and around deposits, assess the total geochemical environment, and refine effective and benign extraction and waste disposal techniques. Both pure- and applied-research ventures play fundamental roles in providing the techniques to manage metal resources and thereby benefit society.

KEYWORDS: exploration, element dispersion, analytical geochemistry, mineral resources

INTRODUCTION

The evolution of our societies and the development of the anthroposphere—that part of the environment modified by humans for use in human activities—have been intimately linked with our ability to extract and exploit metals from the geosphere. As human civilization evolved from the Stone Age on through the Bronze and Iron Ages, our society became dependent on metals for its very existence. Metallurgical knowledge evolved from an art to a science, beginning with the metals used by prehistoric man, such as gold, silver, copper, tin, lead, and iron. Gold and silver were soft, durable, easily worked and visually attractive and so were used for decoration; copper could be hardened by forging and was, therefore, useful as a tool; bronze, an alloy of copper with tin, could be hardened and cast, and so could make more advanced weapons and other tools, which significantly advanced human society. Lead was soft, easily worked, and could be made into vessels and pipes to transport water. Iron, whose name means "stone from heaven" in several languages, so influenced civilization that its discovery led to the transition from the Bronze Age to the Iron Age. The first sources of iron for metallurgy probably came from meteorite finds. Iron oxide ores, like many metals, were discovered when ores were close to camp fires. So began the massive extraction of metals from minerals. Eventually, the development of steel into a material of common use influenced the evolution of our society A nation with steel could conquer a nation without steel (Reardon 2011).

In days gone by, even in the Bronze and Iron Ages, people did not use a significant amount of metal resources per person. However, today, each individual uses or requires an average of 1.4 million kg of resources over their lifetime (FIG. 1). The required resources will increase as populations grow and as the standard of living increases in currently less advanced societies.

When populations grow and advance, more resources are always needed, including mineral deposits. Mineral deposits can be viewed as geochemical anomalies, and, as such, their detection, as well as assessing their impact on the environment, must use geochemical techniques. Areas where geological research, applied geochemistry, and policy intersect in the exploration for and extraction of metals include the following: (1) using element mobility in the near-surface environment to detect deposits at depth (Kelley et al. 2006); (2) revealing element distributions in and around deposits to adequately assess the total chemical environment associated with the deposit and to refine effective and more environmentally benign extraction and waste disposal techniques (Bowell et al. 2011); (3) understanding the effects of both macro- and microenvironments on
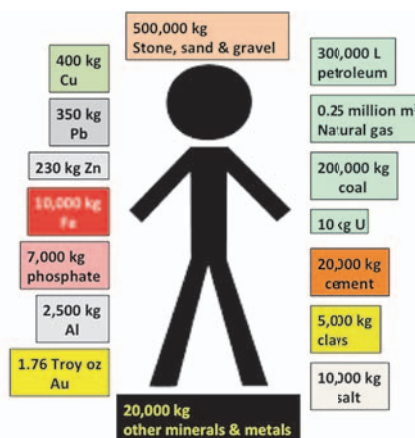
FIGURE 1   Average lifetime consumption of metal and mineral resources for individuals in first-world countries. DATA FROM WWW.MINERALSEDUCATIONCOALITION.ORG.

1   Department of Geological Sciences and Geological Engineering
    Queen's University, Kingston, Ontario, Canada
    E-mail: kyser@geol.queensu.ca

2   Anglo American plc, Technical & Sustainability, Geosciences
    E-mail: john.barr@angloamerican.com

3   Anglo American plc, Technical & Sustainability, Exploration
    E-mail: christian.ihlenfeld@angloamerican.com

element mobility across the geosphere–biosphere interface to define appropriate remediation techniques associated with the extraction of diverse commodities. Geological research, both pure and applied, plays a fundamental role in providing such techniques. Research in applied geochemistry can add value to exploration, extraction, and remediation strategies provided that the results are adequately conveyed to the appropriate individuals in both industry and government and that there is a perceived need to develop new and novel techniques by all concerned. For example, applying isotope tracers to help understand the processes by which various elements move through the geosphere and into the biosphere is a novel area of research with boundless benefits to exploration, extraction, and remediation and will lead to a better understanding of the impact of mining processes on the total environment.

THE BASIS OF GEOCHEMISTRY IN DISCOVERING AND EXPLOITING ORE DEPOSITS

A basic tenet in exploration and environmental geochemistry is that elevated concentrations of metals and compounds in ore deposits or from anthropogenic sources will disperse with time and be recorded as aberrations against "normal" background levels. Environmental and exploration geochemistry have repeatedly proven that this basic tenet is valid because there are numerous cases where the subtle geochemical footprint of an ore deposits goes well beyond the bounds of the ore itself and its associated alteration: it is, in fact, possible to detect "leakage" of elements from deposits at depth (Cameron et al. 2005; Kelley et al. 2006; Coker 2010). The new challenges for geochemists include understanding the processes by which elements migrate (Anand et al. 2014), the rate at which concentrations in the environment change as a result of anthropogenic activity, and identifying those elements or compounds that truly reflect dispersion from ore deposits up to several hundreds of meters below the surface (Coker 2010). There have been very few recent discoveries of ore deposits at the surface (Marlatt and Kyser 2011), which means that most new discoveries will be at depth, which in turn means that we must be able to "see" them from the surface with geophysics and geochemistry. In addition, surface exploration geochemistry for deposits at depth must be able to distinguish elements in metal deposits from elements due to the background geology and from elements in the area that might be from human pollution.

Exploration geochemistry directly benefits society by enhancing the inventory of subsurface metal deposits through new technologies and by tracing element migration in the near surface environment, including across the geosphere–biosphere interface. Amplifying an orebody's footprint so it can be detected at depth or traced near the surface involves two distinct processes (Fig. 2): (1) primary dispersion, which provides information on alteration and primary element dispersion associated with ore emplacement; (2) secondary dispersion, which provides clues about element migration from alteration and ore zones after emplacement. Overall, the most commonly and successfully applied surface media in exploration surveys are stream sediments, soils, tills, ferruginous materials from lateritic profiles, and plants. The emerging field of biogeochemistry, which focuses in part on the interaction of microbes, plants, and other organisms with Earth materials, offers a new dimension by which elements can be traced from the geosphere to the biosphere (Dunn 2007; Kyser 2012).

Primary Dispersion

During primary dispersion (Fig. 2), components in the mineralizing fluids permeate into the country rock, which alter primary minerals and elevate the concentrations of "pathfinder" elements. Several types of deposits have been discovered using primary dispersion haloes, including deposits of "iron oxide–copper–gold", other types of Au deposits, and Pb–Zn and Cu deposits (Kelley et al. 2006). These enrichments relative to background concentrations are sometimes evident in the lithogeochemistry up to several kilometers away from the mineralization (Halley et al. 2015). Hydrothermal alteration minerals associated with mineralizing fluids are normally detected in drill core, outcrop, and from airborne surveys using spectroscopic techniques (Table 1). Lithogeochemistry is widely used in exploration, and recent advances in field-based, real-time analysis (Table 1) have been made using hand-held portable X-ray fluorescence (pXRF) detectors and laser-induced breakdown spectroscopy (LIBS) devices, the results of which, however, should be subsequently verified using certified laboratory analyses. Enrichments and zoning in pathfinder elements specific to an ore-forming fluid may be detected through element isotopic compositions, which reflect the presence of ores and alteration haloes such as H, Li, B, C, O, S, Cu, Zn, Tl, Mo, Pb, and U (Mathur et al. 2009; Barker et al. 2013) or reflect the trace-element composition of specific minerals such as epidote and chlorite (Cooke et al. 2014).

Lithogeochemical methods on an outcrop or on a drill core have been used in regional reconnaissance, and more locally for detecting the far-field effects of mineralization, particularly around blind targets (Lawie 2009). Lithogeochemistry combined with mineralogy is useful in geometallurgical work to more effectively extract the elements of interest from the ore and alteration minerals (Lawie 2009).

Secondary Dispersion

Tracing element migration in the near-surface environment and into the biosphere involves understanding the secondary dispersion of elements, including those associated with anthropogenic activity (Fig. 2). Surface media that can be used to reflect secondary dispersion of ores or alteration minerals include stream sediments, tills (McClenaghan and Cabri 2011), vegetation (van Geffen et al. 2012), and ground waters (Leybourne and Cameron
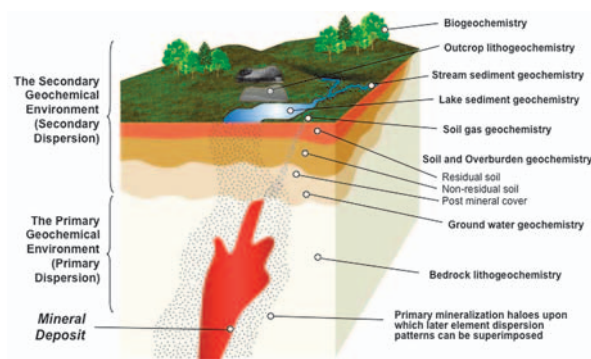

FIGURE 2 Different types of media sampled during exploration and baseline geochemical surveys in the area of a mineral deposit. Proximity of an undercover deposit can be reflected in zoned geochemical enrichments formed during the mineralizing event itself (primary dispersion) or as a result of postmineralization dispersion (secondary dispersion). Primary dispersion haloes can be detected through lithogeochemistry; secondary dispersion haloes can be detected using ground water, soil (till), soil gas, lake and stream sediments, and biogeochemistry.

2010). Studies of such media have led to numerous discoveries of ore deposits over the years (Eppinger et al. 2013), including the Boyongan porphyry Cu–Au deposit (Philippines), which contained over one million tons of copper and was discovered by Anglo American in 2000 (Braxton et al. 2009).

Because most ore deposits are electron-rich and contain elements in reduced forms, they are potential havens for microbes that can mobilize elements during secondary dispersion. Microbe-mobilized elements can involve aqueous or gaseous complexes in the microbe's waste products or from the decay products of dead microbes. Such complexes migrate to the surface, particularly along fractures and faults, become sorbed on clay and Fe–Mn oxide surfaces, and make their way into the biosphere. These complexes have specific element and isotope signatures that reflect the deposit at depth (Cameron et al. 2005). Tracking these elements and determining their migration processes is something of a current research obsession because in areas of thicker or transported overburden, surface geochemistry is notoriously unreliable. With the current poor understanding of the controlling geochemical processes by which elements migrate, applying these techniques in a robust predictive fashion is fraught with uncertainty and requires additional rigorous scientific research. While the direct approach of drilling through cover and sampling the top of the bedrock is more effective, drilling to any level is an expensive venture, so anything reliable and cheaper is much sought after.

CRITICAL ASPECTS IN APPLIED GEOCHEMISTRY

Many in the academic geochemistry community are unfamiliar with what is done by geochemists in the mining industry and unaware of the numerous questions that could benefit from research. Applied geochemists would dearly like to know more about the mechanisms by which elements migrate from deposits, what elements provide reliable vectors back to the primary deposit, and what techniques are most effective at detecting these mechanisms. Geochemistry is a strategic technique throughout the chain of exploration and mining, from initial targeting through to resource definition and on into effective mining and, ultimately, mine closure. There are three main areas of applied geochemistry in the mining industry: (1) exploration geochemistry; (2) mining geochemistry (geometallurgy); and (3) environmental geochemistry. Although the goals of these areas are different, the approaches, applications, and techniques of each are similar.

Environmental geochemistry on mine sites and projects involves determining the geochemical baseline, monitoring surface and borehole water-quality, and characterizing ore and waste rocks for potential acid mine drainage and metal leaching. Fast and relatively cheap multielement analysis by inductively coupled plasma atomic emission spectrometry (ICR-AES) and inductively coupled plasma mass spectrometry (ICP-MS) (TABLE 1) have been some of the major technological developments in the last couple of decades. These techniques allow the generation of large multielement data sets of use in both exploration and mining.

The critical importance of geochemical sampling in applied geochemistry cannot be overstated. Sampling strategies must be devised and implemented based on a holistic understanding of the character of the media being sampled, the style of mineralization, and the overall project requirements. It is not uncommon for billion-dollar decisions on a mining project to be made on the basis of assaying just a few hundred kilograms of rock. It is, therefore, essential to get the geochemistry and the sampling right.

TABLE 1 ANALYTICAL TECHNIQUES IN APPLIED GEOCHEMISTRY

Acronym	Technique	Description
CF-IRMS	Continuous Flow Isotope Ratio Mass Spectrometry	Elements of interest (H, C, N, O, S) are prepared as gases and separated in-line with a stable isotope ratio mass spectrometer
DET CRC Lab-at-Rig	Deep Exploration Technologies Cooperative Research Centre Coiled Tubing Drill Rig with sensors in-line	Trailer-mounted assay system that provides near real-time XRF geochemistry and XRD mineralogy on drill cuttings.
ETV-ICP-OES	Electro Thermal Vaporization Inductively Coupled Plasma Optical Emission Spectrometry	Solids or solutions are evaporated into a plasma and excited atoms and ions emit electromagnetic radiation at wavelengths characteristic of a particular element
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectrometry	Plasma used to excite ions in solutions or solids and excited atoms and ions emit electromagnetic radiation at wavelengths characteristic of a particular element
ICP-MS	Inductive Coupled Plasma Mass Spectrometry	Excited ions in plasma torch are introduced to a mass spectrometer detector for both elemental and isotopic analysis
LA-ICP-MS	Laser Ablation Inductive Coupled Plasma Mass Spectrometry	Laser is used to ablate material that is carried into a plasma torch and the excited ions are introduced to a mass spectrometer detector for both elemental and isotopic analysis
LIBS	Laser Induced Breakdown Spectroscopy	Laser is used to sample material and the chemical composition determined using emission spectra
OA-ICOS	Off-Axis Integrated Cavity Output Spectroscopy	The concentration or amount of an isotopic species in a gas phase is determined by absorption spectrometry with a laser
pXRF	portable X-Ray Florescence	Handheld XRF for in situ chemical compositions
QA/QC	Quality Assurance & Quality Control	Correct and transparent protocols are used in analyses to ensure they are of the appropriate quality
Raman	Raman spectroscopy	Raman spectroscopy uses the vibrational modes of molecules; sometimes coupled with SWIR
SWIR	Short Wave Infrared spectroscopy	Infrared reflectance spectroscopy for mineral identification
Synchrotron-based methods	XRD, micro-XRD, XRF, micro-XRF elemental mapping, computed tomography (CT) and fluorescence CT, extended X-ray absorption fine structure (EXAFS) and micro-EXAFS spectroscopy, scanning transmission X-ray microscopy	Synchrotron light used as a source of intense and energy-tunable X-rays for a variety of techniques
XRD	X-Ray Diffraction (portable)	Closed-beam field portable XRD to provide full phase identification of mineral components; sometimes coupled with a qualitative XRF spectrometer.

The theoretical basis for effective sampling in applied geochemistry was formulated in the 1950s by Pierre Gy (Pitard 1993). Gy's formulation is frequently applied in the mining industry and, in most instances, up to 70% of the total variance in chemical composition comes from field sampling and sampling design, 20% from sample preparation, and 10% or less from the actual chemical analysis. To limit these errors, the mining and exploration industry has adopted sophisticated quality assurance (QA) and quality control (QC) protocols that are reflected in international codes, such as the Australasian Joint Ore Reserves Code (JORC www.jorc.org) and the Canadian National Instrument 43-101 *Standards of Disclosure for Mineral Projects (*NI 43-101 web.cim.org/standards). Having well-written and transparent protocols for sampling and analysis and ensuring that these are followed using the appropriate equipment are part of QA. Quality control protocols include analysis of "blind" blanks, matrix-matched certified reference materials (CRMs), and duplicates (normally performed on 5–10% of the samples). Interlab check analyses are also done. Precision error estimates from duplicate and multiple analyses of the CRMs are normally assessed using an average coefficient of variation approach, which uses the ratio of the standard deviations of the values to their means (Stanley and Lawie 2007).

Grunsky (2010) has given a good overview of the essential methodology commonly followed for data interrogation and visualization. Grunsky advises a two-pronged approach to geochemical data interpretation: a geochemical process-based analysis that tries to understand the controls on element associations and data distribution patterns, plus a statistical-based analysis of empirical inter-element relationships. Although one approach can feed into the other, the real power lies in spatially integrating the geochemical data with the available geological and geophysical data.

GEOCHEMISTRY APPLIED TO EXPLORATION

Mineral exploration is a multidisciplinary team effort in which conceptual geological thinking and traditional geological fieldwork are complemented by the key specialist subdisciplines of geochemistry and geophysics. Examples where geochemical techniques have contributed to the discoveries of deposits, to critical baseline studies, and to environmental impacts abound.

One such successful integrated program is exemplified by the discovery of the Sakatti Cu–Ni–platinum-group element (PGE) magmatic sulfide deposit in northern Finland (FIG. 3). The Sakatti Cu–Ni–PGE sulfide deposit was discovered by Anglo American in 2009 (Brownscombe et al. 2015). Initial area selection was primarily based on a conceptual geological exploration model that recognized the geological similarities between the portion of the Central Lapland Greenstone Belt in which Sakatti is located and the world-class Pechenga Ni–sulfide deposit on the Kola Peninsula (Russia). Public-domain geophysical (e.g. airborne magnetics) and geochemical datasets (surface and basal till) obtained from the Geological Survey of Finland were evaluated to identify and to rank targets within the area. The Sakatti target itself was identified as a magnetic body with ultramafic affinity. Much of the area is covered by glacial deposits with only 2% outcrop, so further exploration relied on geochemistry and geophysics of the overlying deposits to delineate the subsurface geology. Targeting areas to drill was accomplished by sampling the basal till layer immediately overlying the bedrock contact. Initial base-of-till sampling at Sakatti was carried out along lines perpendicular to the strike of the magnetic body, with 300 m line spacing and 25 m sample intervals (FIG. 3). A weak Cu–(Ni)–PGE anomaly in the basal till was followed up with additional base-of-till sampling, first to a line spacing of 150 m and finally to 50 m. As a result of this, a 150 m × 150 m subcrop of the mineralized body was delineated below the till cover. Subsequent
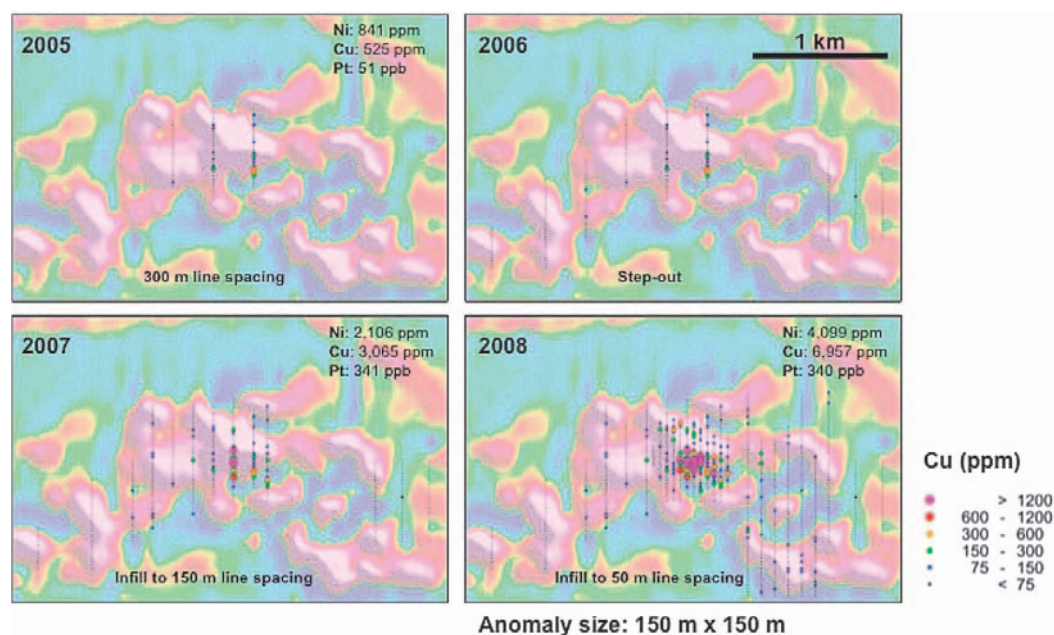

FIGURE 3 Selected results of the base-of-till (BOT) geochemical survey undertaken over the Sakatti deposit (Finland) prior to its discovery (results are overlain on a reduced-to-pole airborne magnetic grid). BOT samples were collected from the basal till layer immediately overlying the bedrock contact. Initial sampling was done at 300 m line spacing along lines perpendicular to the strike of the magnetic body (during 2005 and 2006), followed by additional sampling, first to a line spacing of 150 m (in 2007) and finally to 50 m (in 2008). As a result of this survey, the 150 m × 150 m large subcropping part of the mineralized body was delineated below the till cover, leading to the discovery of the Sakatti Ni–Cu–PGE sulfide deposit. USED WITH PERMISSION OF ELSEVIER FROM BROWNSCOMBE ET AL. (2015).

drilling of the Cu–Ni–PGE anomaly intersected significant magmatic sulfide mineralization leading to the discovery of the Sakatti deposit.

Another example of successful applied geochemistry was in developing new technologies in isotope tracing and gradients in element concentrations (lithogeochemical vectors to ore) as a result of integrating element and isotope geochemistry in a study of the Rosario porphyry Cu–Mo subprovince of the Collahuasi district in northern Chile (FIG. 4). Mineralization in the district involved propylitic hydrothermal alteration of granodiorites, diorites, andesites, dacites, and rhyolites, all of which had previously experienced regional lower greenschist facies metamorphism. In low-grade metamorphic terrains, propylitic assemblages that represent the boundary of an ore system can resemble metamorphic mineral assemblages. However, propylitic alteration can be distinguished from other metamorphic mineral assemblages by high whole-rock $\delta^{13}C$ values and carbon contents that result from the incorporation of magmatic CO_2 during mineralizing events (FIG. 4). The spatial variation in $\delta^{13}C$ values and carbon contents of outcrop samples from the Collahuasi district were used to delineate zones that correspond exclusively to propylitic alteration surrounding economic deposits, regardless of rock type. When combined with lithogeochemical data from the same samples, the relative mobilities of elements resulting from primary dispersion defined a compositional gradient that served as a vector toward the mineralization of the Rosario Cu–Mo porphyry deposit (FIG. 4).

FUTURE DIRECTIONS AND TECHNOLOGIES

Recent novel applications of geochemistry in mineral exploration and remediation include the chemical and isotopic composition of surface media (e.g. till, soils, vegetation) to record element migration, new techniques used for real-time (field-based) analyses and for easier laboratory-based analyses, as well as the development of new approaches to isotope geochemistry, microbial technologies, spectroscopy, and data representation. Among the sample materials currently being examined for tracing element migration are clay minerals in soils (van Geffen et al. 2012); plant matter, such as tree-cores and tree resin; and soil gases (Hale 2010). The novel laboratory analytical techniques of pyrolysis, of electro-thermal vaporization (as a way of introducing samples into ICP instruments), and of faster analysis of isotopic compositions now permit the rapid and accurate analysis of complex materials. Both pXRF and LIBS (TABLE 1) are being employed in various forms to generate real-time data in the field. Synchrotron light-source methods are being increasingly used by geochemists to characterize the speciation and phase associations of ores and the contaminants released as a result of mining activities (Brugger et al. 2010). Research on the interaction between microbes and ore deposits is also a frontier area, which includes identifying microbes through DNA analysis. Microbes, we now know, can mobilize specific ore components and, therefore, have potential for exploration, bio-mining, and remediation.

Portable XRF technology is now well established in the mining and exploration industry and has been validated through initiatives like the CAMIRO (Canadian Mining Industry Research Organization) study (Hall and McClenaghan 2013). With matrix-matched calibration and a proper QA–QC protocol in place, it is possible to generate accurate assay data with the pXRF to allow real-time decisions to be made with reasonable assurances.

LIBS-based field-portable systems are also appearing on the market, and these too will need to be similarly evaluated. The halogens represent a target group of elements in exploration and remediation because they form strong complexes with metals, they tend to be mobile, and they are associated with mineralizing fluids. LIBS is one of the
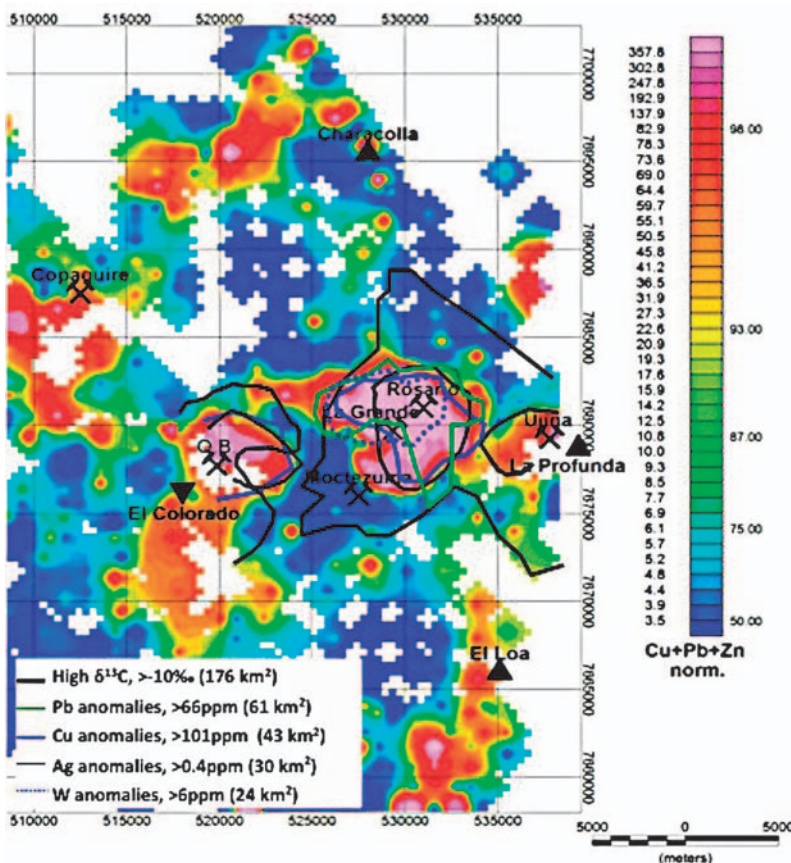

FIGURE 4 Areal extent of anomalous concentrations of pathfinder elements Pb, Cu, Ag and W, and $\delta^{13}C$ values, in outcrop samples at 2 km spacing from the Collahuasi district (Chile) are shown along with Cu+Pb+Zn concentrations normalized to the median value. The major porphyry Cu–Mo deposits of the district – Rosario, Ujina and Quebrada Blanca (Q.B.) – and the epithermal veins of Moctezuma and La Grande are shown, as are the prospect areas of Characolla, La Profunda, El Loa and El Colorado. High $\delta^{13}C$ values delineate zones of high magmatic CO_2 component that correspond exclusively to propylitic alteration (Djouka-Fonkwé et al. 2012). Anomalous pathfinder element concentrations and $\delta^{13}C$ values reflect primary dispersion and define a gradient in anomalous values that serve as a vector toward mineralization.

few techniques that can detect all the halogens. Other field-portable instruments now starting to be routinely used include portable short-wave infrared (SWIR), X-ray diffraction (XRD), and Raman mineral analyzers (Table 1). The potential benefits of real-time geochemical data acquisition are advancing with the Lab-at-Rig project (Hillis et al. 2014) that analyzes the chemical and mineralogical composition of drill material as it arrives at the drill-rig site.

The use of isotopes in applied geochemistry is still not normally routine. A partial exception is for environment-related work where commercial analysis of the light stable isotopes in water is available at a number of laboratories. However, analyzing isotopes as part of standard exploration and mining is sporadic and has been hindered by the lack of suitable machines at commercial laboratories. This is starting to change as the analytical techniques of continuous flow isotope ratio mass spectroscopy (CF-IRMS), off-axis integrated cavity output spectroscopy (OA–ICOS), and automated sample preparation systems are advanced (Table 1). Similarly, laser ablation ICP-MS techniques

(Table 1) have proven useful to exploration; however, cost-effective availability is currently an obstacle to the routine application of this technology to exploration programs.

EPILOGUE

The need to find more economically exploitable mineral deposits is exemplified by the historical use of Cu, a metal critical to the continued advancement of society. Over the past 100 years, Cu production has grown from less than 0.5 million tonnes per year to 18 million tonnes per year. In the past 25 years, we have used half of the copper ever mined. During the next 25 years, we will have to at least double the 600 million tonnes of Cu mined so far, even given the most positive recycling scenarios, to meet growing demands. Thus, the challenge will be to fill the gap between production and consumption of Cu—as well as all mineral commodities—and to do this with minimal perturbation of the total environment. Geochemistry will play a central role in the exploration and management of these resources, and, if applied intelligently, will be a benefit to society. ▪

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