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ABSTRACTS

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ABSTRACTS

A.B. Christie

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Exploration for gold in Australia using Ionex technology

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Exploration for blind ore deposits (more than 10 m cover) is carried out using different geochemical methods of mobile metal forms, including MPF, TMGM, CHIM and MMI. Mapping by Ionex technology is carried out to identify ore geochemical systems characterised by polar zoning in the distribution of ore-forming and siderophile elements. Geochemical systems display fractal characteristics (self-similarity) at all scales. In the Central part of NSW four stages (I to IV) of geochemical exploration were carried out within the study area at the scales 1:500,000, 1:100,000, 1:25,000 and 1:10,000. Initially, the exploration area was 7,700 km^2; the areas in the last stages were 2-3 km^2. Exploration was conducted using the MPF method: a partial extraction technique which is designed to detect leakage of metal ions from bedrock mineralisation through permeable cover to the surface. As a result of over 2 year's exploration, two targets were drilled (five holes) at the two sites. Data obtained from sampling of bedrock (442 samples from 1 m core intervals) showed a high-level of heterogeneity of distribution in a number of ore-related elements: Au, Ag, As, Sb, W, Mo, Nb, Bi, Cu and Ba. An especially significant range of concentration of metals was found in drill-hole 1 (Site 3) and drill-hole 4 (Site 2). A local polar zonality was found within the drill-holes with positive anomalies of those metals in association with zones of reduced concentrations (negative anomalies). The deep levels of Sites 3 and 2 are manifestly promising for gold mineralisation that is probably associated with a hydrothermal vein system.

Geochemical survey of rare earth elements (REEs) in the concealed ore body of Hongcheon, Korea

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Because of the risk of diminishing supplies of REEs worldwide due to China's dominance over REE supply, the necessity of developing domestic resources of REE has been realised in other countries. To explore new ore bodies, a geochemical survey was conducted at an existing carbonatite REE deposit in the Hongcheon area of Korea. Proper sampling strategies and baseline data for the interpretation of the results were determined through a pilot study conducted in the area. Enrichment in the concentration of LREE over that of HREE, which is typical in carbonatite-type deposits, was observed in stream sediments and heavy mineral samples collected during the geochemical survey. Maximum concentrations of LREE were 2,299 mg/kg and 27,798 mg/kg for stream sediments and heavy minerals, respectively. Among LREEs, La and Ce are the dominant components of TREE, comprising approximately 68 % of mean concentrations. Considering the distribution pattern of La+Ce contents and the associations with the existing outcropping ore bodies, the zone of prospective REE mineralisation was determined to be in the south-western part of the area. A detailed follow-up soil survey of the zone found even higher concentrations of La and Ce (2,450 and 3,100 mg/kg, respectively), and suggested the possible extension of the existing ore bodies. Likewise, a systematic geochemical survey for REE is feasible for locating concealed ore bodies in the area, where the mineralisation is mostly covered with soil, and rock outcrops are scarce.

The formation of native metals by methane reduction in greisenised granites, North-Eastern Tasmania

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Small particles of native copper, lead, zinc, tin, nickel, chromium, iron and a variety of alloys have been observed in greisens within the Devonian Poimena granite pluton near Pioneer in northeastern Tasmania. The particles occur in greisens with a still visible granite texture and are mostly associated with fragmented quartz veins and minor sulphides (bornite, chalcopyrite, pyrite, galena, tetrahedrite-tennantite and sphalerite).

Excavations to a depth of 0.8 to 2.5 m were dug by hand after the area immediately around the surface had been cleared of any loose material. The rock samples were broken up by hand using a water spray and then a heavy mineral concentrate was obtained by using a plastic pan. Each panned sample was divided into magnetic fractions using a hand held NdFeB magnet. After inspection by binocular microscope any interesting particles were mounted in epoxy for electron microprobe analysis. The particles vary in length from 10 to 300 µm.

The selected metal particles fall into three main groups: copper-zinc, lead-tin and iron/nickel ± chromium, but some are nearly pure metals. The grains occur as small, irregular grains, some with oxidised coatings and/or quartz inclusions.

The native metals seen here are mostly rare in the earth's crust, zinc in particular. The elements Cu, Pb, Fe, Zn and possibly Ni have been transported as chloro complexes, fixed as sulphides and reduced to their native state by pneumatolytic/hydrothermal methane to their native state. Native Sn and Cr are the result of degradation of stanniferous and chrome bearing micas under similar pneumatolytic/hydrothermal conditions.

Methane occurs in fluid inclusions in quartz veins in granite and greisens, in granite itself, and in Tasmania in hydrothermal silica flour.

Spatial distribution patterns of chromium as a tool to reconstruct sediment pathways: A case study from the Po Plain (Italy)

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Reconstructing sediment transport pathways across a variety of depositional environments requires accurate identification of the sediment sources and their contribution to the downdip components of the dispersal system. Through integrated sedimentological and geochemical analyses of 1,418 samples from the Po Plain (Italy), involving three segments (drainage area, alluvial plain and coastal plain/delta) of the dispersal system, we document that where contrasting source rock compositions are present, trace element geochemistry of surface sediments can play a decisive role in the discrimination of sediment provenance. In this work, we used chromium and nickel to identify the major sources of sediment delivered through distinct tracts of the routing system, from the Apenninic catchments to the Po Delta and the Adriatic coast. Sediment composition from the downstream reaches of the Po River and 23 Apenninic channel-levee river systems is fingerprinted by distinctive chromium concentrations. The natural spatial distribution of chromium can be predicted as a function of three major factors: sediment provenance, grain size and soil maturity. Metal contents vary primarily as a function of the local ultramafic rock contribution. For any constant provenance domain, fine-grained (floodplain, swamp and lagoonal) sediments are invariably enriched in Cr relative to their coarser-sized (channel-related to beach) counterparts, thus reflecting hydraulic sorting by crevasse, overbank and near shore processes. Once the geochemical signatures of the fluvial end-members are established, the relative contribution of the individual detrital sources to the downstream segments of the system can be assessed. This procedure results in a geochemical map that is largely based upon sedimentological criteria, rather than statistical interpolation methods. The reconstruction of source-rock lithology and sediment pathways by combined sedimentological and geochemical studies is highlighted here as the basis for reliable estimates of sediment budgets in a source-to-sink context.

Exploration through transported cover: Can we predict which sample medium works where and why?

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As mineral exploration moves into regions dominated by transported cover, explorers need to know whether they can use surface sample media or if they have to drill deeper to sample weathered or fresh basement. Although surface geochemistry is effective in residual areas, explorers remain sceptical about its application in areas of transported cover. Scepticism is rooted in the possibility that upward migrating elements will not create sufficiently strong anomalies that can be distinguished from variations in the background composition of the cover. Recently there have been advances made in identifying the operating mechanisms (e.g. seismic pumping, electrochemical dispersion, vegetation, termites, capillarity, gases) capable of transferring metals from buried mineralisation upwards through cover to the surface. However, the prevailing climatic regime, nature and age of transported cover, landscape history, presence or absence of supergene mineralisation and depth of groundwater determine which mechanism(s) is likely to operate in a given regolith setting. These mechanisms direct sampling needs and analytical options. Strong geochemical anomalies can form rapidly under experimental conditions, and seasonal variations suggest migration of elements from source to surface may vary in time and intensity. Geochemical anomalies probably form incrementally rather than at a constant rate. Clearly surface anomalies do not form in all environments and alternative approaches need to be investigated where a surface medium cannot be used. An increasing number of studies have shown the importance of mechanical dispersion by using interface sampling and indicator minerals. It is these sample media that provide the under-cover prospecting tool similar to surface exploration that makes use of lateritic gravel, lag, heavy minerals or stream sediment sampling. Secondary minerals (goethite, hematite, alunite) precipitated from groundwaters in the upper sediments and groundwater itself could provide sampling media to search for hydromorphic dispersion from underlying, and deeply buried mineralisation.

Vectoring to basement-hosted uranium mineralisation in the Athabasca Basin, Canada: Methodology, pitfalls, and examples of using Pearce element ratios

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Unconformity-type (U/C-type) deposits of the Mesoproterozoic Athabasca Basin, Saskatchewan, Canada, are the largest high-grade uranium deposits in the world. Most of these deposits are located within major reactivated structural zones at/near the unconformity between the sedimentary basin and the Archean/ Paleoproterozoic basement. Large alteration halos surround these deposits, changing dramatically from proximal to distal, within both the sandstone cover and the underlying basement rocks. The basement-hosted U/C-type deposits, lying variably deeper, are the richest and highest tonnage; occurring with a much smaller halo at greater depths below the U/C. Consequently, the basement-hosted deposits are more difficult to discover, despite new and improved technologies and analytical techniques.

The basement-hosted U/C-type uranium deposits have lithogeochemical vectors that are masked by the large variety of Archean/Paleoproterozoic lithological units in the basement complex and the multitude of alteration events (i.e. regional metamorphism, retrograde metamorphism, high- and low-T metasomatism, paleoweathering, and hydrothermal alteration) that have modified them (i.e. making their lithogeochemistry difficult to interpret and use). Still, after careful evaluation of geochemical data in conjunction with petrography, several oxides, elements, ratios, and isotopes (e.g. Pb isotopes) are determined to be useful for differentiating the various Archean/Paleoproterozoic basement units. Also, based on detailed studies by the first author in the 1990's, the nature and degree of oxide/element mobility can be semi-quantitatively evaluated using Pearce element ratios (PER). Dedicated PER diagrams can be constructed so as to model background variability for discriminating between fresh, altered, and mineralised basement rocks. Here, we will present some examples from drill holes near the Key Lake, McArthur River, Rabbit Lake, and Eagle Point uranium deposits to demonstrate the use of PER diagrams for vectoring towards mineralisation. In conclusion, the use of PER diagrams is a powerful, cost-effective lithogeochemical tool to distinguish basement-hosted mineralisation trends from original primary trends and secondary alteration processes.

Metals – from the mantle source to deposition

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Concentration of metallic elements/oxides may relate to unusual sources and/or particular processes. The majority of crustal ore deposits are ultimately derived from the Earth's mantle. "Large igneous provinces" and associated layered mafic intrusions (LMI) have formed throughout Earth's history, and are attributable to mantle plume activity. Association of base (Ni, Cr, V) and precious metal (platinum group elements; PGEs) ores with komatiites and large LMIs (e.g. Bushveld and Stillwater) with this style of igneous activity is well known. An unappreciated aspect of LMI genesis is the unusual abundance/early phase appearance of orthopyroxene. In modern mid-ocean ridge and hot-spot basalts, orthopyroxene saturation lags considerably behind Cr-spinel-olivine-plagioclase-clinopyroxene. Boninite is the only mantle-derived magma where orthopyroxene crystallises early; boninites are generated by hydrous melting of refractory mantle lithologies in convergent margin settings, and are unusually rich in PGEs. Early orthopyroxene crystallisation can also occur via contamination of mantle-derived basalt with silicic continental crust. Concentration of sulfides/alloys depends on achieving magmatic saturation. Sulfide solubility is critical, dependent on redox state, Fe and S contents. Negative pressure dependence of S solubility means magmas are sulfide-undersaturated during ascent. For relatively reduced mid-ocean ridge basalts, prolonged fractionation in recharging magma chambers results in persistent sulfide saturation and dissemination of crystalline sulfide. In contrast, relatively oxidised arc magmas are enriched in S dissolved as sulfate; reduction associated with magnetite saturation in derivative andesitic-dacitic magmas triggers sulfide precipitation, in temporally and spatially distinct events. The association of “porphyry Cu-Au-Mo” deposits with convergent margins may ultimately be related to these processes. Delayed sulfide precipitation is accompanied by dramatically increased concentrations of base and precious metals in evolved compared with parental magmas. We now know initial metal concentrations in respective parent magmas are not unusually high compared with mid-ocean ridges; process rather than unusual source enrichments via subducted inputs is responsible.

A brave new world? Applying stable isotopes to mineral exploration

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The stable isotope ratios of hydrogen, carbon, oxygen and sulfur have been used extensively to understand sources of fluids and volatiles (e.g. C, S) in hydrothermal systems, as well as help constrain fluid temperatures, and processes responsible for the precipitation of ore. It has also been suggested that changes in stable isotope ratios could also be used to assist with mineral exploration and identify areas of the earth most prospective for ore mineralisation. However, stable isotope measurements have not been made as a routine part of broader mineral exploration programmes due to the time and expense associated with traditional analytical methods for stable isotopes. Recent advances in infrared absorption spectroscopy mean that stable isotope data can be collected more quickly and at much lower cost than has previously possible. We have developed and applied this technology to measure C and O isotope ratios around hydrothermal ore deposits hosted in carbonate rocks. Stable isotope ratios are particularly useful in carbonate host rocks where other exploration vectors (e.g. mineral alteration, lithogeochemical changes) are often very subtle. We demonstrate that stable oxygen isotope ratios can form km+ alteration haloes around Carlin-type gold deposits which can potentially be used to guide mineral exploration. In addition, we show that skarn and related carbonate-replacement deposits form significant isotope alteration haloes parallel to the hydrothermal fluid flow pathways in both carbon and oxygen isotopes. Further studies are underway to apply infrared absorption technology to oxygen and hydrogen isotopes in hydrothermal minerals to evaluate their application in propylitic alteration.

Stable oxygen and hydrogen isotope zonation around epithermal Au-Ag deposits

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The stable isotope ratios of oxygen and hydrogen have been suggested to have potential to be used as exploration vectors for various types of mineral deposits, including porphyry Cu-Au and epithermal Au-Ag deposits (e.g. Criss and Taylor, 1983, Criss et al., 2000). We are determining the distribution of mineralogical alteration (e.g. illite and illite-smectite) and trace element metasomatism around the Martha Mine and surrounding Au-Ag lodes near Waihi, in the Coromandel district of New Zealand (cf. Mauk and Simpson, 2007) as part of an MSc thesis. In addition to this study, changes in stable oxygen and hydrogen isotope ratios in hydrous minerals (e.g. clays) around the gold deposits are being measured using a 1000°C tube furnace, interfaced to an Los Gatos Research Inc off-axis integrated cavity output spectrometer (model IWA-45EP) to enable rapid analysis of the hydrogen and oxygen isotope ratio of the OH and/or H_2O component of clay minerals (cf. Koehler and Wassenar, 2012).

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Trace element and isotopic analysis of shells from the hydrothermal vent mussel *Gigantidas gladius* from seamounts in the Kermadec arc, New Zealand

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Submarine hydrothermal systems are host to rich biological assemblages supported by chemosynthetic micro-organisms that depend upon vent operation for nourishment. Monitoring the flux and intensity of vent systems through time is important in understanding life cycles of these organisms and the variation of normally toxic heavy metals in their environment from associated volcanic systems. However, collecting and analysing vent fluids for time series analysis is both costly and difficult. In this study, we explore the potential of the Kermadec arc hydrothermal vent mussel *Gigantidas gladius* to both record information on the chemistry of the venting systems through time on the Kermadec seamounts and provide insight into relationships between vent activity and mussel growth. *Gigantidas gladius* is found on at least five seamounts in the Kermadec arc: Clark, Macauley, Rumble III, Rumble V, and Tangaroa; as well as at the Calypso vents field in the Bay of Plenty. Differences in mussel shell growth, morphology and geochemistry between the different seamounts are investigated. Individuals from the same site are compared for reproducibility, and individuals collected from the nearby locations seven years apart are used to look for overlap and to extend temporal information for the site. Trace metal concentrations in the shells are measured via solution and laser ablation ICP-MS. Bulk shell analyses are used for comparison between the different venting sites and to the existing literature for other hydrothermal vent mussel species. Micro-analysis across growth banding in the direction of shell growth is used to investigate changes in venting occurring through time, and to examine relationships between vent activity and mussel growth. Oxygen isotope analysis across growth banding is compared to the trace element results to investigate its behaviour and potential as an additional venting proxy. These results are discussed in terms of fluxing of hydrothermal vent systems over time as well as the application of the techniques used applied to environmental monitoring, such as contamination of water bodies from economic tailing waste.

Siderophore-promoted solubilisation of REE, Th and U from igneous rocks and river particulates and the oxidative mobilisation of Ce and U

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The REE are a group of trace elements that have high particle-reactivities, are considered immobile during water-rock interaction and in natural waters are typically associated with particles. In modern surface systems, Ce may be oxidised to Ce^{4+}, resulting in the decoupling of Ce(IV) from the redox-insensitive REE(III). This may produce Ce anomalies in normalised REE patterns. In igneous systems, Th(IV) and U(IV) are closely coupled and most rocks show, therefore, a Th/U ratio of about 4. In surface systems, however, U may be oxidised to U^{6+}, resulting in fractionation of U(VI) from Th(IV).

Explosive volcanic eruptions, such as the 2010 eruptions of Eyjafjallajökull volcano in Iceland, produce volcanic ash which may be an important source of iron and other nutrients for aquatic organisms. To become bioavailable, this iron needs to be solubilised by complexing agents, such as the well-studied biogenic siderophore desferrioxamin-B (DFOB).

Based on results from incubation experiments with glacial meltwaters from southern Iceland, which are rich in suspended volcanic ash from the 2010 eruption of Eyjafjallajökull and that had been incubated with and without DFOB, respectively, we show that siderophores not only enhance the release of iron, but also promote the mobilisation of REE, Th, and U from these particles. In the presence of DFOB, partial dissolution of volcanic ash (and presumably other lithic particles) produces a flux of dissolved REE into ambient waters, that is characterised by depletion of the light REE over the middle REE and by selective enrichment of Ce, due to the formation of dissolved Ce(IV)-DFOB complexes. Formation of U(VI)-DFOB complexes increases the mobility of U and decouples U and Th.

In siderophore-rich environments, this siderophore-bound REE flux has the potential to significantly modify the concentrations and distribution of these elements in glacial meltwaters, river waters and seawater.

Mercury speciation in mine tailings from Patio-amalgamation

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Mercury (Hg) is known as an important element for the environment and human health. However the toxicity of Hg strongly depends on its speciation. Many historical mining sites are heavily contaminated with Hg due to its use for silver or gold amalgamation. The Patio Process was the first application of silver amalgamation on an industrial scale. The method was introduced in Mexico in 1554 and used until the beginning of 20th century, resulting in considerable quantities of Hg polluted mine tailings remaining in the environment. However, the determination of Hg-speciation in those tailings has not been conducted. Therefore the aim of this study is to determine the speciation of Hg in mine tailings where the Patio Process was used. Tailing samples from an old mining district near Fresnillo, Zacatecas, Mexico and Cedral, San Louis Potos, Mexico were analysed using several different methods of X-ray spectroscopy, involving Micro X-ray fluorescence in laboratory and at a synchrotron facility (ANKA Karlsruhe, Germany). Bulk - XRD and micro XRF was used to characterise the geochemical and mineralogical environment. Space-resolved X-ray absorption analysis EXAFS was applied to identify the specification of Hg in the samples. The results show that cinnabar (HgS, trigonal) and meta-cinnabar (HgS, cubic) represent the main Hg-species (>90%) with minor portions of Hg-chlorides (Hg_2Cl_2, $HgCl_2$). The spatial distribution of Hg in the samples is extremely heterogeneous with local concentration maxima (>2%). Those Hg-hotspots are often associated with high concentrations of As, Cu, Fe, Pb or Zn. Due to its high stability, low mobility and poor bioavailability the toxic potential of cinnabar and meta-cinnabar is low. The main risk results from the minor amounts of Hg-chlorides. Both chloride speciations have a higher solubility in water and thus pose a threat to groundwater and may be available for methylation.

Orogenic gold deposits: 50 years of stable isotope geochemistry

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A compilation of 50 years (1960-2009) of stable isotope research on orogenic gold deposits shows wide variation in the stable isotope composition of vein minerals. The $\delta^{13}C$ values of carbonate minerals and inclusion fluids range from -26 to +13‰, with a major mode at -5‰, and a lesser mode at -22‰ that is characteristic of deposits hosted in rocks of the Appalachian/Caledonian orogen. Sulfide and barite $\delta^{34}S$ values range from -30 to +17‰, forming a single population with a mode at +3‰. Quartz $\delta^{18}O$ values range from +5 to +26‰, with two modes, one at +12‰ and characteristic of deposits hosted in volcanic rocks, and the second at +15‰ for deposits hosted in volcano-sedimentary rock sequences. The variance in quartz $\delta^{18}O$ values from deposits hosted in one craton or orogen is typically about 10‰. Similarly large variance in quartz $\delta^{18}O$ values is found at the scale of one district. Other silicates, borates, oxides, and tungstates have $\delta^{18}O$ values ranging from 0 to +17‰. Micas, tourmaline, and actinolite range in δD values -125 to -30‰, with a few values as low as -180‰. The $\delta^{15}N$ values for micas range from +1 to +24‰, where Archean deposits have $\delta^{15}N$ above +8‰ and Phanerozoic deposits values below +8‰. Quartz formed under oxygen isotope equilibrium with micas, tourmaline, and feldspars at temperatures of 300-

400°C. The range in $\delta^{18}O$ and δD values indicates prevalence of high $\delta^{18}O$ metamorphic fluids, but also the admixture of low $\delta^{18}O$ meteoric water or seawater. Carbon, nitrogen, and sulfur are dominantly derived from the regional country rocks.

Interpretation of partial/selective extraction soil geochemical survey results: Why is it so frustrating?

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Strong evidence exists in the recent literature on partial and selective extraction soil geochemistry to show that these methods can detect blind mineral deposits covered by transported overburden that should normally preclude detection, at least according to any conventional understanding of how soil geochemical anomalies form. This communication takes as a given that these methods can work, at least in some cases, but attempts to address why they give results that are so difficult to interpret and why they produce a high proportion of false positive and false negative anomalies. Any explorationist that has drilled such targets can attest to the former and anyone that has done orientation surveys can attest to the latter. To understand why one must consider a soil geochemical survey from the perspective of a measurement system. The variance of results is a combination of the variance of the survey and the variance of the measurement system (which includes all sources of variance from the point of collection to the analysis itself and is cumulative). Conceptually this is the partitioning of variance between sources and can be measured in principal, albeit with difficulty, by collecting sample site duplicates. For an acceptable measurement system the variance of site duplicates should be less than 30% of the variance of the survey and the lower this number the better it will be able to detect variations in the survey. As a comparison, soil surveys based on aqua regia digestion typically give values below 10% but partial/selective extraction methods often have sampling variance exceeding 50% of the survey variance. This leads to excessively noisy data making interpretations very difficult. Methods exist to reduce the variance of sampling but unfortunately in some instances it is the variance itself that is anomalous and may be signalling the presence of mineralisation.

Magmatic volatiles in the Taupo Volcanic Zone, New Zealand

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The extensive magmatism in the central Taupo Volcanic Zone (TVZ) is intimately associated with the high heat flux and active geothermal systems. These geothermal systems have previously been subdivided into two groups: 1) low-gas (i.e., CO_2), high Cl, low B and Li/Cs ratio systems suggested to have chemical affinities with basaltic (and rhyolitic) magmas, and 2) high-gas, low Cl, high B and Li/Cs ratio systems having chemical affinities with andesitic magmas. To better understand the magmatic fluids and their potential contribution to the overlying hydrothermal systems, we analysed volatiles and trace elements in quartz-hosted melt inclusions of the major rhyolitic eruptive deposits, which is by far the predominant magma composition that erupted in the central TVZ.

Based on these new data, the rhyolites can be further subdivided into two distinct groups; R1 which is enriched in Li, Ba and B, and has Cl contents of ~0.2 wt%; and R2, which has lower content of these fluid-mobile elements, but higher Cl contents (0.25 to 0.35 wt%) than R1. These differences in volatile contents are related to distinct parental magmas (i.e. distinct sources for melt generation) with the "wetter" R1 having a higher slab-fluid component (i.e. dehydration of the subducting plate) compared with the "dryer" R2.

A comparison between the new volatile data for the rhyolites and the present-day geothermal systems reveals that the observed differences in the fluid composition of surface springs could be correlated with the composition of the two rhyolite types. We therefore suggest that the variation in geothermal fluids does not necessitate a separate andesitic magma as a source, but is a manifestation of different slab-derived fluid contributions producing distinct rhyolite types. While the correlation observed here is strong, we do not rule out the influence of fluid-rock interaction as a contributor and this remains to be explored.

Copper isotopes from black smoker chimneys at Brother submarine volcano, Kermadec arc, New Zealand

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In the study of copper isotopes, much attention has been paid to environments with low-temperature alteration and Cu-enrichment due to the economic importance of supergene sulfides and because large fractionation patterns accompany these settings. Here, we focus exclusively on δ^{65}Cu values of hypogene chalcopyrite and address the possible mechanisms of fractionation that occur prior to seafloor weathering. That is, variation in the sources of Cu, physico-chemical conditions of fluids that transport it, and depositional processes on the seafloor. We analysed Cu isotopes from a suite of 8 black smoker chimneys collected from the NW Caldera hydrothermal field of Brothers volcano, Kermadec arc. Our results range from δ^{65}Cu = -0.03 to 1.44‰. One chimney has the highest δ^{65}Cu value (1.44‰) in its exterior (older) and a low value (0.13‰) in its interior (younger); another chimney has both high and low δ^{65}Cu values in its interior, while other chimneys have consistently low values (to 0.36‰) throughout their structure. We interpret the population of lower values as representing the magmatic-hydrothermal δ^{65}Cu signature of this deposit (i.e., the source value) and the population of higher values to result from transport or depositional effects, either at the seafloor or subseafloor. As these are the first Cu isotopes to be measured for an active vent field from an intraoceanic arc volcano, our data contributes an important component to the developing global database on Cu isotopes. Through this work and others, Cu isotopes may aid in understanding several challenging questions regarding the genesis of ore deposits worldwide.

The sediment-hosted Au-Pd-Pt deposit of Serra Pelada (Carajás Mineral Province, Brazil): A variant of unconformity related U ± Au ± PGE deposits?

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The Serra Pelada Au-PGE deposit is an unusual, low-temperature hydrothermal Au-Pd-Pt deposit located within the Carajás Mineral Province, Amazon Craton, Brazil. The mineralisation is epigenetic, hosted mainly by carbonaceous siltstones of the Águas Claras Formation. The ore bodies are localised in the hinge of the Serra Pelada syncline, at the intersection of NNE-trending subvertical fault zones with carbon-enriched siltstones. The hydrothermal alteration is divided in three main zones: (1) The ore zone; (2) Distal reducing alteration; and (3) Distal oxidising alteration. Gold, platinum and palladium mineralisation is associated with intense argillic alteration, hematite-rich brecciation and silicification, with the highest grade ore hosted by amorphous carbon-rich breccias. The mineral paragenesis is comprised of kaolinite, quartz, hematite, monazite, rutile, barite, Pb and Ag selenides with pyrite, chalcopyrite, and Ni- and Co-bearing sulfides. Gold is precipitated as fine pureness aggregates or fischesserite (Ag_3AuSe_2), as free standing crystals, or included in sulfides and selenides. Palladium and platinum minerals are arsenopalladinite ($Pd_8(As,Sb)_3$), mertieite ($Pd_{11}(Sb,As)_4$), fine merenskyite-moncheite ($(Pd,Pt)(Te,Bi)_2$) and rare sudovikovite ($PtSe_2$). Major element exchanges during hydrothermal alteration include Si and Mg gains and K depletion with notable introduction of trace elements including LREE, Bi, Pb, U, Co, Ni and As. Fluid inclusion studies show that fluids responsible for the Serra Pelada Au-Pd-Pt ores were low temperature (ca. 170-200°C + possible pressure correction) but highly variable in salinity, ranging from 3 to 25 wt % NaCleq, with detectable trace elements such Pb, As, Ni, Bi, U and Au which are related to the mineralisation. The Ni-Co sulfide inclusions present in the oxidised (hematitic) quartz - carbonate veins indicate that highly oxidised fluids interacted with mafic/ultramafic rocks en route to the ore deposition site. The hydrothermal alteration, element associations, and fluid inclusion data at the Serra Pelada deposit show geochemical similarities with unconformity related U ± Au ± PGE deposits. Despite differences in geological setting and fluid flow geometry, both ore types formed by mixing of fluids that originated from highly oxidised and reduced rock packages.

Taupo Volcanic Zone (TVZ) geothermal exploration: Tools and techniques

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Geothermal systems of the Taupo Volcanic Zone (TVZ) occur in a ‘continental’ setting, and comprise a body of hot rock at depth, with a liquid-dominated hydrothermal reservoir and localised vapour zones. Although the hydrology, geology and structure of TVZ geothermal systems are well known, past evaluation of their resource potential (and later development) has required objective and ongoing application of geoscientific criteria, which has been re-appraised as new information became available (i.e. during exploration and production project phases). For any new geothermal development, in New Zealand or elsewhere, identification of features (e.g. corrosive fluids, potential for scaling, low temperature, or possible ingress of cool near-

surface waters) that might pose a risk or constraint to development is essential. There is a typical size for the TVZ geothermal systems (~5-35 km^2, defined by DC-resistivity and/or MT techniques), which in some cases, combined with extensive surface manifestations (e.g. boiling springs, steaming ground and large surface heat flow) provide the initial (pre-drilling) indication of a resource with potential to support sustainable electricity generation or direct uses. Controls on permeability are defined by alteration mapping, stratigraphic/structural interpretations, air-photograph/satellite imagery, seismic surveys, exploratory drilling (including interpretation of downhole logging data) and analogy with systems in complementary volcano-tectonic settings. Geochemical surveys, including analysis of surface waters and gases, and well discharge fluids, provide (geothermometric) insights on resource temperatures, as well as acidity, silica content and potential for scaling and/or corrosion that may limit the type or scale of resource utilisation. Assessment of proven, probable or possible reserves and hypothetical or speculative resources are based on the geoscience criteria, and support development decisions. A flexible geoscience and exploration strategy, which addresses risk, is used to prioritise development, and is inexpensive compared to drilling costs or failure to recognise issues that could detrimentally impact future field management.

Seawater infiltration at Whakaari/White Island, Bay of Plenty, New Zealand: Using stable isotopes to evaluate the fluid flow dynamics within the crater floor

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Understanding the origin of fluids within a magma-hydrothermal system is important for monitoring geological hazards, developing geochemical and hazard models, and investigating dynamic water-rock interactions. Previous investigations of Whakaari/White Island (WI) have described the hydrothermal system as “chemically sealed” from seawater infiltration despite significant evidence of sea-level change forcing cyclicity in plume CO_2 emissions. However, other assessments have noted that acid brines in the crater floor are related to seawater infiltration into the shallow hydrothermal system. This study aims to delineate the origin of the fluids within the WI system by determining the isotopic signature of carbon, oxygen and hydrogen in soil gas and springs emanating from the crater floor. The two datasets provide a cross examination of the fluid origin with isotopic values for $\delta^{13}C_{CO2}$ and $\delta^{13}C_{DIC}$ ranging from -10 to -2‰ and -6 to -2‰, respectfully. $\delta^{18}O$ ranges from 5-10‰ and for $\delta^{2}H$, 20 to 35‰. A Plot of $\delta^{18}O$ vs. $\delta^{2}H$ show our data falls on an evaporation line from a seawater source. When the $\delta^{13}C_{CO2}$ values are contoured, maximum values (-2‰) are coincident with anomalous soil CO_2 flux (δCO_2 up to 30,000 gm^{-2}day^{-1}) which gives further evidence that seawater is the dominant source of the system fluids (as advectively transported fluids are unlikely to be contaminated). This area of high permeability corresponds with a previous crater rim (fault) and agrees with a model for seawater infiltration within the shallow magma-hydrothermal system at WI.

Biogeochemical expressions of buried rare earth element mineralisation at the Norra Kärr Alkaline Complex, southern Sweden

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Biogeochemical exploration is an effective but underutilised method for delineating covered mineralisation. Plants are capable of accumulating rare earth elements (REEs) in their tissue, and ferns (pteridophytes) are especially adept because they are one of the most primitive land plants, therefore lack the barrier mechanisms developed by more evolved plants. The Norra Kärr Alkaline Complex, located in southern Sweden approximately 300 km southwest of Stockholm, is a peralkaline nepheline syenite enriched in heavy rare earth elements (HREEs). The deposit, roughly 300 m wide, 1300 m long, and overlain by up to 4 m of Quaternary sediments, has been well-defined by diamond drilling. The inferred REE mineral resource, over 60 million tonnes averaging 0.54% Total Rare Earth Oxide (TREO), is dominantly hosted within the pegmatitic “grennaite” unit, a eudialyte-catapleiite-aegerine nepheline syenite. Vegetation and soil samples were collected from the surficial environment above Norra Kärr to address four key questions: 1) which plant species is the most effective biogeochemical exploration medium; 2) what are the annual and seasonal REE variations in that plant; 3) how do the REEs move through the soil profile; and 4) into which part of the plant are they concentrated. *Athyrium filix-femina* (lady fern) has the highest concentration of LREEs and HREEs (up to 125 ppm Ce and 1.03 ppm Dy) in its dry leaves; however, there is better contrast between background and anomalous areas in *Dryopteris filix-mas* (wood fern), which makes it the preferred biogeochemical sampling medium. The REE content in all fern species was shown to decrease from root > frond > stem, and chondrite normalised REE patterns within the plant displayed preferential fractionation of the LREEs in the fronds relative to the roots. Samples collected from an area directly overlying the deposit had up to five times greater HREE content (0.74 ppm Dy) in August than the same plants did in June (0.14 ppm Dy). The elevated REE contents and distinct contrast to background demonstrate that biogeochemical sampling is an effective method for REE exploration in this environment.

Use and abuse of portable XRF in field assessment of mine waste reactivity

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The conventional way for an environmental geochemist to assess the reactivity of mine waste in the field is a simple paste contact test coupled with visual observations such as mineral identification, leached salts or staining from secondary mineralisation. With the advent of portable and robust XRF analysers a new tool has been added to the environmental geochemist’s field tool box. This paper considers the use of two portable XRF analysers from Olympus-Innov-X and evaluates their potential on an assessment of the former lead/zinc mine of Cwmystwyth in Mid Wales. Results of the standard paste contact test indicate that the collected samples release low levels of salinity and the pH values are slight to mildly acidic. This could lead to a classification that the waste is almost inert. However, utilising the portable XRF analyser it can be demonstrated

that there are significant levels of environmentally sensitive metals across the site. Yet as the paste conductivity test suggests, these are not being readily mobilised although there is a constant low level mobilisation due to the size of the mine site that is impacting the river. Field analyses with the portable XRF analyser can be impacted by the inability to prepare samples in the field. However, the internal calibrations appear to be robust for major element detection and can be improved with site specific calibration.

Geochemical assessment of pit backfill at the North Mara Gold Mine, Tanzania

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Sulfide bearing waste rock presents a challenge for acceptable environmental disposal, due to potential for acidic drainage with elevated trace metals, metalloids and sulfate. To prevent this occurring it is necessary to isolate the sulfide minerals from either moisture or oxygen to slow down the weathering process. In a humid tropical environment, isolation from moisture is difficult to achieve but placement of the sulfide rock under a water cover would limit oxygen ingress and so gradually if not completely stop sulfide oxidation.

The Gena pit, on North Mara mine site, is not currently active and contains a pit lake approximately 70 m deep. A geochemical study has been undertaken to determine the impact of placing sulfide bearing waste rock in the pit both above and below the water level to determine what, if any, environmental impacts could occur.

Numerical calculations were undertaken in PHREEQC and predictions indicate that it is unlikely to be impacted by the disposal of potentially acid forming (PAF) waste in the pit lake where the lake water isolates sulfides from chemical reactions and minimise acid generation and metal release. In contrast, disposal of the PAF waste above the water level in the pit is likely to result in the generation of acid run-off, resulting in acidification of the uppermost layer of the Pit Lake and result in an increase of iron, manganese, arsenic and sulfate in the lake chemistry. The predictions supported the disposal of waste rock into the existing pit lake with no net impact to pit lake or groundwater chemistry.

A watershed in geoscience innovation and invention – the Tony Barringer legacy

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Tony Barringer, an economic geologist with a PhD from Imperial College London (where he became a lifelong friend of John Webb) moved to Canada immediately after graduation. With Selection Trust and then Barringer Research he developed the immensely successful airborne EM system – INPUT. However, Tony considered the “false alarm rate” of AEM unacceptably high and set out to complement airborne geophysics with airborne geochemistry, first for minerals, and then for oil and gas. Over a decade this led to development of various versions of Airtrace, which was mounted on both rotary and fixed wing platforms. Initially Airtrace focused on detecting atmospheric gases

such as mercury, sulphur dioxide and iodine analysed in real time. Later versions captured airborne particles, initially in arid areas where particulate loadings were high, and then in vegetated areas. To understand the geochemistry of particulates in vegetated areas, Barringer supported a decade of research at the Botany Department, Imperial College, London.

In-flight samples were collected on sticky tape every few seconds in sufficient quantity for later analysis for up to 32 elements by ICP after laser ablation. Airtrace surveys, supported by Goldfields and later Anglo American, were flown on 3 continents. Subsequently Surtrace, a helicopter mounted system for “ground truth” of Airtrace anomalies was developed. This system collected the surface micro-layer and/or material vacuumed off plants, depending on the area. A further refinement was a backpack unit of Surtrace for yet more detailed follow-up. Results of Airtrace and Surtrace surveys from a variety of settings and for different styles of mineralisation are described. Brief reference is made to “spinoff” methods from this work for related targets like: explosives and drug detection; remote sensing of gases for environmental monitoring; and other instrumentation.

Mineral exploration in an underdeveloped country: Benchmarking a project development using data from a field portable XRF to that of a commercial laboratory

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Portable XRF instruments are effective tools to provide ‘fit-for-purpose’ qualitative chemical data that are precise but typically very inaccurate. The advancement over the past decade in handheld or portable XRF instruments allows for real time ‘fit-for-purpose’ data to be collected allowing for real time assessments and decisions to be made assuming the instruments are used correctly and their limitations understood by the user. Within the mineral exploration industry the ability to make an objective assessment and decision on the significance of a sample’s chemistry can take days to months through a commercial laboratory by the time a sample is prepared, analysed and results reported. Remoteness and poor infrastructure in underdeveloped countries are an added challenge to mineral explorers. Through regional soil sampling and the application of a portable XRF instrument in an underdeveloped county we will demonstrate how a mineral explorer has been able to map out significant geological terrains over a 50 km strike length and identify robust base-metal drill targets in less than a complete field season. The advancement of the project using ‘fit-for-purpose’ qualitative chemical data from a portable XRF is benchmarked against the shipment too and turnaround of results from a commercial laboratory.

Performance comparison of portable XRF instruments: A mineral exploration industry prospective

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Under standardised test conditions, the analytical performance of portable XRF instruments varies significantly between individual instruments from the same manufacturer, and between manufacturers using similar instruments. The precision of the instruments to repeat a constant element concentration from a single sample is typically very good (<5% RSD); however, the accuracy is generally poor to very poor with huge concentration differences in some elements.

Repeat analysis by the same instruments under the same conditions after a two month period shows a measurable deterioration in element concentration, with elements of lower atomic number, Al and Si, the worst affected. This deterioration in the instruments' performance was observed in all instruments evaluated.

Lithium-ion battery packs, a key to the instruments' portability, can have a measurable effect on the precision and accuracy of the data during a routine battery pack change.

Each instrument provides uniquely individual data that should not be combined with data from any other units without appropriate post-processing or recalibration. To significantly improve the quality and value of the pXRF data, a calibration procedure appropriate to the material(s) being evaluated should be implemented with regular baseline data collected to ensure instrument and data stability. Over time, matrix calibrations need to be verified with the instrument undergoing a manufacturer's recalibration when control limits deteriorate significantly.

Geochemistry of chromite-PGE and nickel mineralisation in the Dun Mountain Ophiolite Belt, East Nelson, New Zealand

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The Dun Mountain Ophiolite Belt (DMOB) in east Nelson contains numerous chromite occurrences, some of which were mined historically (1859-1908) on a small scale. Chromite occurs as podiform deposits in a lower zone of serpentinised dunite and harzburgite at the top of a peridotite tectonite unit from Wooded Peak (Dun Mountain) south to little Ben. Chromite lenses and layers also occur in an upper dunite-rich zone at Lowther Creek in the Red Hills massif and at Baldy Ridge in a southern outlier of the east Nelson DMOB. Fourteen podiform chromite occurrences in the DMOB between Dun Mountain and Red Hills, and at Baldy Ridge, were sampled and analysed for PGE, Cr, Al, Fe, Ni, Cu and other elements. Chromite samples from Wooded Peak to Little Ben and Lowther Creek showed elevated concentrations of Ir (12-83 ppb) and Ru (22-154 ppb), with generally low concentrations of Rh, Pt and Pd. These levels are similar to those found in podiform chromite deposits in ophiolites worldwide. Chromite samples from Baldy Ridge are distinctly different in having elevated concentrations of Rh (50-58 ppb), Pt (717-1069 ppb) and Pd (287-531 ppb), in addition to Ir (57-81 ppb) and Ru (159-162 ppb). Reflected light microscopy and electron microprobe analysis showed that chromite grains are altered around their margins to ferritchromite and magnetite. Samples from Lowther Creek and Baldy Ridge contain composite grains of pentlandite + magnetite ± pyrrhotite ± pyrite ± chalcopyrite that are intergranular to olivine and/or chromite and appear to represent intercumulus blebs of magmatic sulphide. Serpentine in samples from Baldy Ridge, Wooded Peak and Dun Saddle contains minor awaruite (Ni_3Fe) ± magnetite ± heazlewoodite (Ni_3S_2) that have formed from serpentinisation of primary olivine. These observations suggest that the chromites of Baldy Ridge have exploration potential for platinum group elements.

Geothermal systems and epithermal ore deposits – a history

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A relationship between high temperature geothermal systems and epithermal ore deposits was first recognised by Don White of the USGS in 1955. (Economic Geology, 50th Anniversary volume, 99 – 154). In the years following, experiments showed that gold and silver were transported primarily as bisulfide complexes in these systems. Many measurements were made of gold and silver concentrations in hot springs and the outflow of geothermal wells. However, the concentrations that were measured were always too low for an economic gold or silver deposit to form in the lifetime of a geothermal system. In 1986, an orifice plate was recovered from a well test at the Ohaaki geothermal field. Orifice plates offer a constriction that serves to reduce pressure in a geothermal fluid flow. The recovered orifice plate had a scale deposited on the downstream side that consisted of 4.5 wt% gold and 26 wt% silver in a matrix of chalcopyrite, with lesser galena, sphalerite and pyrite. Geochemical thermodynamic calculations revealed that there was an order of magnitude decrease in the gold solubility as the fluid flowed through the orifice plate. Further calculations showed that the gold concentration was approaching the theoretical solubility in the geothermal reservoir, which meant that an economic gold deposit could easily be transported in the fluid flow of a geothermal system. The gold and silver are deposited primarily as a result of boiling where the H_2S is distributed from the liquid phase into the vapour phase. This removes the ligand from the gold according to:

$$Au(c) + H_2S\,(aq) + HS^- = Au(HS)^{2-} + \tfrac{1}{2} H_2\,(g)$$

and the gold (and silver) then deposits. Later experiments with a pilot extraction plant showed that the gold deposited rapidly within 0.2 – 0.3 seconds. This, and later work led to more focused exploration methods for these types of gold and silver deposits.

One size does not always fit all: The risks associated with mining-derived wastes in a residential suburb, Thames, New Zealand

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The Moanataiari subdivision, Thames, was reclaimed from the Firth of Thames between the 1870s and 1970s, in part using waste from historical mining activities. Due to this geological heritage, arsenic, cadmium, lead and thallium concentrations in Moanataiari soils exceed their respective Soil Contaminant Standards incorporated by reference in the National Environmental Standard for Assessing and Managing Contaminants in Soil to Protect Human Health.

However, the generic Soil Contaminant Standards can be over-protective at many sites because they must be applicable to a range of different situations. The principal contaminant was arsenic. Elevated concentrations of lead, cadmium and thallium were also present in some samples. At Moanataiari, arsenic and lead bioavailability were assessed using the Relative Bioaccessibility Leaching Protocol and found to be 27 % and 57 % respectively – significantly less than the 100 % assumed in the derivation of the generic soil standards. Considering site-specific factors, the estimated health risks were calculated to be substantially less than indicated by the Soil Contaminant Standard.

This assessment reinforces the need to consider the geochemistry of a contaminated soil. Based on this “Tier 2” site-specific contaminated land health risk assessment, soil contamination in western areas of Moanataiari does not generally appear to pose a significant health risk, once bioavailability is taken into account.

The Moanataiari experience shows that biogeochemical considerations can have great real-world significance. In particular, the experience highlights the need for effective communication of highly technical information, meaningful community engagement, and how to bring together science, policy, and community perception to allow effective collaboration between agencies with diverse drivers.

Early dark micaceous alteration in the Radomiro Tomic porphyry copper deposit: A mineralogical, lithogeochemical and thermodynamic study

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In porphyry copper deposits around the world, descriptions of early high temperature hydrothermal alteration types commonly include Early Dark Micaceous (EDM) veins, also termed as Green Mica Veins (GMV), in addition to the traditionally described “white quartz-sericite” association that defines phyllic alteration. Green mica veins (sericite/muscovite) are dark, as compared to phyllic alteration, but the causes of color differences are not clearly described. In the Radomiro Tomic porphyry copper deposit, Chuquicamata district, various hydrothermal alteration types containing sericite have been recognised, these discriminated in two main groups: green sericite and white sericite. These determinations are based on the proportions of these minerals, but mineral overprints of white sericite over green cause mapping and interpretation uncertainties. To aid mapping techniques and mineral discrimination, a lithogeochemical, mineralogical and fluid inclusion study of both alteration types was carried out, together with determination of genetic and time evolution differences of these two alteration types. By means of lithogeochemistry, calibrated to mineralogical characterisation, easy, low cost and observer independent techniques were developed to provide quantitative mineral determinations that may aid geological mapping and refine geological models in porphyry copper systems. In addition, recognition of distinct mineral associations, lithogeochemical differences, and determination of formation temperatures and salinities, have allowed interpretation of the hydrothermal alteration evolution pathways from high temperature GMV veins to lower temperature white sericite alteration.

Use of field portable XRF in chemostratigraphy and lithogeochemical vectoring towards mineralisation, Kulumadau epithermal gold deposit, Woodlark Island, PNG

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The Kulumadau low-sulfidation epithermal gold deposit (3.8 Mt @ 2.3 g/t) is located within the Papuan Island Terrane of Woodlark Island, Papua New Guinea. The deposit is hosted within milled matrix brecciated lenses and veins which cut the mid-Miocene andesitic Okiduse Volcanics. These units are in turn overlain by the Quaternary Kiriwina Formation and colluvium. Defining the spatial continuity of the various volcanic rock types of the Okiduse Volcanics from drill core is complicated by the pervasive nature of hydrothermal alteration, post-mineralisation faulting and the extremely humid conditions, which have almost completely oxidised sulfide-bearing diamond drill cores recovered as recently as 2012. To help define the stratigraphy of the Kulumadau deposit, chemostratigraphy has been constructed using fpXRF data using various forms of cluster analysis and compositional data analysis on log-ratio transformed data. These techniques were also used to quantify the effects of hydrothermal alteration, identify faults (palaeo-conduits for mineralised fluids) and indicate vectors towards higher grade mineralised zones. Immobile element analysis has been able to identify cryptic alteration facies. The spatial distribution of these facies suggest that propylitic assemblages defined by chlorite ± hematite and pyrite are the product of rock-buffered alteration related to the infiltration of meteoric fluids into the hydrothermal system. Propylitic facies are typically barren of Au and base metal mineralisation, whereas those areas with phyllic to argillic assemblages exhibit elevated gold and base metal contents and are the result of fluid buffered alteration related to the interaction between the andesitic host rocks and high-level magmatic derived fluids. High gold contents appear to have a spatial affinity with areas approaching the juncture of phyllic/argillic and propylitic altered zones; in these zones, fluid mixing appears to be an important mechanism in the precipitation of Au and base-metals.

Multiscale analysis of regional geochemical data

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This paper presents a method of multiscale analysis of regional geochemical data. A shift-invariant stationary wavelet transform (SWT) was used to undertake multiscale decomposition of regional geochemically-interpolated grids using an optimal selection of the wavelet basis function. The optimal decomposition level occurs when the resulting statistical distribution approximates a uniform distribution. At each scale, the approximation surface is not directly taken as the geochemical background, which will vary in accordance with geochemical anomalies determined by the corresponding detail coefficients of SWT of the regional geochemical data. The lower limiting value of geochemical anomalies from multiscale detail coefficients of SWT can be determined using statistics methods. The multiscale detail coefficients of SWT of the regional geochemical data are plotted on cumulative frequency graphs, and anomaly

thresholds are defined by the upper inflexions of the plots. Areas containing more multiscale geochemical anomalies are more favorable to mineral prospecting. Fine structure and local variation of regional geochemical anomalies can thus be acquired using the method of multiscale analysis, assisting the identification of geochemical anomalies relating to mineralisation. This method is illustrated by using regional geochemical data from the Jiangxi and Yunnan provinces, China.

Regional geochemical anomalies at Simao Cenozoic rift zone, SW China

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Regional geochemical anomalies can distinguish major tectonic units, helping to unravel crustal evolution and assist mineral exploration. The Simao Cenozoic rift zone has recently been considered to be an active continental rift, resulting from thermal upwelling of the asthenosphere. This interpretation is supported by structure, the sedimentary record, the geochemistry of igneous rocks and geophysical data. A large regional geochemical data set of about 15,900 evenly distributed stream sediment samples, each representing a 2 km to 2 km area, collected and analysed by the Chinese national geochemical mapping project during the 1980s, was used to outline the Simao Cenozoic rift zone. The geochemical anomalies clearly reflect the rift zone, and show that it is enriched in F, B, K_2O, Na_2O, MgO, Co, Ni, Cr, Fe_2O_3, V, Ti, Mn, Cu, Hg, Sb, Mo, Bi, Sn, Nb and Y, but depleted in Ag, Pb and Zn. Multivariate statistics and spatial interpretation of the geochemical data suggests three major factors associated with the geological evolution of the Simao Cenozoic rift zone. The enrichment of siderophile elements (Co, Ni, Cr, Fe_2O_3, V, Ti, Mn and Mo) in the rift zone is attributed to upward migration of mantle material. The distribution of K, Na, Mg, B and F coincides with late Cenozoic basins that infill grabens, as well as with salt deposits. The chalcophile elements (Cu, Hg, Sb, Bi and Sn) display dispersion patterns associated with clusters of economically interesting Cu deposits. Multi-disciplinary methods were used to investigate the structure and tectonic evolution of the Simao Cenozoic rift zone, assisted by the regional geochemical patterns.

Geostatistical analysis of geochemical and organo-geochemical data applied to mineral exploration in Northern Chile

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Within a joint Codelco-Chile and University of Chile research program, systematic soil gas sampling was undertaken in three exploration prospects lying beneath transported overburden and post mineralisation rocks in northern Chile. Sampling was carried out along 400 x 500 m grids using ORE HOUND GOCC collectors. The collectors are passive devices buried in the soil, especially designed to capture free ions and gaseous hydrocarbon compounds that have migrated from depth and that deliver, in a short period of time, a response to the presence of covered underlying

ore bodies. From the collectors, 72 chemical elements and 162 hydrocarbon compounds were assayed, for a total of 314, 417 and 618 samples in the respective exploration areas. The multivariate database was used to define exploration targets and determine geological, geochemical and/or organo-geochemical relationships between samples. In the first data processing stage, a thorough quality control evaluation was completed, to ensure that the assayed variables possess suitable confidence levels, commonly reducing the number of variables to study. The second stage corresponds to a multivariate statistical analysis in order to interpret the relationships between variables and to detect anomalous data. This analysis is complemented by a factorial kriging analysis, by incorporating the spatial information and by distinguishing different scales of spatial variation, as given by the set of direct and cross variograms of the variables under study. This way, it is possible to filter out measurement errors (nugget effect), local and regional trends, and to independently observe the contrast anomalies of interest. In the studied prospects we have recognised the influence of structural factors, in the migration path of gases and free ions toward surface, plus lithological and hydrogeological control in shaping contrast anomalies.

Geochemical methods in studies of recent and past environmental changes

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A multi-proxy approach is advocated in studies of recent and past environmental changes, as the use of too few diagnostic criteria often leads to misinterpretations. Geochemistry is a powerful tool which, when combined with other proxies, can provide information on short- and long-term changes preserved in the sedimentary record. Geochemical methods used in the studies presented here include ion chromatography, ICP-AES, ICP-MS, portable-XRF and X-ray core scanning. While IC, ICP-AES and ICP-MS are well established techniques, P-XRF and X-ray core scanning have only recently been used in geosciences, particularly in Australasia. The latter, coupled with magnetic susceptibility, produces a continuous record along the length of a core with high resolution fingerprinting of environmental changes, albeit with qualitative data. Portable-XRF is a rapid non-destructive method, but results are semi-quantitative. Here we discuss the application of these two methods in recent studies.

Long- and short-term environmental changes in Moawhitu Wetland, d'Urville Island, New Zealand, were reconstructed using a suite of multi-proxy analyses. It was high resolution X-ray core scanning though that provided the geochemical evidence for tsunami inundation into the wetland, beyond the extent of any sand deposit. ICP-AES and ICP-MS analyses of selected samples were also used to quantify and corroborate the results of the X-ray core scanning.

Portable-XRF is more commonly used in archaeological studies, although it has recently been used to map the inundation limit following the 2011 Tohoku-oki tsunami, and to assess the longevity of marine chemical markers in different sediment types. Concurrent analyses of water-leachable ions by IC and ICP-AES were also used to corroborate the results of p-XRF analysis, confirming the occurrence of saltwater indicators in the sediment.

Geochemical mapping of tsunami inundation: Beyond the sand

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Tsunami deposits range from mud to boulders, depending upon the material available for transport by these devastating waves. As sandy beaches are most often eroded, many of the reported tsunami deposits are dominated by sand, and are identified in the geological record as an anomalous sand layer within a soil or peat profile, a bit like a layer cake. However, recent post-tsunami surveys have shown that the sand layer may extend up to only 60-70% of the tsunami inundation limit, and is thus not representative of the magnitude of the event. This invariably leads to underestimates of the size of the tsunami and the generating event. As shown by the 2011 Tohoku-oki tsunami in Japan, this can have devastating outcomes. While the inundation limit can be mapped immediately after the event using the extent of debris, salt-burned vegetation and water marks, this evidence is often lost over time and is therefore absent in the geological record.
Here we report on two studies, where the tsunami inundation limit was mapped using geochemical methods. Six months after the 2010 Maule Tsunami in Chile, the limit of inundation was identified based on chemical and microfossil data. In Japan, geochemical markers allowed the precise limit of inundation to be identified in the absence of any sedimentological evidence. Follow-up studies also revealed that the marine geochemical signature was preferentially preserved in the mud component of the tsunami deposit which is found inland beyond the limit of sand deposition. As no marine microfossils were recovered in this area of Japan, geochemical mapping is proving to be the only means by which tsunami inundation maps can be redrawn allowing tsunami mitigation measures to be re-assessed.

Phosphorus speciation in soils peripheral to meltwater ponds of Victoria Land, Antarctica

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Meltwater ponds are the most common habitat for terrestrial biota on continental Antarctica. The productivity of benthic cyanobacteria (the dominant biomass) is considered to be limited by phosphorus availability in inland areas, but sources of P and factors limiting its bioavailability are poorly understood. Consequently, it is difficult to predict how productivity will be affected by climate change-induced increases in pond size and volume. As part of a larger research programme to determine the P biogeochemical cycle for meltwater ponds, this study has explored P concentration and speciation in the soils near the ponds, to identify additional potential sources of P to the pond water during periods of increased temperature and greater meltwater volume. Over three years (2011 – 2013), soils were collected (together with sediments, waters and biological material) from 15 ponds from 3 areas of the Dry Valleys, and from 7 ponds in the McMurdo Ice Shelf / Ross Island region in Victoria Land, representing inland and coastal meltwater environments, respectively. Concentrations of P were up to an order of magnitude higher in the soils of coastal ponds (mean = 2.2 g/kg), compared to inland pond soils (mean = 0.32 g/kg). Phosphorus speciation, determined using standard sequential extraction methods, indicated

that <3% of the P in the soils was in a form that might be readily released during flooding or during the seasonal anoxia that develops in meltwater ponds. However, up to 10% was in a form that could be released under alkaline conditions (pH>10), as can occur during periods of intense photosynthesis over summer. The remaining P (70 to 99%) was refractory and less likely to be readily dissolved during soil flooding, though weathering of apatite and/or dissolution of refractory oxide phases may release P in the longer term, particularly from the relatively P-enriched coastal soils. In coastal ponds on the McMurdo Ice Shelf, pond sediments had <25% of the readily exchangeable P concentration in adjacent soils, and up to 40% less total P, confirming immediate and longer term release of soil P into pond water.

Biogeochemical orientation surveys in the Reefton Goldfield, New Zealand

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Biogeochemical orientation surveys were conducted in two areas near Reefton in the South Island of New Zealand: the T38 target (T38) and the Blackwater Creek (Waiuta) prospects, both potential orogenic gold quartz vein systems. Six common plant species were sampled: black beech (*Nothofagus solandri*), red beech (*Nothofagus fusca*), silver beech (*Nothofagus menziesii*), Westland quintinia (*Quintinia acutifolia*), ferns (*Blechnum spp.*) and rimu (*Dacrydium cupressinum*). 169 samples were analysed for 53 elements. At the T38 target prospect, foliage from three species of beech was analysed and the element distributions plotted. Two northwesterly trending zones of enrichment were identified, one with coincident enrichments in Ca, Ba, As, Sb, Cu, Li, Cs and Rb, and the other with coincident enrichments in Au, Co, Mo, Mn, Se, REE and Pb. However, in general, element concentrations were not particularly remarkable, except for one site yielding 4.8 ppb Au in dry tissue – about 50 times background levels of Au (<0.2 ppb Au). This was coincident with slightly elevated levels of several other elements commonly occurring as pathfinder elements for Au (e.g. Bi and Se). At the Blackwater Creek prospect, foliage from the small tree Quintinia was analysed. No indications of Au mineralisation were identified, although it appears that Quintinia is less sensitive to many elements than the beeches. There are two zones of distinctly different chemical composition: 1) in the north there are relative enrichments of B, Ba, Cd, Cu, Hg, Li, Mg, Ni, P, Rb, Sb, Sr and Zn; 2) in the south the coincident suite of elements is Ca, Cr, Cs, Mn, Mo and Pb. Additional information on the relative uptake of elements by ferns (notably high levels of REE) and the conifer, rimu, provides what is probably a first database for New Zealand on multi-element concentrations in these common species, providing a baseline dataset for future surveys.

Sulphide minerals in waste rock used as construction fill and their effect on groundwater chemistry at the Martha Au-Ag mine, Waihi, New Zealand

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Chemical and isotopic characterisation of groundwater, as well as geochemical testing of waste rock was used to identify sources contributing to increased levels of sulphate in shallow monitoring wells at the Martha Mine tailings storage facility, Waihi, New Zealand. Waste rock is used as construction fill and contains pyrite (about 0.3 wt%) and goethite, the latter indicating that the deposits are in an advanced stage of oxidation. X-ray diffraction and shake flask tests of the fill material indicate the main soluble sulphate minerals are gypsum, epsomite as well as iron and manganese sulphates. On average, about 0.04 wt% water-soluble sulphate is present in the fill, but amounts vary spatially; concentrations up to 0.12 wt% are present in restricted areas within the deposit. Net acid generation tests and acid base accounting confirms that some localised regions of fill are potentially acid forming; however, most samples are classified uncertain. Analysis of isotopic signatures ($\delta^{18}O$, δD, $\delta^{34}S$) indicates groundwater sulphate, which currently ranges from ~3 to 100 mg/L, is predominantly the result of mixing between two primary sources: (1) pyrite present in the oxidised waste rock (average $\delta^{34}S$ of 2.1‰), and (2) atmospheric sulphate derived from precipitation (average $\delta^{34}S$ of 20.9‰). In wells affected by pyrite oxidation, isotope dilution calculations suggest between 3 and 78% of the sulphate is sourced from pyrite oxidation, with an average contribution of 25%. In a few of the monitoring wells, some of the sulphate is derived from other sources resulting in anomalous stable isotope compositions. Minor amounts of additional sulphate, with $\delta^{34}S$ values similar to that of atmospheric sulphate (~20.9‰), yet depleted in ^{18}O ($\delta^{18}O$ of 0 to -1‰), are incorporated through the oxidation of organic sulphur in carbonaceous layers beneath the fill. Once in the shallow groundwater, bacterial sulphate reduction is a locally important process resulting in removal of sulphate and metals.

Platinum stable isotopes in ferromanganese crust and nodules as a paleoceanographic tracer

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In the modern oxic ocean, many trace metals are concentrated in hydrogenetic ferromanganese crust and nodules relative to upper continental crust (UCC) (Hein et al. 2012). This enrichment, combined with an increased industrial demand for platinum group elements (PGE), REEs, and other metals, is leading to growing interest in these sediments as a potential economic resource. These slow-growing ferromanganese oxyhydroxides are also being utilised as archives of changing ocean chemistry recording elemental concentration and stable isotopic variations (Goldberg et al. 2009). Ferromanganese oxhydroxides are the primary sink for platinum

with 80 times enrichment over pelagic sediments and up to 1300 times over UCC concentrations (Goldberg et al. 1986). Changes in seawater chemistry due to changes in source fluxes, ocean redox state, etc. may lead to small variations (< ±1‰) in the platinum stable isotopic composition. Platinum is a non-bio-essential, highly siderophile metal with six naturally occurring isotopes with several oxidation states. A method has been established using MC-ICPMS to precisely measure Pt isotopic compositions using a ^{196}Pt-^{198}Pt double spike to correct for instrumental mass bias. Pt is separated from the Fe-Mn oxyhydroxide component of the sediments by means of anion exchange chemistry, with ≥ 80% yields and ≥ 85% purity, as determined for three natural nodule standards and the IRMM 010 Pt isotopic standard. Analyses of natural and experimentally synthesised ferromanganese oxyhydroxides will be conducted to evaluate the speciation, incorporation and isotopic composition of Pt, which will aid in the overall understanding of Pt in the marine environment.

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From tree-tops to massive sulphide in the Mabel Lake area, British Columbia, Canada

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Located in southern British Columbia, the Mabel Lake area is an extensive region with dense forest and rugged terrain that poses significant problems to conventional exploration and mapping. Glacial deposits cover metamorphosed calcareous rocks, quartzites, biotitic and graphitic schist of the Monashee sequence that host Zn-Pb deposits such as Kingfisher and Ruddock Creek. In 2005, the Geological Survey of Canada conducted a reconnaissance survey to provide a biogeochemical dataset for this region. 562 Douglas-fir tree top samples were taken from a helicopter over c.700 km^2. Analysis of the tissues indicated significant Tl and Cd anomalies east of Mabel Lake and detailed follow-up sampling using Western Hemlock bark outlined a Tl anomaly some 300x400 m across. In 2010, Ah soil sampling within the Tl anomaly identified anomalous Mo and Zn concentrations in addition to the Tl-Cd association. In 2011, trenching across the centre of the biogeochemical anomaly revealed a gossan-rich zone, 10-35 wide and >50 m long, composed of quartzitic marble with sphalerite, graphitic and micaceous quartzite, and semi-massive gossan and sulphides. Best concentrations included: Zn – 3 m @ 8.98%; Re – 580 ppb; Mo – 1339 ppm, and anomalous Cd, Cu, Bi, Ni, Sn, Tl and W. A HeliTEM electromagnetic survey was flown to outline the extent of the anomaly and to explore other adjacent areas. Results showed a significant electromagnetic conductor and magnetic responses in the area of the trenching, and anomalies of similar magnitude elsewhere that have yet to be investigated. In 2012, a reconnaissance diamond drilling programme intersected Zn-rich massive sulphide beneath the trenches, and prospecting also discovered more Zn-rich gossan 200 m southeast of the drill sections. This grassroots study demonstrates the successful linkage between biogeochemistry, geophysics and geology to identify significant mineralisation.

Preliminary results of an environmental risk perception carried out in the industrial city of Estarreja, North Portugal

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This study presents preliminary data from an environmental risk perception study. The study received ethical approval from the National Committee for Data Protection (CNPD). We are investigating the public's perceived health risks associated with environmental pollution from a number of identified sources. A sample of 20 subjects was interviewed and a questionnaire was voluntarily filled out by the participants. This questionnaire included specific questions related to subject characteristics, to household and neighborhood characteristics and to perceived risks of certain environmental hazards to human health. All subjects confirmed that they were concerned with the environmental quality of the region. Unlike some men, all the women interviewed considered that the region is polluted. The majority think that the air is the most polluted pathway providing exposure to contaminants, while less polluted pathways included soils (men) and water (women). In general, the participants thought that they received enough information about environmental issues from the stakeholders (the local authority). All participants suffering from heart, bladder, skin or respiratory diseases identified the industrial Chemical Complex of Estarreja (CCE) as the major environmental pollution source. The results also showed that people have some perception of the risk posed by air and water contamination, but seem to be unaware of the risk posed by soil contamination. Most participants attributed liabilities to the Portuguese state rather than to industry, and thought that the most effective mitigation measure to reduce the environmental burden of the region is through the application of penalties. This information will become crucial at the stage of risk communication.

Thallium geochemistry during acid mine drainage treatment

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Thallium (Tl) is a toxic Group 13 element, which can be an environmental issue in some acid mine drainage (AMD) systems. Thallium can enter AMD systems either directly from sulfide oxidation or indirectly if it has become concentrated in acid neutralising materials used to treat AMD. The use of industrial waste materials as cost effective neutralents for AMD needs to be tempered by an understanding of the impact of these wastes on trace metal loadings that leave the AMD treatment system. Thallium exists in aquatic systems predominantly as the highly soluble monovalent cation with a 1st hydrolysis constant of 10^{-13} but it can form an insoluble trivalent species at high EH. Monovalent Tl^{+} is expected to be very mobile in AMD systems and, unlike other toxic cations such as Pb^{+2} and Cu^{+2}, have a low affinity for the surfaces of the Fe^{+3} and Al^{+3}

hydrous oxides that precipitate during neutralisation. This means that there is a need for extra caution with regards to the thallium content of AMD neutralents. In this work we explore the geochemistry of Tl during laboratory scale AMD neutralisation experiments with a focus on a waste $Ca(OH)_2$ product with a known elevated level of Tl.

Contrasting geochemistry of orogenic gold deposits in Yukon, Canada and Otago, New Zealand

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The Yukon-Tanana Terrane (YTT) of western Yukon Territory in NW Canada and the Otago Schist belt (OSB) of South Island, New Zealand share similar geological evolutionary histories as convergent margin orogenic belts. Both belts host orogenic gold deposits of mainly Jurassic to Early Cretaceous age. Jurassic mineralisation in the YTT occurred during accretionary orogenesis and stacking of previously-metamorphosed (Paleozoic) greenschist-amphibolite facies metasediments, metavolcanic rocks, and metagranitoids. Approximately coeval OSB mineralisation occurred in the latter stages of collision of terranes that comprised essentially un-metamorphosed turbidites with minor basaltic rocks. Metamorphism of the OSB turbidites mobilised gold and abundant As, Sb, and W, primarily under greenschist to lower amphibolite facies conditions. In contrast, the YTT rocks had little As, Sb, or W available for mobilisation in the Jurassic, and consequently orogenic deposits are distinctly lacking in these pathfinder elements. Arsenic, Sb, and W in the YTT may have been earlier removed from the rocks during the initial Paleozoic metamorphism. The YTT host rocks, particularly metagranitoids, have anomalous levels of Mo, and many orogenic deposits contain elevated Mo, predominantly as molybdenite. The OSB turbidites have elevated Mo, along with elevated Au and As, in diagenetic pyrite, but this Mo became largely dispersed through the metamorphic pile as metamorphic grade increased and pyrite transformed to pyrrhotite. The OSB orogenic deposits have only marginally elevated Mo, no molybdenite, and the accessory scheelite in these deposits is distinctly Mo-poor. Only minor mobilisation of base metals occurred in the orogenic belts, and orogenic gold deposits contain only traces of base metal sulfides. Deposits in the YTT and OSB differ in that gold and other anomalous ore-related elements in many of the orogenic deposits were remobilised from relatively local sources (e.g., pre-Jurassic Cu-Mo-Au porphyry or VMS mineralisation) in the YTT, whereas metals were homogenised from larger volumes of rock at depth in the OSB.

Applied geochemistry: Current trends and issues in Africa

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The total output in Applied Geochemistry (AG) for the Africa region, in terms of research, publications and industrial utilisation, continues to be limited, and far out of proportion in relation to the huge potential benefits that would accrue in applications to mineral exploration programmes, investigation of environmental chemical phenomena, agriculture, health and land use planning. The dearth of activities in this important branch of geoscience is manifested in many ways, a situation that has not changed significantly during the last decade, despite the growth of

commercial laboratories offering diverse high quality analytical facilities around the continent. In spite of the increased interest in mineral exploration projects by numerous mining companies, the rate of discovery of new deposits is still relatively low in comparison with areas of the world with less favourable geology in terms of mineralisation potential. For instance, South Africa, considered the world's top mining country, lags far behind Russia, Chile, United States, Canada, Australia, and the UK in total output from AG programmes. The number of research articles on Africa appearing in leading AG journals continues to be below 15 percent of world total. These statistics are surprising, given that it was in Africa (Zambia and Sierra Leone), Eire and the UK that John Webb first observed several important correlations between geochemical patterns, mineralisation, soil type and the incidence of agricultural disorders. Addressing the issues would engender a concerted effort by African governments and pertinent geoscientific institutions in training an adequate number of highly skilled applied geochemists, and concomitant massive investment in analytical geochemical infrastructure. In the short term, however, more use should be made of the high quality geochemical facilities offered by commercial laboratories, now readily available in most parts of the continent.

Distribution of lithium in Australian regolith: An indicator of potential lithium resources in salt lake brines?

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Lithium concentrations in catchment outlet sediment samples were measured as part of the National Geochemical Survey of Australia (NGSA; www.ga.gov.au/ngsa). Samples were collected at or near the outlet of 1186 catchments covering ~81% of Australia during 2007-2009. At each site a top outlet sediment (TOS) sample (0-10 cm depth) and a bottom outlet sediment (BOS) sample (~60-80 cm depth) were collected; each split into a 'coarse' (<2 mm) and a 'fine' (<75 µm) grain-size fraction. Lithium data are available for the Mobile Metal Ion (MMI®; TOS 'coarse' only) and aqua regia (AR) digestion techniques. Censored data (reported to be below the lower limit of detection (LLD) account for 32% of the MMI® dataset (LLD = 0.005 mg/kg) and are absent from the AR dataset (LLD = 0.1 mg/kg); replacement values were imputed using a nearest neighbour method. The median MMI® value is three orders of magnitude lower than the median AR concentration. Further, there is an increase in median Li for the AR digestion following the order TOS 'coarse' < BOS 'coarse' < TOS 'fine' < BOS 'fine'; in other words the deep or 'fine' samples have higher Li concentrations than their surface or 'coarse' counterparts. In order to assess the 'availability' of Li, the ratio of MMI® to AR Li (Li_Mi/Ai) was calculated and plotted. Li availability ranges from almost non-existent up to 14%. The map of Li_Mi/Ai shows that the regions of high Li availability correspond to the Yilgarn Craton, much of eastern South Australia, the southernmost, westernmost and central Northern Territory, south and western Queensland, western New South Wales and Victoria and a few coastal areas. These commonly are regions where salt lakes occur. However, assessment of Li content of source rocks and groundwaters and absence of active hydrogeological setting highlight limitations for the potential for Li-rich brines in Australian salt lakes.

Metalloids in waste rocks and waters of the mined mesothermal gold deposit, Globe Progress mine, New Zealand

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Arsenic and antimony are two metalloids commonly associated with mesothermal gold deposits and their enrichment in surficial environment may cause environmental concerns. The open-pit Globe-Progress Mine was developed on the site of historic underground workings and has been in operation since 2007. Historically, the targeted ore comprised auriferous quartz veins characterised by abundant arsenopyrite and little stibnite. At present, the mined ore is composed predominantly of sulphide-rich fault breccias with abundant stibnite.

The waste rocks at the mine are managed depending on their 'arsenic generating potential' and they are divided into non arsenic generating (NAG, <0.2 Au/t, estimated As <2000 ppm and Sb <1000 ppm) and potentially arsenic generating (PAG, <0.65 Au/t), with the latter being stored separately in a clay-lined waste pile. Analyses of waste rocks throughout the different stages of mining operations reveal metalloid concentrations up to 0.6 wt% As and 0.1 wt% Sb in NAG and up to 2.4 wt% As and 10.8 wt% Sb in PAG waste. Only 0.2% of NAG-classified rocks were found to exceed the aimed threshold for As and 2.4% exceeded the estimated Sb limit which suggests that the method of waste rock separation at the mine proceeds rather successfully.

The advent of modern mining has resulted in chemical evolution of waters draining the mine which are now characterised by circumneutral pH, high bicarbonate and sulphate and, most notably, metalloid signature of Sb/As near to or greater than 1. The natural shift from the historic Sb/As <1 was further enhanced by a ferric chloride treatment system for process waters that preferentially removed more As than Sb. The treatment of process waters is also responsible for the removal of iron from water which in turn prevents potential further metalloid attenuation through adsorption onto iron oxyhydroxide precipitates.

Lake sediment geochemistry over complex landscapes: A case study over the 'Ring of Fire' deposit area, Ontario, Canada

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Mineral exploration using lake sediment geochemistry has proven successful throughout Ontario and most recently in detecting evidence of the world class 'Ring of Fire' (RoF) chromite and Ni-Cu deposits in the McFaulds Lake area of northern Ontario. The landscape in the McFaulds Lake area is complex; coverage with peat deposits is extensive and overlies Quaternary glacial and marine deposits up to 76 m thick. Detailed lake sediment sampling over and down-ice of the mineral deposits has revealed the presence of a dispersal plume developed in the complex drift that covers the region. The use of lake sediments as a proxy to till geochemistry is particularly advantageous over such landscapes where till is inaccessible or very difficult to sample due to thick accumulations of overlying peat deposits. The lake sediments were also analysed for soil gas hydrocarbons (SGHSM) a proprietary technique offered by Activation Laboratories. Unique hydrocarbon signatures, possibly related to bacterial biomass, are thought to develop in the overburden above mineral deposits, perhaps in response to the presence of redox gradients (electrochemical cells). The SGHSM analysis was performed on 287 lake sediment samples collected over the region and submitted blind to the laboratory along with blind quality control samples for independent assessment of data quality. Quality control charts demonstrate that the variance of the unknowns greatly exceeds the variance in the performance of the standards; therefore, it is concluded that the majority of the signal is related to real variations in the concentration of the hydrocarbon compounds in the samples. An area centred on the RoF deposit area was identified as the most significant SGH anomaly. These results indicate, despite the complexity and thickness of the cover material, the known chromite and Ni-Cu-PGE deposits are imparting a significant signal that was detected by the SGH analysis of lake sediments.

Exploration geochemical studies at the concealed Pebble porphyry Cu-Au-Mo deposit, Alaska, part I: Active soil gases determined with GORE modules

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Collaborative exploration geochemical and geophysical studies by the U. S. Geological Survey and Pebble Limited Partnership (PLP) include a soil gas study completed in 2012. The concealed Pebble deposit consists of two contiguous zones: the shallow Pebble West (PW), and the deeper Pebble East (PE). From PLP, measured plus indicated resources are 5,942 million metric tons (Mt) at 0.42% Cu, 0.35 g/t Au, and 250 ppm Mo, with an inferred resource of 4,835 Mt at 0.24% Cu, 0.26 g/t Au, and 215 ppm Mo, plus significant Ag, Re, and Pd concentrations. The Pebble district consists of Jura-Cretaceous argillite, siltstone, and graywacke cut by a northeast-trending belt of multiple granitic intrusions. Late Cretaceous subalkalic granodiorite intrusions (91-89 Ma) are genetically related to mineralisation. Post-mineralisation Tertiary volcano-sedimentary rocks (300-600 m thick) unconformably overlie PE. Quaternary glacial deposits up to 50 m thick blanket the area. Active soil gases were collected using 130 proprietary GORE modules (GORE sorbers). Modules were placed in the ground along traverses across the deposit, at sites where soils had previously been collected for partial leach studies. After 28 days, the modules were collected and sent to GORE's analytical laboratory for determination of 85 organic soil gas compounds by thermal desorption-gas chromatography-mass spectrometry. Several soil gas compounds show depletion or enrichment trends over the shallow PW. No trends were observed over the deeper PE. Principal components analysis reveals the presence of distinct geochemical signals spatially related to PW. An inverted factor 4 (loaded strongly positive for CO_2 and negatively for disulfide and nonane) gives a good anomaly compared to background. A similar strong response was found for an inverted factor 5 (loaded strongly positive for dimethyldisulfide, dimethylsulfide, and benzothiazole, heptane-1 and to a lesser extent CO_2). These data suggest that a reduced chimney overlies the sulfide body at PW.

Tungsten mineralisation at the Macraes orogenic gold deposit, Otago, New Zealand

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Scheelite ($CaWO_4$) is commonly found as an accessory phase in many orogenic gold deposits. A study was performed at the Macraes gold deposit in Otago, combining geostatistics, petrography, and geochemistry to characterise the tungsten mineralisation. The mineralisation was modeled on a pit scale using grade control samples from the active open pit. These samples were analysed for gold using traditional fire assay, and re-analysed for a suite of 18 elements, including tungsten and arsenic, using a portable XRF. Two distinct domains were identified in the data: the Northern domain was characterised by high gold and tungsten grades, and the Southern domain had high gold grades, but was essentially barren in terms of tungsten. A pod of scheelite was identified in the Northern domain that extends for more than 200 m and is open both laterally and at depth. Scheelite is confined to gold-bearing quartz veins, which are closely associated with the major shear zones that host the deposit. Scheelite and quartz within these veins show evidence of ductile deformation, indicating that vein formation occurred early in the history of the shear zone during uplift through the brittle–ductile transition zone. Scheelite samples were analysed for Nd isotope composition and yielded a narrow range of $^{143}Nd/^{144}Nd$ values between 0.512407–0.512499. The calculated ε_0Nd values between -2.7 and -4.5 coincide with published εNd data from the Torlesse terrane that range from -1.9 to -4.7. This suggests that the underlying schist pile was the source of the mineralising fluid or that the Nd isotopes reached full isotopic equilibrium with the host rocks.

The use of soil gas to map concealed faults and veins: Examples from the Hauraki Goldfield New Zealand

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The mobility of gas from soil has made soil gas an attractive exploration tool in the search for geologic structures and mineral deposits concealed by post-mineral cover. We have collected more than 500 soil gas samples, measuring Hg, CO_2 and O_2, from the Hauraki Goldfield, North Island, New Zealand to critically assess the usefulness of soil gas geochemistry in a humid subtropical environment. At epithermal deposits, and over faults, soil gas Hg anomalies have been found within 25 to 50 meters of mapped faults and veins, even where the faults are covered by as much as 800 meters of sedimentary fill. Therefore, soil gas Hg can be used quickly and inexpensively to confirm or identify faults accurately in covered terrain. Repeat sampling of soil gas along established lines five times on a monthly basis demonstrated that the amplitude of soil gas Hg anomalies varies widely, but the location of anomalies remains constant. Observed variations in the soil gas Hg were consistent with fluctuations in the intensity and duration of rainfall events, with increased concentrations of up to two orders of magnitude in soil gas Hg in the dry season and depleted concentrations in the wet season. Variations of O_2

concentrations in the soil gas primarily reflect the relative amount of soil aeration, whereas $\delta^{13}C$ values of CO_2 show that its concentration is controlled by microbial degradation of organic matter. In the Hauraki Goldfield humid subtropical climate, soil gases O_2 and CO_2 do not relate to enrichment along fault zones, and do not reflect oxidising epithermal deposits.

Quantitative evaluation of ore mineralogy in the world-class epithermal Waihi vein system, New Zealand

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The Waihi vein system is a group of adularia-sericite epithermal deposits that formed as part of a single hydrothermal system between 6.0 and 6.1 Ma**.** The Martha deposit, including the Edward lode, is situated in the north-west of the vein system, while Favona lies to the north-east, and Union Hill and the vein sets of Correnso form the central portion. Gold-silver ore is hosted in quartz veins, which fill fault-fracture networks in a 10-km^2 area of hydrothermal alteration. Although mineralised vein sets have formed in a 1.5 km radius from each other, petrographic, microprobe, and quantitative evaluation of minerals by scanning electron microscopy (QEMSCAN) results show significant variability of ore mineralogy. Mineralogical commonalities of electrum, acanthite, pyrite, sphalerite and galena occur in Martha Hill, Favona and Union Hill deposits. The abundance and distribution of these minerals is variable and base metal sulfide minerals display an increased abundance in deeper samples. In the Waihi vein system, less abundant ore minerals of tetrahedrite, stephanie-pyrargyrite-prousite $[(Cu,Ag)_{10}(Zn,Fe)_2(As,Sb)_4S_{13}]$, pearceite-polybasite $[(Ag,Cu)_6(As,Sb)_2S_7][Ag_9CuS_4]$ $[(Ag,Cu)_6(Sb,As)_2S_7]$ $[Ag_9CuS_4]$, aguilarite, Au-Ag sulfides, Au-Ag selenides, stromeyerite-mckinstryite-jalpaite and a unnamed CuAgFe sulphide have been identified. The distribution and abundance of these minerals varies within veins; Au selenides and stephanie-pyrargyrite-prousite are more abundant at shallow depth in Correnso, Martha and Edward vein samples. Vein-to-vein variability in the distribution of silver-bearing minerals also occurs among the samples: tetrahedrite is most abundant within veins of Favona and Moonlight, whereas stephanie-pyrargyrite-prousite and pearceite-polybasite are most abundant in the Martha and Edward samples. Mineralogical variations produce changes in the concentrations of Se, As, and Sb in the ores that have important metallurgical and environmental implications; areas that are enriched in Se, such as Favona, required particular care during processing. Available fluid inclusion data indicate that the veins formed at approximately the same temperature, and therefore the variability in the ore mineralogy presumably reflects variations in the chemistry of hydrothermal fluids from place to place, and perhaps through time.

A holistic approach to understanding ore deposits using portable X-ray fluorescence data

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The amphibolite-facies metabasaltic rocks that comprise the Mine Mafic Package at Plutonic Gold Mine (Plutonic), Marymia Inlier, Western Australia, contain some 9.5 million ounces of gold. For the last five years, Plutonic has adopted a systematic approach whereby all underground face samples and diamond drill samples have been analysed by portable X-ray fluorescence (pXRF). This provides a dataset of over 200,000 multi-element analyses, which enables us to comprehensively enhance our understanding of the deposit's lithostratigraphy, alteration and mineralisation.

We review our current understanding of Plutonic, focusing on what has been gained through pXRF geochemical analyses, and present our latest advances in understanding of the deposit based on this technique. Recent work has focused on generating a geochemical logging schema to objectively log diamond drill core, and the characterisation of dolerite dykes. These advances enable both gold mineralisation and the late-stage intrusive rocks to be modelled more rigorously and accurately than was previously possible.

By interrogating the pXRF database at Plutonic, significant advances in the understanding of the geometry, stratigraphy, and geometallurgy have been gained; additionally, the geometry of the sometimes complex orientation of the dolerite dykes has been better understood. Incorporation of pXRF data into day-to-day geological modelling at Plutonic has resulted in more robust models than would be possible to achieve without this dataset.

Geochemical pattern of mineral systems from regional to local-based exploration by Ionex technology

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The foundation of geochemical exploration of mineral deposits, theory and practice, is based on verifying the presence of anomalous (above background) metal concentrations. Appraisal of such favorable areas involves: the magnitude of the values, the size of the area, and the geochemical zonality of the ore elements. However, uncertainty around this issue remains, in spite of extensive work and empirical data on the subject. Our proposed approach could add to the information value of the geochemical method through the use of the new model of the primary halo, termed polar geochemical systems. Such a model includes both enrichment zones and adjacent depletion zones for some ore metals. Such zones are spatially conjugated in a unified polar geochemical system. The positive anomaly of ore-forming elements is the nucleus of the systems. The ferrous group of elements formed negative anomalies in the nuclear and positive anomalies surrounding mineralisation. Such polar geochemical systems are established for regional-scale metallogenic provinces, for example gold provinces in China, the zinc metallogenic provinces of Alaska, the Leninogorsk and Zyranovsky VMS Ore Region of Kazakhstan; ore field and deposit-scale examples include the Bendigo Gold Field of Australia, the giant Strelzovsky uranium deposits of Russia, and others. A good correlation exists between the dimensions of a depletion zone of the ore-forming elements and the content of these elements in the associated enrichment zone. This correlation could be one key criterion for assessing a favorable region. Formation of such polar systems implies a frontal migration of ore elements from the periphery of the system to the centre of precipitation. Such processes can be explained by electrical energy that is generated in the Earth. For example, fluid movements form a streaming electrical potential field. There are other sources of electrical energy, when blocks of rock are stressed in active geo-dynamic environments. It may generate electrical currents of up to 105 amperes per km^3.

Recognition and evaluation of geochemical anomalies in mineral prediction

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Establishment of a prospecting model, and recognition and evaluation of geochemical anomalies are three key components of mineral prediction. This study concentrates on the recognition and evaluation of geochemical anomalies. Key technologies used for these purposes involve the use of contrast and ratio values, both of which have been fully discussed in geochemical literature. Three other geochemical parameters: the normalised areal productivity (NAP), the similarity coefficient, and the denudation coefficient, have also been used to successfully evaluate geochemical anomalies. Results show that contrast values can identify weak geochemical anomalies, and ratio values of appropriate element pairs can recognise different mineralisation types. Similarly, the NAP is an effective parameter to trace main ore-forming and pathfinder elements for common mineral deposits. Lastly, similarity and denudation coefficients are crucial parameters in the evaluation of the extent of similarity and denudation between 'observation samples' (forecast area) and 'standard samples' (known deposit).

The lithogeochemical footprint of the Relincho Cu-Mo porphyry deposit, Atacama Desert, Chile

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Porphyry copper deposits (PCDs) typically have large alteration haloes that extend several kilometers from economic mineralisation. Lithogeochemical characterisation and quantification of such alteration haloes is an important exploration tool and may be critical for discovery. The Relincho PCD in the Atacama Desert, Chile, contains six known Paleocene Cu-Mo mineralised centers hosted by four distinct porphyritic lithologies that intrude the Los Morteros granodiorite batholith (64±2 Ma). Contacts between the porphyries and the granodiorite are marked by hydrothermal breccias. The dominant alteration types observed within the system include potassic, propylitic and phyllic assemblages defined by secondary biotite + magnetite + incipient K-feldspar ± glassy limonite (after chalcopyrite), epidote + chlorite + hematite ± albite ± calcite ± pyrite, and chlorite + quartz + sericite ± calcite, respectively. Three hundred surface rock samples were collected in a grid covering a 64 km^2 area centered over the mineralised porphyry centers, with proximal spacings of 250 m and distal spacings of 500 m.

These samples were used to assess the suitability of surface rocks as a medium for determining alteration type and intensity via lithogeochemistry. Aqua regia, pressed pellet XRF, and fusion-ICP results, combined with short-wave infrared spectra, feldspar staining, petrography and field observations, were used to classify lithologies and identify and quantify hydrothermal alteration. Molar element ratio diagrams distinguish the effects of fractionation from metasomatism, allowing for hydrothermal alteration characterisation and quantification. These plots indicate that minor Ca loss and minor K addition accompanied the selective/incipient muscovite alteration of the calcic component of plagioclase, the phlogopitic alteration of hornblende, and the incipient K-feldspar alteration of plagioclase. This is interpreted as a manifestation of phyllic and potassic alteration, the latter of which is strongly associated with economic Cu-Mo mineralisation.

The Ambient Groundwater Geochemical mapping programme in Ontario: Multiple controls on groundwater geochemistry

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The Ambient Groundwater Geochemistry mapping programme of the Ontario Geological Survey is characterising groundwater quality in rock and overburden aquifers at a consistent density of 2 samples per 10x10 km ‘node’; one sample each from a well finished in glacial overburden and bedrock. Samples are analysed for field parameters, major ions, trace elements, bacteria, dissolved gases and isotopic parameters including enriched tritium. In order to determine true geochemical background concentrations, many of the trace analyses have extremely low detection limits; in some cases below 1 part per trillion. Sampling began in 2007 and analytical results for southwestern Ontario were published in 2011. The 2013 field season completes the sample coverage for all of southern Ontario with more than 2000 samples collected across an 80,000 km^2 area. Publication of the remaining data is scheduled for 2014 with all data available both database and ‘OGS-Earth’ format. Results show that, with several notable exceptions, bedrock water chemistry is controlled by aquifer composition. The lithological influence of shale, carbonate, evaporites, sandstone and crystalline Precambrian shield rock are easily differentiated one from another. Within each lithotype, major and trace element chemistry varies sufficiently that the influence of particular units and formations can often be differentiated. The exceptions to lithological control on water chemistry include: (1) areas of Pleistocene Champlain Sea influence in eastern Ontario, (2) areas where karstic flow predominates, and (3) the ‘Niagara anomaly’; a >2000 km^2 zone of intensely degraded water quality possibly related to leakage of historic gas wells in the region. The influence of the Champlain Sea is evident, among other factors, by halogens concentrations that range up to those of almost pure sea water. However, in the case of iodide, concentrations regularly exceed those of seawater by up to 100 times.

Exploration geochemical studies at the concealed Pebble porphyry Cu-Au-Mo deposit, Alaska, part II: Self-potential, soil partial leaches, and reduced chimneys

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Surface geochemical methods were tested on transects across the shallow Pebble West (PW) and deeper Pebble East (PE) zones that comprise the Pebble Cu-Au-Mo porphyry deposit in Alaska. Methods include Soil Gas Hydrocarbon, GORE module (GORE Sorber), and seven commercially available partial leaches that measure weakly bound metals across a range of strengths. Surface electrical geophysical data are also available, including spontaneous potential (SP) and resistivity, which allowed the development of a model for subsurface electrical current sources. All geochemical methods show responses across the PW zone, which is exposed at one location but otherwise is concealed by younger rocks and glacial deposits. The SP response related to PW along the geochemical transect is distinct, with a -25 mV baseline response punctuated by three strongly negative zones as low as -300 mV. The electrical current source model identifies subsurface centers of strong electrochemical activity. Soil geochemical results show clear patterns related to the strong current sources, with opposite responses for cationic and anionic species. For example, several partial leach extractions show the cation Cu has the strongest response at the center of the negative current sources, whereas the anion Cl has the strongest response coinciding with adjacent, but weaker, positive current sources. Therefore, along the transect, the anionic anomalies have a rabbit-ear morphology. The electrochemically influenced soil anomalies at PW and a large fault-localised geochemical anomaly over the PE zone result in the juxtaposition of two soil geochemical signatures that are related to two distinct mechanisms. The GORE Sorber data for CO_2 show a clear and uniform depletion across the deposit with elevated concentrations near the edges. Considering the extremely low carbonate content of the soils, and that GORE Sorbers measure true active gases, this signal may be related to microbial activity in the soil substrate near the deposit edges.

Children's blood lead levels (BLLs) in urban and suburban areas of China from 1997 to 2010

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Lead poisoning is an important environmental disease that can have life-long adverse health effects. It can result in serious toxic reactions in the infant human body, and children are more vulnerable to lead exposure than adults. Most people are exposed to lead through breathing air which contains very fine particles of lead and/or through swallowing dust or dirt that is contaminated with lead. Recently, BLLs (Blood Lead Level) of children from developed countries have been sharply reduced. In contrast, in developing countries, the lead pollution situation is more serious. This study presents the results of BLLs of Chinese children from urban and suburban areas and its related factors. Some of the instructive conclusions that have been drawn include the following. BLLs have decreased significantly since 2000, when the Chinese government banned the use of leaded gasoline. Strong correlations between BLLs and lead

concentration in soil and dust of 26 cities of China were obtained. BLLs also showed a linear correlation with annual average PM10, especially when PM10＞100µg/m^3. Coal accounts for much of China's energy consumption, and this can cause serious lead pollution of air and soil. The reviewed data shows a good correlation between the coal consumption of different provinces and BLLs. Meanwhile, the total oil consumption of 30 provinces did not correlate with BLLs. We conclude that coal use is the dominant factor influencing lead exposure for children, after the phase-out of leaded gasoline. Overall, although the lead phase out regulation has reduced the BLLs of Chinese children, lead control in China has not been vigilant. Vast reservoirs of lead still exist in air, soil, dust, and house paint which will continue to contribute to the children's lead burden for many years to come.

Geochemical and mineralogical dispersal in till from the Mount Polley Cu-Au porphyry deposit, central British Columbia, Canada

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The Mount Polley Cu-Au deposit is a calc-alkaline, silica-under saturated porphyry deposit, owned by Imperial Metals Ltd. It is hosted by intrusive rocks of the Quesnel terrane and situated within the Interior Plateau of British Columbia, Canada. Drift prospecting is the exploration tool used to detect buried mineralisation in glaciated terrain. Glaciers are dynamic, eroding the underlying bedrock, modifying, transporting and depositing it as till, down-ice from the source rock. If the glaciers eroded mineralised bedrock, its signature will be present in till. The aim of this research is to apply drift prospecting methods to characterise the geochemical and mineralogical signature in till from Mount Polley. This research is funded by the Geological Survey of Canada's Targeted Geoscience Initiative (TGI-4) program. Till samples were collected up ice, overlying and down ice from the Mount Polley deposit and the geochemical and mineralogical data from these samples were plotted to map the dispersal. Elements associated with the mineralisation, which could be useful in drift prospecting include Ag, Cu, Mo and Zn. Similarly, associated minerals commonly referred to as porphyry indicator minerals (PIM's), include chalcopyrite, epidote, garnet, and red rutile. Results reflect elevated contents near mineralisation, progressively decreasing towards the northwest, which is also the dominant ice flow direction in this region. These include elevated copper content in the clay-sized fraction (maximum 1525 ppm), elevated gold grain content in the silt and fine-sand fraction (up to 105 grains per 10 kg), and chalcopyrite in the 0.25-0.5 mm fraction (up to 12 grains per 10 kg). The epidote content (up to 267 grains per 10 kg) in the 0.25 – 0.5 mm fraction reflects the propylitic alteration and might become a key indicator of buried propylitic alteration associated to porphyry mineralisation.

Surficial geochemical patterns above blind mineralisation in glaciated terrains: Some thoughts on their formation and preservation

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Exploration geochemistry in glacial terrains has traditionally relied on basal till sampling to detect down-ice dispersal trains of mineralised rock or 'indicator minerals' derived from subcropping mineralisation. Indeed, many discoveries have been made using this approach. For local scale exploration however, till geochemistry has some significant drawbacks. First, the necessity to collect very large samples (>10kg) means that it can be expensive and logistically complicated. Second, till samples require specialised and expensive processing to extract indicator minerals. Third, a good understanding of the ice-flow history and glacial sedimentology are important for optimising survey design and sampling. Finally, and perhaps most importantly, till geochemistry provides little or no information about the bedrock geology directly below the surface. To 'see through' till and other types of glacial sediment cover 'Deep Penetrating' geochemical methods need to be used.

This presentation describes strategies for deep penetrating geochemistry in glacial terrains and discusses possible mechanisms by which metal ions migrate to the surface through sometimes considerable thicknesses of glacial sediment cover and bedrock. It describes the different manifestations of the 'mineralisation signal' that may be found in the near surface environment and illustrates them with recent case histories from northern British Columbia and Ontario. Finally, the role of organic media in the capture and concentration of mobile metal ions is examined and a model explaining the formation and preservation of observed geochemical patterns in the upper parts of the soil profile above blind mineralisation is proposed.

The use of organic media in the geochemical detection of blind porphyry Cu-Au mineralisation at the Woodjam Project, British Columbia, Canada

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Plant exudates can contain metals translocated from underlying mineralisation. These materials (saps, transpired fluids, salts and particulates on leaf surfaces) may provide simple and cost-effective sample media for detecting mineralisation through transported cover. A Geoscience BC-funded study carried out at the Woodjam project in central BC tested the geochemical response of exudates and spruce tissues collected over the blind Deerhorn porphyry Cu-Au system. HR-ICP-MS was required to obtain low ppb and ppt detection limits for some ore and pathfinder elements in the exudates. Results are compared with data from Ah horizon and soil charcoal samples. Over mineralisation, spruce samples showed elevated levels of Au, Cu, S and Sb. Cesium anomalies appeared to indicate the position of potassic alteration associated with mineralised zones. Similar results were obtained in charcoal samples collected from the bottom of the A horizon, notably for Rb, Ca, As and Cu. Transpired fluids were anomalous in Cu, S and Tl over the mineralisation. Congealed sap collected from the surface of spruce trees was enriched in Cu and the pathfinder elements W, Hg and As. Of note is that non-essential and potentially toxic elements commonly associated with mineralisation, such as

As, Hg, Tl and W, can enter plants via their roots and be translocated through the plant. Analysis of plant tissues shows that a portion of these elements precipitates in plant cells, but a significant portion continues through the plant in solution to be exuded with sap and transpired fluids.

Marine rare earth element deposits: Complementing the global rare-earths wealth

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Rare Earth Elements (REEs) are critical for a large array of green-technology and energy applications. Over the past decade, China has supplied the global market for REEs; but increasing internal demand for REEs and China's change to higher-value manufactured products has caused a significant decrease in exports that is expected to continue. Consequently, other sources for land-based REEs are being explored. Deep-ocean mineral deposits can offer a partial solution to this projected shortage. We provide quantitative comparisons in terms of grade and tonnage of marine and land-based deposits. The Clarion-Clipperton Manganese Nodule Zone (CCZ) in the NE Pacific and the central Pacific Prime Ferromanganese Crust Zone (PCZ) are compared with the two largest land-based REE mines, Bayan Obo (Obo) in China and Mountain Pass (MP) in USA. These land-based deposits are much higher grade but lower tonnage of ore (MP 0.48 x 108 tonnes at 7.0% Total REEs as Oxides (TREO); Obo, 8.0 x 108 tonnes at 6% TREO) compared to the CCZ (211 x 108 tonnes at 0.07% TREO) and PCZ (75.3 x 108 tons at 0.21% TREO). These grades and tonnages correspond to tonnes of TREO of 4.8 x 107 Obo, 0.34 x 107 MP, 1.5 x 107 CCZ, and 1.6 x 107 PCZ. The fractionation of light and heavy REEs is also important. Large land-based deposits have less than 1% heavy REEs (HREEs), whereas the CCZ has 26% HREEs and the PCZ, 18%. The prices for the HREEs are much higher than for the light REEs. An important environmental concern is the high levels of radioactive thorium in the land-based deposits (100s of ppm) in contrast to low thorium in marine deposits (mean 15 ppm CCZ; 12 ppm PCZ). REEs in the marine deposits would be recovered as byproducts of Ni, Cu, and Co mining. An additional potential source for marine REEs is REE-rich muds discovered recently in the Pacific; however, they are unlikely to be economically recoverable without being accompanied by a large-market main metal.

Behaviour of arsenic in the sediments of New Zealand lakes

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Although arsenic is commonly attributed to specific sources, a survey of 28 lakes shows that it is also present in the sediments of all New Zealand lakes where it is remobilised and recycled as part of natural diagenesis. In the Taupo Volcanic Zone arsenic is commonly discharged into waterways from both natural geothermal discharges and waste waters from geothermal power production. Arsenic V stripped from the water column is transported to the sediments of both volcanic lakes within the Taupo Volcanic Zone and to lakes filling hydro-electric dams on the Waikato River. Particulate organic matter produced within the lakes also settles lowering the redox potential within the sediments and results in iron, manganese and arsenic concentrations to increase markedly within the pore waters, causing these elements to be constantly recycled up the sediment column. Increasing eutrophication appears to accelerate this process. As a result of the diagenetic recycling, the concentration of arsenic generally exceeds drinking water tolerance in the bottom waters of most of the lakes surveyed.

Recycling of silicon from New Zealand lake sediments

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Intact sediment cores taken from the deepest basins of 28 New Zealand lakes show that the Si concentrations in pore waters and the flux of Si to the overlying lake water can be modelled assuming first order kinetics for the rates of dissolution or precipitation and Fick's Law. We have applied the model developed for silicon transport ($cx = c\infty + (c0 - c\infty)\exp(-x\sqrt{(k/D)})$; Pearson et al. (in press)) using gradients of the pore water concentration (cx) of silicon measured in the sediments of lakes ranging in trophic state from oligotrophic to supertrophic. The model simulated the Si transport gradient with high precision ($r^2 > 0.95$, $p > 0.01$) in lakes with uniform sediment lithology or no significant geothermal discharges to the lake water. The lithology of the sediments was a significant determinant in the steady state pore water concentration of silicon as observed at depth within the sediments. Sediments dominated by diatomaceous ooze or rhyolitic glass shards achieved steady state concentrations ($c\infty$) of 25 – 30 mg Si L^{-1}. Sediments dominated by greywacke, granite or schist silts had much lower $c\infty$ values. The extent of the flux of Si was also found to be controlled by the trophic status of the lake, being greatest in eutrophic lakes where diatom populations were able to reduce epilimnitic silicon concentrations (c0) to < 1 mg L^{-1}. The pore waters of lakes with significant geothermal fluid influxes also fitted the Pearson et al. model but with the sign reversed to allow precipitation rather than dissolution. Evidence for this process was observed in the sediments of Lake Rotomahana where diatoms are encrusted with clusters of micron diameter silica spheres.

Plentiful parameters promoting pathfinder performance for plant picking prospectors: Accounting for environmental variables for biogeochemical techniques for mineral exploration in semi-arid Australia

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Although biogeochemical exploration techniques can offer an efficient and effective provision of subsurface geochemical information, they have had a more limited uptake and application in Australia. This is despite transported cover providing one of the greatest exploration challenges for this continent! This presentation examines some of the reasons for this limited uptake and application as well as ways that they have been addressed in recent research. Some of the main perceived limitations to the application of biogeochemical exploration techniques in Australia include:

- High species diversity and limited range of some species across Australia;
- Poorly constrained sampling and analytical procedures specific to Australia;

- Temporal and spatial variations in results, independent of underlying substrate variations; and,
- Greater popularity and familiarity with other exploration methods, such as soil, calcrete, ferricrete geochemistry, hydrogeochemistry and geophysical approaches.

Many of these limitations were perceived during biogeochemical exploration trials in the 1970s to early 1990s, while at the same time biogeochemical exploration techniques became more widely adopted in other parts of the world. More recently there have been important increases in the knowledge of the Australian landscape that hosts biogeochemical media, as well as biogeochemical characterisation and application in Australia. Some of the research highlights that address these limitations and also provide valuable insights into biogeochemical techniques, include:

- An emerging portfolio of biogeochemical characteristics for regionally important media, such as widespread and abundant flora species and genii, including Eucalyptus / Corymbia, Acacia, Triodia, Casuarina, Maireana and Atriplex;
- Characterisation of biogeochemical differences in plant organs and variations within individual plants towards a more robust and representative sampling procedure that best takes advantage of analytical technology;
- The significance of regolith-landform settings and seasonal climatic changes and their significance for plant biogeochemical characteristics; and,
- The value of adding biogeochemical surveys to other exploration techniques within an integrated exploration program.

Regolith geochemistry of the Rustenburg Layered Suite, south western Bushveld Complex, South Africa

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The present study focused on the Rustenburg Layered Suite of the south western Bushveld Complex, which forms part of the annual technical programme of the Council for Geoscience. The aims of the research was to determine the geochemical background values in soils derived from mafic-ultramafic rocks, delineate geochemical patterns that correlate with underlying geology and identify mineral target zones of the south western Rustenburg Layered Suite of the Bushveld Complex. The soil samples were dry sieved and powder briquettes prepared for analysis. The X-ray Fluorescence Spectrometer was used to analyse for TiO_2%, Fe_2O_3T%, MnO%, Sc, V, Cr, Co, Ni, Cu, Zn, As, Rb, Sr, Y, Zr, Nb, Sn, Ba, W, Pb and Th. The median and mean + 2*Std values were used as univariate element threshold values. The element background values of residual soils from Rustenburg Layered Suite Zones were defined as the median for each element, because most element datasets have positively skewed histograms. The multi element correlation matrix reflected four significant principal components that geochemically fingerprint and reflect the bedrock of different Rustenburg Layered Suite Zones. The Lower, Critical, Main and Upper Zones are best defined by PC1 (Ni, Co, MnO, Fe_2O_3T), PC2 (Cr, Ni, Co, MnO), PC3 (Sr) and PC4 (TiO_2, Fe_2O_3T, Sc, Cu, V) respectively. The Critical Zone was delineated as having potential mineral targets of platinum group metals and chromium, whereas the Upper Zone has potential mineral target of vanadium. Regolith geochemical mapping was efficient in determining geochemical background values and mineral target zones for platinum group metals, chromium and vanadium deposits of the Rustenburg Layered Suite, Bushveld Complex. High density soil geochemical survey, magnetic survey and lithogeochemistry are recommended as further mineral exploration and target generation methods.

Biogeochemical exploration using *Triodia pungens* (Spinifex) in the Tanami Desert, Australia

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The Lower Proterozoic Granites-Tanami Province in Western Australia and the Northern Territory contains numerous significant gold deposits, but recent exploration for additional deposits has been hampered by deep weathering of the basement and extensive Tertiary and Quaternary cover. Biogeochemical exploration has rarely been attempted in this environment, with soil sampling and drilling being the principal exploration methods. This paper outlines the methodology and results of a biogeochemical exploration programme utilising *Triodia pungens* (soft spinifex), a perennial, hummock-forming grass, widely found throughout much of arid and semi-arid Australia. This species possesses several attributes which make it suitable for biogeochemical exploration: it is ubiquitous in the area, readily harvested, and possesses an unusually deep root system.

Systematic sampling has been undertaken at 50 m intervals on widely spaced lines over several prospect areas. Collection of large samples (~300 g) from numerous plants at the sample point is critical to overcome an apparent nugget effect (especially for Au) possibly due to variable rooting depths and the likelihood of gold nucleating within the plant itself. Initial multi-element analytical work utilising small samples (2.5 g) of dried and shredded vegetation did not allow sufficient resolution of anomalies with most results for Au and Pt being below detection levels. However, ashing of substantially larger samples (~30 g) has allowed anomaly thresholds for those elements to be more readily defined. The species displays extensive geochemical variability for precious metals, pathfinders, base metals and major cations suggesting it offers much promise as a sampling medium. Test sampling traverses across known gold occurrences confirm the effectiveness of the technique in areas of thick cover sequences and suggest that the method is more effective than traditional soil sampling. Two issues requiring further investigation are the changes in accumulated metal contents with maturity and seasonal variability.

A probabilistic approach to forensic provenancing with isoscapes

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Isotope maps, or isoscapes, have shown to be valuable for the study of the origin and migration of natural materials and organisms. The potential of using this information not only for scientific pursuits but also to aid forensic investigations was realised early on. However, when porting scientific results to real world applications with potential serious consequences for those being investigated, the scientific models need to be properly validated. Essential for use in law enforcement is that any outcome should be presented in such a manner that jurors, lawyers and law enforcement officers can make proper use of the statements made. Scientifically it has become evident that the hydrogen and oxygen isotopic composition of rainwater is related to a limited number of well-understood spatial parameters. Models of the hydrogen and oxygen isotopic composition in precipitation have been validated globally and now the regional composition of groundwater and food products can be predicted with a useful level of accuracy, enabling discrimination of latitudinal distances in the 200 km range. Other parameters can be linked to existing information already captured in maps, e.g. existing geochemical stream sediment and soil maps and the associated samples, to increase spatial discrimination. Recent research has shown that the radiogenic isotopic composition of elements like strontium and lead in soil can be linked to the isotopic composition of a local foodweb. The often relatively well-understood behavior of these isotopes enables researchers to make spatial predictions of the isotopic profiles in target tissues and objects. The presentation will use results of recent forensic investigations performed with light and heavy isotope maps to discuss strategies how to combine different isotopic parameters and other relevant information to construct spatial likelihood models that are scientifically correct, provide a tool for investigators and suits the legal process.

Integrating regional geochemistry and biogeochemistry with geological survey for the Mt Painter – Lake Frome uranium and base metal mineral systems of semi-arid South Australia

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As part of the Geological Survey of South Australia's geological mapping of the Mt Painter region a range of geochemical and biogeochemical media were analysed for integration with the final mapsheet data release. This includes regional sampling of silcretes, ferricretes, gypcretes, kaolin, and regolith carbonates. Over 1300 plant biogeochemical samples have also been collected and analysed, thereby representing one of the largest and most comprehensive regolith geochemical and plant biogeochemical integrated mapping programs in Australia. The objective here has been to test and provide a greater pre-competitive mapping framework for regolith-dominated areas flanking the Flinders Ranges and extending onto the Lake Frome Plains. These areas represent the major exploration frontier in this region but also host sedimentary uranium mineralisation as well as the geochemical dispersion pathways and "footprints" for buried sedimentary uranium and base metal (including Broken Hill and IOCG-U) mineral systems. Many of these geochemical sampling media have shown to be part of the oxidised, surficial expression of mineral systems that include important redox and acid-sulphate weathering processes, found elsewhere with sedimentary uranium and sulphide-hosted mineralisation. The oxidation and acidity of weathering of these systems has facilitated a re-organisation of geochemical and mineralogical components to create distinctive silcrete-kaolinite-ferricrete-gypcrete weathering zones (or "alteration haloes"). These media are conveniently accessible for sampling at the contemporary landsurface. The plant biogeochemistry data set provides a more "penetrative" expression of buried substrate geochemistry and in many cases can be shown to represent the chemical reduced parts of these mineral systems.

Research on soil organic carbon changes and soil erosion of Wuyu'er River Basin, China

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Our focus has been the study of the effects of soil erosion and re-deposition of soil organic carbon in the watershed. The Wuyu'er River is China's second largest endorheic river and soil erosion is a very serious issue in this watershed. We had soil organic carbon data for 4994 samples from the Second National Soil Surveys conducted in the 1980s and in this study we re-sampled 276 top soils (0-20 cm). The soil organic carbon contents of the new samples were determined and compared with the data measured 30 years ago on samples from similar depths. We also collected four river sediment profiles and measured their organic carbon contents, ^{210}Pb and ^{137}Cs. The results show that the soil organic carbon density (SOCD) of top soils had declined sharply. In the 1980s the SOCD of meadow soil and black soil were 4.98 and 5.90 kg/m^2, however, they have decreased to 3.53 and 4.95 kg/m^2, respectively. The top soil in the study area has lost 1.24 x 10^7 t of organic carbon. In the 1980s, the temperature and rainfall showed obvious correlation with the soil organic carbon, but data from the present samples show a weak correlation. This indicates that there are other factors controlling the loss of soil organic carbon besides temperature and rainfall. The distribution of ^{210}Pb and ^{137}Cs in river sediment profiles indicate that sediment of about 45 cm depth formed over the last 30 years. The average organic carbon content of these sediments is 1.13% (n=92). The amount of organic carbon stored in over-bank deposits is very large (1.03 × 10^{10}kg). This information is being used to constrain models of erosion-related carbon fluxes in a small catchment.

The role of geochemistry in the discovery and exploration of the Sakatti Cu-Ni-PGE deposit (Finland)

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The Sakatti Cu-Ni-PGE deposit in northern Finland is a significant grassroots discovery made in 2009 by an Anglo American exploration team led by Jim Coppard. Mineralisation at Sakatti is magmatic, predominantly ultramafic-hosted and consists of disseminated, vein, semi-massive and massive sulphides. The mineralised body sub-crops below a thin glacial till cover and plunges as a coherent body at an angle of 45° towards the northwest. Mineralisation has been traced for over 1,500 m, but remains open to the west, north, south and at depth. The topography of the region is generally flat, with extensive bog coverage and mixed pine-birch forest. Most of the region is covered by a till veneer of variable thickness (<1 m to >15 m) and outcrops are generally less than 2% of the surface area. At the Sakatti project, geochemistry forms part of an integrated multi-disciplinary exploration approach and has played an important role from initial targeting through to resource definition. Following early orientation work, Base-of-till (BOT) geochemistry, which involves the collection of till samples at the till-bedrock interface, proved to be the most effective geochemical tool. Drill testing of a BOT geochemical anomaly over the eastern portion of the Sakatti target, coincident with an aeromagnetic anomaly, ultimately led to the intersection of economic mineralisation. In addition, BOT geochemistry also assists with the lithological mapping of the concealed bedrock. As exploration drilling at Sakatti progresses, geochemistry continues to add value to the project. Recognition of spatial zonation in the composition of sulphide mineralisation may provide a useful vectoring tool for further exploration drilling and helps with the definition of geometallurgical domains, while lithogeochemistry provides valuable insights to improve the geological model of the deposit.

Weathering of black shale and subsequent releases of metals in a shale mining district – effects of pH and presence of natural organic acids

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Mining of black shale (alum shale) of Late Cambrium age for the extraction of aluminium and iron sulphate started in the early 17th century in Sweden, and starting in the late 19th century there was an extensive use of shale, with its content of organic carbon in the range 15-18%, as fuel in lime-burning processes. Recovery of oil from black shale started in 1873. Full-scale recovery of hydrocarbons took place in Kvarntorp during 1942-66, and recovery of uranium in Ranstad during 1965-76. There are remains from the mining and processing of black shale at about 50 major shale deposits. The Kvarntorp deposit, still burning after more than 50 years, contains some 40 million m^3 of crushed unprocessed as well as processed shale residues. There are also large areas covered with crushed shale, used for example, as road fill material.

Studies of the natural weathering of processed and virgin shale due to exposure to the atmosphere and water with pH within the natural range (from 3 to 12.5) indicate a high leachability at low pH (cationic elements) as well as at high pH (anionic elements). The presence of organic complexing acids of natural origin (microbial exudates – citric acid, oxalic acid, as well as humic acids and cellulose degradation products) may give an enhanced leaching, particularly at pH above 8, when the hydroxy-groups would constitute active metal binding sites. Results from the weathering and leaching of black shale of various origins are presented, and consequences in terms environmental impact on the former shale mining sites and the surroundings are assessed.

Exploration for porphyry deposits in glaciated environments: A case study from the Iliamna/Audn region, southwest Alaska, with comparisons to the Pebble district

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The discovery of the ~90 Ma Pebble deposit, one of the largest Cu-Au porphyry deposits in the world, highlights the importance of middle Cretaceous porphyry development and has led to focused interest in this highly prospective region of southwest Alaska. Recent geochemical and geophysical studies at Pebble provide information about the surficial expression of the deposit; extrapolating these characteristics to regional scales is critical for defining additional targets. The Iliamna and Audn prospects are 90 km southwest of Pebble. Both are entirely concealed by up to ~210 m of glacial materials; only the Iliamna prospect has been drilled. Similar to Pebble, the prospects lie on the edge of a broad regional aeromagnetic anomaly that initially targeted the area. Upward continued reduced-to-pole (RTP) aeromagnetic compilations that emphasise deep magnetic sources diminish the anomaly and suggest that most magnetic material lies west of

the Iliamna/Audn region. Granodiorite samples from Iliamna drill core have low magnetic susceptibilities compared to compositionally similar intrusions at Pebble. Like Pebble, chalcopyrite, molybdenite, and pyrite are disseminated or in veins, but Iliamna has more abundant pyrrhotite. Biotite from mineralised granodiorite at Iliamna yielded $^{40}Ar/^{39}Ar$ plateau ages of 62.4 +/- 0.2 and 62.1 +/- 0.2 Ma. Porphyry Cu indicator mineral and hydrogeochemical studies best delineate buried mineralised zones. Tills down ice of mineralised areas contain abundant pristine or modified gold grains. Pond, stream, and spring waters contain high (>75th percentile) concentrations of Cu (310-7,780 µg/L), Ag (3.1-17 µg/L), and V (457-1,930 µg/L), similar to water samples in and around Pebble. Atypical of Pebble are waters with high arsenic concentrations (0.5-1,610 µg/L). The younger age and subtle differences in geochemical and geophysical properties indicate that the Iliamna/Audn mineralised system is part of a compositionally distinct younger suite of porphyry deposits, although drilling at Audn is required to fully document this.

Experimental mobilisation and secondary mineralisation of antimony and arsenic from gold ore, Reefton New Zealand

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Antimony (Sb) and Arsenic (As) are toxic metalloids commonly associated with Au in mesothermal mineral deposits. Occurring principally in stibnite (Sb_2S_3) and arsenopyrite (FeAsS), mobilisation and/or secondary mineralisation occurs when As-Sb-bearing rock is exposed at the surface. This study investigates potential mobility and re-mineralisation, based upon experimental leaching trials over an eight month period. Ore collected from the ROM pad at Globe-Progress gold mine was categorised using XRF into As-rich (mean = 24,764 ppm) and Sb-rich (mean = 99,449 ppm). Samples were placed in three kinetic leach columns (As-rich, Sb-rich and control) and watered weekly. Leachate was collected and analysed at monthly intervals using ICP-MS to determine dissolved metal concentrations. Preliminary results indicate that after eight months, only a small proportion of total As and Sb has been leached (<1%). Over the course of each month, the leachate became highly acidic, reducing from pH ~7 to pH ~3 at collection. As expected, dissolved As concentrations were higher than Sb in the As-rich sample, up to 16.1 mg/L compared with up to 0.3 mg/L. Dissolved Sb concentrations were higher in the Sb-rich sample, up to 11.8 mg/L compared with up to 1.4 mg/L As. The high acidity of the leachate may be a limiting factor in As dissolution. SEM analysis and imaging of the samples after six months showed significant arsenolite (As_2O_3) precipitate (>80 wt% As) forming on the surface of the As-rich sample, in addition to secondary mineralisation of Mg-, Na-, Fe-sulfates with minor Ca and As, and tabular gypsum ($CaSO_4.2H_2O$). Analysis suggests the majority of mobilised As is forming transient arsenolite. Secondary mineralisation in the Sb-rich sample is predominantly tabular gypsum and acicular Al-sulfates with minor Mg and Fe. Sb-oxides are entirely absent in the Sb-rich sample, indicating that mobilised Sb is not being removed by secondary mineralisation.

Geochemistry of uranium in lakes of west Mongolia

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In the arid climate of western Mongolia, where evaporation is 2-3 times higher than the amount of precipitation, evaporation concentration processes contribute to the growth of salinity and concentration of U. However, our investigation indicates a significant role in uranium accumulation in the waters of the upper hydrodynamic zone is provided by aquifer rocks in the lake catchments. Geologically, granite massifs (Harhiraa, Achitnursky, Oshkinsky, etc.) are widespread in the studied territory, which are known to possess natural radioactivity. But lithology is not the main factor. The time of water/rock interaction, which determines the degree of accumulation of U in the lakes is more important. Specifically, the equilibrium-nonequilibrium state of the water-rock system determines the potential for U concentration in the water during the time of its interaction with rocks: the longer interaction time, the more uranium will be concentrated in the water, all the other things being equal. Analysis of lake waters in equilibrium with uranium minerals shows that only a few can precipitate out of solution and only three lakes with total salinity more than 300 g L^{-1} equilibrium with the investigated minerals. Water stores U by getting into the rocks of any composition and dissolving them. Uranium, in turn, forms complexes with carbonate-ions and migrate to the lakes, and precipitates in lake sediments by the influence of evaporation and water-sediment interaction. In this case, the more uranium accumulated in the water along the entire migration path to the lake, the greater the amount that will be precipitated. Consequently, the lakes are a unique geochemical barrier for the migration of uranium, which forms oxides, hydroxides, carbonates, phosphates, fluorides and other minerals in lake sediments.

Exploration of uranium deposits by integrating isotope data with geologic and other geochemical data

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Among the new techniques to unravel fluid histories from deposition to later alteration and the role of the biosphere in forming uranium deposits is isotope tracing. The isotope systems being used include Li, C, N, Mo, Tl, Pb and U, all of which reflect different, but overlapping, processes. Although Pb isotopes have been used to understand the evolution of the deposits, Li, C, N, Mo, Tl and U isotope systems are new ways to analyse deposits and barren areas and to reveal their precise redox mechanisms. For example, $^{238}U/^{235}U$ ratios of uranium minerals from volcanic-metasomatic-, unconformity- and sandstone-related uranium deposits vary as a function of the type of uranium deposit. $^{7}Li/^{6}Li$ ratios in muscovite and chlorite associated with mineralising events are distinct from background ratios, with the lowest values reflecting the beginning of hydrothermal alteration systems whereas the highest values are indicative of the terminal flow of hydrothermal fluids. The isotopic composition of C indicates microbial interactions with the uranium deposits, which may be the process by which elements are mobilised out of the deposits and into the surrounding environment for us to use as vectors to ore. The goal is to be able to use isotopes to reflect a definitive process that occurs in the deposit and not in barren systems, and then to relate these to something that is easier to measure, namely elemental concentrations.

Tracing the mobility of metals from a buried VMS deposit using Cu and Zn isotopes in soils and vegetation

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The utility of Cu and Zn isotopic systems in soils, clay minerals, tree bark and moss above the Talbot VMS deposit, Canada, have been evaluated. The deposit sits at a depth of 100 m below Phanerozoic carbonates and a thin veneer of till. The Cu contents for the various media showed no anomalies, whereas anomalies in the Cu isotopic compositions occur in soil samples over a fault transecting the ore body and over the ore. Anomalous Zn concentrations were found in clay samples collected over the fault and over the deposit, whereas other media did not show any Zn enrichment above background. Soils collected over the fault and over the ore deposit have anomalous Zn isotopic compositions compared to background samples. In general, Cu isotopic compositions in different media are more variable above the Talbot deposit relative to Zn isotopic compositions in the same samples due to the preferential adsorption of Cu on the surface of minerals as well as reduction of Cu(II) to Cu(I). The Talbot case study shows that Cu and Zn isotopic systems, in conjunction with trace element data, can elucidate the processes of element migration from deeply buried deposits to the surface and potentially add value to exploration for deposits buried at least 100 m or more.

Mineralogical and geochemical assisted bedrock mapping in glaciated terrane: The Bald Eagle intrusion, Minnesota, USA

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The Bald Eagle intrusion (BEI) is a 250 km^2 layered intrusion within the 1099 Ma Duluth Complex of northeastern Minnesota, USA. The BEI is composed predominantly of troctolite with lesser olivine gabbro and anorthositic and mafic volcanic megaxenolith phases. In common with other Duluth Complex intrusions, the BEI is prospective for orthomagmatic Cu-Ni-PGE deposits. The BEI is glaciated with poor bedrock exposure, and the meager exposure is inferred to be unrepresentative of the full range of bedrock lithologies. However, till cover is generally thin and characterised by a low mean transport length. Till composition therefore closely reflects that of underlying bedrock. To evaluate the prospectivity and geology of the BEI, an extensive B-horizon till sampling programme has been undertaken. Geochemical analyses follow a standard 4-acid digestion of the <63 µm fraction with multielement ICP-MS finish. Heavy mineral sampling utilises small (c. 3 kg) samples, from which >3.2 s.g. heavy mineral concentrates (HMC) were separated from the 63-125 µm fraction using 2-stage LST liquid separation. HMC yields averaged 5.5%, ranging from 1 to 30%. The bulk modal mineralogy of the HMC is determined using QEMSCAN® Bulk Mineral Analysis. Distinct HMC populations within the BEI are distinguished by relative concentrations of ilmenite, olivine, clinopyroxene, orthopyroxene, Fe-oxides, amphiboles, epidote, and chromite. Multivariate analysis (factor analysis) of geochemical and HMC data identified a number of underlying factors describing variability in BEI samples. The spatial distribution of factor scores clearly delineates breaks corresponding to numerous previously unrecognised contacts internal to the BEI. The resulting geochemical/HMC pseudo-geological map highlights previously unrecognised geological complexity in the BEI, and provides a guide for further geological and geophysical investigations.

Standard till geochemical methods augmented by QEMSCAN® bulk modal mineralogy of fine-grained HMC are proving effective tools to advance greenfields exploration in poorly exposed and mapped glaciated terrane.

Hydrothermal footprints around magmatic nickel-sulfide deposits: A case study at the Miitel deposit, Yilgarn craton, Western Australia.

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The remobilisation of metals during hydrothermal alteration of magmatic nickel-sulfide deposits could result in large geochemical haloes, potentially enlarging the detectable footprint of this ore type. The Miitel komatiite-hosted nickel-sulfide deposit (Western Australia) was used as a case study to investigate the nature and 3D geometry of this footprint. Portable XRF (pXRF) analyses on basalt samples, close to the contact with overlying komatiites, up to 200 m away from the mineralisation, detected the presence of anomalous Ni concentrations, associated with elevated As, Co, Pt and Pd. A petrographic study of the samples containing anomalous concentrations, combined with SEM-EDS techniques and elemental mapping, associated the elevated Ni concentrations with the presence of Ni-As rich phases. Gersdorfitte, and minor nickeline, are concentrated within small quartz and carbonate veinlets within the footwall Lunnon basalt. They are interpreted as forming during the circulation of arsenic-rich hydrothermal fluids through the mineralised horizons and subsequently along the footwall contact into the basalt. Results from in situ LA-ICP-MS analyses on gersdorffite and nickeline also indicate high PGE concentrations (Pt and Pd mainly) within these phases. This PGE enrichment suggests that the massive nickel sulfides from the Miitel ore bodies, rather than the adjacent barren komatiite, are the source of the remobilised Ni. This cryptic Ni-PGE-As signature in immediate footwall rocks could constitute an effective vector to mineralisation for magmatic nickel sulfides deposits in an As-enriched environment.

Geochemical mapping of Alaska

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Alaska has an area of 1.7 million km^2, and regional to local geochemical surveys have been undertaken by state and federal agencies. We present a new compilation of geochemical data that have been collected since the early 1960s, including (1) 65,993 sediment samples from the National Uranium Resource Evaluation (NURE) program, (2) samples from the US Geological Survey including sediments (90,360), soils (6,869), rocks (108,966), heavy-mineral concentrates (48,096), and minerals (7,470), and (3) samples from the Alaska Division of Geological & Geophysical Surveys including sediments (10,919), soils (100), rocks (12,437), and heavy-mineral concentrates (1,063). Sample density varies significantly on a local scale, but averages 1 site per 11.6 km^2 for the entire state. Legacy data in our compilation have highly variable accuracy, precision and associated detection limits due to the steady and significant improvement in analytical methods during the last 50 years. For example, older geochemical data are associated with relatively high analytical detection limits, so data for many elements are highly censored, with some having more than 90 percent of their values at levels that are less than the detection limit. Thus, the heterogeneous nature of the data in our compilation presents challenges for geochemical interpretation. On the other hand, robust statistical methods allow for the identification of anomalous element concentrations. In some places, groups of samples with anomalously enriched element concentrations correlate with geology. For example, areas that are enriched in Ni and Cr generally coincide with belts of mafic to ultramafic rocks, and the greatest enrichments of Th and REE are associated with alkaline igneous rocks. Taken together, these results suggest that careful treatment of legacy data can provide significant and revealing geochemical maps for large areas.

Establishing a regional background for geochemical exploration surveys: Regional-scale metasomatism in the Fortescue Group, Hamersley Basin, Western Australia

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Regional reconnaissance surveys are commonly used to recognise distinct zones of hydrothermal alteration that may be related to economic mineralisation. However, alteration indicative of major ore deposits may be subtle and must be distinguished from background regional variation in rocks independent of any mineralising system. The mafic volcanics of the Fortescue Group which, to date, are believed to be unmineralised, provide a background against which areas of potential Au mineralisation may be compared, in order to determine whether an anomaly truly exists. A regional burial metamorphic gradient extends across the Hamersley Basin, from prehnite-pumpellyite facies in the north to epidote-actinolite greenschist facies in the south and west. Superimposed on this metamorphic gradient, regional-scale metasomatism has affected extensive areas of the Fortescue Group. Metasomatised rocks are characterised by well-developed pumpellyite-quartz, epidote-quartz and albitised assemblages that contrast with least altered, massive mafic rocks. Metasomatic alteration is most conspicuous in the lower grade metamorphic zones as pumpellyite-and epidote-rich rocks are green to yellow-green in outcrop. In the higher grade metamorphic zones, epidote-clinozoisite is almost colourless and pumpellyite is much less abundant. Whole-rock geochemical data indicate that metasomatism is associated with strong depletions in alkali metals, Mg and the first transition series metals, with a significant enrichment in Si and variable mobility of Ca and volatiles. Such geochemical trends, particularly depletions in Fe, Mn and base metals, along with metasomatic mineral assemblages, are comparable to those associated with the sub-sea floor circulation of sea water, particularly in relation to base-metal depleted root zones of volcanic-hosted massive sulfide deposits. This study shows that hydrothermal alteration is not always associated with mineralisation and helps explain why some hydrothermally altered areas are mineralised and some are not.

Geobotanical vegetation anomalies within the Roseby Corridor, N.W. Queensland: Is 'Copper Grass' still a valid exploration tool?

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The Roseby Corridor, located 50 km north of Cloncurry, offers some of the clearest examples of geobotanical indicator plants in N.W. Queensland. Several key regional mineralisation styles are present in this 20 km x 10 km zone including Little Eva (IOCG), Dugald River Zn-Ag-Pb (SEDEX) and Roseby Copper Horizon (structurally hosted, low-sulphidation) styles. The presence of numerous indicator species has directly aided the identification of metalliferous lithological units and can be used to directly infer base metal anomalism in soil.

Regolith within the corridor varies from outcrop and colluvium to overbank alluvial and black (smectitic) soil. The region has a dry savannah climate with a yearly maximum temperature above 40°C and average annual rainfall of 400-500 mm, which mostly falls in the wet season between December and March. Observations recorded during the 2009-2012 field seasons identified numerous plant species whose distribution is directly linked to mineral occurrences and geochemical soil anomalies. The most common and widespread surface geochemical anomalies are Cu, but vegetation anomalies have also been well documented in areas of Zn-Pb enrichment, with accompanying variations in plant growth and form. Common copper indicator species include 'copper grass' (*Eriachne mucronata* and *Bulbostylus barbata*), 'copper bush' (*Polycarpea glabra* and *Polycarpea spirostylis*) and 'copper weed' (*Tephrosia supina Nova*).

The continued demand for world-class ore bodies and the decreasing chance of discovering outcropping ore deposits increases the need to embrace all data. Despite the availability of advanced surface geochemical techniques, the results from this case study clearly highlight the continued relevance of including 'traditional' biogeochemical techniques in the explorer's toolkit.

Geochemical trials in weathered overburden: Defining exploration parameters for Mount Isa-style and IOCG mineralisation in NW Queensland, Australia

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The continued demand for world-class ore discoveries and the decreasing chance of finding outcropping ore deposits increases the need to explore for potentially buried mineralisation in areas of thick overburden and cover sequences. The development of new geochemical methods continues to advance the ability to geochemically explore in covered terrains. Field trials were conducted to test established and recently developed geochemical techniques designed to measure the surface geochemical expressions of buried and blind mineralisation in a range of regolith settings. This study aimed to determine the most effective and appropriate methods and to define characteristic pathfinder element associations over the two principal NW Queensland ore-deposit styles (Mount Isa Cu and Ernest Henry IOCG Cu-Au). Trial locations varied from blind targets under thick cover sequence lithologies (50 m+) to targets with shallow (<5 m) transported or residual soil cover. Seven techniques were chosen for trial and included those that sample gas compounds released from oxidising ore minerals at depth, commercially available partial extraction methods from different laboratory groups and more traditional acid digest soil sampling methods. Despite the availability of advanced soil-gas techniques the project has clearly highlighted the continued relevance of ‘traditional’ geochemical techniques, especially for chalcophile elements in areas of thin to moderate cover. All partial leach techniques trialled provided increased resolution in areas of thick cover and identified litho-geochemical variations through thick (50 m+) cover sequences. The results from these field trials have also highlighted the importance of a thorough, systematic and repeatable sampling procedure with regular collection of QA samples. Results from this study and follow-up surveys has helped guide current exploration geochemistry procedures and sampling techniques and have delivered exploration success in a range of regolith settings. On-going active sampling and research into existing deposits represents a constant learning-curve towards geochemical best practice in the Mount Isa Inlier.

Characterisation of the spatial distribution of gold concentrations using fractal models in regolith over the Jinwozi Goldfield, NW China

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Characterisation of the spatial distribution of element concentrations in overburden that conceals ore deposits is necessary to understand the mechanisms that enable the use of deep-penetrating geochemistry in mineral exploration. The aim of this study is to identify the spatial distribution features of gold concentrations in regolith over the Jinwozi goldfield, northwestern China, by applying the number-size (N-S) and the concentration-volume (C-V) fractal methods to 979 samples from 63 overburden drill holes analysed for Au. Both the N-S and C-V models distinguished four different enrichment states defined by Au thresholds of 0.8, 3.2 and 79.6 ppb for the former, and 1.6, 7.9 and 39.9 ppb for the latter. Results using these thresholds indicate that a prominent zone of high gold concentrations is elongate horizontally in a NE-SW orientation along a ductiley-sheared belt of hydrothermal alteration, and is symmetrically distributed in a vertical pattern directly above the concealed deposit, with gold enrichment in the top and bottom layers of the regolith. Three other zones were identified by the N-S and C-V models that exhibit weak-to-moderate gold enrichment. Comparison of the results from N-S and C-V methods indicates that the spatial delineation of the C-V fractal model is more accurate than that of the N-S fractal model. Nevertheless, both Au concentration spatial distributions defined by these fractal models coincide well with the underlying geology and characteristics of deep-penetrating geochemistry in arid terrains.

Gold and calcrete: 25 years of successful exploration geochemistry – what have we learnt?

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Gold and calcrete are strongly associated. The CSIRO discovery of this peculiar and extraordinary relationship between two disparate components of the soil goes back to 1987. The discovery has led to the unearthing of billions of dollars' worth of gold. It is currently being applied to the delineation of gold mineralisation in the Albany Fraser Belt of Western Australia. Recent advances in our understanding of the gold-calcrete phenomenon suggest that several mechanisms are operating at different scales: at the micron scale gold may not be directly associated with calcrete but with biotic components of the soil; at the soil sampling scale the strong relationship between gold and calcrete must be considered in order not to overlook a deposit; geochemical mapping of gold-in-calcrete anomalies requires an understanding of landscape evolution and geomorphology. Thus, gold anomalies that have formed in calcrete directly over mineralisation with the help of deeply rooted plants are subject to landscape processes that create subtle but larger footprints to mineralisation. However, these geochemical anomalies in depositional terrains may become spatially isolated and dispersion trains overly complex making interpretation of their origins difficult to resolve. Synchrotron XRF, isotope geochemistry (C, O and Sr), luminescence dating, laser ablation inductively coupled mass spectroscopy and conventional geochemistry will illustrate the concept of scale associated with evolving Au in calcrete anomalies from a range of gold prospects including Edoldeh Tank, Barns, Bounty and Earea Dam. While this research has been restricted to Australia, it is highly likely that these processes apply in other auriferous calcreted terrains of the world but need to be investigated.

Polytopic Vector Analysis as a valuable tool for determining magma/fluid sources in geochemical processes by comparison of whole-rock versus mineral chemistry

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Geochemical modifications taking place in the continental crust are usually complex scenarios involving a variety of processes deriving elements from different sources. The effect of that combination is a 'mixture' where the characteristics of individual sources are usually irretrievable using conventional analytical and petrological methods. However, a number of mathematical algorithms exists that enable extraction of the unknown information, such as fractal statistics, linear equations and Polytopic Vector Analysis (PVA). PVA is probably the most simple and straightforward method where the influence of the user is limited in comparison to other methods. PVA is an algorithm that allows defining the number and composition of the sources contributing to a particular system, along with the relative proportions of each source in every given sample. It can be applied to any geochemical concentration that results from mixing of several end-members. We discuss advantages and disadvantages of the PVA method using a magmatic system example that has undergone mixing of mantle- and crust-derived melts. The method was applied to both whole-rock and apatite geochemistry; apatite was used because it constitutes the only accessory mineral present in each stage of magma differentiation, the trace-element composition of which can record the changes in the dynamics and chemistry of the magma. The results of PVA applied to the whole-rock geochemistry are consistent with previous studies employing other modeling approaches and are in accord with the magma-mixing model. However, the apatite compositions do not reflect the same trends demonstrated by the whole-rock chemistry, especially in the case of the REE's, which exhibit chaotic distribution patterns likely resulting from local saturation of the melt. In this case, other factors like variations in partition coefficients, diffusion rates, and the presence of other accessory phases have to be taken into account in order to obtain satisfactory results.

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Chemical weathering in the upper Yangtze River Basin: Impact factors and CO_2 consumption

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The upper Yangtze River Basin has received particular attention as a carbon sink, because of heavy weathering caused by abundant rainfall, large elevation differences and complicated geology. In order to quantify these effects, river water, suspended solid and sediment samples from the upper reaches of the Yangtze River were collected and the ions flux model and GEM-CO_2 model were applied to evaluate CO_2 consumption. The results indicate that the rivers of the area are typical carbonate rivers, and Cl^- and SO_4^{2-} ions have increased sharply compared to previous work as a result of anthropogenic activities.

In general, the dissolved ion composition is affected by rock type, precipitation, and human activities. The ions flux model was established based on the value of F^-, Cl^-, NO_3^-, Mg^{2+}/Na^+, and Ca^{2+}/Na^+ to calculate the contribution of precipitation, evaporites, silicate rocks and carbonate rocks to the total dissolved ion load; which were 3.84%, 31.11%, 16.88% and 48.56%, respectively. The contributions of agricultural activity to total dissolved ion load of the Minjiang River in the wet and dry season were 6.08% and 7.07%, respectively. Chemical weathering rates of different rivers in this basin varied between 26.61 t km^{-2} y^{-1} and 102.58 t km^{-2} y^{-1}, which were mainly controlled by the rock type and annual runoff. Based on the ions flux model, total CO_2 consumption is 6.702 x 10^{11} mol y^{-1} in the whole basin with the consumption rate of 529.68 x 10^3 mol km^{-2} y^{-1}. The Tuotuo River has the minimum value and the Xiaojiang River has the highest. The total CO_2 consumption is 2.261 x 10^{11} mol y^{-1} calculated with the GEM-CO_2 model, consistent with the ions flux model.

Overall, the regional atmospheric circulation was changed by the uplift of Tibetan Plateau, which accelerated the regional chemical weathering process. The following carbon sink effect should not be ignored and needs to be fully investigated.

The environmental behaviour of indium at metal mine sites, northeastern Australia

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Indium is a rare, post-transition metal that is widely used in modern technological applications such as liquid crystal displays and photovoltaic solar panels. It is one of a number of so-called "e-tech" elements whose supply is considered to be insecure. By contrast, the geology and geochemistry of In is poorly understood. Moreover, there are currently no environmental guidelines with respect to In; the element is rarely monitored and its behaviour in the environment is poorly known. This is despite the fact that there is considerable evidence suggesting that In compounds have significant, if not extreme toxicity. This study reports on the sources and sinks of In in acid rock drainage environments at metal mine sites, northeastern Queensland, Australia. Sulfide-rich materials comprising the ore and waste at metal mine and processing plant sites have undergone extensive oxidation prior to and after mining. Rocks and wastes are invariably enriched in In (Baal Gammon Cu-Sn-Ag up to 270 g/t In, Orient Camp Ag-Pb-Zn up to 120 g/t In; Montalbion Ag-Pb up to 90 g/t In; Jumna Sn up to 19 g/t In). Indium is thereby hosted in cassiterite, sphalerite, stannite, chalcopyrite, and sulphosalts of Sn, Pb, Cu or Sb. Rare occurrence of indite ($FInS_4$), roquesite ($CuInS_2$), sakuraiite $(CuAg)_2(In,Sn)(Zn,Fe)S_4$ and dzalindite $In(OH)_3$ have also been reported. ARD development leads to mobilisation of In into acid waters (max. 0.12 mg/l, pH 2.5). Subsequent oxygenation of ARD waters and hydrolysis of Fe lead to the formation of Fe-rich precipitates (schwertmannite, goethite, amorphous Fe compounds) that, through adsorption and coprecipitation, preferentially incorporate In. Thus, In displays significant mobility in ARD environments, with its mobility constrained by Fe precipitation. There is a need to understand mining fluxes of In and identify In pathways and sinks in the mining environment, also in the context of improved processing technologies and environmental protection.

PGE-enriched Fe-Ni sulfide droplets in volcanic glass from the central Atlantic: Possible implications for magmatic PGE-Ni-sulfide deposits

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The origin of large accumulations of nickel and platinum group elements (PGE) in some continental magmatic rocks is ultimately linked to silicate-sulfide liquid immiscibility. While there is much experimental evidence of such immiscibility, direct observation of coexisting primary silicate and sulfide melts from this early stage is difficult because of their small volume and transient nature, and because of magmatic overprinting. Here we report the discovery of Fe-Ni sulfide melt globules highly enriched in noble metals (Pt, Pd, Au; 120 ppm total PGE) within unusual high-Mg andesitic glass ("BTJ", with 8.2 wt% MgO, 57.3 wt% SiO_2) dredged from the southern Mid-Atlantic Ridge. The composition of this unaltered glass indicates a high-temperature (1250°C) parental silicate melt derived from a garnet pyroxenite mantle source with pronounced "continental" isotopic (Pb, Sr, Nd, Hf, Os, O) signatures. Fe-Ni sulfide globules (mostly <5μm, largest 180μm) have compositions consistent with being a quenched primary sulfide-hydroxide liquid. PGEs occur as alloys and reach concentrations (100% sulfide basis) ~2x higher than in sulfide globules in oceanic basalt glasses, and higher or similar to bulk sulfides in major Ni-Cu-PGE deposits. The specific chemistry (high Si, high Ni, low Fe) of primary melts generated from garnet pyroxenite sources promotes sulfide saturation at low pressures, without extensive fractional crystallisation and late-stage crustal contamination. The combination of high primary Ni content, sulfide saturation at low pressure, high temperature and high PGE-Au content suggests that the type of melt represented by BTJ glass may be an attractive model for the transition from magma to ore in magmatic Ni-sulfide systems, particularly those with inferred non-peridotite lithospheric sources.

Columbite-tantalite and pyrochlore minerals as potential indicators in exploration for specialty metal deposits

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Columbite-tantalite series minerals are a main constituent of Ta and Nb ores. They are also present in Li, REE, Be, Zr, W, Sn, and Cs -bearing deposits associated with granitoids, pegmatites, carbonatites, peralkaline intrusions, in saprolites overlying these deposits, in associated stream and lake sediments, and in till. Compositionally, following classification of Černý and Ercit (1989), based on Ta/(Nb+Ta) and Mn/(Mn+Fe) atomic ratios, members of the columbite-tantalite series can be divided into tantalite-(Fe), columbite-(Fe), columbite-(Mn), and tantalite-(Mn). Li-F-Rb-Cs-Be-Nb-Ta-REE-Sn-U-Th-Zr enriched granites are known to contain predominantly columbite-(Fe) with a Mn/(Mn + Fe) atomic ratio > 0.2, columbite-(Mn), and tantalite-(Mn). Pegmatite-related deposits are known to contain tapiolite, all major varieties of tantalite, and Ta-rich end members of columbite. There is a paucity of columbite analyses from carbonatite-hosted deposits; however, preliminary compilation suggests that they contain Nb-rich columbite-(Fe) with Mn/(Mn+Fe) atomic ratio ≤0.2. Mineral groups belonging to the pyrochlore supergroup (betafite, microlite, and pyrochlore) as defined by Atencio et al. (2010) are associated with the same deposits as columbite-tantalite minerals. Betafite group minerals [$(Ca,U)_2(Ti,Nb,Ta)_2O_6(OH)$] are common in granite pegmatites and present in some carbonatites; microlite group minerals [$(Na,Ca)_2Ta_2O_6(O,OH,F)$] are found predominantly in rare element pegmatites and in miarolitic cavities in granites; and pyrochlore group minerals [$(Na,Ca)_2Nb_2O_6(OH,F)$] are characteristic of carbonatites, but are also present in other alkaline rocks. Discrimination diagrams based on composition of columbite-tantalite and/or pyrochlore minerals may allow exploration geologist to relate mineral chemistry of these minerals to established deposit models. For example, Nb-rich pyrochlore and columbite-(Fe) with Mn/Mn+Fe atomic ratio ≤0.2 are expected in carbonatite-related specialty metal deposits, while tapiolite, microlite and Ta-rich betafite are characteristic of pegmatite-related mineralisation. Weathering is known to affect chemical composition of minerals belonging to the columbite-tantalite series and pyrochlore supergroup and should be taken into consideration.

Progressive silica mobility enhances lithologic contrasts during mineralisation, Macraes mine, New Zealand

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The Macraes mine is a world-class orogenic gold deposit located in a regionally extensive shear zone that is hosted in a package of folded, lower greenschist facies metasedimentary rocks. The mineralised shear cuts through two end-member schist types: massive quartz-rich quartzofeldspathic schist and more fissile micaceous schist. Rheological differences between these two types are important in focusing and controlling the style of mineralisation within the shear zone. Gold and scheelite are concentrated in low angle shears and foliation-parallel veins within more fissile units, as well as in high angle extension veins that are generally confined to massive quartz-rich units. Both mineralisation styles are coeval and were preceded by, and were a consequence of, silica mobility during and after metamorphism. Progressive deformation during ductile folding of quartz- and mica-rich segregations resulted in the development of an anastomosing strain-slip cleavage surrounding quartz-rich fold hinges. Pressure solution caused thinning of fold limbs and general thickening of quartz in fold hinges. Ductile shearing and quartz removal were concentrated along the limbs of folds, whereas fold hinges became the sites of quartz redeposition. Silica mobility and subsequent recrystallisation occurred at quartz grain boundaries and along intragranular fractures. Mineralising fluids used the strain-slip cleavage as channelways for deposition of shear–parallel veins and quartz infill at brecciated quartz-rich hinges. Subsequent ductile shearing continued to deform the hydrothermal quartz. Migration of hydrothermal and metamorphic quartz into hinge zones continued to accentuate the rheological differences between fissile micaceous schist and quartz-rich schist. Late-stage mineralised cataclastic shears affect both schist types, but they are concentrated along pre-existing ductile shears that anastomose around the edges of massive schist pods and pre-existing quartz veins.

Geochemical exploration in the Shamanikha-Stolbovsky gold cluster (Magadan Region, Russia)

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The Shamanikha-Stolbovsky gold cluster is located in the North-East of Russia, in the basin of the Kolyma River. In 1933, gold placers were discovered, but the search for significant gold targets for more than 50 years failed to yield positive results. From 2009 to 2011, geochemical and geophysical studies, mining and drilling were conducted within this cluster.

Because of complicated landscape conditions (thick Quaternary sediments and widespread permafrost), geochemical exploration was carried out based on superimposed secondary sorption-salt haloes (sampling density of 250x250 m, 250x50 m, 250x20 m) using the superfine fraction analysis method (SFAM). The method consists of extraction of the superfine fraction (<10 µm) from unconsolidated sediment samples followed by transfer to a solution of sorption-salts and analysis using quantitative methods.

The main results of the work in the Shamanikha-Stolbovsky area are:

1. Geochemical exploration using the superfine fractions analysis method with a sampling density of 250x250 m allowed the identification of areas of anomalous geochemical fields (AGCF) and the discovery of gold mineralisation (Nadezhda, Timsha, and Temny prospects). These AGCF are characterised by the following three-zonal structure (from the centre to the periphery): nucleus zone – area of centripetal element concentration (Au, Ag, Sb, As, Cu, Hg, Bi, Pb, Mo); exchange zone – area of centrifugal element concentration (Mn, Zn, V, Ti, Co, Cr, Ni); flank concentration zone – area of elevated contents of centripetal elements with subbackground centrifugal elements.
2. Detailed AGCF studies with sampling density of 250x50 m (250x20 m) in the Nadezhda, Timsha, and Temny prospects made it possible to refine the composition and structure of anomalous geochemical fields, identify potential gold zones, and determine their formation affinity.
3. In all these prospects, mining and drilling penetrated gold ore bodies within the identified potentially gold zones. The Nadezhda target now has the status of a gold deposit.

Mobile Metal Ion (MMI®) geochemistry of European agricultural soils

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Over two thousand agricultural (Ap) soils, at a sample density of approximately one sample per 2500 km^2 taken as part of the GEMAS project over continental Europe, have been analysed after MMI® extraction for more than 50 elements. For many elements MMI® analysis is a proxy for “bioavailability”. In a number of samples, high levels of Ce (>1 ppm) are shown to be derived from granitoid substrate in the Scandinavian Shield, Scotland, parts of France and north-west

Spain and Portugal, whilst in others high levels of nickel (>8 ppm) coincide with ophiolites in northern Italy, Bosnia, Herzegovina, Slovenia and Greece. A large number of soils associated with limestone in the eastern UK, France, Spain, Italy, Germany and the Ukraine show high levels of MMI® calcium (>800 ppm). Weathering patterns are apparent in the MMI® distribution patterns for a number of elements, particularly Fe, Ti and Al, which display higher values in soils in northern Europe where rainfall is higher and evaporation a minimum. Calcium in general is higher in southern and eastern European soils where annual evaporation exceeds annual precipitation. Examples highlighting the local presence of mineralisation are evident for Fe at Kiruna and Malmberget in Sweden, Au in north-eastern Portugal, Ag near Rio Tinto in Spain and Cd near Navan in Ireland. In the case of Pb, the highest value (58.3 ppm) is for a soil in an old lead mining district in Derbyshire, although the influence of anthropogenic activity cannot be discounted. Similarly the highest values of copper (>50 ppm) occur in French vineyards, including the Bordeaux district where Cu-based fungicidal sprays have been used. Other examples of anthropogenic activity are the effects of fertiliser on soil contents of P, S, Cd and K.

Variable-scale geochemical anomalies related to gold-bearing systems: Methods of indication, evaluation, interpretation and case studies

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A system approach to geochemical prospecting for gold generally implies stage-by-stage indication and evaluation of gold-bearing systems of different ranks: ore clusters, ore fields, and ore deposits, with their primary halos. These systems are manifested in different scale geochemical anomalies which are determined by means of sequential geochemical surveys. The typical sequence includes: (a) stream sediment geochemical prospecting at reconnaissance stage; (b) soil geochemical prospecting at follow-up stages; and (c) rock geochemical exploration at final stages. It has been shown that productive geologic systems with economic gold deposits differ from non-productive ones based on the principal features of geochemical anomalies. As a rule, the inherent feature of the multi-element geochemical anomaly of a productive system is an arranged structure with sharply manifested geochemical zoning (regular spatial relationships between anomalies of different indicator elements) and a combination of enrichment and depletion zones. Expression of this common feature is specific for each rank of a gold-bearing system and, correspondingly, a scale of multi-element geochemical anomaly. Other differences appropriate to stream sediment and soil anomalies depend on the type of cover and other supergene conditions.

Natural processes of rare earth element fractionation and implications for soil development

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Natural biogeochemical processes can be reconstructed by their effects on the distribution of rare earth elements in a wide variety of materials. At high temperatures, the REE concentrations of minerals are strongly controlled by the systematic variation in lattice strain related to the changes in ionic radii of the trivalent rare earths. The ability of Eu and Ce to undergo changes to divalent or tetravalent states and their accompanying changes in distribution coefficient into minerals is revealed by the presence of either positive or negative anomalies in the abundance of these elements relative to that exhibited by the simple trivalent REEs. Chemical weathering results in residual enrichment of REEs in soils relative to their parent rocks because of the insolubility of REEs in surface waters. In highly leached tropical laterite soils, REE concentrations may become elevated to the level of an ore deposit. Although residual enrichment occurs, additional factors must be involved, both by simple mass balance and the fact that the REEs can be significantly fractionated during weathering. REE fractionations have been attributed to the production of microenvironments of varying pH and redox potential in the root zone and variable uptake into different types of vegetation. A complication is the addition of either natural or human materials. Wind-blown dust may be locally reworked or long-travelled and can therefore have variable REE patterns. Furthermore, many cultivated soils are treated with amendments that contain REEs, either by intentional application or as an incidental constituent. Combining REE abundance patterns of the resultant soils with their Sm-Nd isotope systematics can prove useful in deconvolving both the sources and processes involved in soil formation.

Government's role in applied geochemistry – a Canadian perspective

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Government geochemical data are independent impartial datasets that reduce risk for decision makers in mineral exploration, environmental assessment, urban planning, protected area selection, agriculture or public health. In Canada, the initiation of large-scale centre-lake and stream sediment surveys in the 1970s is an early example of government recognising the need for geochemical data. Since then, more than 110,000 lake and 90,000 stream sediment samples have been collected by Canadian government agencies as a cost effective means of assessing regional scale mineral potential. Geochemical surveys in Canada additionally employ till, soil, and vegetation. Canadian exploration successes directly related to government geochemical surveys include the discoveries of the Kudz Ze Kayah, Star Lake and Brewery Creek deposits and, more recently, the Rainy River gold deposit. Stream sediment surveys have facilitated protected areas decision making, including the identification of high mineral potential in the South Nahanni River area. Governments use geochemical surveys to identify areas at risk due to natural or anthropogenic contamination. Recent surveys in southern Ontario have identified groundwater contaminated by historic gas production and areas with natural fluoride contents that exceed the drinking water criteria. On the Canadian Prairies, elevated contents of cadmium in wheat indicate natural contents in soil and bedrock. Since the explosion in diamond exploration activity and discoveries in northern Canada in the 1990s, indicator minerals have become an important part of government geochemical surveys supporting mineral exploration. Government agencies have helped adapt diamond indicator mineral methods for exploration for magmatic Ni-Cu-PGE, VMS, IOCG, MVT and intrusion-hosted Cu, Mo and W deposits. The Canadian Geochemical Surveys website is an example of how large volumes of geochemical data for different media, analytical methods and government jurisdictions can be linked and delivered to the public using modern web-based tools, including plotting data as KML files in Google Earth™.

A closer (and closer) look at iron indurated cover sequences for mineral exploration

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The Murray Basin in SE Australia is a shallow sedimentary basin concealing large tracts of bedrock prospective for gold and base metals. Decades of work have constrained the tectonic and stratigraphic history of the basin, yet there is no comprehensive geochemical study of the region. Samples have been collected from an extensive (140,000 km^2) Late Miocene-Pliocene strandplain known as the Loxton-Parilla Sands. Bulk geochemistry, XRD, HyLogger^{TM} hyperspectral mineralogy, isotopic analysis, and morphological and chemical microanalysis all combine to provide new insight into the metal mobilisation and weathering history of the western Murray Basin. Bulk geochemistry via ICP-MS and XRF show the vertical and chemical heterogeneity within the same unit, for example, 0.5% to 80% Fe_2O_3, 0.6 ppm to 1,100 ppm As, and up to 60 ppb Au. Highly variable trace element chemistry is observed in parts of the formation rich in iron oxides, distinctive components of the cover often used as exploration sample media. Microanalysis including SEM and LA-ICPMS complement bulk geochemical analyses and shows how minor mineral phases host trace elements like V, Ni, U, Th, and Cu, and how the bulk geochemistry is influenced by the heavy mineral content of the sand. The HyLogger^{TM} core and rock chip scanner is a rapid, non-destructive method to determine mineralogy from reflectance in the VNIR, SWIR, and TIR spectral range. It shows a number of clay minerals dominated by kaolinite as well as nontronite, montmorillonite, and smectite, and iron oxides of hematite and goethite. It is supplemented by XRD analysis for more detailed information on mineral crystallinity and abundances. This work brings together data and observations from the basin scale to the micrometre scale to demonstrate the value of understanding dispersion mechanisms and landscape evolution in mineral exploration.

Element accumulation and fractionation processes in ferruginous lag: Implications for geochemical exploration

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Surficial lag is a widely used sampling medium for geochemical exploration in semi-arid, low relief terrains. Key hosts for many target and pathfinder elements in this lag are the iron oxides/oxyhydroxides. Understanding how elements are accumulated and preserved in this ferruginous material is of fundamental importance for interpreting geochemical anomalies detected by lag sampling. Ferruginous lag is derived from a range of regolith components, but particularly the underlying mottled zone, pedogenic nodules, ferruginous duricrust and in some cases gossan. During weathering, ferruginous mottles and nodules fix target and pathfinder elements leached from the surrounding saprolite or introduced by groundwater. When these elements are substituted/incorporated they become less leachable compared to absorbed or weakly bound cations (e.g. on clays) and preserve this geochemical signature. Gossans retain a signature of elements by a similar process, after most of the target and pathfinder elements have been leached. Lag accumulates by surface deflation, bioturbation and differential movement related to shrink-swell of clay and soil creep. It then undergoes physical and chemical maturation from mechanical reworking, transport and geochemical/biogeochemical processes. This results in progressive decrease in clast size and rounding, mineralogical changes and loss of soluble components, precipitation of additional iron oxides and residual element concentration. Analysis of mottles, nodules and lag from 10 sites in the Cobar area reveals chemical fractionation during uptake of elements in the weathering zone, dependant on lag mineralogy, followed by additional fractionation during surface modification. This fractionation has concentrated some target and pathfinder elements from background values to what might be misinterpreted as mineralisation related anomalies. The study shows that it is critical to understand the transport history, mineralogy and chemical fractionation of lag in order to assess lag geochemistry. Fractionation templates constructed for background and mineralised sites can assist normalisation and correct interpretation of lag geochemical data.

Arsenic in the urban environment, Canberra, Australia: Understanding anomalies and dispersion processes

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Urban areas of Canberra contain numerous arsenic soil anomalies. Since their detection in the 1990s, these areas of elevated arsenic have raised concerns with residents and development agencies. More than seven sites have been linked to contamination or potential contamination from historic sheep dips, but others have no history of anthropogenic contamination. Investigation of an anomalous site in the suburb development of Lawson has shown arsenic in the A and upper B horizons of the soil to be derived by a two-stage process of leaching and dispersion from weathered sulphide mineralisation. Arsenic concentrations above 100 ppm were initially detected in two soil profiles. Petrographic examination and analysis of soil fractions revealed that arsenic in one profile is hosted by ferruginous (hematite-goethite) pedogenic nodules. Arsenic in the other profile appears to be in recently mobilised colloidal form. Subsequent field mapping and sampling, located a quartz-ironstone gossan and ironstone fragments down slope. Ferruginous nodules were also observed as lag in areas of recent soil erosion. The ironstones contain 127-2831 ppm As, elevated Cu (308-731 ppm), Zn (178-911 ppm) and Bi (4-19 ppm), with trace gold (30 ppb). They contain low Mn (<120 ppm) and Ba (<100 ppm). Pedogenic nodules down slope are enriched in As (up to 315 ppm), but those more distal show a systematic decrease in As (to 40 ppm) with distance from the ironstone. The nodules contain elevated Mn (725-3577 ppm) and Ba (58-285) relative to the ironstones. The ironstones represent hydrothermal vein or skarn-type sulphide mineralisation that has released arsenic during weathering. Some arsenic has been absorbed onto iron minerals in the pedogenic nodules. Arsenic bioavailability from the ironstones and nodules is low (<0.1% by ASLP) indicating low risk to humans. The study highlights the importance of understanding arsenic sources, forms and dispersion processes in environmental assessments.

Geology, geochemistry, terroir, and wine – the science of good taste

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Mounds of grape seeds in prehistoric caves testify that early people had more than a passing acquaintance with wine. The records of the ancient Egyptians and Greeks also contain observations that certain regions seemed to produce better wine than others. This observation carries through to modern times where the question is brought into sharp focus by the rather simple occurrence of two vineyards, side by side, that share most obvious aspects of climate, slope, and viticulture, yet produce crops that are vastly different. Examples abound but perhaps the most spectacular are the vineyards of Burgundy, where Grand Cru wines such as Romanee-Conti have been highly valued for centuries (some bottles sell for thousands of dollars), while nearby vineyards produce wine that is sold as vin ordinare for less than a dollar a bottle. The simple question is, "Why?" Although to some extent the terroir of each vineyard is unique, there are some common threads that are shared among better vineyards. Probably the most important factor is the restricted availability of water and nutrients – grape vines need to be stressed to a critical level for best results (the “Goldilocks” approach: just the right amount – not too much, not too little). Clearly, climate is the first order control of water, and it is an observational fact that there are no vineyards in rain forests or where root zones are saturated – this is too much water! Where natural precipitation is moderate to sparse, however, it is the drainage of that water from the root zone of the vines that becomes most important. This is one connection to the predominance, in quality vineyards, of coarse clastic sediments/rocks, typically of alluvial, fluvial, or glacial origin. This is seen in the alluvial fans of Napa Valley, California and Tuscany, Italy; the glacial-fluvial terraces of Bordeaux and Gimblett Gravels, New Zealand; and the glacial-lacustrine sediments of British Columbia, New York, Ontario, Oregon, and Washington. Another important terroir factor is nutrient availability from soils and bedrock. Mineralogical and chemical composition, as well as soil/bedrock textural properties, can all affect wine quality. At a broader scale, depositional processes such as floods and young glacial outwash are likely to restrict the amount of certain nutrients, such as those resulting from the slow decomposition of organic material, relative to residual soils developed over long periods of time. This, in addition to drainage, will have an impact on vine vigour such that the overall physical environment becomes inseparable from the ultimate characteristics and quality of wine.

Boron and lithium isotopic signatures of basement lithologies of the eastern Athabasca Basin: Implications for understanding fluid source and fluid flow

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Boron (B) isotopic signatures, preserved in refractory minerals such as tourmaline, can aid in determining the source of fluids and P-T conditions during crystallisation, whereas lithium (Li) isotopic fractionation is indicative of weathering, hydrothermal alteration, and/or igneous and metamorphic processes. The objective of this research is to measure the bulk δ^7Li and δ^{11}B isotopic signatures of the basement lithologies and to determine the potential insight that Li and B isotopic signatures can provide for fluid source and fluid flow beneath the Athabasca

Basin in proximity to unconformity-type (U/C-type) uranium deposits. The majority of the largest U/C-type uranium deposits in the world are located within the eastern margin of the Proterozoic Athabasca Basin in northern Saskatchewan. Many researchers agree that oxidised basinal brines transporting uranium flowed through the basement rocks, but the mechanics of deposition and source of uranium are still highly debated. A suite of fresh to strongly altered samples was selected from multiple sites in the eastern Athabasca Basin. Bulk chemical Li concentrations range from 28 to 591 ppm, whereas B concentrations range from 12 to 11300 ppm. Elevated concentrations of Li and B are expected because of the presence of hydrothermal clay minerals and tourmaline. Also present are magmatic and/or metamorphic tourmaline, which contribute to this B and Li isotopic budget. Granitic pegmatites display δ^7Li values between +3.94 to +18.4 ‰ and δ^{11}B from -5.3 to +16.1 ‰. The δ^7Li range for metasediments is slightly less, between -0.40 to +12.7 ‰, with δ^{11}B ranging from -16.3 to +17.0 ‰. The significant variations in δ^7Li and δ^{11}B are interpreted to be representative of multiple fluid sources or mixing of magmatic/metamorphic and hydrothermal components in these bulk samples pre/post U deposition.

Temporal and spatial variability of element concentrations within *Eucalyptus camaldulensis* leaves in a semi-arid region and the effect that El Nino has on biogeochemical sampling

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Australia is well known for extreme weather conditions, these extreme conditions have, in part, been attributed to the El Nino – La Nina phenomenon. Many studies into the effect of the El Nino – La Nina phenomenon on the vegetation of Australia have been conducted as have studies into the temporal and spatial variation in the chemistry of trees however there is a gap in the research when it comes to the effect these conditions have on biogeochemistry of Australian flora when used as a mineral exploration tool.

Pine Creek is a north to south flowing ephemeral creek system 10km south-east of Broken Hill, NSW. The creek flows along the eastern margins of the Pinnacles Pb-Zn mine, cutting through shallow mineralisation. *Eucalyptus camaldulensis* (River Red Gum) grow along its banks and within the channel. Leaves from these trees have been sampled to define the presence of the mineralisation, measure the extent of lateral dispersion along the creek, as well as the effects of temporal and climatic variation on biogeochemical characteristics. Samples were collected over two periods; 2005 when the previous year's annual rainfall was 187.8 mm (El Nino period), and 2012 when the previous year's annual was 605 mm (La Nina period). This long period of sampling has allowed an investigation into the effect of rainfall availability on the biogeochemical results of the River Red Gum in a mineral exploration context.

Analysis has shown that during El Nino climatic conditions the Eucalyptus trees can store up to an order of magnitude higher concentrations of lead (411 ppm) and zinc (338 ppm) than in high rainfall years of La Nina conditions (Pb 89 ppm and Zn 83 ppm) in samples collected directly overlying mineralisation. The change in available water for uptake by the plants plays a significant role in the resulting biogeochemistry of the trees and the potential implications for sampling programs that may spread over several field seasons.

The petrology, geochemistry and ore genesis of the alkaline REE Toongi deposit, Dubbo NSW

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The Toongi rare metal deposit is located approximately 20 km south of Dubbo in central New South Wales, and is one of the world's largest in-ground resources of Zr, Hf, Nb, Ta, Y and REE. The deposit is one of several Triassic trachytic intrusions in the Dubbo area, yet is one of only two igneous bodies with economically viable rare metal contents. The trachyte bodies form elliptical, flat-topped sills and flows that often feature concentric flow banding. Petrographic analyses of 15 alkaline bodies reveal the trachytes are comprised of K-feldspar, albite, aegirine – augite and alkali amphibole phenocrysts surrounded by a fine-grained feldspathic trachytic groundmass. The rare metals are hosted in intergranular, texturally complex natroniobite, REE carbonates and zirconium gels that either form colloform precipitates in vesicles/vugs or replace an as yet unknown mineral with hexagonal habit (possibly eudialyte). Bulk-rock major and trace element concentration data (acquired by XRF and LA-ICP-MS, respectively) are used to test the relationship between mineralisation and igneous and hydrothermal processes. For most of the igneous bodies, crystal fractionation, as monitored by decreasing TiO_2 contents and Eu anomalies, correlates with increasing rare metal concentrations. However, Y, REE, Zr, and Nb concentrations in the Toongi deposit are nearly an order of magnitude higher than in the most fractionated unmineralised trachyte bodies. Furthermore, there is no correlation between fractionation indices (i.e. Eu* or TiO_2) and metal concentrations in the Toongi deposit, which indicates that a separate process has amplified the ore metal grades. The proposed model for genesis of the Toongi deposit involves the shallow emplacement of highly fractionated trachytic magma, possibly during extension and/or mantle plume activity. During or soon after emplacement, influx of fluorine-rich hydrothermal fluids, exsolved from a deeper-level magma reservoir(s), are inferred to have transported the bulk of the ore metals into the Toongi igneous body. Rare metal precipitation from the fluid may have resulted from pressure and/or temperature changes, or reaction of the fluid with the trachytic host rock.

The timing of gold anomaly formation in regolith, east Wongatha area, Western Australia

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A regional regolith geochemistry programme in the east Wongatha area of Western Australia identified several samples with anomalous gold concentrations in the fine (<50 μm) fraction of regolith, including one sample with an aqua regia gold concentration of 14 ppb. At this sample site, regolith is characterised by at least 10 m of dominantly eolian quartz-rich sand. Samples from a pit excavated to a depth of 1.8 m were collected for geochemistry and optically stimulated luminescence (OSL) dating of quartz. Fine-fraction aqua regia gold concentrations, ranging from 7 to 31 ppb, gradually increase with depth. The lowest concentration of 7 ppb is found in a sample at 15 cm, which is less than the upper level of background of 9 ppb established from the regional program. Gold concentrations following deionised water digestion show a strong positive correlation with aqua regia data, but there is no correlation between Au and Ca, indicating no carbonate control on the distribution of gold. OSL dating shows an age range from 6.7 ± 1.8 ka at 60 cm depth, to 38.9 ± 19.7 ka at 120 cm, to 90.9 ± 19.0 ka at 180 cm. Over this depth interval, the vertical change in gold concentration is approximately 1ppb/7,600 years, with an average sand accumulation rate of 1 mm/70 years. The correlation of gold concentrations by aqua regia and deionised water techniques in the <50 µm fraction indicates gold is microparticulate and/or water soluble. Gold concentrations in regolith at shallow depth are in the background range, which has implications for the depth of sampling in regional programs; shallow regolith may be too young to have acquired a signature of buried mineralisation, which results from vertical migration from bedrock-hosted mineralisation.

Chemistry of thermal waters – examples from the Rotorua geothermal field

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The composition and the chemistry of discharging fluids from a geothermal field reflect its hydrology and thermal history. The geochemical methods used to interpret the data rely heavily on the utilisation of two opposing properties of the chemical and isotopic constituents, which can be either "reactive" or "conservative". Reactive constituents tend to equilibrate with other reactive constituents and/or rocks and minerals and give information on the state of the geothermal system (e.g. temperature). In contrast conservative constituents are tracers which are largely unaffected by physical and chemical changes in the reservoir and once in the fluid phase they remain there. The use of these techniques is illustrated for the Rotorua Geothermal Field (RGF). The RGF is unique in that it contains New Zealand's last remaining area of major geyser activity. A significant decline in thermal activity since the 1970s due to excessive exploitation led to a bore closure programme beginning in 1986. However, to date, the recovery of natural features has been mixed, with most of the large failed geysers showing no signs of recovery. There are pronounced East to West chemical gradients across the RGF with Cl decreasing from over 1000 mg/kg to 300 mg/kg, inversely correlated with HCO_3 which reaches a maximum of ~400 mg/kg. The B/Cl ratio decreases by a factor of three between East and West and, as both constituents are conserved, suggests steam loss or dilution cannot explain the chemical difference. The chemical and isotopic evidence supports previous work that indicates that there are two separate plumes making up the overall RGF. The main upflow is to the Nth East at Napuna were Cl is highest and low relative concentrations of CH_4 suggest boiling and steam loss. A smaller separate upflow in West to the Kuirau area is chemically distinct with low Cl, high HCO_3 and high relative concentrations of CH_4.

Unravelling the nitrous oxide biogeochemistry in Southwest Pacific Ocean using stable isotopes

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Nitrous oxide (N_2O) is a potent greenhouse gas whose concentration in the troposphere is increasing at a rate of 0.25% annually. Oceans account for most of its global flux, however, the biogeochemical pathways leading to its formation are poorly understood. Nitrification and denitrification dominates N_2O production with the N_2O source output varying with oxygen availability. This paper describes the dissolved nitrous oxide concentration and its changes with apparent oxygen utilisation (AOU). Samples were collected from three different water masses around New Zealand. For the first time novel stable isotopic methods including $\delta^{15}N_{bulk}$, $\delta^{18}O$, $\delta^{15}N^{\alpha}$, site preference (SP-which is the difference between $\delta^{15}N^{\alpha}$ and $\delta^{15}N^{\beta}$) for N_2O and dissolved oxygen. N_2O concentration at all depths was above air saturation. Maximum N_2O concentration was observed in the deep oxygen minimum zone. Isotope values give important clues for upper nitrification production and lower denitrification. Isotopomeric results helped to understand the production mechanism and revealed that the area is neither a good source nor a sink for nitrous oxide.

Soil and stream sediment geochemistry of the B8 Olifants Catchment, Giyani, South Africa

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The Olifants primary catchment area, which consists of about eight sub-catchments marked from B1 to B8, straddles the border between South Africa and Mozambique and, has a total area of approximately 87,000 km^2. The B8 catchment is where most of the legal and illegal gold mining activities occur, surrounding the major town of Giyani in the Limpopo Province, South Africa. Although industrial and agricultural activities are also important contributors, pollution from the mining activities within the area is significant and yet its contribution is not fully quantified. A multi-disciplinary project is underway to investigate (1) the severity of the mining impacts on the water resources and (2) the levels of exposure to the toxic metals. One of the techniques adopted at the screening level for pollution assessment includes soil and stream sediments as sample media. Analyses were done by SXRF and ICP-MS for metal concentrations. We determined from the regional soil chemistry, which was sampled at a density of one sample per square kilometer, that the communities around Giyani are exposed to As (range from 32 to 1040 mg/kg in soils and 56 to 237 in sediments), Co (range from 50 to 213 mg/kg in soils and 134 to 493 mg/kg in sediments), Cr (range from 885 to 7880 mg/kg in soils and 1220 to 1700 mg/kg in sediments), and Cu (range from 92 to 375 mg/kg in soils and 99 to 300 mg/kg in sediments). The metal sources are clearly defined. The concentrations of these metals were higher than the 95th percentile, at levels above the required concentrations listed in soil quality guidelines. The stream sediment data also indicate the extent of downstream migration of these metals, and other associated metals.

New insights into the origin and distribution of phosphate deposits on the Chatham Rise

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The Chatham Rise is a narrow topographic high extending east from Banks Peninsula to the Chatham Islands, rising from more than 2000 m water depths to ca. 400 m across the central Rise. A distinctive feature of the Rise is a nodular phosphate deposit which shows great promise as a mineable resource. Delineating the resource requires updating and summarising the geological history of the Chatham Rise in a geological model. Questions to be answered include: What triggered phosphatisation? Was there more than one phase of phosphatisation, and if so does each phase cover the same area? The geological history of the Chatham Rise reflects that of New Zealand, while paleoceanographic changes may reflect changes around Antarctica. The Rise has a core of Permo-Jurassic greywacke, which was rifted and block faulted as Zealandia separated from Gondwana during the mid Cretaceous. In Paleogene to middle Miocene times, the central Rise saw mostly chalk deposition, interrupted by periods of non-deposition and erosion, coincidental with major paleoclimatic events such as the mid-Late Oligocene opening of the Southern Ocean and middle Miocene expansion of the Antarctic cryosphere. In the Chatham Rise region, this meant cooling temperatures and the establishment of the modern currents including the Subtropical Front and expansion of Antarctic Intermediate Water. Extensive hardgrounds were developed in the Oligocene and Miocene, with phosphatisation and subsequent glauconitisation events in the Miocene and possibly the Pliocene. Chatham Rock Phosphate enabled a series of surveys of the central Chatham Rise in 2011 and 2012, gathering geophysical data as well as sediment sampling. This data, including phosphate nodule concentrations, geochemistry, and grain size and shape, combined with results previous cruises from the 60s to 80s, will help elucidate the history and extent of the phosphate deposit.

Arsenic release from neutralised tailings: Implications for mine closure

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Understanding the processes controlling metal contaminant mobility is essential to successful remediation of metalliferous mine sites. This study investigated the geochemical and mineralogical processes controlling arsenic mobility in tailings at a historic tin mine (Royal George, Tasmania). The acid-generating tailings contain elevated concentrations of environmentally significant elements (>100 ppm mean concentrations of As, Cu, Mn, Pb, S, Sn and W; <100 ppm of Ag, Bi, Cd, Co, Sb, Th, Tl, U and Zn). Efforts to prevent acid rock drainage (ARD) from the tailings repository and to encourage natural colonisation of the tailings surface by native plants were carried out by statutory authorities in 2006, through the application of limestone and phosphate fertiliser pellets. Scanning electron microscopy and electron microprobe analyses of both limestone- and fertiliser-amended, and non-amended tailings identified scorodite and iron oxide phases as the dominant arsenic rich phases. The solubility of arsenic species in the amended and non-amended tailings was evaluated by a series of chemical extraction techniques. The results showed that in some extractions arsenic release was significantly reduced by the limestone and phosphate fertiliser amendment, relative to the non-amended tailings. However, at high sulphate concentrations, typical for ARD environments, arsenic mobility was significantly greater (3x) in the amended tailings versus non-amended tailings, possibly due to arsenic desorption from iron oxide mineral surfaces. Similarly, the amendment of tailings with soluble phosphate fertiliser pellets may enhance arsenic mobility from the wastes. Results of this study demonstrate that successful closure of metalliferous mine sites and their waste repositories requires consideration of the mineralogical and geochemical properties of wastes prior to remediation.

Rate-controlling species in dissolution of stibnite in reducing, sulfide-containing aqueous solutions at 30°C

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The modelling of antimony sulphide (stibnite, Sb_2S_3) precipitation and dissolution in geothermal power station infrastructure are generally based upon batch solubility studies (Krupp 1988) in which an antimony sulfide dimer, $Sb_2S_4H_w$ (w = 0 - 2) controls stibnite solubility over the pH range from 3 to 10 in reducing solutions containing 0.1 to 0.001 mol/l total dissolved sulphide ($S^{2-}_{total} = HS^- + H_2S_{(aq)}$). A general reaction can be written for stibnite dissolution to this species at basic pH:

$$2Sb^{3+} + 4HS^- + (w)H^+ = Sb_2S_4H_w\ (w-2)$$

Our current studies of stibnite solubility using a flow-through experimental apparatus suggest that the kinetics of stibnite dissolution at pH ~ 7.5 and from 0.05 to 0.1 S^{2-}_{total} are independent of sulphide content. For example, at pH = 7.5 and 0.1 S^{2-}_{total}, the solubility (flow-through measurements) of stibnite is 3.5 ppm, which is somewhat lower than the value (Sb ~ 15 ppm) measured by Krupp (1988) for these conditions. These results indicate that $Sb_2S_4H_w$ may not be the first-step dissolution product at weakly alkaline pH but instead suggest that a hydroxy-thioantimonite species such as $Sb_2S_3OH_w$, could be the first-step dissolution product of stibnite via a reaction such as:

$$2Sb^{3+} + 3HS^- + OH- = Sb_2S_3OH_w\ (w-2) + (4-w)H^+$$

A hydroxy-thioantimonite complex may control stibnite precipitation patterns in systems where geochemical conditions favour kinetic control of dissolution/precipitation processes.

Krupp, R.E., 1988. Solubility of stibnite in hydrogen sulfide solutions, speciation, and equilibrium constants, from 25 to 350°C. Geochimica et Cosmochimica Acta 52: 3005-3015.

Increasing your greenfields to project development advantage using simple lithogeochemistry applications – examples from Au and Cu-Au systems around the world

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Multi-element assay data spans the entire Greenfields to mining-geometallurgy continuum; however it is often under utilised in the quest to turn an ever increasing amount of data into actionable information. Here, we demonstrate how interpretation tools such as Principal Component Analyses (PCA), Pearce Element Ratios (PER) and General Element Ratios (GER) can help assess fertility, vector to ore and provide vital geometallurgical information. Applying PCA to data from a greenfields exploration project for Au-veins allowed development of a custom classification diagram that discriminated barren- from Au-bearing basalt. Trace elements were used to increase confidence in vector development as sampling intervals masked trends and alteration due to veining. Plots of GER (K+Na/Al vs Fe+Mg/Al) and PER (Al/Ti vs K/Ti) were applied to data from a brownfields Cu-Au-U system to compare distal-, proximal- and deposit-hosting geochemical signatures. A clear trend away from alkali-feldspar towards muscovite and then chlorite is observed as mineralisation is approached. This trend is mirrored by changes in trace element chemistry. Importantly, these diagrams expand the deposit footprint beyond the commonly (and sometimes exclusively!) used commodity halo. The identification of such an alteration system is of great importance to vectoring to ore. Geometallurgical studies are typically sparse on spatially representative data; therefore leveraging the data-rich exploration environment can add significant value. Application of PCA on data from two ore zones of a Cu-Au system revealed significant differences not identified in hand sample. Early identification of deleterious elements, the presence/absence of acid consuming minerals and other indice-proxies are important in assessing project viability. The use of PCA, PER and GER plots add instant value and insight. Importantly, these diagrams can be easily and quickly applied to new and expanding datasets and provide a constant point of reference, such that reliable comparisons can be made.

Solid-phase distribution and oral bioaccessibility of cobalt and lead in outdoor dusts of Estarreja city, north Portugal

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Estarreja has typical urban metal sources, but is also strongly influenced by an Industrial Chemical Complex, which includes several chemical industries such as a chlor-alkali plant. A total of 21 outdoor dust samples were collected throughout this industrial city. The study of the solid-phase distribution was carried out using a Selective Sequential Chemical Extraction (SSCE) method. A study on the oral bioaccessibility of Pb and Co in outdoor dusts was carried out using the Unified BARGE Method. Dust pH and organic matter (OM) content, and other physico-chemical properties, were determined in all samples. The pH of the dusts varies between 6.44 and 7.6 while the OM content ranges from 1.24 and 20.6%. The solid-phase distribution, for both Co and Pb, is highly variable between samples. Near total and bioaccessible concentrations are higher for Pb (average values of 109.6 mg/Kg and 63.3 mg/Kg for near total and bioaccessible concentrations, respectively) than for Co (average values of 4.4 mg/Kg and 1.68 mg/Kg for near total and bioaccessible concentrations, respectively). There is a good positive correlation between near-total and bioaccessible concentrations for both elements. Comparing the results of the solid-phase distribution with the bioaccessibility estimates, it is clear that only the silicate residue is never solubilised by the gastric fluids. The solubilisation of other Co host phases varies between samples. There is some evidence that the bioaccessibility of Co is controlled by two coincidental factors: a pH value below 7 and a major fraction of the Co hosted by OM, which render the highest bioaccessibility fractions; a pH value above 7 and Co associated only with carbonate phases, provide the lowest bioaccessible fractions. A different result is obtained for Pb as the bioaccessibility of this metal seems to be controlled mainly by carbonates.

Geochemistry in prospectivity modelling: Investigating epithermal gold mineralisation in the Taupo Volcanic Zone, New Zealand

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Prospectivity modelling of epithermal gold mineralisation has been completed over the Taupo Volcanic Zone (TVZ). The TVZ is unique in that it is the present-day analogue of the environment in which epithermal ore deposits, such as those in the Coromandel Peninsula, are created. The model utilises newly compiled digital data including historical exploration data, geological data from the GNS Science QMAP Rotorua mapping project, recent Glass Earth geophysics data and abundant geochemical data including rock chip and stream sediment analyses. The weights of evidence modelling technique was used to determine spatial correlations between known deposits and predictive maps, created from the available data, representing each component of the currently accepted mineral system model for epithermal gold. There are a number of active geochemical processes occurring in the TVZ; changes in state, redox reactions and rock-water interactions all play a part in the dissolution, transport, and deposition of gold in hydrothermal environments. Exploration geochemistry is used to find chemical element enrichment that commonly occurs around a mineral deposit. The enrichment may be part of a primary envelope related to host rock alteration by hydrothermal fluids, and/or a secondary dispersal pattern, developed by weathering and erosion of a deposit. The primary envelope and secondary pattern form pronounced geochemical anomalies that present a larger exploration target than the mineral deposit itself. Predictive maps created from geochemical data collected in the TVZ provide a powerful tool in the identification of areas of gold mineralisation. The resulting prospectivity model over the TVZ confirms that the TVZ has potential for gold mineralisation, despite the limited coverage of several datasets. The most prospective areas are those associated with active and inactive hydrothermal alteration. Areas over the Rotokawa, Waiotapu and Ohakuri hydrothermal centres have been identified as highly prospective, and are present day analogues for epithermal ore deposits.

Isotopic insights into the behavior of gallium in hydrothermal systems

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In hydrothermal systems around the Taupo Volcanic Zone (TVZ), many metals are found in elevated concentrations in hot spring and geothermal well discharge precipitates. The metals include gold, silver, mercury, thallium and gallium, and are frequently associated with amorphous silica and arsenic and antimony sulfide precipitates. Gallium occurs in concentrations ranging from 8 to 150 ppm in surface samples of geothermal fields across the TVZ (Weissberg et al., 1979; Krupp and Seward, 1987). Weissberg et al. (1979) reported a gallium concentration of 700 ppm in one of the well-head (silencer) precipitates of the Ohaaki/Broadlands geothermal system. The Rotokawa geothermal system contains gallium in hot spring precipitates and geothermal well deposits up to 150 ppm and 15 ppm respectively (Krupp and Seward, 1987).

Little is known about the chemical behavior of gallium in natural systems or of its isotopic fractionation, especially under hydrothermal conditions. The gallium isotopic composition of hydrothermal precipitates, hot spring waters and geothermal well discharges (both liquid and steam phases) as well as natural Ga-containing mineral samples have been analysed using inductively coupled laser mass spectrometry (ICPMS). The gallium was quantitatively separated using an AG-50W-X4 cation-exchange resin to reduce isotopic interferences during ICPMS analysis. The results will be discussed in terms of phase separation and mineral precipitation processes in geothermal environments at elevated temperatures.

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Heavy mineral studies in Petäjäselkä, northern Finland

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Regional geochemical mapping was carried out in Petäjäselkä, northern Finland in 1982-1994. As a result several gold anomalies were found in the fine fraction of glacial till. This initiated an exploration project in the area in 2002. The study area is situated in the Paleoproterozoic Central Lapland greenstone belt on the northern continuation of the Porkonen iron formation. The bedrock has undergone hydrothermal alteration, resulting in sulfide-carbonate-quartz-rich veinlets enriched in gold. Bedrock is covered by a pre-glacial weathered surface from some centimeters to several meters thick, and is overlain mainly by basal till. During the last glaciation, Central Lapland was located in the ice divide zone characterised by weak glacial erosion and short transport distances by glacier. Thus, the till composition reflects the underlying bedrock quite well. In addition to geological, geophysical and systematic geochemical studies, test pit sampling (c. 200 test pits) was carried out in the area. Geochemical and heavy mineral samples were taken from the till and the weathered bedrock. Two different methods were used to concentrate the heavy mineral samples: Knelson concentrator with heavy liquid separation and spiral concentrator. The concentrates were examined under a binocular microscope to identify gold grains, sulfides and other heavy minerals. Some samples were analysed using a semi-automated Scanning Electron Microscope with an EDS detecting unit (SEM-EDS) and INCA Feature software to get an overall mineral composition of the heavy mineral fraction. Furthermore, c. 50 gold grains were analysed with the SEM-EDS. The results showed a large variation in the Au/Ag ratio of the gold grains in different parts of the study area consistent with a diverse source for gold. Furthermore, semi-automated mineral identification provides a good way for a total indicator mineral determination and an estimation of transport distance of till.

High resolution mapping of soil geochemistry at a regional scale (Wallonia, South Belgium)

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In many countries, government agencies rely on soil maps of trace metal background concentrations to implement soil protection policies. In Wallonia (South Belgium), regional regulations require extremely detailed background concentration maps. The main obstacles to obtaining these maps are the large variations in local background concentrations over short distances, mainly due to the high diversity of soil parent materials, and the atmospheric deposition of pollutants around former base metal smelters. Here we outline the methodology to produce the required geochemical maps, and present an example of the resulting geochemical maps at the land parcel scale. The methodology established for the geochemical mapping of soils involves three steps. Firstly, we divided the Wallonia area (17,000 km²) into pedogeochemical units of soil based on (1) the soil map of the Wallonia (1:20,000), (2) geological maps (1:40,000 and 1:25,000), and (3) literature data and surveys results about soils and geology of Wallonia. Secondly, we gathered about 17,500 georeferenced soil analyses from environmental surveys (that we carried out) or from regulatory analyses (required for agricultural use of sludge from sewage plants). Thirdly, we compiled the maps using a geostatistical model based on the map of the pedogeochemical soil units and the georeferenced trace metal analyses. The resulting maps show that Wallonia has higher Ni background concentration in soil than average values in Europe (according to the values of Geochemical Atlas of Europe), principally because of elevated geogenic background levels. Also, higher Zn and Cd values are found, principally due to atmospheric deposition of pollutants originating from former base metal smelters. Due to their resolution, the maps make it possible to predict, for instance, the risk of exceeding threshold metal concentrations in any particular land parcel in Wallonia.

Geochemical variations in the Sams Creek gold prospect, NW Nelson, New Zealand

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MOD Resources, in a joint venture with OceanaGold, are currently exploring a gold prospect at Sams Creek in NW Nelson. Gold mineralisation is hosted by a microgranite dike that extends 7 km along strike and is up to 60 m in thickness. Exploration has included programmes of field mapping, stream sediment, soil, and rock chip sampling, geophysical surveys and the drilling of over 120 diamond drill holes. Drill core samples a kilometre of vertical relief facilitating observations of large scale variations. In this study, we focus on geochemical relationships from which we interpret enrichment trends and document general spatial distribution of ore related elements. Analyses of 1 m half-core sections for Au, Ag, As, Cu, Pb, Zn, Mo, Bi, S, and Sb show that a Au-As-Sb assemblage is anomalous over the full scale of the deposit. Zoning patterns of Ag, Pb, and Zn are seen throughout the range of elevations sampled. Ag increases with elevation, while Pb and Zn decrease with elevation. At low elevation: Pb and Zn correlate and Mo is seen at its highest average values. At the upper level of elevation sampled we see a correlation of Ag and

Cu and the highest of these values occur. Scanning Electron Microscopy (SEM) shows gold typically occurring as an alloy with silver as small growths in-filling micro-veins which locally cross cut arsenopyrite (the most abundant ore mineral). Mineral hosts for the enrichment and variation of gold-related geochemistry include arsenopyrite, pyrite, galena, sphalerite, chalcopyrite, pyrrhotite, and molybdenite. All Sams Creek Dike (SCD) samples are highly enriched in Light Rare Earth Elements (LREE) moderately enriched in Heavy Rare Earth Elements (HREE) have a distinct negative Europium anomaly and no significant variation between stages of alteration. SEM imaging has substantiated a recent discovery of “hydrothermal zircons” present in the mineralising system. We interpret these zircons as precipitates formed when zirconium, native to the unaltered Sams Creek Dike, was remobilised by hydrothermal fluids.

Mobility of gold during metamorphism: Otago and beyond

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The sources of metals for orogenic gold deposits have long been debated, but much recent research has supported the metamorphic devolatilisation model where metal-rich fluids are produced during prograde metamorphic dehydration and related reactions. Investigations of a number of orogenic belts, including the Otago and Alpine Schists in New Zealand and the Dalradian Metasedimantary Belt (DMB) in Scotland, show that considerably more gold is mobilised than is trapped in orogenic gold deposits in these regions. The metamorphic mobilisation of gold and other elements associated with orogenic gold deposits, such as As and Sb, is shown through systematic depletions of these elements with increasing metamorphic grade. Recrystallisation of sulfide minerals during prograde metamorphism, in particular the recrystallisation of pyrite to pyrrhotite, is considered to be the driving force for the release of metals into the metamorphic fluids. Metamorphic processing of Torlesse terrane source rock beneath the Southern Alps of New Zealand probably mobilised thousands of tonnes of gold in the past five million years, with only a fraction of that gold being trapped in the gold deposits observed in the Southern Alps. In the DMB, systematic depletions of the same suite of elements have been observed, with approximately 1.5 t Au mobilised from every 1 km^3 of source rock during greenschist to amphibolite facies metamorphism. The DMB, which covers an area in excess of 15,000 km^2, is poorly endowed with orogenic gold deposits. These investigations indicate that the production of gold-rich fluids is not the major control on generation of large orogenic gold deposits and provinces, but that other processes, such as efficient fluid focusing and potent precipitation mechanisms, may be the key.

Environmental and medical geochemistry in urban disaster scenarios

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In addition to the physical damages, casualties, injuries and psychological effects they cause, urban disasters can also produce large volumes of hazardous materials. These disaster materials can be geogenic (e.g. volcanic ash, landslides), geoanthropogenic (e.g. polluted flood sediments, smoke and ash from wildland-urban fires), and anthropogenic (e.g. industrial chemical releases, dusts and debris from building collapses, and smoke and ash from building or industrial fires). Environmental and medical geochemists can collaborate with hazards, emergency management, and public health experts to: characterise the physical, chemical, and microbial makeup of disaster materials; fingerprint and assess relative contributions of materials from multiple sources; elucidate how environmental processes modify disaster materials; monitor, map, and model the dispersal and evolution of disaster materials in the environment; characterise pre- and post-disaster environmental conditions; help understand exposure pathways and toxicological implications of disaster materials for urban populations and ecosystems; and, help identify appropriate disposal options for disaster materials to minimise additional health impacts or exposures. Environmental and medical geochemists can also contribute substantially to interdisciplinary urban disaster scenarios, which are increasingly used by hazards experts to help governments and communities prepare for future disasters. This presentation, growing from the outstanding efforts of many collaborators, will summarise urban environmental and related health implications of several such scenarios. These include the Southern California ShakeOut (which modelled the impacts of a hypothetical 7.8 magnitude earthquake on the southern San Andreas fault), ARkStorm (which modelled the impacts of a hypothetical weeks-long winter storm hitting southern and central California), and a California teletsunami triggered by an Alaskan offshore earthquake. Helping understand the plausible sources, types, environmental behavior, and health implications of natural and anthropogenic contaminants and pathogens that are involved in these disaster scenarios will ultimately enhance preparedness for and resilience to environmental and health consequences of future disasters.

Medical geology and geochemistry insights into the global potential for lead poisoning linked to artisanal or recreational metal mining

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Over the last decade, price increases in gold and other metals have caused artisanal mining to burgeon globally. Mercury contamination and its and associated environmental impacts have been widely recognised in artisanal gold mining areas around the globe, due to the use of mercury amalgamation to extract the gold. However, in 2010 Médecins Sans Frontières discovered a previously unrecognised result of artisanal gold mining and processing in northern Nigeria—an outbreak of lead poisoning that has killed ~400 young children and affected thousands more. The lead poisoning resulted from contamination of soils, living areas, water supplies, and foodstuffs by the processing of weathered, lead-rich gold ores with abundant, highly gastric-bioaccessible secondary lead carbonate minerals (Plumlee et al., 2013, Env. Health. Persp. http://ehp.niehs.nih.gov/1206051/). At Kabwe, Zambia, thousands of people were similarly affected by lead poisoning, which resulted from artisanal re-mining of and environmental exposures to wastes from historical lead-zinc mining and smelting (Branan, 2008, Geotimes). As with Nigeria, secondary lead carbonates are a significant component of the ores and wastes at Kabwe. Recreational mining is also a common practice in a number of developed countries, and although not carried out at the same scale or intensity as artisanal mining, may pose some similar health concerns. Economic geology analysis of artisanal or recreational mining areas around the world helps identify those where workers may be at higher risk for lead poisoning and needing medical surveillance. Of highest risk are lead-rich deposit types that have abundant carbonate gangue, occur in carbonate host rocks, are low in acid-generating iron sulfides, and/or are located in dry climates where surface waters and ground waters are alkaline—characteristics that promote weathering of minimally bioaccessible primary lead sulfides to form abundant, highly bioaccessible, secondary lead carbonates. Examples include polymetallic replacement deposits, some polymetallic vein deposits, and Mississippi-Valley Type lead-zinc deposits. Artisanal re-mining in historical mining camps with prior uncontrolled smelting of lead-rich ores will have high bioaccessible lead and high lead poisoning risk regardless of deposit type.

Substantiation of the property of soil cover's geodynamic memory and its practical applications

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Late Pleistocene-Holocene geodynamics are a factor in soil formation, with the resulting soil type linked to the development of relief. Velocities of vertical tectonic movements greater than 0.5-1 mm/year, up or down, significantly modify the soil cover in terms of its composition, texture and properties of the soil horizons. Thus, besides the influence of vegetation and climate, the effect of recent geodynamics is also significant. The geochemical evolution of soils is linked with the geodynamic regime. Areas undergoing uplift are characterised by simple soils, whereas areas undergoing subsidence and oscillatory movements have complex soils. Geostructures with oscillatory movements are covered by polycyclic soils with relicts of the past geochemical conditions. Changes in the composition, properties and types of soils over the newly-generated landforms correlate with the geomorphological and geodesic parameters. Applications of this concept of a geodynamic record or "memory" in soils include: a) identification of recent movements by mapping the soil cover structure; b) specifying areas of geodynamic risk for engineering projects; c) forecasting the geochemical background, anomaly thresholds, and associations of elements for exploration; and d) distinguishing the tectonic induced geochemical anomalies in surveys for hydrocarbon and mineral exploration. The successful examples of the employment of these applications in Dnipro-Donets Depression and Carpathians are presented.

Integration of geochemistry and IR reflectance data for improved understanding of alteration by ore-forming fluids and improved mineral exploration strategies

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Infrared reflectance data in the visible-near infrared and short wave infrared (vis-NIR-SWIR) are now an accepted data set used extensively by the exploration and mining industry worldwide. These data provide not only mineral identification of a wide range of mineral groups but can also provide data on certain mineral characteristics such as composition and crystallinity, and on variations in relative mineral proportions. These data, combined with geochemical data, such as assay and multi-element data, provide geologists and geochemists with an in depth understanding of alteration and mineralisation systems at all stages of development from exploration to mining. This presentation will discuss examples and case studies where integration of geochemistry and IR data have been modelled both in 2D and 3D and have provided geologists with powerful predictive information for targeting and planning drilling programs.

Modeling hydrothermal alteration facies of Earth's oldest hydrothermal setting: The 3.5 Ga North Pole Dome, Western Australia, Australia

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The North Pole Dome in the Pilbara Craton, Western Australia, is well known for hosting stromatolitic cherts of the 3.48 Ga Dresser Formation. These overlie a thick package of komatiitic basalts that are transected by a dense swarm of chert-barite veins.

Migrating acid steam-heated fluids altered footwall pillow basalts to hydrothermal kaolinite, possibly indicative of a high-sulfidation system. This is contrasted by fluid inclusion studies on epithermal quartz within the cores of chert-barite veins, suggesting a low-sulfidation system, typified by near-neutral fluids.

Recent mapping at the North Pole Dome has revealed regions of quartz-sericite-pyrite (phyllic) alteration focused around the most dense concentration of chert-barite veins, with hydrothermal kaolinite-quartz (advanced argillic) alteration restricted to the very apex of the system. More distal is an envelope of carbonate-chlorite-sericite (propylitic) alteration. Localised Fe-chlorite indicates a distinct alteration facies at this level, while carbonate alteration increases towards the paleosurface, reflecting the influence of circulating seawater.

We present a 3D geological model of the system, illustrating the spatial distribution of the hydrothermal alteration facies beneath the Dresser Formation and lateral stratigraphic variations within the formation. The results show that the Dresser Formation was deposited in an evolving extensional system. After initial uplift and shallow water deposition of stromatolitic carbonates, extension caused basin deepening, extensive fracturing of the footwall and hydrothermal circulation.

New Zealand coal mine drainage: Downstream chemical evolution and aqueous speciation

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Water rock interactions in areas disturbed by mining can lead impacts on water quality downstream of the mine. The reactive minerals and geochemistry of the processes that lead to mine drainage impact have been studied for the last 30-40 years and are well understood. However, mine drainage management, remediation as well as secondary minerals and long term geochemical processes are active fields of research. Changes in chemistry of mine drainage from the zone where AMD forms into the receiving environment is controlled by secondary minerals and aqueous chemistry related to these minerals has implications for management and treatment of mine drainage.

In New Zealand's acidic coal mine drainages, several common and predictable changes in mine drainage chemistry occur between the zone where oxidation of sulphide minerals takes place and the downstream environment. Roughly from upstream to downstream, these processes include oxidation of Fe(II)to Fe(III), partial neutralisation by alumino-silicate minerals, precipitation of a series of Fe minerals, partial adsorption of trace elements, substitution of Al for Fe as the dominant Lewis acid, precipitation of Al minerals, and complexation of trace elements. These processes can take place over a relatively short distance (~100 m) at an active mine site or several kilometres at legacy mine sites and the degree to which they occur define an evolution process for mine drainage chemistry.

Data used to identify mine drainage chemical evolution comes from laboratory based leach testing, field analyses at mine seeps, laboratory based mine drainage neutralisation tests, field observations in downstream environments and aqueous speciation modelling studies. Thorough understanding of the chemical evolution processes for mine drainage chemistry is used to:

- identify most appropriate mine drainage management options;
- improve the efficiency and effectiveness of active treatment;
- optimise the selection and performance of passive mine drainage treatment systems; and
- better understand the environmental impacts of mine drainages.

Ant nest geochemistry used to locate silver-lead-zinc mineralisation buried beneath 40+ metres of barren rock

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In the 6th century, Varaha Mihira, an Indian astronomer, mathematician, and astrologer described the importance of termite mounds as indicators of both groundwater and gold mineralisation. However, only during the last few years have termite and ant nests been actively investigated as geochemical indicators of buried mineralisation.

This paper describes the geochemistry of meat ant nests (Iridomyrmex purpureus) and termite nests located in a semi-arid climate of mixed eucalypt forest with barren sandstone cover rocks (<1 ppm Ag, 10 ppm Pb, <25 ppm Zn, and <44 ppm As) overlying (40-60 m) epithermal silver-lead-zinc mineralisation of the Bowdens Silver Deposit (NSW, Australia).

Metal contents of ant nests are in all cases much higher than in the surrounding soils and outcropping/subcropping rock. Ant nests are anomalous in Ag, Pb, Zn, As, Mn and Cd and reflect the composition of the buried mineralisation.

One ant nest (A4) located 40-50 m directly above high -grade mineralisation (>200 ppm Ag) is also anomalous in Sb, W, and Co. Comparison of nest samples (with surrounding soils) for this nest include:

4.19 ppm Ag of nest sample, (0.11 ppm Ag in soil), 269 ppm Pb (16.7 ppm Pb soil), 260 ppm Zn (11 ppm Zn soil), 89.2 ppm As (47.2 ppm As soil), 416 ppm Mn (59 ppm Mn soil) and 0.98 ppm Cd (0.03 ppm Cd soil).

A mechanism for metal accumulation by ants during extended periods of drought is proposed. Both ants and subterranean termites can have substantial underground nests/passages and after lengthy dry periods eucalypt tree root penetration into a fluctuating groundwater table may have provided these ants with access to a deep water source through joints and fractures.

Processes of metal accumulation are clearly different for ants and termites. Termites obtain food and moisture from vegetation and can accumulate metals in body parts via elevated metal content in foliage and branches of their cellulose food source.

Geothermal prospecting on a Type B Volcano - Mount Tangkuban Perahu area – West Java, Indonesia, using a geological and geochemical approach

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Indonesia, as one of the countries on the Ring of Fire, has numerous areas of geothermal activity. One of these, with potential geothermal resources, is in the area of Mount Tangkuban Perahu, West Java, Indonesia, and located at latitude 6.77 °S and longitude 107.6 °E. Mount Tangkuban Perahu is composed of intermediate composition lava flows and pyroclastic breccias that are locally hydrothermally altered. The lithological sequence is mapped as Old Volcanic Product, Breccia (Qyl); Undifferentiated Young Volcanic Product (Qyu); Pumiceous Tuff (Qyt); and Sandy Tuff (Qyd). The structure is dominated by the Lembang normal fault that influenced the formation of the Lembang Depression and Mount Tangkuban Perahu during the Quarternary.

The Indonesian volcano classification divides volcanoes into 3 types: Type A, Type B, and Type C. In general, geothermal exploration is usually done on volcanos of Type C. Geothermal prospecting on Type B volcanos such as Mount Tangkuban Perahu has only recently commenced. Mount Tangkuban Perahu volcano has no recorded magmatic eruption since 1600, although it still shows symptoms of volcanic activity. The active geothermal system was discovered by the presence of chloride (Cl) waters and acid sulphate waters (SO_4) representing the upflow area, bicarbonate waters (HCO_3) representing the outflow area, and fumarols. This study aims to undertake geothermal prospecting of the area by geological mapping surveys and geochemical surveys.

Spatial-temporal distribution of elements in clastic sedimentary rocks in a transect across South China: Implications for the W, Sn metallogenic province

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South China is comprised of the Yangtze and Cathaysia blocks bounded by the NEE-SWW extending Jiangshan-Shaoxing fault. In order to have a better understanding of the abundance and distribution of each element in South China, a geochemical investigation across a 2500 km transect in South China was conducted since 2008.

Samples of 539 fine-grained clastic sedimentary rocks of all the Mesoproterozoic to Cretaceous ages from the Yangtze to Cathaysia block have been collected at a spacing of 1 site/1-4 km. Both sandstones and mudstones are characterised by significant fractionation of LREE and HREE, negative Eu anomaly, high Th, U, Ba, and Zr relative to upper continental crust. The significant depletion of Ca, Na and Sr, and the pre-metasomatism CIA values suggest intensive chemical weathering of the source rocks. Discrimination diagrams involving La, Th, Sc, Co, Ti, Al, and Hf indicate a multiple lithological source including TTG-like, granitic, andesitic and felsic volcanic rocks. Compared to the Yangtze block, the Cathaysia block has lower Cr/Zr ratio and higher La/Co and Th/Sc ratios, due to contribution of more felsic materials.

Large-scale tungsten and tin mineralisation took place mostly in the Cathaysia block. Along the transect, the contents of W and Sn decrease from south to north and change abruptly at the South China orogen belt. The Cathaysia block have high W and Sn relative to upper continental crust and peak values occur in the Mesoproterozoic-Ordovician rocks. High background of contents of W and Sn in the Cathaysia block have provided for formation of the world’s largest W, Sn metallogenic province.

Deeply weathered profiles, an alternative interpretation and consequences for geochemical exploration for gold

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Deeply weathered profiles cover approximately ¼ of the current land masses and were more extensive in the recent geological past. The intense oxidation and leaching associated with these profiles poses challenges for mineral exploration. The exposed surface of such deeply weathered profiles is the logical first medium for mineral explorers to sample. In commonly accepted profile interpretations, a lateritic duricrust (sometimes non-genetically described as a ferruginous duricrust) overlies mottled clay, overlying upper and then lower saprolite, saprock and finally unweathered rock. This paper examines the timing of the development of the duricrust and the consequences this may have for mineral exploration, especially for Au. In the present day tropical rainforest environment, a duricrust capping to a deeply weathered profile is rare. The upper portions of the profiles are dominated by red brown latosols and one or more stone lines, frequently overlying saprolite. The duricrust capping and mottled clay zones are generally found in areas where the climate is drier, notably in the savannah regions which border the tropical rainforest belt. Understanding the processes that give rise to the profiles preserved in tropical and once tropical environments is essential for making informed decisions on whether or not to sample on a given duricrust surface and what to expect to find beneath such a surface. When sampling for exploration purposes it is essential to discriminate the null result from the negative result. For this to be done effectively, some knowledge of processes of profile formation is essential.

Geochemical maps of New Zealand

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New Zealand is yet to undertake a national geochemical baseline survey where background levels of chemical elements and compounds are systematically collected and analysed from soils, rocks and stream sediments. Such a survey (which is planned) is seen as an important component of future mineral exploration as well as contributing to environmental, human and agricultural health assessment and monitoring. In the meantime there are existing national geoscience datasets that, in combination, can be used as a proxy for a more comprehensive geochemical survey. Following extension of existing database designs and thorough standardisation of content, stratigraphic unit names from the New Zealand Stratigraphic Lexicon database, whole rock geochemical data from the PETLAB geoanalytical database and spatial extents from the QMAP Seamless GIS geological map unit dataset have been combined. Mean, minimum, maximum and standard deviation of all measured major and trace element concentrations for each New Zealand stratigraphic unit have been calculated and made accessible as SQL-generated database views. While some of these calculations are based on few measurements and are not statistically robust, more than 170 stratigraphic units covering c. 38% land area of the South Island have five or more analyses each. These values can be portrayed using GIS software to create geochemical variation maps of parameters such as weight percent SiO_2, ppm As or Sr/Y ratio. Of the geological map units in the South Island that either have not been geochemically analysed or which lack a stratigraphic name, 75% by area are Quaternary sediments. These sediments most commonly underlie agricultural and urban areas and should be a priority for future sampling and geochemical analysis.

Does low density geochemistry (1 site / 2500 km^2) deliver relevant information for the explorationist? Results from the GEMAS project

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Geochemical Mapping of Agricultural and grazing land Soil (GEMAS) is a cooperative project between the Geochemistry Expert Group of EuroGeoSurveys and Eurometaux. During 2008 and until early 2009, a total of 2108 samples of agricultural (ploughed land, 0-20 cm) and 2023 samples of grazing land (0-10 cm) soil were collected at a density of 1 site/2500 km^2 each from 33 European countries, covering an area of 5,600,000 km^2. All samples were analysed for 52 chemical elements following an aqua regia extraction, 41 elements by XRF (total), and soil properties, like CEC, TOC, pH ($CaCl_2$), following tight external quality control procedures. In addition, the agricultural soil samples were analysed for 57 elements in a mobile metal ion (MMI®) extraction, Pb isotopes and magnetic susceptibility. The results demonstrate that robust geochemical maps of Europe can be constructed based on low density sampling. At the European scale element distribution patterns are governed by natural processes, most often a combination of

geology and climate. The geochemical maps reflect most of the known metal mining districts in Europe. In addition, a number of new anomalies emerge that may indicate mineral potential. The size of some anomalies is such that they can only be detected when mapping at the continental scale. For some elements completely new geological settings are detected. Taking the famous step back to see the whole picture at the continental scale may hold unexpected promise for mineral exploration.

Assessing exposure and health risk associated with lead in urban soil and outdoor dust collected in recreational areas used by children in Lisbon city, Portugal

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A number of studies have been showing that soil Pb is an environmental hazard because adults and children are adversely affected when Pb is absorbed into the body (bioavailability). Children are more vulnerable to Pb toxicity than adults due to their physiological and behavioral characteristics. Lead loading in urban environments is particularly high due to traffic volume, housing and industrial facilities. Urban concentrations of soil Pb can be several orders of magnitude higher than background values, and urban soils represent an important pathway of exposure to Pb. Another important pathway that must not be disregarded is urban outdoor dust. Because dusts are a mixture of displaced soil, urban wastes, pavement debris and airborne particles (possibly metal laden) that settle at ground-level, sometimes outdoor dusts show higher Pb loads than soils. This study uses 102 soil and 50 outdoor dust samples collected in urban recreational areas used by children. Near total concentrations of Pb were analysed by ICP-MS. Nineteen topsoils and eight outdoor dusts were selected to carry out an oral bioaccessibility testing using the Unified BARGE Method. The soil ingestion recommendations of US EPA [1] assume ingestion of a combination of soil and outdoor settled dust, without distinguishing between these two sources. The inhalation and subsequent swallowing of soil particles is accounted for in these recommended values, and therefore this pathway does not need to be considered separately. In this study, exposure and health risk of Pb in soil and dust were assessed using the same model of risk assessment. The considered routes were ingestion and dermal contact, for soil and outdoor dust. The results show that the estimated health risk is higher for Pb in outdoor dust than in soil, and suggest that both pathways of exposure should always be considered.

[1] US Environmental Protection Agency (EPA), 2011. Exposure Factors Handbook:, 2011 Edition. National Center for Environmental Assessment, Washington, DC; EPA/600/R-09/052F. Available from the National Technical Information Service, Springfield, VA, and online at http://www.epa.gov/ncea/efh.

Lithological and mineralogical controls on REE patterns in the soils of Cyprus

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Rare earth elements are widely applied as tracers to assist in modelling various geochemical processes in the primary and secondary environments. REE patterns in the soils of Cyprus are largely controlled by the composition of the parent lithologies, which range from ultramafic rocks to limestones, and samples form distinct statistical clusters. The similar concentrations of top soil (0-25 cm) and subsoil (50-75 cm) samples indicate limited REE mobility under weathering conditions. In soils derived from marine carbonate units, such as the Lefkara Formation, REE are largely bound up in carbonates or clay exchange sites yielding a high percentage of REE extractable by aqua regia (ar-). In soils derived from mafic to ultramafic intrusive rocks of the Troodos Ophiolite Complex (TOC), REE are mainly associated with Fe-oxyhydroxides and clays. Normalised ar-REE plots display LREE enrichment, strong positive Ce anomalies and patterns in most rock units similar to saponites from seawater-altered basalts. Apart from a few samples from the TOC, ar-REE typically exceeds 50% of total REE and, with a high correlation between total REE and Th, indicate the main primary hosts to the REE to be carbonates (e.g. bastnasite) or clays and other seafloor alteration minerals. Five imbricated structural blocks in Cyprus are inferred from major fault patterns. The major boundary faults are characterised by elevated ar-REE and offset REE trends. The most westerly of these structures has the strongest ar-REE anomaly which coincides with elevated soil Cu values in both pillow basalts and the underlying mafic intrusive sequence containing sheeted dyke complexes.

Exploration of an Au-Ag-base metal mesothermal vein system in an eroded volcanic intrusive complex, Western Java, Indonesia

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The Indonesian (Banda) Volcanic Arc, encompassing Java, Bali, Sumbawa and Lombok, is renowned for active and older eroded volcanic-intrusive centres. Rapid erosion in response to tectonic uplift of the magmatic arc exposed numerous occurrences of base and precious metal mineralisation hosted in shallowly-eroded epithermal and more deeply-eroded mesothermal vein and porphyry systems. The eroded intrusive centres may be blanketed by recent volcanic ash and soil, potentially masking mineralisation. Level of exposure influences the approach to exploration. The Cikondang Mine, 125 kilometres SSE of Jakarta, was discovered by gold panning in 1927. Mining commenced in 1939. Intermittent exploration between 1974 and 1996 produced a resource of 760,000 tonnes @ 13.5 g/t Au, 43 g/t Ag, 0.85% Cu, 4.9% Pb and 9.2% Zn (average grades) along 900 metres of strike. Development has been curtailed by modest Au prices, metallurgical issues and financing during the Asian financial crisis and the 1990s infamous Bre-X scandal. Paramount Mining commenced new exploration and drilling in August 2011 as part of a due diligence programme and inferred Au resources now exceed 630,000 ounces to a vertical depth of 220 metres (still open) over 900 metres within 2500 metres of mineralised vein and breccia strike. Historic mapping describes volcanic lava, agglomerates, dykes etc., implying a

shallow eruptive-intrusive environment. New work indicates microdiorite intrusives, intrusive and milled breccias, pebble dykes, hydrothermal magnetite and base metal veins suggesting connection to a porphyry system at depth consistent with the presence of mesothermal veins and hydrothermal breccias hosting mineralisation. Parallel “veins” are indicated by artisanal workings through soil cover. Rock and soil sampling, alteration mapping and magnetics put the recognised mineralisation into a coherent geological context. Veins and alteration in drill core indicate the mineralisation event was late in the intrusive history and vein types and grade can be resolved from soil geochemical signatures.

Recognition of tectonic pathways for intrusions, mineralising fluids and location of Au-Cu skarn mineralisation in an active volcanic arc, Aceh Province, Indonesia: Implications for exploration

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The Indonesian (Banda) Volcanic Arc is a classic arc system extending some 4500 kilometres. In Sumatra, at the western end of the Arc, the Sumatra Fault demarks the limits of upthrust basement exposure and active volcanism. A simple exploration model can be demonstrated in which active oblique compression along the western section of Sumatra has upthrust and exposed to erosion the Palaeozoic basement and continental margin sediments and limestones. During periods of relaxation the structures have opened enabling intrusives and mineralised fluids to rise from a deep sub-crustal level through the rock package introducing mineralisation.

In Southern Aceh, west of the Sumatra Fault, field evidence of volcanic eruptives is lacking, but extensive exposure of deeper-seated mafic-microdioritic intrusive bodies, local diatreme breccias and porphyry dykes constrained by structures which parallel the arc are seen. These cut continental shelf facies including reefal limestones, clastics (conglomerates to shales), basement metamorphics and older deep intrusives. Many of the early phase intrusives are magnetite bearing microdiorites with associated Fe-rich fluids from which hydrothermal magnetite was precipitated within tectonic pathways from depth. These microdiorites frequently contain magnetite endoskarn near their margins which locally host Cu-Au-Mo mineralisation. Exoskarns at limestone contacts are generally pyrite-garnet-pyroxene or rarely wollastonite skarn enveloped within epidote (and other retrograde) alteration. Non-magnetic Au-Cu-rich skarns are also present. Connection to large deeper porphyry bodies is demonstrated only in limited cases.

Hydrothermal magnetite within the regional structural fabric is highlighted by airborne magnetics in rugged dense tropical jungle. The structures and more massive magnetite bodies offer targets for geological and geochemical assessment as well as the associated intense magnetic lows. The high-grade of some of the skarns merits drill assessment. Stream, soil and rock chip geochemistry accompanied by careful mapping of rock type and alteration characteristics help resolve the geological setting and target mineralisation.

Biogeochemical exploration for Cu-Ag-Au skarn mineralisation using Palo Verde trees, Sonora, Mexico: Methods and results

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In 2012, a biogeochemical orientation survey using Foothills Palo Verde (FPV) trees was undertaken by MMG in the Sonoran Desert of northwest Mexico. It was conducted to assist in the delineation of Cu-Ag-Au skarn mineralisation overlain by Tertiary andesite. The skarn mineralisation crops out in a small window but elsewhere is overlain by younger andesite and alluvium.

Thin healthy twigs (<4 mm in diameter) ranging from 10 to 15 years in age were collected, as metals accumulate in the bark rather than woody cellulose. Preparation of PV samples included drying, milling, ashing, and digestion prior to analysis by ICP-MS. Results from an initial PV orientation survey detected a Cu, Mo, Zn, Ag anomaly, with anomaly to background contrast ratios of 1.63 (Cu), Mo (17.5), 2.97 (Zn), and 3.00 (Ag). A skarn rock chip sample collected within 5 m of the anomalous tree has Cu, Mo, Zn, and Ag values of 108, 103, 969, and 0.98 ppm, respectively and a sample within 20 m has 10700, 31, 444, and 13.4 ppm, respectively. Comparatively, the median Cu, Mo, Zn, and Ag andesite (background) values are 38, 1.04, 199, and 0.20 ppm. Based on the success of that orientation survey, a larger, 6.25 km^2 survey with 100 x 200 m spacing was undertaken in spring 2013 over a broad covered area surrounding the exposed skarn zone. Results from this larger survey indicated anomalous elements including LREEs, Mn, Re, Pb, Au, Ba, along mapped and interpreted structures. These results suggest either mineralisation related to structure or the deep tap roots of PV plants are drawing up groundwater that has interacted with mineralisation, which has then preferentially travelled along structures. The biogeochemical data delineate two separate zones of anomalous pathfinder elements where colluvium cover exists: one zone is high in Cu, Fe, K, and Ag, and is coupled with the existence of jarosite and kaolinite, suggesting potassic alteration and perhaps close proximity to porphyry mineralisation. A second zone at the opposite end of the survey (3 km north) is anomalous in Pb, Zn, As, Sb, and Re, and may suggest lower temperature, more distal skarn mineralisation. Overall our results indicate that biogeochemical exploration using PV plants are highly effective for exploration in covered terrain.

Regional exploration for VHMS deposits using lake sediment and water geochemistry in the Slave geological province, Canada

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MMG undertook a regional scale lake sediment and lake water geochemical programme over several 2.72 to 2.58 Ga greenstone belts of felsic to mafic composition within the Slave geological province in the Canadian arctic. The purpose was to define new exploration targets in regional proximity to MMG's Izok Lake, Hood, and High Lake Cu, Zn, and Pb bearing volcanogenic hosted massive sulfide deposits, and along the proposed road route that would connect the Izok Lake deposit to the arctic coast.

Our data demonstrates that lake water geochemistry is a valuable addition to regional lake sediment surveys. In lake water samples, less mobile dissolved elements (i.e. Cu^{2+}, Pb^{2+}) tend to exhibit smaller dispersion footprints from known historical showings compared with those same elements in lake sediments, likely due to complexation, adsorption, and dilution processes. This more discreet footprint can provide greater accuracy in the delineation of potential exploration targets.

Lake water geochemistry also does not appear to be impacted by covered terrain compared to lake sediment geochemistry. The mean, median, and maximum values for several chalcophile elements including Cu^{2+}, Zn^{2+}, and Pb^{2+} in lake waters do not change with variations in the cover thickness. However, sediments collected in regions with thick till cover are significantly lower in chalcophile elements compared to regions of little/no cover, likely due to residual material dilution of geochemical signals. The independence of aqueous geochemical values in lakes located in both bare and covered terrains suggest that lakes might be partially fed from groundwaters that have interacted with bedrock below the cover. If geochemical anomalies are present due to metal transport as dissolved ions, a weak leach of the lake sediment rather than aqua regia digestion might be appropriate, especially since arctic lake sediments in this survey are on average composed of only 12% organics. Metal contents in lakes sediments are more dominantly controlled by Fe and Mn-oxyhydroxides.

Preliminary study of epithermal mineralisation in Purnama deposit, Martabe District, North Sumatra, Indonesia

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Seven epithermal prospects have been discovered during exploration in the Martabe district in the south-western part of North Sumatra, with resources to date of 8.05 Moz Au and 77 Moz Ag. The Purnama deposit is the largest deposit in this district, with 4.53 Moz Au and 58.46 Moz Ag at grades of around 1.7 g/t Au and 22 g/t Ag. At Purnama, high sulfidation epithermal type mineralisation is mainly hosted in andesite to phreatic breccias, and exhibits strong structural control of both the mineralisation and hydrothermal alteration. We infer that magmatic evolution and activities related to the Great Sumatra Fault complex were responsible for the formation of the deposits providing the heat source for the mineralisation in the study area. The Purnama deposit was controlled by the Purnama and Sipiramanuk faults, which are extensional structures of the Great Sumatra Fault complex. Preliminary assessment has identified ore mineral assemblages dominated by enargite-luzonite and pyrite. These minerals are the main associations for gold mineralisation in the Purnama deposit. Sulphide minerals that formed in the irregular ore body occur in vugs in the andesite and in cavities in the breccias. Hydrothermal alteration is characterised by acid-sulphate types, predominantly alunite ± kaolinite ± pyrite, vuggy silica and silicification, indicating that the deposit was formed in an acidic pH environment. In contrast, the southern Purnama area contains massive and colloform-banded quartz veins with local lattice textures, which indicate mineralisation by near-neutral chloride fluids.

Passive removal of nanoparticulate iron from AMD

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This study demonstrates the potential applicability of a siliceous gravel (20-10 mm) filter, termed here a Vertical Flow Reactor (VFR) as a means to remove iron from AMD. A 1 m^3 pilot-scale VFR was constructed and deployed at Cwm Rheidol, an abandoned zinc mine in Wales, UK. The VFR was gravity-fed with mine water discharging from the lower number 9 adit at Cwm Rheidol. The discharge is typically circa pH 3 with average Zn and Fe concentrations of 50 – 90 mg/l and 50 – 120 mg/l respectively. The flow rate through the VFR was throttled by a ball-valve, the volume of water in the VFR was controlled by a swan neck mechanism, typically the swan neck has been kept at 0.2 m below the height of the inflow. Results of the field trial have demonstrated that the VFR has consistently removed 60-70% of the Fe at pH circa 3, with a retention time of ≥6 hours. Iron precipitates accumulated in the tank as a blanket, iron removal in the system is circa 20 $g/m^2/day$ (the maximum quoted for wetland design). After an initial decline in permeability over the first 4 weeks, the system continues to remove iron for 12 months without further appreciable decrease in bed permeability. Spectrophotometric analyses of Fe (II) and Fe(III) concentrations conducted in the field demonstrated that circa 1 mg/L of the total Fe was present as Fe(II) and that this was being oxidised within the tank with half-life of approximately 1hr, indicative of microbial catalysis. The removal mechanism in the VFR is thought to be predominantly filtration of nanoparticulate Fe (III) (<0.2 µm) that agglomerate in the tank to form ochreous sludge. XRD analysis indicates amorphous iron (oxy)hydroxides. Samples of the ochre from the VFR have extremely fast settling rates and have similar physical appearance to sludge from high density active treatment even though no reagents have been added. Microbiological analyses indicate an abundance of stalked bacteria which may contribute to both the removal of nanoparticulate iron and the sludge characteristics.

Advanced till geochemical and heavy mineral methods for mineral exploration in glaciated terrain in Finland

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Surficial geology, till geochemistry and heavy mineral studies have been used in exploration of glaciated terrains for nearly one hundred years. Till is a useful sampling medium due to it being a mixture of fresh bedrock, pre-glacially-weathered bedrock, and older sediments. Lithologic and geochemical characteristics of dispersed till are effective in estimating transport distances and deposition processes of the till and the mineralised material contained within. Heavy mineral investigations support and elucidate till geochemical studies. Research by the Geological Survey of Finland involves development of new sampling and analytical techniques for utilising till in geochemical and heavy mineral exploration. The purpose is to develop new effective surficial methods for regional and/or target-scale exploration that are nature-friendly in environmentally sensitive Arctic or Subarctic regions. One focus is to have very low environmental impacts related to exploration activity. Another focus is to decrease analytical costs and increase sample efficiency. Traditional till geochemistry in ore exploration involves using specific till size fractions, total- and partial-leach dissolution methods, and analysis by methods

such as ICP-AES, ICP-MS, and GFAAS. However, these procedures are often expensive and time-consuming. To more effectively assess bedrock mineral potential, new techniques are being utilised, including portable X-Ray Fluorescence (pXRF) and automated heavy mineral analyses. Advancements in modern pXRF analysers over the last decade include increased sensitivity that allows determination (at ppm scale) for a large group of elements, and increased portability that results in light-weight equipment (like ScanMobile®) that is easy to take in the field or use in truck-supported systems. SEM-EDS and MLA methods are effective techniques to analyse a wide range of indicator minerals from the heavy mineral concentrates. Several successful exploration studies from northern Finland prove the effectiveness of these methods in glaciated terrain.

Natural geochemical characteristics of soil at different scales in Finland

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Chemical and physical characteristics of soil are determined by the geology and geological processes that form the foundation to the natural ground. Chemical characteristics result from a combination of natural mineralogical composition, element concentrations, and organic content in the soil. However, the element contents can vary widely at different scales. This is the case in Finland, where bedrock is mainly composed of crystalline Archaean and Palaeoproterotzoic rocks that range from granitoids and granite gneisses to volcanic, calciferous and sedimentary rocks. After pre-glacial chemical weathering followed by several glacial periods involving erosion, transport, and deposition, the bedrock is almost totally covered by till and other glaciogenic sediments. Based on European-scale soil geochemical datasets, such as the FOREGS Geochemical Atlas of Europe, the overall content of most elements in northern Finland is considered the lowest in Europe and Scandinavia. However, a closer look at the Finnish national geochemical database shows high regional differences between the areas having high ore potential and the surrounding background areas. This phenomenon is even stronger comparing data at regional and detail scales. Arsenic, for example, forms several strong geochemical anomalies in till related to mineralised schist belts in different parts in Finland. However, the levels of harmful elements, such as heavy metals and radioactive elements, seldom reach high concentrations of concern for nature and people. Although the ground is considered naturally clean in Lapland, human acts can disturb the natural element balance and raise element contents over the recommended levels. Agricultural and forestry soil treatment, metal and mineral mining, and raw material quarrying, for example, can cause these harmful effects. Generally, the influence of these acts on nature—animals, fish, berries, mushrooms, and other vegetation—is usually local and relatively temporal.

REE and gold exploration using surficial geochemistry in northern Finland

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The Tana Belt in northern Finland is one of several regions in northern Europe that have rare earth element (REE) and Au potential. It has prominent La and Y anomalies in regional surficial- and litho-geochemical datasets. High Y content indicates enrichment of heavy REE in bedrock of the Tana Belt. The area is also mineralised in Au, as reflected by large paleoplacer gold deposits. The

strongly deformed Tana Belt comprises amphibolite, garnet-biotite and arkose gneisses that were thrust together with the Lapland Granulite Belt onto the Central Lapland Greenstone Belt at 1.9 Ga.

Due to repeated glaciations in the northern hemisphere, bedrock is largely covered by glaciogenic sediments, mainly till. During the last (Weichselian) glaciation, subglacial erosion was weak and the transport distance of till short. In this regime, geochemistry of till, pre-glacially-weathered bedrock, stream water and sediments, and surficial weak leach geochemistry, are effective in exploration. Furthermore, indicator mineral studies support and elucidate the till geochemistry.

The region including the Mäkärä and Vaulo targets has been explored for several decades through 2011. Gold contents in pre-glacially-weathered saprolite and glacial till have strong positive correlations with positive electromagnetic anomalies that are caused by sulphidic bedrock. The highest La and Y contents in till correlate well with equivalent-Th maximums found in radiometric datasets. Exploration studies revealed two REE targets: a Au-hematite-quartz vein with 3 ppm Au and 0.04-0.1% REE at Mäkärä and elevated REE contents up to 0.4% in the fine fraction of till at Vaulo. The elevated REE content at Vaulo resembles that of ionic adsorption clays in China. Typical REE minerals are monazite, rhabdophane, xenotime and kaolinite. Regional geochemical results indicate REE potential in much of the Tana Belt; the Mäkärä-Vaulo area covers only a very small part of the Belt.

Validity of low-density continental-scale surveys – discovering new geochemical features in sediments from Western Australia

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The National Geochemical Survey of Australia (NGSA) involved the collection and analysis of 1315 catchment outlet sediments covering approximately 81% of Australia at an average density of one site per 5200 km^2, with 276 samples (21%) from Western Australia. Analyses of different parts of the sediment profile and different grain size fractions of each sample by a total of eight analytical techniques resulted in a comprehensive geochemical dataset.

In Western Australia, most samples from older cratonic and orogenic areas are composed of weathered silicate-rich material, whereas samples from younger sedimentary basins (e.g. the Eucla Basin) usually have high carbonate contents and elevated pH. Bottom of hole samples have higher silt and clay contents and contain the highest concentrations of most elements.

The NGSA data highlight several largely undocumented anomalies for several elements. A cluster of samples with anomalous Pb and REE concentrations are found in an area of lacustrine sediments in the central Yilgarn Craton, which has no documented mineralisation. Here, anomalous Pb and REE are associated with sulphate-rich evaporates and resistate minerals such as garnets, derived from basement gneisses and granitic rocks. Elevated concentrations of high field strength elements (HFSE) such as Zr, Nb and Ta are found in samples from coastal areas, well known for their heavy mineral sand deposits. This association is consistent with the low extractability of HFSE following aqua regia digestion.

NGSA data are also used to lithologically subdivide the Archean Yilgarn Craton. The gneiss-dominated South West Terrane is characterised by higher alkalis (K and Na), REE and HFSE contents than the more greenstone-dominated terranes farther east, which have stronger ferro-alloy and chalcophile element signatures.

Passive seismic estimates of cover thickness—essential information for geochemical surveys in regolith-dominated terrains

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Mineral exploration in greenfields areas are hampered by the extent and thickness of regolith and sedimentary rock cover, which accounts for 80% by area of continental Australia. As the effectiveness of surface geochemistry decreases with increasing cover thickness, knowing the thickness of cover is essential, yet data are either sparse or non-existent (e.g. drilling), or imprecise (e.g. regional seismic). The Geological Survey of Western Australia (GSWA) has addressed this issue using a rapid, portable, and non-invasive passive seismic system (Tromino®) to estimate cover thickness.

In comparison to conventional surveys using reflectance seismology, the passive approach does not require a controlled seismic source. Instead, it measures the natural, ambient noise (or vibration) caused by wind and waves, as well as noise generated by distant anthropogenic activities, all of which are present in the subsurface. The Tromino® records two horizontal (E-W, N-S) and the vertical spectral components of the ambient noise over a certain period of time. The spectral ratio of the averaged horizontal to vertical components is used to determine the site resonance frequency of the subsurface. A change in lithology, for example, induces an impedance contrast, resulting in a change in the horizontal/vertical ratio, which can be equated to depth.

Results from two trial programs in Western Australia, have provided convincing cover thickness estimates which correlate well with known thicknesses from drilling data, covering depths from 5 m (regolith) to >800 m (regolith and sedimentary rock cover). Passive seismic cover thickness determination provides valuable data for planning geochemical surveys, and interpreting survey results. Ultimately, a combination of regional geochemical mapping programmes and passive seismic surveys could enhance exploration in greenfields areas by providing data on both anomalous geochemical surface expression and estimates of cover thickness over basement at the same time.

Future international organic stable isotope reference materials for the IAEA and the USGS

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The need for international organic H, C, N stable isotope reference materials

Currently there are few hydrogen, carbon, and nitrogen organic international stable isotope reference materials (RMs) available from the International Atomic Energy Agency (IAEA), the US Geological Survey (USGS) or the US National Institute of Standards and Technology (NIST). In the absence of suitable pairs of organic reference materials for proper 2-point calibrations along isotopic VSMOW, VPDB and AIR scales, many laboratories have to resort to questionable practices, for example by using 'reference gas pulses' for isotopic calibrations that violate the principle of identical treatment of sample and standard (see Elsner et al., 2011, Analytical and Bioanalytical Chemistry 403 (9), 2471-2491. http://dx.doi.org/10.1007/s00216-011-5683-y). In 2011, the US National Science Foundation (NSF) funded an initiative of 10 laboratories from 7 countries to jointly develop much needed new organic RMs for future distribution by international outlets such as the IAEA and the USGS.

Targeted organic compounds

The selection of targeted RMs attempts to cover various common compound classes of broad technical and scientific interest. We had to find compromises to approach the ideal of high chemical stability, lack of toxicity, availability, and price of raw materials. Hazardous gases and liquids were avoided in order to facilitate international shipping of future RMs. In most cases we are developing 2 or 3 isotopic variants of each compound for 2-point calibration: 3 hexadecanes, 3 glycines, 3 L-valines, methyl heptadecanoate, 3 caffeines, 2 high-quality vacuum pump oils, polyethylene powder. With the exception of polyethylene and vacuum pump oil, all organic RMs are individual, chemically pure substances which can be used for compound-specific measurements in conjunction with liquid and gas chromatographic interfaces. Glycines and L-valines are isotopically spiked with ^{2}H and/or ^{13}C at different molecular sites to serve as future isotopic site-specific RMs.

Origin of natural gas-fed “eternal flames” in the Northern Appalachian Basin, USA

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Introduction

Hydrocarbon gas seeps are surface expressions of petroleum seepage systems, whereby gas is ascending through faults and conduits from pressurised reservoirs that are typically associated with sandstones or limestones. The region around the states of New York and Pennsylvania marks the birthplace of commercial gas production from shales dating back to the 19th century.

Methodology

We sampled and analysed two burning seeps in New York and Pennsylvania that had not yet received geochemical scrutiny, including compound-specific stable isotope ratios of hydrogen and carbon.

Results and Conclusions

A spectacular “eternal flame” in western New York State marks a natural gas macroseep of dominantly thermogenic origin emanating directly from deep shale source rocks, which makes this a rare case in contrast to most Petroleum Seepage Systems where gas derives from conventional reservoirs. The main flaming seep releases about 1 kg of methane per day and seems to feature the highest ethane and propane (C2+C3) concentration ever reported for a natural gas (~35 vol. %). The same gas is also released to the atmosphere through nearby invisible and diffuse seepages from the ground. The synopsis of our chemical and stable isotope data with available gas-geochemical data of reservoir gases in the region and the stratigraphy of underlying shales suggests that the thermogenic gas originates from Upper Devonian shales without intermediation of a conventional reservoir. A similar investigation on a second “eternal flame” in Pennsylvania suggests that gas is migrating from a conventional sandstone pool and that the seep is probably not natural but results from an undocumented and abandoned gas or oil well.

The stability of metal-containing oxyanions under geothermal conditions

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A number of group 6 transition metals (Cr, Mo and W) as well as group 15 metals such as As (a metalloid), Sb and Bi occur ubiquitously as fellow travellers in geothermal and ore depositing systems but their hydrothermal chemistry/ geochemistry is still poorly known. Of interest as well, is the well known association of these elements with other metals such as gold in hydrothermal ore deposits.

In aqueous solution at 25°C, the values of pK_1 for $As(OH)_3(aq)$ and $Sb(OH)_3(aq)$ ionisation are 9.25 and 11.28 respectively, indicating that the fully protonated, neutral species predominates from acid to weakly alkaline pH's. At 300°C however, pK_1 for $As(OH)_3$ deceases to 7.11 (Zakaznova-Herzog et al., 2006), suggesting that the deprotonated arsenite species, $As(OH)_2O^-$, may play a role in hydrothermal arsenic transport, especially in fluids which have undergone phase separation(boiling). For Sb and Bi hydrolytic equilibria at elevated temperatures (Zakaznova-Herzog and Seward, 2006; Tooth et al., 2013), the fully associated $Sb(OH)_3(aq)$ and $Bi(OH)_3(aq)$ predominate over the range of pH's characteristic of hydrothermal fluids in the Earth's crust. However, in dilute aqueous molybdate and tungstate solutions at elevated temperatures, the simple $H(Mo,W)O_4$- and $(Mo,W)O_4^{2-}$ species predominate over a wide range of pH's (Minubayeva and Seward, 2010; Wesolowski et al. 1984).

The transport and deposition of these oxyanion species in hydrothermal fluids in the Earth's crust will be discussed in light of new experimental data. In addition, the importance of thio- and halogenido-substituted analogues will also be considered.

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Application of hard and fuzzy clustering methods for interpretation and processing of geochemical data, Dalli Cu-Au deposit

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Proper interpretation of geochemical data and subsequent delineation of valid anomalies requires application of new multivariate techniques. Numerous multivariate methods have already been used for this purpose, such as principle component analysis (PCA), factor analysis and so on. In this study, the hard and fuzzy clustering methods are used in order to process geochemical soil samples of the Dalli copper and gold deposit, which is located in Markazi province, Iran. In this paper, K-means clustering is used; this is considered as one of the most applicable and fastest hard clustering methods. This method clusters the samples to a certain number of classes based on similarity and dissimilarity criteria (distance, correlation coefficient, angle between samples and clusters center) and each sample belongs exclusively to a single cluster. But, in fuzzy schemes (such as the fuzzy c-means clustering technique that is used in this paper) a sample belongs simultaneously to more than one cluster. The fuzzy c-means algorithm assigns data points to each cluster by using fuzzy memberships. The number of clusters is specified as a priori knowledge in these methods. Choosing the wrong number of classes can lead to incorrect clustering. In this paper we have used the Basic Sequential Algorithmic Schemes (BSAS) for estimating the number of clusters. The estimated numbers of clusters are used as a priori knowledge in k-means and fuzzy c-means algorithms. Ultimately, clustering results are compared with drilling exploration in this study. Comparisons of results demonstrate that this method is acceptable, simple and quick for investigation and interpretation of geochemical data.

Geology, mineralogy and geochemistry of the Chahnaly low sulfidation epithermal gold deposit, SE Iran

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The Chahnaly low sulfidation epithermal gold deposit is located to the northwest of the Bazman semi-active stratovolcano at the western end of the Makran Volcanic Arc. Chahnaly is hosted by early Miocene syn-subduction, calk-alkaline volcanic-volcaniclastic rocks of the Bazman volcano. Lack of a significant negative Eu anomaly, listric shaped LREE patterns and moderate La/Yb ratios of the host suit rocks may indicate a high magmatic water content of the source magma. Gold minerals, including free gold and Au-rich electrum, are present in a series of 030°-striking sub-vertical siliceous veins and hydrothermal breccias that are temporarily and spatially related to chalcedony-adularia alteration assemblages within altered volcaniclastic rocks. ^{40}Ar-^{39}Ar geochronology of ore stage adularia suggests that the alteration and mineralisation at Chahnaly appears to be up to 1.5 million years younger than volcanic host assemblage.

Petrographic studies followed by LA-ICP-MS analyses of pyrites show that there are at least three generation of pyrites in the Chahnaly host suit rocks, with the second and third generations carrying high gold contents. Analyses by LA-ICP-MS show that gold occurs as nanoparticles in the pyrite lattice and as inclusions in pyrite when concentrated at higher levels. Additionally gold minerals are hosted by quartz in siliceous veins within the hydrothermal breccia.

Homogenisation temperatures of fluid inclusions in gold bearing quartz range between 132.5°C and 350.2°C, and salinities range from 0.17 to 1.82 wt% NaCl equiv. The $\delta^{34}S$ values of pyrite samples are between -0.1 to 4.2 per mil, consistent with a magmatic source for sulfur. Oxygen isotope values of gold bearing quartz samples range from 1.5 to 4.5 per mil. Moderate temperature, low salinity and the absence of detectable gases by laser Raman spectroscopy in quartz hosted primary fluid inclusions, as well as the quartz oxygen isotope values suggest a meteoric source for the hydrothermal fluids.

Handheld X-Ray fluorescence spectrometry in the exploration and development of carbonatite-related niobium deposits: An example from Aley Carbonatite, British Columbia, Canada

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This study evaluates the suitability of handheld (hXRF), the Thermo Scientific Niton XL3t GOLDD+ analyser, in the exploration for carbonatite-hosted pyrochlore- columbite-fersmite containing deposits. Results obtained by conventional sampling and laboratory methods (CSLM) are compared to: 1) results of hXRF on selected pulp samples; 2) results of averaged multiple hXRF spot analyses directly on 10-15 cm long pieces of drill core; and 3) results of drill core scanning.

The best correlation exists between hXRF measurements on rock pulps and CSLM for Nb (r^2=0.99), La (r^2=0.97), Ce (r^2=0.67), Y (r^2=0.93), and P (r^2=0.89). The values of r^2 for Pr and Nd are 0.19 and 0.38.

The multiple spot analyses directly on the drill core are used to confirm the presence of ore-bearing minerals and for determining the grade of homogeneous materials. Averaging of multiple, regularly-spaced spot readings partially eliminates the effect of heterogeneities on typical drill core, but this method is inferior to hXRF pulp analyses, and to hXRF scanning for determining ore grades.

The hXRF drill core scanning (single beam) is non-destructive (no sample preparation) and can be done in the field. The scanning reduces wide variations associated with spot analyses, but the data quality is limited by the inability of the operator to maintain constant scanning speed. At Aley, the scanning results correlate well with CSLM for Nb (r^2=0.88), Th (r^2=0.80), Fe (r^2=0.84), Sr (r^2=0.74), Ba (r^2=0.73), Y (r^2=0.59), and Zn (r^2=0.75). The r^2 for La, Ce, Pr, and Nd were 0.31, 0.26, 0.01 and 0.03, respectively. These low r^2 values are due to combination of low REE concentrations and erratic distribution of REE-rich fluorocarbonates and zircon throughout the core. The hXRF methods are not a substitute for CSLM in ore reserve calculations; however, they provide interpretable and instantaneous results for field-based decision making.

Portable X-ray fluorescence instrument in exploration and development of rare earth element deposits

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Portable X-ray fluorescence (pXRF) provides rapid, non-destructive chemical analyses in the field. This study evaluates the merits/limitations of pXRF technology in exploration of REE-bearing deposits. It is based on the Thermo Scientific Niton XL3t GOLDD+ analyser, Standard Reference Material NIST 2780 from the National Institute of Standards and Technology (Gaithersburg, USA), Certified Reference Material “TRLK” Rare Earth Ore “CGL 124” from the Mongolia Central Geological Laboratory, Reference Niobium Ore OKA-1 (CANMET), and a 99.8% silica blank from Alpha Aesar (Ward Hill, USA). Each standard was analysed more than 100 times. These analyses, in combination with orientation surveys, an inventory of chemical signatures of the main REE deposits, and the ore grades reported from 37 advanced REE projects outside of China, indicate that the pXRF is suitable for use in exploration and development of carbonatite-related lanthanides and Y (REY) deposits, such as Mountain Pass (California, USA), Bayan Obo (Inner Mongolia), Wicheeda Lake, St. Honoré, and Eldor (Canada) and peralkaline intrusion-related deposits, such as Kipawa, Nechalacho and Strange Lake (Canada). By extension, the pXRF is also suitable for the exploration of apatite-monazite veins, such as Steenkampskraal (South Africa). A commercial pXRF, without a radioactive source, can analyse a wide range of elements from Mg to U (including Y) however it cannot analyse most of the heavy lanthanides. Yttrium can be used as a pathfinder for these elements. Limited but effective use of pXRF in exploration of ion adsorption clay deposits, such as those of Xinxui and Heling areas (China) that can grade as low as 500 ppm total REY also appears possible. The pXRF can definitely be used for delineation of REE-enriched zones within sedimentary phosphate deposits and probably for estimation of REY concentrations in quartz-pebble conglomerate type uranium deposits (Elliot Lake, Canada).

Vein textures in the world-class epithermal Waihi vein system, New Zealand

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The Waihi vein system occurs within Hauraki goldfield as a series of adularia-sericite epithermal Au-Ag veins, including the world-class Martha mine. Critical comparison of quartz textures within eight major veins of the Waihi district show significant textural variations among veins. The western (Martha) and eastern (Favona, Moonlight, Cowshed and Silverton) veins contain abundant colloform, cherty, and black quartz fill textures, with minor crustiform and massive quartz. Between these two groupings, the Amaranth, Trio and Union veins contain predominantly massive and crustiform textures with minimal colloform and cherty quartz and black quartz fill, and these veins are also commonly coarser grained. Observed textures are consistent with formation of the Amaranth, Trio and Union veins at a deeper structural level than western or eastern veins. Scanning electron microscopy-cathodoluminescence (SEM-CL) was used to further evaluate textures in the Waihi vein system. Common textures, including zonal

patterns in coarse-grained euhedral quartz, are seen in CL and petrographically, and previous studies elsewhere have shown that CL zonation typically reflects fine-scale variations in the concentrations of trace elements such as Al, Li, Na, K, and Sb. Cathodoluminescence also shows brittle deformation in Waihi samples that is not apparent under the microscope; combined these textures suggest that quartz veins experienced intense deformation and subsequent annealing. Careful examination of the CL zonation may suggest that at least some trace element zonation patterns in hydrothermal quartz can survive the annealing process. Furthermore, previously unrecognised brittle fractures may have provided areas of significant permeability that enhanced hydrothermal fluid flow during vein formation and mineralisation.

Determining a constituent release index from overburden material via laboratory weathering experiments

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The Appalachian coal industry is currently under scrutiny for water quality issues related to high concentrations of total dissolved solids (TDS). Current recommendations of blending acidic and alkaline overburden have successfully minimised water quality issues such as acid mine drainage; however this practice can actually increase TDS release. Although the coal industry has been successful in developing technologies to identify, handle, treat, and isolate overburden material that may promote acid mine drainage, technologies for predicting TDS do not currently exist. Our objective was to develop quick laboratory methods for predicting TDS release from overburden materials in the Appalachian region by comparing two extracting solutions and one digestion technique to Acid-Base Accounting (ABA) parameters, Virginia Tech leaching columns, and University of Kentucky field studies. Forty-one overburden samples were collected from surface mines in West Virginia, Virginia, and Kentucky. Ground samples were mixed with a dilute nitric acid (HNO_3 0.016 M) solution or Ethylenediaminetetraacetic acid (EDTA 0.5 M) solution, and shaken for up to one week to simulate weathering. Microwave digestion (USEPA Method 3051) using nitric and hydrochloric acids was performed to provide the upper limit on TDS release. Supernatants were extracted and filtered to be analysed for pH, electrical conductivity (EC), cations (Al^{3+}, Fe^{3+}, Mn^{2+}, Mg^{2+}, Ca^{2+}, P, Na^+ and K^+) by Inductively Coupled Plasma-Optical Emission Spectroscopy, as well as anions (Br^{1-}, Cl^{1-},NO_3^{1-}, PO_4^{3-}, and SO_4^{2-}) by Ion Chromatography. ABA parameters, which measure percent sulfur (% S) and neutralisation potential (NP), were compared to results from our weathering tests. Results showed that predictions of TDS from the ABA were similar to the actual release of constituents in our weathering study. Samples highest in % S and NP released the highest concentrations of elements, including Fe, Al, and Mn, and Ca. Samples with lower sulfur and NP contents released lower quantities of TDS. Samples shaken with dilute HNO_3 released two to six times more constituents than samples shaken with EDTA. Microwave digestion on average released three orders of magnitude more constituents than the two shaking solutions, however this may be the quickest test for predicting the relative TDS release potential of overburden material.

Crystal growth morphology versus composition: 3D depiction of geochemical data

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The growth morphology resulting from crystallisation in a geochemically heterogeneous environment is defined by growth zones. These may be modified by hydrothermal processes producing an overprinting re-growth pattern. Trace element geochemical data may be used to develop raster-based digital distribution models to show the heterogeneity of element concentrations resulting from environmental changes during crystal growth. Cathodoluminescence can also be used to illustrate such changes. During crystal formation-transformation processes, chemical exchange between the environment and the crystal proceeds at different rates for different elements. Simultaneous measurements of their concentrations, inter alia by LA-ICP-MS, and further data processing enables the tracking of such differences. However, because elements are partitioned into the crystal with different concentration, their absolute concentrations are not the best measure of such differences, and normalisation is commonly required. The proposed normalisation employs a threshold separating the local minimum from the neighbouring local maximum, and can be used to determine the degree of spatial concordance or discordance in the behaviour of two elements, where they exhibit similar or different behaviours, respectively. Thus, crystal areas can be identified as having concordant or discordant element behaviours. Using the boolean spatial distribution of ‘positively’ and ’negatively’ correlated values, an output model can be constructed identifying areas of mutually concordant and discordant behaviours. This model has been used to measure the intensity of hydrothermal changes within a single phase, enabling the understanding of individual element behaviours during crystal-fluid interaction and the calculation of the approximate composition of the fluid from which the crystal grew.

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Geochemical prospecting using the superfine fraction analysis method under complex landscape conditions

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In closed areas characterised by thick unconsolidated sediments overlying mineralisation, special mineral exploration techniques are used to identify superimposed secondary haloes from data of mobile or sorption forms of elements occurring in the unconsolidated cover. The superfine fraction analysis method developed at FGUP VSEGEI (2003) is among such techniques (MASF).

Aqua regia is used as the extraction reagent in the MASF technique because it dissolves salt, sorption and metal forms of elements. Thus, the MASF technique may identify both the sorption-salt and secondary mechanical dispersion halos. The method has been used in varying landscape conditions to identify mineral occurrences of a wide range of elements in open and closed areas.

In open areas, the success of the method from mechanical haloes with a bulk analysis of element concentrations, is confirmed by:

- selective analysis of ore minerals that is similar to that predicted by mineralogical and geochemical methods; and
- analysis of bulk contents in the superfine fraction of unconsolidated sediments.

In closed areas, the success of the method based on the study of sorption-salt forms is confirmed by:

- the regular location of sorption-salt halos in geological space;
- the correlation of halos, and identification of the presence of geochemical structures both in open and closed sections of a specific area; and
- agreement of predicted results obtained by the MASF technique with results from drilling and mining.

In the past 10 years, many geochemical anomalies, ore occurrences and deposits, prospective for economic mineralisation were identified in Russia using the MASF technology.

Lithogeochemical exploration in the Pioneer-Pokrovskoe gold cluster (Far East, Russia)

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Studies in the Pioneer-Pokrovskoe gold cluster (the Upper Amur Region) allowed the identification of some geochemical characteristics of the gold mineralisation location:

1. The main gold trace elements have been identified based on chemical analyses of ore samples (ICP MS). So, for example, in the Pioneer deposit, the ore association of the Bakhmut and Andreevsky ore zones is similar: it is represented by Au, Ag, As, Sb, with a subordinate role of Pb, Hg, Mo, Bi, but the Bakhmut zone is dominated by Au and the Andreevsky zone by Ag. Ti, Co, V, Zn, Cr and Ni contents are lower than the background. Geochemically, the Zheltunak ore occurrence (Krest Prospect) is characterised by the principal geochemical association of Au, As, Sb, Ag, with subordinate Hg, Mo, W, sharply reduced U, Bi, Mn, Th contents relative to the background concentration (according to A.P. Vinogradov), and slightly lower Pb and Sn contents.

2. The study area is characterised by complicated landscape conditions of the geochemical surveys (bogginess, thick Quaternary sediments). Therefore, to find gold mineralisation in the area of the deposits, lithogeochemical soil sampling (horizon B) was carried out using the superfine fraction method to identify the superimposed sorption-salt haloes of gold and trace elements (MASF technology). The identified mineralised zones are fixed by haloes of centripetal elements supply (Au, Ag, Sb, As, Bi, Cu, Hg, Pb, Mo, Bi) and haloes of centrifugal elements removal (Ti, Mn, Zn, Co, Cr, V). The mineralised zones are most reliably established from haloes of complex geochemical indicators such as TiMnZn, TiVCoCrMnZn (for haloes of removal) and AuAgAsSbCuHg, AuAgAsSbCuHg/TiVCoCrMnZn (for haloes of supply). In addition, cut-off values of these indicators were determined to identify potential gold-bearing zones and bodies.

The geochemical criteria listed above allowed the identification of noble metal ore-bearing zones (Au, Ag), some of which have been confirmed by geological surveys.

In-situ measurements of soil helium to detect leakage patterns through transported regolith

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Elevated He is commonly associated with hydrocarbon and some U-bearing deposits. Being chemically inert, He tends not to be absorbed by mineral material and is highly mobile. Helium movement through sedimentary rocks and regolith is largely controlled by permeability but may be affected, at various time-frames, by the amount of pore water or soil moisture and other climatic factors such as air pressure. Faults and fractures can act as preferential pathways for the migration of He. This study compares soil He contents over hydrocarbon-rich sedimentary units in various regolith settings. The study area near Dalby in southern Queensland contains a series of hydrocarbon deposits (mainly coal-bed methane) hosted in deformed sedimentary units. Most areas are overlain by alluvium with depths up to 50 m. The land is used for agricultural purposes and is regularly ploughed. In-situ measurement of He, using a (portable) Varian PHD-4 detector, were made on a 200x200-m grid and at some higher density traverses at the soil surface and in subsoil (70-80 cm depth) using thin tubes hammered into the ground. Helium values ranged from ~ 5 ppm to >500 ppm. The spatial patterns suggest He is leaking (vertically) through the alluvium along conjugate fault structures. There is high correlation but large differences between surface and subsoil values. Irrigation of the fields suppressed the He soil concentrations, but did not affect the general trends in the He patterns. By comparison, maximum He in similar surveys run over major hydrocarbon deposits covered by different transported regolith types at study sites in Corsicana, Texas displayed peak values of <100 ppm, though there are again large differences between surface and subsoil, whereas in various study sites in W. Siberia, there was less variation between surface and subsoil values but distinct spatial patterns that appear to reflect buried structures.

Geochemistry of pediment over the Toki porphyry copper deposit, Atacama Desert, Chile

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The absence of vegetation in arid portions of Chile allows visual inspection and satellite imagery to be successful in locating gossans developed over exposed porphyry copper deposits (PCDs). Unfortunately, deposits covered by pediment or pyroclastic materials are more difficult to discover. Over the past 15 years, exploration techniques have been developed to more easily locate buried deposits; one such technique is partial digestion pedogeochemistry. This procedure uses weak reagents to extract metals that are loosely bound to the surfaces of soil particles. These metals are most likely transported from PCDs at depth by circulating groundwaters, and thus produce anomalies with geochemical contrasts that are higher than those obtained using total digestions.

In this research, fine-grained (<125 µm) soil samples were digested using total (fusion/ICP) and partial (aqua regia and mineral deionised water) methods. Samples were collected every 10 cm

down trenches up to 2.5 m deep that were dug into pediment up to 60 m thick over/adjacent to the Toki PCD near Calama, Chile. Aqua regia results indicate that pediment is strongly contaminated in Cu and weakly contaminated in Mo, Pb, Zn, Ni, Ag, Cd, and Bi to a depth of approximately 50 cm, probably due to wind-blown dust from nearby PCDs, mines, concentrators, and/or smelters. This contamination masks any surface anomalies that might exist above the underlying Toki PCD. If contaminated samples (from less than 50 cm depth) are not considered, aqua regia analyses of deeper samples exhibit geochemical anomalies defining the classic metal zoning pattern observed at PCDs. Fusion/ICP results illustrate that calcite and gypsum are important caliche minerals above and below 50 cm depth, respectively; subordinate natron is also present. These observations suggest that caliche minerals precipitated due to evaporation of groundwaters brought to the surface either by capillary action, or by hydraulic head from adjacent uplands.

Lithogeochemistry of host rocks to the Bisha and Harena Cu-Zn-Au volcanic hosted massive sulphide deposits, Eritrea

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The Bisha mining camp is hosted by the Neoproterozoic Western Nafka Terrane of the Arabian-Nubian Shield in western Eritrea, and contains four volcanic hosted massive sulphide deposits (Bisha, Harena, Bisha NW, and Hambok). The largest deposit (Bisha) is partially weathered, containing 27.3 M tonnes (measured and indicated) in: (i) an oxide zone of 4.8 M tonnes grading 7.0 g/t Au and 30 g/t Ag; (ii) a supergene zone of 7.5 M tonnes grading 4 % Cu, 0.7 g/t Au and 32 g/t Ag; and (ii) a hypogene zone of 15.0 M tonnes grading 6 % Zn, 1 % Cu, 0.7 g/t Au and 48 g/t Ag. Hydrothermal alteration, metamorphic recrystallisation, and deformation impede identification of primary volcanic compositions and textures in host rocks to these deposits, and thus complicate correlation of stratigraphy across the mining camp. Conserved element ratios, constrained by petrographic observations, were used to evaluate the lithogeochemical data and assist in recognition of the lithologies. These ratios are unaffected by lower greenschist to amphibolite metamorphism and hydrothermal alteration, and so allow identification of precursor rock compositions in an effective and compelling manner, so they can be traced across sections through the deposits. Molar element ratios were then used to investigate and understand the compositional controls in mafic, intermediate and felsic volcanic rocks, to identify the different hydrothermal alteration styles present in these rocks, and to quantify their intensities. Results indicate that the Bisha and Harena deposits do not occur at the same stratigraphic level. Nevertheless, both hangingwalls are muscovite altered and both footwalls exhibit chlorite alteration. A new 'aluminous' alteration zone in the immediate footwall of the Harena VHMS deposit is quartz deficient, and consists of chloritite or an andalusite-chlorite-muscovite-calcite assemblage. This new alteration style is the most intense and proximal hydrothermal alteration zone observed in the camp.

Detecting fine-grained gold in pedogeochemical samples from the Fifteen Mile stream gold property, Nova Scotia

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Pedogeochemical exploration for gold is impeded by the 'nugget effect', a sampling error that causes extremely variable Au grades due to the presence of large, rare gold nuggets. Thus, the 'nugget effect' adds noise to geochemical data that obscures dispersal patterns and makes exploration for gold extremely challenging. A conventional method that avoids the nugget effect involves collection and analysis of large samples, as these likely contain numerous coarse-grained gold nuggets, and thus exhibit reproducible grades. An alternative method, developed in China for regional stream sediment gold exploration involves a different rationale whereby fine-grained fractions of small samples are analysed. This method ostensibly circumvents the 'nugget effect', by lowering the probability of including large, rare gold nuggets in samples. In this research the small sample method was applied to B-horizon soil samples developed over a known Au anomaly to determine if the small sample approach can be used effectively in pedogeochemical exploration. Gold grain size distributions were determined in 15 soil samples using 14 size fractions (from 0 to 250 µm), and sixteen small (0.3 g) replicate samples were analysed from these same samples. Results confirm that small samples exhibit a 'nugget effect' smaller than that observed in large samples. Because small samples lack large nuggets, they also under-estimate grade, and so exhibit lower geochemical contrasts. Unfortunately, the smaller nugget effect in small samples is still large enough, relative to geochemical contrast, to impede data interpretation. This prevents the small soil sample strategy from out-performing conventional (large sample) analysis in gold exploration. A possible explanation for this contradiction between soils and stream sediments is that hydraulic segregation in streams may alter gold grain size distributions such that a small sample Au analysis exploration strategy can be effective in stream sediments but not in soils.

Using oxygen isotopes in vein calcite to map the distribution of fluid flux in exhumed fault systems: An example from the Dar Al Baydah fault system, northern Oman

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When fault ruptures breach overpressured fluid reservoirs, fluid pathways are controlled by the distribution of fracture-permeability in rupture zones and hydraulic connectivity of high permeability sites to fluid reservoirs. Little is known about the geometry and distribution of fault-controlled fluid pathways and how they evolve during successive seismic cycles. Oxygen isotope signatures in fault-related veins provide potential for exploring the spatial and temporal distribution of flow in these systems.

The Dar Al Baydah (DAB) Fault, and an associated array of smaller faults, is exposed within a limestone sequence in NE Oman. The DAB Fault has a strike extent of 30 km, is segmented at various scales, and has a maximum dip separation of 800 m. The early slip history involved normal slip, whereas later activity involved sinistral strike-slip. The fault system exhibits widespread development of calcite fault-fill veins along with calcite extension veins in lateral damage zones. The exposed structural levels of the fault system record deformation at depths of approximately 10-13 km, and temperatures up to 250 °C.

Vein calcite from the DAB Fault is ^{18}O-depleted by up to 12‰ relative to limestone host rock, indicating the fault breached a deeper-level, externally-buffered fluid reservoir. During normal slip, the formation of low δ^{18}O vein calcite, and high fluid flux, was localised preferentially at major fault segment boundaries and fault terminations. During subsequent sinistral reactivation, the distribution of low δ^{18}O vein calcite and high fluid flux was more variable. The low displacement part of the network also was connected to the external fluid reservoir and hosted significant fluid flux. Reactivation of normal fault relays as dilatant and contractional jogs during late sinistral slip in the low displacement fault network has played a key role in localising permeability enhancement and fluid flow late in the evolution of the fault system.

A summary of recent isotopic investigations employed for ore genesis and environmental purposes at the Navachab Gold Mine, Namibia

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The aim of this abstract is twofold: i) to present the latest Re-Os molybdenite dating of Navachab and; ii) to discuss a stable (D/H, O) and Sr isotope data set used for aquifer fingerprinting.

Navachab is the largest non-Witwatersrand gold resource in southern Africa. A late-kinematic, auriferous, quartz-vein swarm and associated Ca-Mg-Fe-Mn skarn (sensu lato) alteration crosscut the Neoproterozoic Damara Sequence (Adelaidean equivalent), which comprises the metamorphic equivalents (upper amphibolite-facies grade) of continental quartzites, glaciogenic mixtites and pelite ± carbonate shelf rocks. Re-Os dating (by Geospec Consultants) of rare traces of molybdenite in a sphalerite+pyrite-bearing aplite yielded Cambrian Re-Os ages (2σ) of 525 ± 2.4 Ma and 523 ± 2.1 Ma. Molybdenite-bearing, NNE-dipping, extensional auriferous quartz+bismuth+pyrite+pyrrhotite veins (garnet selvage) have Re-Os ages (2σ) of 520 ± 2.1 Ma and 519.4 ± 2.1 Ma. The gold-mineralising event occurred slightly after the collisional metamorphic peak at 530 Ma, but subsequent gold redistribution and even ore mineral melting of the Au-Bi minerals at the late-stage peak of the Damaran HTLP tectonothermal event is considered likely. The “standard” greenschist dewatering model (Groves - Goldfarb) cannot explain the ore-forming process at Navachab.

An ^{87}Sr/^{86}Sr groundwater and rock database (spanning the Sturtian and Rapitan cryogenic events), as well as rain, sump and groundwater stable isotope values (O, D/H) were collected as part of a groundwater monitoring program. Hydrogeological management of the centrally located ~100 m-thick quasi-karstic Okawayo Formation (also a fractured-rock aquifer), is essential to minimise water ingress into the mine. Strontium (rock ^{87}Sr/^{86}Sr value range of 0.707777 to 0.903491) and stable isotope signatures of waters in the most important hydrological units can be used for aquifer discrimination. The sheeted quartz vein and reduced, deep-level, pyrrhotite-dominated gold skarn orebody have relatively low sulphide contents and groundwaters are buffered by voluminous carbonate aquifers. Therefore, environmental liabilities at Navachab are low compared to other gold deposit types.

Comparative analysis of three types of insect nest structure as a sample medium for the discovery of ore deposits

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Previous research has demonstrated that small mounds of the termite *Tumulitermes tumuli* (Froggatt) can successfully be used as geochemical sample media for the discovery of Au deposits (Stewart et al., 2011). This finding is in contrast to the typical use of large mound forming species for exploration in northern Australia and Africa. Large areas of Australia not only have small mound forming termites present but also have subterranean termites. These termites can have large nests hidden sub-surface. When foraging they sheath their food sources in earthen material. We investigate the use of this material, along with nest material from an ant species as sampling media for mineral exploration in the Yilgarn Craton, Western Australia.

We collected samples of all three sample types along a transect at the Garden Well Au deposit in the Duketon Belt of the Yilgarn Craton in Western Australia. Elevated Au concentrations (above a background level ~2 ppb) were found in all 3 nest structure types over the mineralisation. *Tumulitermes tumuli*, which forms small mounds to 60 cm in height, had up to 7.4 ppb Au in the mound material. The subterranean termite (*Schedorhinotermes actuosus*) had up to 8.4 ppb in the sheath material, and an ant species (*Rhtidoponera mayri*) recorded Au up to 24.4 ppb in the nest material. Vertical movement of the anomaly from at least 1.4 m deep is supported by evidence in the form of XRD studies and mineral grain counts of nests. These show vertical movement of calcite associated with elevated Au.

This is the first investigation of the suitability of subterranean termites for use in mineral exploration. Results suggest that along with mound forming ants and termites they are potentially useful for mineral exploration.

Stewart, A.D., Anand, R.R. and Balkau, J., 2012. Source of anomalous gold concentrations in termite nests, Moolart Well, Western Australia: implications for exploration. Geochemistry: Exploration, Environment, Analysis 12, 327-337.

Volcanic ash impacts on urban areas: Hazards from leachable elements

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An estimated nine percent of the world's population lives within 100 km of a historically-active volcano, with this proportion likely to increase in the future. Although volcanic eruptions can produce a wide range of hazards, with phenomena such as pyroclastic density currents and surges, lahars and ballistics block being the most destructive and dangerous, volcanic ash is the most widely-distributed product and can affect large numbers of people because of the large areas than can be covered by ashfall. However, volcanic eruptions tend to be infrequent and somewhat exotic occurrences and in many cases civil authorities may not have devoted serious consideration to management of a volcanic crisis.

As part of the immediate emergency response, there should be rapid dissemination of information about the physical and chemical properties of the ash and its hazardous potential. However, there is a wide range of components that can be tested for which can lead to confusion about whether or not a health threat exists. To help address this uncertainty, an international working group has recently developed a hazard assessment protocol for the analysis of volcanic ash samples to assess the hazard from leachable elements. The purpose of this protocol is to recommend clear, standard and reliable methods for the rapid assessment of hazards from leachable elements. This presentation will outline the new protocol and describe its application to recent eruptions that have affected urban areas.

The biogeochemical expression of bedrock in a regolith dominated environment: An example from regional surveying on Kangaroo Island, South Australia

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Although Kangaroo Island has a relatively well constrained basement geology determined from geophysical techniques and coastal exposures, the majority of the Island has a thick layer of regolith which obscures the full characterisation of bedrock. The regolith includes deep weathering profiles as well as Permian to recent sediments, typical of many of the transported cover exploration frontiers of Australia. Regional scale biogeochemical surveys have been undertaken across Kangaroo Island, South Australia, with an aim of identifying the expression of the buried bedrock geochemistry and associated mineral systems. The main plant types sampled include Eucalyptus trees and the grass tree Xanthorrea, mostly from remnant vegetation along roadside verges. The plant biogeochemical results show a strong localised expression of previously known base metal and gold mineralisation, mostly associated with the Cygnet-Snelling Fault Zone. In some cases these are a more repeatable method of surveying than the ferricretes (”laterites”) on the island, which are limited by their variable availability and greater chemical heterogeneity. In the areas away from the known mineralisation there is the possibility of the expression of the buried bedrock geochemistry being expressed in the ‘background levels’ of the biogeochemistry. This has important implications for defining the broad geological settings associated with mineral systems and broad scale exploration targeting. Other major advantages of biogeochemical techniques on the island have been their time and cost efficiency and low environmental impact.

The importance of redox condition in the formation of the Archean Red Lake gold deposit, Ontario, Canada

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Archean lode-gold deposits are a significant source of gold, but exploration for these deposits is hindered by their poorly understood geochemical features. The Red Lake gold deposit, located in northern Ontario, Canada, was studied to provide new information about its geochemical evolution and genesis, using mineral and whole rock chemistry. Red Lake is an Archean basalt-hosted lode-gold deposit with an estimated 49 Mt of material at 19 g/t Au, and is characterised by superimposed hydrothermal and metamorphic events. Three distinct events are identified. First, an early widespread (>7 km) hydrothermal event is characterised by a reduction of the basalt with FeO, MgO, K_2O, SiO_2 and S enrichment that likely represents a seafloor-hydrothermal event. The interaction of seawater and magmatic-hydrothermal fluids with the basalt caused formation of Fe-chlorite-carbonate and advanced argillic alteration assemblages respectively. Second, subsequent peak-regional metamorphism created a greenschist-amphibolite facies from the chlorite-carbonate alteration and a quartz-muscovite-andalusite assemblage from the advanced argillic alteration. Finally, a post-peak regional metamorphic event of structurally-controlled hydrothermal alteration along a narrow corridor (1-km-wide), formed <10-m-wide ore zones with abundant ankerite-calcite-quartz veins hosting pyrrhotite-pyrite-arsenopyrite-magnetite-gold-quartz with Mg-biotite alteration halos. The ore-forming fluids caused enrichment in CaO, MgO, SiO_2, K_2O, Au, Ag, and Sb in the basalt. Mineralised samples of basalt are furthermore characterised by a lower Fe^{2+}/Fe_{total} molar ratio compared to barren greenschist-amphibolite equivalents. This change in Fe^{2+}/Fe_{total} molar ratio reflects oxidation of Fe^{2+} in the host basalt to form a more Fe^{3+}-rich ore assemblage consisting of pyrrhotite and magnetite. The association of gold with the pyrrhotite-magnetite assemblage indicates that the interaction of a relatively oxidised ore-forming fluid with the Fe^{2+}-rich host basalt was the main influence on gold precipitation at Red Lake.

Geochemistry of ore-forming fluids at the Tui Zn-Pb-Cu epithermal deposit, Hauraki goldfield, New Zealand

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The Tui deposit in the Hauraki goldfield, North Island, New Zealand produced 163,000 tonnes of ore at 17% Zn, 7% Pb, 0.6% Cu, and 36.5 g/t Ag; it is a deep-level adularia-sericite epithermal deposit hosted by hydrothermally altered andesite. The two main veins, the Champion and Ruakaka, contain coarsely-crystalline quartz that is brecciated and cemented by sphalerite, galena, chalcopyrite, and pyrite. Base metal sulphide minerals are also brecciated and cemented by cryptocrystalline and later comb quartz with minor cinnabar and barite.

Microthermometry, Raman microspectroscopy, and laser ablation-inductively coupled-plasma mass spectrometry (LA-ICP-MS) have been used to determine the temperature, apparent salinity, and composition of fluids trapped in individual fluid inclusions in sphalerite and quartz.

Sphalerite and quartz were deposited from Na-K-Ca-Cl aqueous solutions with no detectable CO_2 or other volatiles. Na/K and Na/Ca molar ratios range from 0.6 to 149.8 and from 0.7 to 932.0, respectively. Lithium, Sb, As, and Ba occur in quartz- and sphalerite-hosted inclusions at concentrations up to 1114, 471, 109, and 33 ppm, respectively. Quartz-hosted inclusions contain up to 1900, 69, and 34 ppm Zn, Cu, and Pb, respectively. Homogenisation temperatures for primary, pseudosecondary, and most secondary inclusions in sphalerite and quartz overlap and range from 253° to 291°C and 240° to 287°C, respectively. Final ice melting temperatures (Tm) for quartz range from 0.0° to -4.0°C and correspond to salinities up to 6.4 wt. % NaCl equiv. In contrast, Tm values for sphalerite range from -2.6° to -8.2°C showing that ore-forming fluids contained 4.3 to 11.8 wt. % NaCl equiv. The greater salinity values for the sphalerite-hosted inclusions, combined with previously published stable isotope data, are consistent with base metal sulphide mineralisation from periodic incursion of a magmatic-hydrothermal fluid into a hydrothermal system that was predominantly meteoric water.

Geochemical and microbiological factors leading to increased arsenic release during uranium bioremediation

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Bioremediation has been the strategy employed at the former mill site in Rifle, Colorado, USA to immobilise uranium. Acetate injections were used to stimulate microbial growth and reduction of mobile U(VI) to immobile U(IV). While bio-stimulation was successful in attenuating uranium below the maximum contaminant level of the site, the subsurface change in redox conditions resulted in arsenic concentrations increasing several-fold over the background (up to 9 µM vs. <1 µM). Groundwater samples were collected from 10 wells down gradient of the injection wells and analysed for general water chemistry constituents and arsenic speciation to provide insight into the reason for, and nature of, arsenic released during bioremediation. Laboratory experiments were conducted to evaluate the effects of iron, sulphate and microbial activity on arsenic release in bach systems and flow-through columns designed to simulate conditions at the field site. It was found that arsenic release was strongly correlated with sulphate reduction in wells exhibiting the highest concentrations of arsenic ($r = -0.91$, $p < .001$). Thioarsenic species, which were found to form from arsenite and sulphide, dominated speciation during this arsenic release. Laboratory columns using field sediments did not produce levels of arsenic as significant as some of the field wells (<2 µM). However, the results were analogous to wells receiving limited acetate concentrations, exhibiting stronger correlations of arsenic release to the reductive dissolution of Fe(III) minerals. Disparities between field and laboratory column data indicated factors contributing to the observed increase in aqueous arsenic concentrations; these include arsenic source, redox chemistry, active microbial communities, and mineral precipitation. To successfully remediate the mill site in Rifle, Colorado using bio-stimulation, care should be taken to optimise in situ levels of acetate in order to reduce uranium without creating the conditions favourable for thioarsenic formation and release.

SGH – Spatiotemporal Geochemical Hydrocarbons self-organise to display the hydrocarbon flux pathways from effects of the electrochemical cell in redox zones to locate mineralisation

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Projections indicate that the supply of mineral resources will be insufficient in the near future, thus new technologies for exploration are needed to locate resources under deep and exotic cover. Research has proven that bacteria are ubiquitous and are associated with mineral and petroleum targets. Their growth depends on the use of inorganic elements which catalyse reactions to synthesise organic hydrocarbons to support growth. Experiments have proven that in the death phase of the life cycle of these microbes, cell membranes decompose and intracellular hydrocarbons are released. The hydrocarbons migrate to the surface and provide a forensic signature for identification of their food source as the type of mineralisation or petroleum target found at depth. It is accepted that redox conditions in the overburden and the subsequent electrochemical cell is associated with buried geological bodies, however the detection of redox cells is not sufficient evidence to pursue expensive drill programs. Over fifteen years of observations has resulted in an understanding of the relationship of the electrochemical cell and its effect on migration of these hydrocarbons. As relatively neutral species, the fluxes of hydrocarbons is shaped by electro-potential gradients that self-organise into predictable chemical class zonations dependent on the residence time of migration through the overburden. The analysis for hydrocarbons at ultra-trace concentrations from samples in a survey grid has illustrated highly symmetrical anomalies that provide a control to interpretation of these spatiotemporal geochemical hydrocarbons at a very high level of confidence. This 3D-SGH interpretational approach, coupled with the hydrocarbon signature of mineral identification, has resulted in a geochemistry that has accumulated a history of a very high level of success in independent reviews. This deep penetrating geochemistry confidently locates and identifies blind mineral and petroleum targets.

SGH – The ultimate geochemistry for sampling in difficult surface terrain and areas of exotic overburden

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Although the Soil Gas Hydrocarbon (SGH) name implies the exclusive use of soils, this geochemistry is also able to use other sample media such as humus, peat, sand, till, submerged sediment, etc., in the same survey. Snow surveys can also be done. As these hydrocarbons are relatively neutral species, the state of the flow of hydrocarbons that migrate and geochromatographically disperse through the overburden can be captured by the surface area of a wide variety of sample media. This capability is vital in areas of difficult terrain where a complete sample survey may cover swamps, lakes, peaty areas or conversely forests, sand dunes, and caliche. This multi-media survey can be processed and mapped together without data leveling, thereby significantly reducing the bias in the interpretation due to survey areas where sampling was traditionally not able to be conducted due to the limitations of other geochemistries.

The SGH geochemistry has been scientifically shown to detect those hydrocarbons released from the decomposition of bacteria at the end of their life cycle. From a 'you are what you eat' perspective, the 162 specific hydrocarbons in the C5 to C17 carbon series range provide an information-rich forensic signature of identification from the biofilms of bacteria that feed and grow on a wide variety of mineral deposits.

The forensic signature of hydrocarbons in this na noscale geochemistry can dramatically delineate and identify mineralisation through barriers such as a basalt cap and permafrost and has been able to help differentiate geophysical targets such as between barren and ore-bearing conductors and for those of kimberlites from naturally occurring signals from granite gneiss or dunite.

SGH is a robust geochemistry that is very easy to sample regardless of terrain, has highly confident results, and allows a more economic sampling program.

Use of field portable XRF in assessing the biogeochemical response to contamination from the Woodlawn Cu-Pb-Zn deposit, New South Wales

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Mining waste is a major source of trace metal contamination in the surface environment that may affect soils, groundwater and various organisms such as plants. Vegetation is a sampling medium that offers potential to map the extent and level of such elevated metal patterns. This study examined the spatial distribution of selected metals in vegetation around the Woodlawn base metal deposit in southern NSW. An fpXRF was used for in situ analysis of organs of *Acacia mearnsii* (Black Wattle) and *A. dealbata* (Silver Wattle) in the (former) Woodlawn Mine area and surrounding region. High levels of contamination for a number of elements related to the deposit itself (Cu, Pb, Zn, Ag) occur in the bark in a zone extending up to 1 km away from the tailing ponds. There is a close correlation between trace elements in the leaves and twigs, but weaker correlation between those organs and bark, in both ore and non-ore-related elements. Trace elements are typically more elevated on the side of the trees facing the tailings ponds than away from it and there are correlations between trace and major elements, indicating the main source of metals in the bark to be derived from dust. Laboratory tests indicate the penetration distance for X-rays from the fpXRF to be in the order of 3 mm for compressed leaves or bark. There is a close correlation for most elements between the fpXRF and laboratory-based XRFs.

Arsenic behavior in lacustrine sediments of the Bolivian Altiplano of Oruro

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Oruro Department is located in the Bolivian high-plains at 3800 m.a.s.l. and is one of the most unexplored, mineralised and historic mining towns of the world. The Altiplano experiences high inter-annual and seasonal climatic variations, which has been linked to El Nino events (ENSO).

To determine arsenic behavior in sediments and interstitial waters of Oruro, two coring campaigns were performed, during the wet (WS) and the dry seasons (DS). Northern and southern borders of the lake Uru Uru (Altiplano, contaminated site) and Cala Cala lagoon (Eastern Cordillera, reference site) were sampled, obtaining a total of 91 sediment and 222 interstitial water samples. Sediments were subjected to selective single digestions to determine the solid state partitioning (SSP) of As. Arsenic quantification was performed by ICP-MS.

Interstitial water behaviour and diffusive fluxes suggested that lake Uru Uru sediments are an arsenic source to the water column. In the reference site, As is found in residual (immobile) and Fe-Mn oxy-hydroxides fractions. In northern lake Uru Uru, sediments are sensitive to seasonal changes and there are also changes in the solid state partitioning of As between dry and wet seasons as the water column is not present during the dry season. In southern lake Uru Uru, solid state partitioning of As is similar during both, dry and wet seasons because this area does not experience the absence of the water column during the dry season.

As a consequence of the intricate and complex redox processes and climatic variability of the Altiplano, we conclude that lake Uru Uru sediments work as an As source to the water column and that the fate of the dissolved As will depend on the competition between its removal and transport in the water column.

Impact of volcanic ash on REE, Zr, Nb, Hf, and Th input into seawater from glacial meltwater rivers

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One of the consequences of climate change is retreating glaciers. These melting glaciers are connected to the ocean via glacial meltwater rivers. The chemical composition of glacial meltwater rivers in Iceland is affected by volcanic eruptions due to the input of colloid- and nano-particles from volcanic ashes. In 2010, we sampled river waters and volcanic ashes from southern Iceland to characterise the geochemistry of glacial meltwaters (especially the behaviour of REE and other high-field-strength-elements, HFSE), to investigate the impact of colloids and nanoparticles from volcanic ashes on water chemistry, and to study the behaviour of REE and HFSE during estuarine mixing. The REE and HFSE are highly particle-reactive and show low solubilities, and are therefore not truly dissolved in surface waters, but associated with particles. Comparison of the trace element distribution of river particulates (>0.45 µm filter residues) and volcanic ash to that of the respective glacial meltwater (<0.45 µm filtrates) reveals very close similarities, indicating that REE and HFSE bound to colloids and nanoparticles dominate the dissolved trace element distribution in Icelandic meltwater rivers.

We then did laboratory mixing experiments with 0.2 µm-filtered glacial meltwater from Markarfljöt River and seawater. Admixture of minute amounts of seawater (resulting in a salinity of 3.4) already has a strong impact on the REE and Y (REY) signature of the water. Besides a significant decrease of REY concentrations, the REY input develops all the features typical of the REY distribution in seawater as salinity progressively increases. After the initial drop, REY concentrations tend to increase again with increasing salinity, probably due to REY desorption from or incongruent dissolution of aggregated former colloids and nanoparticles. Our results strongly suggest that the REY input into the ocean is characterised by a specific REY distribution pattern that is rather independent of the lithology of the catchment.

Strong increases in rare earth elements as emerging contaminants in drinking water: Increasing anthropogenic gadolinium levels in tap water of Berlin, Germany, between 2009 and 2012

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Xenobiotics and high-tech metals have become emerging contaminants of the hydrosphere. In this study we focus on the distribution and behaviour of the rare earth elements (REE), especially gadolinium (Gd), in tap water of Berlin, Germany. First reported in German rivers in 1996, contamination of surface waters with anthropogenic Gd has become a typical feature of industrialised countries with highly developed health care systems. The sources of anthropogenic Gd are Gd-based contrast agents used in magnetic resonance imaging (MRI). Gd-based contrast agents are injected into the bloodstream of patients and are released in urine within 48 hours. Since these highly stable and water-soluble Gd-complexes cannot be removed in waste water treatment plants, they are transferred to surface and ground waters, and eventually into tap water. Anthropogenic Gd is therefore a tracer for the presence of waste water-derived substances, which may have a high (eco-)toxicity. An initial study from 2009 reported shale-normalised REE patterns in tap water from the western districts of Berlin, with large anthropogenic positive Gd anomalies. In contrast, the eastern districts exhibited no distinct anomalous Gd behaviour, indicating the absence of waste water-derived contaminants. Considering that anthropogenic Gd levels in the Havel River have increased significantly in the past decade, it was predicted that the contamination of Berlin's tap water with anthropogenic Gd would continue to increase in the near future. Updating the study from 2009, we report results for tap water samples taken in December 2012. Between 2009 and 2012 anthropogenic Gd increased significantly. The smallest increase was observed in Zehlendorf (1.5 times) in the western districts, while the maximum increase was observed at Jungfernheide (11.5 times). The strong increase of anthropogenic Gd in tap water between 2009 and 2012 demonstrates the increasing impact of high-tech metals, such as the REE, on the environment.

Regional background concentrations of indicator and pathfinder elements in soil: A case study from the Hauraki Goldfield, New Zealand

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Soil geochemistry is an important exploration method employed in the detection of subsurface mineralisation. Critical parts of interpreting soil geochemical data lie in determining background ranges, threshold values and in the recognition of geochemical anomalies. At the Hauraki Goldfield, where epithermal Au-Ag deposits are present, soil samples from sites where bedrock lithologies have not been hydrothermally altered during mineralising events were analysed for 19 pathfinder elements by ICP-MS, following dissolution by Aqua Regia. The soil profile including A, B and C horizons have been sampled at each of these sites. The geochemical data have been treated with classical statistical methods and exploratory data analysis techniques to define regional background ranges for the 19 key pathfinder elements and to calculate threshold concentrations above which these elements may be considered as anomalous. Within the Hauraki Goldfield a regional geochemical background database founded on samples collected beyond the known areas of hydrothermal alteration has been established in this study for the first time and represents a foundation that may be used for comparative purposes during regional- and local-scale mineral exploration. The threshold values that have been calculated provide a measure of the minimum background concentration within the southern Hauraki Goldfield. Element concentration values that are significantly elevated in comparison to this threshold database may be considered as significant. B Horizon soils typically show element enrichment relative to the A and C Horizons. Threshold values for B Horizon soils developed over unaltered andesite bedrock, determined by the median + 2 median absolute deviation method (expressed as ppm except where noted as pbb or %) are: Ag (0.09), As (9.9), Au (0.10 ppb), Ba (217.5), Bi (0.41), Cu (23.25), Fe (0.45%), Hg (0.29), Mn (0.04%), Mo (1.53), Pb (21.72), S (0.09%), Sb (0.28), Se (1.8), Te (<LDL), Tl (0.23), U (2.5), W (0.1), Zn (48.3).

Biogeochemical "fingerprinting" of Voisey's Bay Ni-Cu-Co sulphide mineralisation, northern Labrador, Canada

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In areas with exotic overburden, by definition there is no geochemical relationship between mineralised bedrock and the overlying material. Some species of vegetation, however, have the capacity to absorb metals from groundwater, and hence underlying bedrock, via their root systems. Metals can be concentrated to varying extents in needles, leaves, twigs and bark. The analysis of vegetation may, therefore, be used to locate hidden mineral deposits. The Voisey's Bay (VB) Ni-Cu-Co sulphide deposits in Labrador, Canada, were originally discovered as a gossan in an till-covered area. The sulphide mineralisation is hosted by a troctolite dyke feeder and magma chamber system, the Voisey's Bay Troctolite (VBT), which intruded older gneiss. An investigation was undertaken over the VB deposits to establish the usefulness of biogeochemistry as an aid in Ni-Cu-Co exploration. Twigs with needles, and bark of black spruce, *Picea mariana*, were collected from a series of traverses extending over areas of mineralisation and background. The dried samples were ashed and analysed by ICP-MS for a suite of 44 elements. The results indicate strongly anomalous responses to mineralisation in the twigs, bark and needles. Metals are preferentially concentrated in twigs relative to bark and needles. On the basis of these results it is concluded that biogeochemistry constitutes a viable exploration procedure in the search for sulphide mineralisation in areas of shallow exotic till where conventional methods have proved to be of limited use.

Nano gold nuggets in natural arc volcanic glasses

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Most seafloor massive sulfide deposits contain significant proportions of magma-derived metals (i.e. Au, Ag, Cu, Mo, Bi, Sb, As), which relate to the composition of the associated (host) magmatic rocks. The composition of the host rock therefore must have a strong influence on the composition of the seafloor massive sulfide deposit. We present new EMPA major and LA-ICPMS trace element data from submarine volcanic glasses recovered from the Kermadec arc volcanic centers Monowai, Brothers, Healy, Cotton, Rumble II West, Rumble III and Clark. The new data show that most glasses have an order of magnitude higher metal contents compared to whole rock analyses of the same element. But more importantly, nano-sized nuggets with high metal contents were identified during time-integrated laser ablation analyses. LA-ICPMS mapping of respective glass charts revealed that the nano-nuggets are mostly located along imperfections, such as glass-microlite boundaries, which may act as nucleation sites. Field and experimental evidence suggest that gases exsolve from magmas and accumulate as bubbles, and act as metal carriers. Due to changes of melt characteristics, flow regime, temperature and pressure during ascent and quenching, the bubbles may collapse, subsequently depositing metals in the glass. The localised occurrence and different composition of the nano-nuggets also suggest heterogeneous metal content in the exsolved gas phases, which is likely to relate to a heterogeneity in the carried gas composition. This early metal deposition process is likely to represent a syn-eruptive process and may indicate ore forming capabilities of magmatic sources.

Landscape and regolith evolution in hyper arid regions of northern Chile: Implications to geochemical exploration in areas of transported overburden

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In northern Chile mining exploration has reached a mature state of development; most outcropping and obvious exploration targets have been long explored and evaluated. Well known giant porphyry copper districts occur along north-south (NS) metallogenic belts, among these, the Paleocene and upper Eocene to lower Oligocene porphyry copper belts. Within the belts, porphyry copper districts occur mostly as clusters, with large expanses of land between them. Despite obvious NS exploration trends, much of these expanses are covered by transported overburden, and indirect exploration methods are required, including conceptual geology of surroundings, evaluation of NS linear trends of main fault and/or metallogenic trends, and use of geophysics and geochemistry. Indirect geochemistry relies on soil/cover samples and is based on the development of geochemical signatures at surface, from deposits beneath cover, by means of metal migration to surface, be it by hydromorphic, gaseous, tectonic pumping, electrochemical or other mechanisms. Resulting geochemical signatures at surface from such sources may develop geochemical variance and eventually contrast that could lead to discovery. However, contrast from such processes tends to be subtle and hard to discriminate from other sources of variance and contrast. At the Inca de Oro porphyry copper deposit, located in the Atacama region, in order to better interpret sources of natural variance, geochemical and mineral studies of regolith were carried out. Seven regolith/gravel units were recognised, each with unique mineralogical associations and geochemical signatures. These units cut and cross each other, from youngest to oldest, implying geochemical variance associated with regolith and landscape evolution processes. Geochemical and mineral characterisation of regolith may aid the interpretation and application of exploration geochemistry. In particular, this characterisation provides insight on surface dispersion processes and recognition of surface related regolith/ landscape geochemical patterns, both important in discriminating surface regolith expressions from that generated by underlying mineralisation.

Antimony removal by two passive treatment techniques – sulphate-reducing bioreactors and adsorption chambers, Globe Progress Mine, West Coast, New Zealand

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Two passive treatment methods for the removal of antimony from mine water discharge were tested in field trials at a gold mine in New Zealand. One involved adsorption onto iron oxides consisting of a precipitate of goethite and ferrihydrite from AMD at an abandoned coal mine. The other method involved sulphate reduction and formation of antimony sulphide (stibnite) using a sulphate-reducing bioreactor. Each system was contained in a 1000 L tank. The loading ratio of iron oxide in the adsorption chamber was 253 g precipitate per L of water. The bioreactor contained equal parts of post peel, bark and compost and a small amount of inoculant. Inlet antimony concentrations ranged from 0.3 to 2.3 mg /L. Hydraulic residence times (HRTs) ranged from 3 min to 14 h (adsorption chamber) and 2 h to 30 h (bioreactor). Removal rates in the adsorption chamber were 14% at HRTs of only 3 min and were up to 95% at HRTs greater than 2.5 h. As the experiment progressed, removal rates by the adsorption chamber decreased with time suggesting that adsorption capacity was being approached. Removal rates in the bioreactor were greater than 80% at HRTs above 15 h. The greatest removal rate was 98% at an HRT of 30 h, lowering Sb concentrations from 1.7 to 0.014 mg/L. Even at short HRTs of only 2 h, removal rates were up to 81%, lowering Sb concentrations from 0.75 to 0.14 mg/L. Analysis by XRD confirmed the presence of stibnite in the bioreactor. Contrary to the adsorption chamber, bioreactor performance continued to improve with time, likely due to multiplication of sulphate-reducing bacteria, resulting in increased sulphate reduction rates. These results show that passive treatment can be a successful treatment method for antimony at gold mine sites.

Discovery of the Mesel, Batu Hijau and Elang deposits, Indonesia: Results of successful greenfields exploration

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In 1986, Newmont identified three blocks of favourable terrane in Indonesia; in North Sulawesi, Lombok and Sumbawa islands in the eastern Banda Arc, and Bengkulu Province in southwest Sumatra. A comprehensive multi-method, multi-element, regional-scale drainage sampling program was implemented to ensure that a single visit would be sufficient for most sites sampled.

In Bengkulu, it was recognised at an early stage that the abundant gold anomalies generated by the drainage survey were not being reflected in the local geology. Coarse pannable gold and erratic anomalies indicated placer gold, and auriferous conglomerates were subsequently recognised on ridge tops. With this understanding it was easy to rapidly assess the remaining anomalies, and terminate the Contract of Work (COW) when no primary sources for the gold were located.

Work on the North Sulawesi COW commenced with both a regional drainage survey, and detailed exploration around an historic Dutch mine at Hais. This zone hosted epithermal veins and visible gold, which generated strong stream sediment anomalies and extensive surface eluvial gold deposits, which were exploited by the Dutch and then by thousands of local miners. In contrast, the carbonate-hosted, micron-size gold in jasperoidal silica at the Mesel deposit had a very weak stream sediment anomaly and restricted outcrop. Mesel was mined between 1996 and 2004, and resources are now exhausted.

The initial regional drainage survey in Nusa Tenggara Barat generated 36 anomalous clusters of drainages. The top-ranked target was around Bukit Ladam, which subsequently proved to be an epithermal overprint on the margins of a very large porphyry Cu-Au deposit at Elang. Elang is at a resource definition stage.

Discovery of Batu Hijau in West Nusa Tenggara in 1990 was based on the persistent follow-up of rare copper-stained diorite float. Batu Hijau is a classically zoned porphyry deposit which commenced operation in 2000 and continues today.

Diurnal trace element cycles at Champagne Pool, Waiotapu, New Zealand: Control of sulfur on the solubility and speciation of antimony and arsenic

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Champagne Pool, a sulfidic hot spring associated with the Waiotapu Geothermal System in New Zealand, exhibits distinct diurnal variations in antimony (Sb) and arsenic (As) concentrations. Total Sb concentrations increase during daytime, while As concentrations experience a decrease over the course of the day. To investigate the trigger for these diurnal cycles and their potential link to the sulfur (S) redox chemistry in this sulfidic environment, we sampled the waters of Champagne Pool over a full 24 hour cycle. Every two hours, filtered and unfiltered samples were taken at five sites from the pool itself as well as along the drainage channel. Total trace element concentrations were analysed by ICP-MS and speciation of Sb, As and S was determined by IC-ICP-MS.

Sulfur speciation was found to undergo significant diurnal variations, with thiosulfate and sulfide dominating in the fluid at night and sulfate dominating during the day. The daylight dependent transformations among S species suggest that the observed diurnal cycle is governed by phototrophic sulfur-oxidising bacteria. These bacteria catalyse the oxidation of sulfide and the disproportionation of thiosulfate, leading to increasing concentrations of sulfate and, as suggested by modelling with PhreeqC, elemental sulfur during the day. As a result of sulfide consumption during the day, the geothermal fluid becomes undersaturated with respect to antimony sulfides and additional Sb is released into the fluid. Compared to Sb, diurnal variations for As were found to have a more pronounced effect on the actual speciation than on the total As concentration. During the day, monothioarsenate forms from arsenite and elemental sulfur. At night however, As speciation is dominated by the formation of di- and trithioarsenate from sulfide, which accumulates due to the inactivity of phototrophic bacteria. Sulfur speciation was thus identified as a key factor in controlling both total concentration and speciation of Sb and As in geothermal fluids.

Hydrothermal evolution of the Titiribi Mining District, Columbia

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The Titiribi mining district is located on the western margin of the central cordillera, 70 km south west of Medellin, Colombia. It is part of the Middle Cauca metallogenic belt, which contains Cerro Vetas, Chisperos, Porvenir, Juntas and El Zancudo deposit. Cerro Vetas, Porvenir and Juntas deposit have shown feautres in common with porphyry-copper systems. Hydrothermal alteration in Cerro Vetas consists of a deep sodic-calcic alteration zone characterised by actinolite + albite + magnetite, and a widspread area of potassic alteration marked by biotite + K-feldspar. Mineralisation consists mainly of disseminated magnetite, pyrite, chalcopyrite, with minor amounts of galena and Ag-sulfosalts. Juntas and Porvenir have a potassic alteration zone characterised by biotite + magnetite overprinted by a chlorite-sericite alteration zone, in turn locally overprinted by smectite. Mineralisation consists of pyrite, magnetite, Fe-rich sphalerite, and trace amounts of chalcopyrite, ?covellite, galena and Ag-telluride.

The Chisperos and El Zancudo deposits exhibit hydrothermal alteration characteristic of a low sulfidation epithermal system. Diorite porphyry and breccia samples from Chisperos deposit record a widespread propylitic alteration zone characterised by the association of epidote + chlorite + carbonate, overprinted by sericitic alteration characterised by sericite + carbonate. Calcite, quartz ± chlorite veins hosted in the breccia unit, and associated with the sericitic alteration, contain Ag-Pb-Zn-Sb ore mineral assemblages including sphalerite (Fe-rich and Fe-poor), galena, stibnite, electrum and silver sulfosalts. At the El Zancudo deposit, an alteration mineral assemblage of quartz – illite is present. Vein mineralogy consists of quartz, carbonate, Fe-rich sphalerite, pyrite and arsenopyrite, which is consistent with low sulfidation epithermal mineralisation.

Considering the elevation differences between the low sulfidation epithermal systems (Chisperos and Zancudo deposits) and porphyry systems (Cerro Vetas, Porvenir and Juntas), a tectonic event of exhumation and subsequent erosion between the two hydrothermal events is suggested. A later epithermal event may have overprinted the porphyry style mineralisation introducing part of the precious and base metal content.

Performance of sulphate-reducing bioreactors treating mine influenced waters using waste mussel shells

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The ability of sulphate-reducing bioreactors using waste mussel shells to treat acid mine drainage from an active coal mine has been evaluated. Eight bioreactors (each 30 L) were tested using a semi-continuous upward flow-through experimental design. The effect of two different hydraulic retention times (2.2 days and 6.6 days) as well as two different reactive substrates containing a mixture of organic materials (Pinus radiata bark, compost and bark mulch) and either mussel shells or limestone as a source of alkalinity was monitored. Several physical and biochemical properties of the substrate mixtures were examined before the experiments commenced.

Numerous geochemical analyses were performed on influent, effluent and pore-water samples (pH, ORP, EC, alkalinity, COD, metals, sulphate and sulfide concentrations) to evaluate the ability of the different systems to increase the pH and to remove the metals and sulphate. Preliminary results show that all systems are effective at increasing pH and alkalinity, with those containing mussel shells and/or with a longer hydraulic retention time generate more alkalinity. Effective sulphate and metal removal is observed in each system. Assessment work on the bioreactors includes mineralogical analyses of the precipitates (SEM and sequential extractions), geochemical modelling of the aqueous phase using PHREEQC, and characterisation of the different organic fractions of the substrate mixture (pre- and post-treatment).

Post-glacial processes causing upward element migration from a buried massive sulphide source

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For geochemistry to be applied effectively in mineral exploration, it is essential that all the processes acting in a given environment are understood and tested for in orientation studies. Furthermore, as exploration efforts are increasingly focusing on deep targets and under transported cover, the targeted geochemical signals at the surface become increasingly subtle and distinguishing their source becomes more complicated. A study of the multi-element geochemistry and Pb-isotope ratios of various sample media from the Talbot Lake prospect in the Flin Flon-Snow Lake terrane was conducted to identify pathfinders from a Proterozoic sulphide source, through Paleozoic carbonates, in the overlying till and organic media. The results of this research cannot be explained by conventional methods of element migration as described in the geochemical literature. A process described in hydrological studies of glacial moraine formation provides an alternative mechanism and a plausible explanation for the observed phenomena at the Talbot Lake prospect: During deglaciation, the glacial load is removed much faster than isostatic rebound of the lithosphere can compensate for. As a result, remnant hydrostatic pressure on buried aquifers remains very high until the overlying strata become permeable, either through opening structures or through the melting of permafrost. In such an event, deep groundwater is propelled upwards along permeable pathways, transporting materials both in solution and in suspension, and depositing them in the near-surface environment. Influx of pathfinder elements and Pb-isotope ratios typical of VMS mineralisation into the till, directly over structures in the carbonate cover, is supportive of the proposed mechanism having occurred at the Talbot Lake prospect.

Assessing the usability of geochemical data originating from multiple databases for mapping the background concentration of metal in soil at regional scale

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When undertaking mapping of trace metal concentrations in the soil at a regional level, it is often found that several databases already exist. These databases, usually quite large, were obtained for instance because of an environmental protection regulation (requiring soil analysis) or in the course of geochemical characterisation surveys. The use of all the available databases is often a necessity if one has to provide high resolution maps of the pedogeochemical background.

However, analyses from these geochemical databases were generally carried out by different laboratories at different time periods. Although these laboratories are required to follow strict protocols and quality control procedures, the precision and the accuracy of a particular laboratory can vary in time. This can be due to variations in the analytical equipment, the analytical procedure or the analyst. In addition, there may also be interlaboratory biases. Exploiting multi-laboratory geochemical databases can therefore be a tricky task. Here we outline a generic procedure and the series of guidelines that proved to be useful for this purpose.

The procedure consists in two sets of checks: (1) relevance checks, and (2) accuracy checks. The latter also comprises the correction of the dataset, if needed. The checks for relevance pertain to analytical protocol, georeferencing, temporal variability, spatial structure and the presence of censored values. The checks for accuracy involve testing the existence of interlaboratory bias by a method that takes into account the geochemical characteristics of the study area. An interlaboratory bias correction method is proposed and discussed. The procedure is illustrated with a soil geochemical database of about 17,000 georeferenced analyses of trace metal elements carried out by 13 different laboratories in Wallonia (South Belgium). The cases of Cd (atmospheric deposition), Ni (geogenic origin) and Zn (both origins) are discussed.

Integration of geochemical data from handheld XRF analyser, ICP-OES and AAS with mineralogical techniques to characterise a porphyry Cu-Mo deposit in Chile

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The mining of porphyry copper deposits in Chile enables its mining sector to stand out as one of the largest worldwide. To maintain this position, it is necessary to optimise the mineral extraction processes. This may be assisted by the integration of geological, mineralogical and geochemical information that contributes to the understanding of the geology of the deposits and enables the establishment of relationships between the nature of the material and processing features. This knowledge may be used to predict the behaviour of the material and generate models to optimise mine planning and mineral processing. The gangue mineralogy is particularly important in determining the behaviour of the rock during mineral processing.

This study, using samples from the Relincho Porphyry Cu-Mo deposit, investigates the application of a variety of analytical techniques that, in conjunction, provide a comprehensive geometallurgical model. In our study, hydrothermal alteration and lithology are analysed using portable XRF, AAS and ICP-OES. The mineralogy is characterised qualitatively and quantitatively by core logging, petrographic techniques and QEMSCAN® (Quantitative Evaluation of Minerals by SCANning electron microscopy). The description of lithological and alteration mineralogy present at the site, in conjunction with analyses of bulk geochemical assay data using statistical tools, allows the linking of the geochemical distribution of elements and specific qualitative and quantitative characteristics of the rock. A multivariate study is done to define relationships of elements, using the handheld XRF analyser, and compared with ICP and AAS data. The geochemical contrasts and ratios are analysed to indicate a change in the geological features, such as hydrothermal alteration, mineralisation and lithology, supported by the mineralogical description of the rock, integrating macroscopic, petrographic and automated techniques.

QEMSCAN analysis of core samples to characterise paragenesis, hydrothermal alteration and mineralisation in the Relincho porphyry Cu-Mo deposit in Chile: Potential applications in geometallurgy

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Chile is the world's largest copper producer, primarily through production from porphyry copper deposits. To maintain economic production it is necessary to optimise the mining and mineral extraction processes. Information on the ore geology, mineralogy and geochemistry can be critical in this endeavour. In our study, the qualitative and quantitative mineralogy of rocks from the Relincho Porphyry Cu-Mo deposit in Chile were characterised via core logging, petrographic techniques and QEMSCAN® (Quantitative Evaluation of Minerals by SCANning electron microscopy) analyses. Representative samples were obtained from drill cores and examined petrographically in thin section. Subsequently, the polished thin sections were analysed with QEMSCAN®, in Fieldscan mode, to provide information on the modal mineralogy of the samples, ore characterisation, estimated grain and particle size, mineral association and elemental distribution. The resulting information may be used to predict the geometallurgical response of the material to be processed. The analysis shows that the mineralisation consists essentially of primary copper ores, such as chalcopyrite and bornite, and some traces of chalcocite and covellite. There is no strong association with copper oxides or secondary sulphides, which is convenient for the flotation process. Other positive features are the low content of pyrite and the presence of molybdenite as the molybdenum ore. The principal gangue minerals are potassium feldspar, quartz, plagioclase, chlorite, epidote, calcite, muscovite and clays. The data provide valuable quantitative information on the mineralogical association of copper and in particular, the minerals that could interfere with its extraction.

Geochemical exploration in carbonatitic and felsic xenoliths associated with pegmatites, NW of Sierra El Roble, Cordillera de la Costa, Atacama region, Chile

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The study area is located at about 26° 56'S, 70° 37'W in the Cordillera de la Costa, Chile. The Cordillera de la Costa is along the western continental margin of the Atacama region, and is predominantly composed of Devonian to Carboniferous rocks that have been metamorphosed to low grade conditions in an accretionary prism and intruded by granitoids of late Permo-Triassic to Jurassic age. Activation of the subduction zone in the early Jurassic caused the emplacement of the intrusive bodies, which include a variety of tonalites, diorites, granites, and gabbros. Intrusive bodies of Middle Jurassic to Lower Cretaceous age in the study area are classified as calc-alkaline, metaliminous, I-type granitoids with initial Sr isotope ratios of $^{87}Sr/^{88}Sr$ 0.07041-0.7059, indicating great compositional variability.

Pluton Sierra El Roble (Jmtd) is an intrusive body with variable composition, including melanocratic diorites, amphibole monzodiorites, quartz-bearing diorites, and tonalites containing hornblende and biotite. The quartz-bearing diorites have phaneritic texture and subhedral to anhedral, holocrystalline phenocrysts. The tonalites have microcrystalline, holocrystalline, inequigranular, and poikilitic textures, and contain crystals of hornblende and medium to coarse grained biotite that vary from subhedral to anhedral. There are two xenoliths in Pluton Sierra El Roble, one of carbonatitic composition and the other of felsic composition associated with post-magmatic processes, Pegmatitic-neumatolitic stages, where crystals of biotite are approximately 20 cm across, have been identified.

Lithogeochemical exploration in both xenoliths, using a portable analyser (FRX, Bruker S1 TITAN) has revealed important concentrations of rare earth elements, mainly yttrium, lanthanum, and cerium.

The application of partial extraction geochemistry for base metal exploration in thick loess covered region, Gansu

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Loess covers c. 630 000 km^2 in northern China. The Jiaolongzhang polymetallic deposit, located in Eastern Gansu, is under loess, varying in thickness from <50 m to >200 m. The mineralisation zones are totally covered by loess and by a red soil layer. A soil survey along Line 48, sampling at a depth of 30 cm, and employing a total digestion technique, gave no response for the deposit-related elements Pb, Zn, Cu, and Ag. Although results of a MSG (metals in soil gas) survey showed that Cu, Pb and Bi exhibit strong anomalies above the buried ore bodies (Wang et al., 2008), selective leaching of soil by conventional procedures in use at that time by IGGE for extracting geochemical phases, including both exchangeable and carbonate-bound, did not reveal responses before 2008.

Following the 2008 studies, to decipher selective leaching geochemistry in loess terrain, different leachants and leaching procedures for top soil were tested and over 30 elements were analysed by ICP-MS. A specific leachant (so called SE-A) was found to be very effective for indicating buried mineralisation. The results show strong multi-point anomalies for a dozen elements over concealed orebodies. The highest Cu, Pb, and Zn concentrations in anomalous samples reach to 800, 2000, and 8000 ppb, respectively, while these elements in background soils are homogeneous with concentrations around 200, 70, and 400 ppb, respectively. The elemental distribution patterns identically correspond with MSG results. Interestingly, most pH values of soil in the background samples are higher than 8.45 but the pH values for anomalous samples above the buried bodies are lower than 8.45, which corresponds with a pattern of reduced chimneys (Hamilton, 1998).

Nano-scale insights into the migration mechanism of gold and copper through cover

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Deep-penetrating geochemical surveys have revealed that anomalies do exist at the surface overlying mineral deposits covered by transported regolith. We do not yet fully understand the migration mechanism. Recently, nanoparticles of metals were widely observed in gases, soils and ore rocks at copper and gold deposits using a transmission electron microscope (TEM) equipped with an energy dispersive spectroscope (EDS). Particle diameters range from 10 to 200 nm, with crystal structures observed by the TEM. The particles tend to form assemblages that are shaped like a grape cluster. In situ analysis by EDS shows that the particles from the copper-nickel deposit are composed of native copper and compound metals of Cu-Fe, Cu-Fe-Mn, Cu-Ag,Cu-Cr,Cu-Ni with Si, Al, Ca, O, P. Compounds from the gold deposit are Au, Cu-Au, Cu-Fe, and Cu-Ti. The nanoscale copper particles with crystal shape and ordered arrangements of atoms indicate that they originated from the concealed endogenetic Cu-Ni deposit. A migration model is therefore proposed that suggests that nanoparticles have properties that may overcome gravity to float in a liquid, have high surface area to volume ratios to maintain a tremendous force adsorbed onto surface of gas bubbles for diffusion, and which are migrated with an ascending flow of gas or water bubbles upward to the surface. Once at the surface, part of the particles persist in the soil gases whereas others are trapped by soil geochemical barriers. The findings provide nano-scale insights into the migration mechanisms of metals. This new method for separation of nanoparticles from soils is important for deep-penetrating geochemistry and the search for concealed deposits.

How to use geochemical baselines to quantify environmental changes?

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Geochemical databases and accompanying element distribution maps represent a geochemical baseline against which can be quantified future human-induced or natural changes to the chemistry of the Earth. How can “Geochemical Baselines” be used to quantify these changes? The authors take the datasets and maps obtained by the Environmental Geochemical Monitoring Networks project (EGMON) in 1994-1995 and China Geochemical Baselines project (CGB) in 2008-2012 for example to quantify environmental changes. Heavy metals such as As, Cd, Cr, Cu, Hg, Ni, Pb and Zn, and CaO were selected for study. The results show that 1) The medians for each element are consistent. The median ratios of CGB to EGMON range from 0.9-1.20. This implies slight bias in terms of sampling and analysis between the two projects. 2) The contents of heavy metals in top soils significantly increased, for example average values of Cd and As by the CGB are 2.7 and 1.6 times that by EGMON respectively. 3) The percentages of anomalous areas relative to the total surveyed areas significantly increase, for example Cd from 10.9% to 22.7%, Hg from 24.4% to 30.7%, As from 5.8% to 10.7%, Cu 4.3% to 11.8%, Ni 3.9% to 7.1%, Zn 5.8% to 8.3%. 4) The average concentration decreases from 0.53% to 0.41%, area of Cao <1% from 872,000 km^2 to 1.073,000 km^2, increasing 23%, due to leaching of $CaCO_3$ by acid rains induced particularly by coal burning. The facts show that geochemical baselines by using comparison data (values) and distribution maps (area of anomalies) can be applied to quantify environmental changes induced by human activity.

Geochemistry for improved environmental management at mining operations

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The mining industry is in an arena of constant environmental responsibility and scrutiny. This has resulted in longer timeframes required for project approval associated with greater consideration of environmental effects. This has cascaded into increasing costs associated with the approval process, operational management, monitoring, and reporting of performance and compliance. Applied geochemistry practitioners are an essential part of the mining industry providing answers and solutions that facilitate better environmental management outcomes and significant cost reductions.

A key issue facing the mining industry globally is acid and metalliferous drainage (AMD) manifesting as a multi-billion dollar challenge worldwide. It is a common, yet complex geochemical issue at many coal mining operations. Understanding the geochemical complexities of AMD at Solid Energy mines, including the likely occurrence, forecasting acid loads, prevention, treatment, and closure planning has involved significant input from research students, academic experts, consultants, and Solid Energy's environmental team.

Geochemical research has included fundamental geochemistry principles of AMD formation, improvement of acid base accounting techniques and long-term kinetic testing ranging from benchtop laboratory trials (2 kg) through to field based instrumented operational engineered landforms (> 400,000 bcm) to understand the acid mine drainage evolution profile.

Prevention techniques (low permeability covers) have been developed to reduce AMD formation based on reduced oxygen flux. Passive and active AMD water treatment technologies have been developed where, in one catchment alone, up to 8,000 tonnes per annum of acidity are treated annually. Research into the beneficial reuse of waste streams have enabled the recycling of coal ash, cement kiln dust, mussel shells, and high-grade biosolids.

This paper discusses a decade of geochemical research at Solid Energy New Zealand Ltd and how this has contributed to improved environmental outcomes. Further research should be vigorously pursued as this is an area of opportunity to improve performance and reduce costs.

Understanding the biogeochemical contributors of oil sand tailings materials for successful reclamation

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The recovery of bitumen from Alberta Oil sands generates enormous volumes of oil sands process material (OSPM). After bitumen extraction, tailings are pumped into retention ponds, where the sand fraction settles, and most of the aqueous slurry (i.e. fines consisting of silts, clays and residual hydrocarbons) slowly densifies which is termed fluid fine tailings (FFT). Both the chemistry and the microbial community structure within oil sands tailings material is complex and not well understood. There is a clear need for detailed systematic studies bridging the governing physical (mineralogy) and chemical (redox chemistry cycling of Fe and S) components with the microbial ecology for accurate long term predictive models on how these settling basins will function long term. In this research we apply a combination of field investigations in parallel with laboratory microcosms to predict the biogeochemical development. Novel micro-electrodes and molecular tools (i.e. T-RFLP with qPCR; Terminal Restriction Fragment Length Polymorphism with quantitative polymerase chain reaction) have been used to assess the chemical and biological evolution of several oil sands tailing ponds over time. These results will be used to optimise treatment based on biogeochemical responses to waste type and will contribute to the development of future prediction models being developed for large end pit lake systems. Details of this research project will be discussed.

Bacteria mineral-metalloid interactions: Investigating redox transformations of selenium

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A number of metal species, including selenium (Se), can be incorporated into the jarosite structure. Selenium can be found as a trace nutrient in some environmental systems and can be toxic in relatively low doses to humans, microbes, and other fauna. Selenium geochemical behavior is similar to arsenic, and can exist in aqueous systems since it will readily form as the oxyanions, selenate and selenite (SeO_4^{2-} & SeO_3^{2-}). As in the case of As, Se behavior in mining environments is still not well understood. Since it will form as an oxyanion it has a tendency to be incorporated into a range of low temperature geochemical mineralisation reactions in these exotic mining environments. For example the sulphate group can be completely substituted for selenate in jarosite minerals ($NaFe_3(SO_4)X(SeO_4)_{2-X}(OH)_6$). Under certain environmental conditions (e.g. pH, ionic strength, anaerobic environment), bacteria will use these metals as potential electron acceptors increasing the mobilisation and reduction of the jarosite mineral compounds. Several species of bacteria have been observed to reduce Se oxyanions to nanoparticulate elemental Se, which is insoluble under most environmental conditions. This pathway potentially poses a vector for mobilisation and transport at Se-contaminated sites. The mechanisms pertaining to this research along with toxicity thresholds to the model organism used will be discussed in the presentation.

Modelling the distribution and abundance of calcium carbonate in the Australian regolith using environmental covariates

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Regolith carbonate or secondary carbonate is a key component of the regolith, particularly in many Mediterranean, arid and semi-arid regions of Australia. National maps of regolith carbonate distribution have been compiled from regional soil, regolith and geological mapping with varying degrees of confidence and consistency. Here we apply a decision tree approach based on a piecewise linear regression model to estimate and map the near-surface regolith carbonate concentration at the continental scale. The model is based on relationships established from the 1311 field sites of the National Geochemical Survey of Australia (NGSA) and 49 national environmental covariate datasets. Regolith carbonate concentration (weight %) was averaged from the <2 mm grain size-fractions of samples taken from two depth ranges (0-10 cm and ~60-80 cm) at each NGSA site.

The final model is based on the average of 20 runs generated by randomly selecting 90% training and 10% validation splits of the input data. Results present an average coefficient of determination (R2) of 0.56 on the validation dataset. The covariates used in the prediction are consistent with our understanding of the controls on the sources (inputs), preservation and distribution of regolith carbonate within the Australian landscape. The model produces a continuous, quantitative prediction of regolith carbonate abundance in surficial regolith at a resolution of 90 m with associated estimates of model uncertainty. The model-derived map is broadly consistent with our current knowledge of the distribution of carbonate-rich soil and regolith in Australia. This methodology allows the rapid generation of an internally consistent and continuous layer of geoinformation that may be applicable to other carbonate-rich landscapes globally. The methodology used in this study has the potential to be used in predicting other geochemical constituents of the regolith.

The Taupo Volcanic Zone: An introduction

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The Taupo Volcanic Zone (TVZ) represents the southern, continental termination of the Tonga-Kermadec arc system, and is divisible into three segments. The northern and southern segments are conventional, with andesite-dacite composite cones and limited geothermal activity. The central ~120 km segment is an extraordinary area of silicic volcanism and associated magmatism that matches Yellowstone in its productivity. The average magma eruption rate for the last ~61 kyr exceeds 12 km^3/kyr, and the modern thermal flux through geothermal systems is around 4.5 GW. Notable features of the central TVZ include the following. (1) Rapid (for an arc setting) rates of rifting (7-14 mm/yr); (2) a thin (15-16 km) quartzo-feldspathic upper crust overlying a more mafic lower crust; (3) a dominance (~90 %) of rhyolite in the eruption products; (4) a rapid frequency of rhyolite eruptions (~1 per 900 yr over the past 61 kyr); and (5) a wide range of eruption volumes, from <0.01 to >2000 km^3, including four of the ten known global Quaternary supereruptions. Magma bodies that feed the volcanic and geothermal systems are scattered spatially throughout the central TVZ, but the two highly active volcanic systems (Taupo, Okataina) are at its northern and southern extremities. Between Taupo and Okataina is a ~75 km by ~40 km area where volcanism has been sparse in the last 50-100 kyr, but is highly active magmatically and tectonically. The western side of this area has relatively low heat flow, but abundant surface faulting (Taupo Fault Belt), while the eastern side (Taupo-Reporoa Basin) has an exceptionally high heat flux (~2 GW) and little surface faulting. There are inter-relationships between magmatism, volcanism and tectonism on a range of temporal and spatial scales, including syn-eruptive tectonic modulation of large eruptions. Despite decades of research, many still unanswered questions remain about how the central TVZ operates.

2013 Review of the Waikato Regional Geothermal Geochemistry Monitoring Programme (REGEMP II)

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Waikato Regional Council recently commissioned the third four-yearly review of its Regional Geothermal Geochemistry Monitoring Programme (REGEMP), which was re-established in 2006. In this third review, emphasis was placed on three dimensional spatial analysis and an assessment of temporal trends at sites for which relatively complete long-term records are available. Despite a difference in approach, the results of spatial analysis of REGEMP data in three dimensions were consistent with those reported in previous reports, principally because the drivers of spatial trends were the depth of source waters, magmatic intrusion and saline influences. The relative influence of these drivers was evident in the results of hierarchal analyses, in which Kawhia, which is strongly influenced by saltwater intrusion was shown to be distinct from other features. Spatial analyses have revealed difference not only between broad areas (e.g., sites north of the Taupo Volcanic Zone (TVZ) compared to sites north of the TVZ), but on a smaller scale, such as the influence of Hauraki Rift Zone. Although data records for some sites stretch back to the turn of the 20th century, interpretation of temporal trends was restricted by infrequent and incomplete data records for many sites. Where long term records are available, the trends for most parameters at most sites indicate that geochemical states of Waikato surface features have been relatively stable over at least the last 60 years. The overall outcome of the review is that the REGEMP is generally comprehensive. As the programme develops greater insight into regional geothermal geochemistry trends is anticipated.

Isotopic monitoring of carbon sequestration within hydromagnesite and hydrotalcite-group minerals in mine tailings from the Mount Keith nickel mine, Western Australia

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At the Mount Keith Nickel Mine, Western Australia, the hydrated Mg-carbonate mineral, hydromagnesite [$Mg_5(CO_3)_4(OH)_2\ 4H_2O$], precipitates within mine tailings as a result of mineral processing. We have used quantitative mineralogical results, the three-isotope system of $\delta^{13}C$, $\delta^{18}O$ and $F^{14}C$, and reactive transport modeling to quantify fixation of atmospheric CO_2 within hydromagnesite and to study the mechanism by which it forms. Quantitative mineralogical results and simulations indicate that hydromagnesite production is governed by the abundance of brucite [$Mg(OH)_2$] within tailings and the rate of brucite dissolution. Stable isotopic results indicate that dissolution of atmospheric CO_2 into mine tailings water is kinetically limited, which suggests that the passive rate of carbon mineralisation in hydromagnesite could be accelerated. Based on our assessment, approximately 39,800 t/yr of atmospheric CO_2 are being trapped and stored in the tailings at Mount Keith, which represents an offsetting of approximately 11% of the mine's annual greenhouse gas emissions.

Atmospheric CO_2 may also be sequestered within hydrotalcite-group minerals, such as iowaite [$Mg_6Fe^{3+}{}_2Cl_2(OH)_{16}\ 4H_2O$], which are common at Mount Keith. Anion-exchange experiments on iowaite indicate that complete exchange of interlayer Cl^- for dissolved inorganic carbon (DIC) is achieved within 46 hours in stirred-tank reactors open to CO_2 exchange with the atmosphere. All experiments produced pyroaurite [$Mg_6Fe^{3+}{}_2CO_3(OH)_{16}\ 4H_2O$] via uptake of atmosphere-derived DIC. Although $F^{14}C$ data clearly indicate a modern atmospheric source for carbon in this mineral, experimentally produced pyroaurite shows a marked depletion in ^{13}C. Stable isotopic fractionation factors have not previously been measured for hydrotalcite-group minerals; however, this may reflect a preference for light carbon and/or a kinetic control on carbon capture during this anion exchange process. Consequently, CO_2 uptake into hydrotalcite-group minerals may best be recognised using radiocarbon data and could potentially be accelerated to further offset greenhouse gas emissions at Mount Keith.

Quantitative mineralogy of sulfide mineral breakdown and glacial transport at the Voisey's Bay Ni-Cu-Co deposits, Labrador, Canada

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The Voisey's Bay nickel-copper-cobalt sulfide deposits are hosted by feeder dykes of the ca. Ma Voisey's Bay Troctolite. The bowl-shaped (~300 m in diameter) Ovoid deposit was buried beneath 20 m of till, and geological models suggest that it was much larger, but the upper portion was essentially sliced off and removed by the last glacial advance. Glacial transport was to the east, but previous attempts to identify any remnants of this sulphide mineralisation in tills down-ice have failed as the sulphide minerals seem to have essentially been destroyed. When the surface of the Ovoid was exposed in preparation for mining, however, it was found to be remarkably intact, with no alteration/oxidation whatsoever, compared to nearby gossans associated with the Disco Hill deposit. In fact, glacial grooves/straie on the massive sulphide surface of the Ovoid ore body were preserved, and thus the Ovoid was sealed off from not only the atmosphere, but also from circulating, oxidised groundwaters. Using SEM-MLA (Mineral Liberation Analyser) analytical techniques we have examined: (i) the 'sealing' of Ovoid; (ii) the breakdown of sulphide phases during weathering in a complete section from massive sulphide ore through till cover in the Mini-Ovoid Deposit; and (iii) the distribution of sulphide (and other) indicator minerals in till samples from split-spoon drill-holes in the immediate vicinity of the Ovoid Pit , a sonic hole drilled to bedrock from north of the Ovoid, and, drill-core samples through the Disco Hill gossan. Results indicate that: 1) the differential breakdown of sulphide phases in gossan through till samples can be mapped; 2) there is a quantifiable presence of different sulphide phases in till cover down-ice from the Ovoid; and 3) the glacial clay seal on the Ovoid surface is cemented by calcite.

SEM-MLA (Scanning Electron Microprobe – Mineral Liberation Analyser) analysis of indicator minerals in till surveys from Labrador, Canada

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Standard geochemical exploration techniques in northern Canada are based on the examination of indicator minerals in Heavy Mineral Concentrates (HMCs) from tills collected in regional surveys. The rationale being that unique robust indicator minerals associated with different styles of mineralisation can survive glacial transport, and can be concentrated in a till HMC due to their relatively high density and abundance. Hence, if the correct indicator minerals are detected in a till HMC, and knowing the glacial directions, mineral exploration can be directed to trace back to a hidden source. The standard analytical procedure for indicator minerals involves the field collection of 25-40 kg samples, sieving the samples, and then concentration of a HMC from 0.5-2 mm size fractions through gravity settling and then heavy liquids. The resultant HMC would then be examined under a binocular microscope by an analyst who would manually count and then pick the grains of interest in the HMC; in general, the survey would be designed to only look for specific indicator minerals. We have developed MLA-SEM techniques that evaluate and identify robust indicator minerals in an automated, systematic fashion such that quantitative mapping of the mineral phases from a till HMC separate can be accomplished in a sample; essentially providing a digital point count of all mineral phases, and in particular indicator minerals. The SEM-MLA detects the presence of a large range of indicator minerals in a single sample and quantifies all mineral phases present within a given grain mount. The SEM-MLA will routinely analyse and identify 7,000 to 20,000 particles in the 125-180 µm grain size fraction from an individual grain mount. Also a range of minerals, including sulfides, uraninites and REE-bearing phases, that are generally destroyed in the glacial transport environment have been found to survive as inclusions encased within more robust phases.

Comparison of catchment/floodplain sediment geochemical datasets obtained by global-scale projects in Australia, China and Europe

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Integrated data are critical to the generation of a global geochemical baseline map. In this paper, catchment/floodplain sediment geochemical datasets from Australia (NGSA), China (EGMON) and Europe (FOREGS) were compared in terms of sampling media, elements determined, analytical methods, detection limits and percentage of reportable values, and certified reference materials. Twenty eight elements (As, Ba, Ce, Co, Cr, Cu, La, Nb, Ni, Pb, Rb, Sr, Th, V, W, Y, Zn, Zr, Al_2O_3, CaO, K_2O, MgO, MnO, Na_2O, P_2O_5, SiO_2, TFe_2O_3, TiO_2) are comparable from the 35 elements analysed by all the three projects according to the criteria proposed in this paper for selecting elements with global comparability.

The medians of 28 elements in three datasets have the relationship of NGSA>FOREGS>EGMON, except Zr, SiO_2 and TiO_2 (NGSA<FOREGS<EGMON). The median ratios of EGMON to FOREGS for 28 elements range from 0.98 to 1.94, whereas the median ratios of NGSA to FOREGS or EGMON for soluble elements such as CaO, Na_2O, MgO, K_2O, Zn and As are more than 2. These soluble elements are easily migrated with water and depleted in the floodplain sediments collected by China and Europe in relatively wet regions. However, the soluble elements in the catchment sediments collected in Australia are not significantly leached in relatively dry terrains.

In order to get globally comparable datasets for establishing global geochemical baselines, unified sample media should be collected, detection limits must be lower than the crust abundance values, and international or exchanged standard materials are greatly recommended to be analysed in the future new geochemical mapping projects.

Soil selenium distribution and its influencing factors in main farming areas of China

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Selenium (Se) is an essential nutrient of fundamental importance to both human and animal health, but has a low threshold in terms of toxic concentration. Based on data from the National Multi-Purposes Regional Geochemical Survey project, this paper discusses the distribution of Se and its controlling factors in soil in the main farming areas of China.

The results show that that the mean value of total Se concentration in surface soil was 0.22 mg/kg. The surface soil in Central-south China has the highest mean value of Se content in the studied areas, reaching 0.31 mg/kg. North China has the lowest, about 0.18 mg/kg. According to the recommended standard by Tan's research, 12% of the farmland is classified as Se-deficient, 21% is Se-moderate, 52% is Se-sufficient, 9% is Se-rich and 0.04% is Se-excess.

The distribution of Se in surface soil is influenced by many factors, e.g. parent rocks, soil types, land use types, atmospheric precipitation and the contents of iron and aluminum oxides etc. The type of parent rocks is one of the main reasons for fractionation of Se. At the same time, we found that the distribution of Se content in Se-rich areas was related to the content of iron and aluminum oxides in soil. It was also found that the bioavailability of Se is controlled by several factors including soil pH, Eh, texture, soil organic matter, Fe and Al oxides etc. Higher content of soil organic matter would reduce the bioavailability of Se in the Kaschin-beck and Keshan disease area.

Landscape zoning in accordance with conditions of geochemical studies using GIS and remote sensing data (case study of the southern Far East, Russia)

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In the south of the Russian Far East, exploration aimed at identifying not only ore deposits (gold, base metals), but also oil and gas has been actively carried out in recent decades. A peculiar feature of geological and geochemical activities in the area is complicated geological structure (geological formations of different ages, thick Quaternary sediments (up to 200 m), neotectonic processes, etc.) and specific climatic conditions (widespread bogs, thick forest coverage, permafrost). At present, geochemical exploration is widely used to evaluate the prospectivity of different areas for various types of mineralisation.

Previous studies showed the possibility of using morphometric analysis of relief for the zoning based on the use of GIS technologies with the digital model of the topography (DMT). Enhanced functionality of this approach became possible by using remotely sensed data. Radar and hyperspectral survey data provide information on the Earth's surface with high accuracy (up to several tens of meters), describing, for example, areas of hot springs and volcanic activity, anthropogenic impact areas, topographical and geological structures, landforms etc. Based on a comprehensive analysis of spatial data using GIS, landscape zones were characterised. Their morphometric and spectral parameters were given; the features and distribution of some types of Quaternary sediments and soil cover were refined that allowed assessment at a new and qualitative level, of the most suitable geochemical methods at regional stages of studying mineral resources and during detailed exploration. In conclusion, the proposed procedure of landscape zoning in accordance with conditions of geochemical studies based on the analysis of spatial data using GIS can be easily integrated into other GIS systems, allowing the extension of original databases and possibilities of comprehensive analysis of geological information.

LA-ICP-MS analysis of major and trace element compositional variations in simple solid solutions through cross-correlation with an EPMA-characterised working standard

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Determining correlated major and trace element zoning profiles is an important goal in modern microanalysis, and is critical to some geospeedometric applications. It will be shown that a precise determination of relative variations in major element compositions of simple solid solutions is possible by LA-ICPMS, and that low accuracy can be corrected for through cross-correlation with EPMA-characterised working standards. Further, it will be shown that the relative uncertainties on binary or quasi-binary solid solution endmember proportions are always lower than the relative uncertainties on the ratio of the principle substituting elements by at least a factor of 2. In calcic plagioclase, for example, the relative uncertainty on XAn is a factor of (1-XAn) smaller than the relative uncertainty on Ca/Na. Using a concentrically zoned bytownite crystal as an example, we compare reproducibilities of FE-EPMA and W-EPMA analyses with 2 µm beam diameter and LA-ICP-MS with 16 µm beam diameter. While the accuracy of LA-ICP-MS analyses is low (analytical bias), the precision of LA-ICP-MS analyses is slightly higher than that of FE-EPMA data and comparable to that of the W-EPMA data. EPMA-corrected LA-ICP-MS data can thus be used to characterise major oxide compositional variations and potential covariations with trace elements within individual crystals.

The geochemical exploration model of the Jiama polymetallic copper deposit, Tibet

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The exploration of the Jiama polymetallic copper deposit achieved a major breakthrough in a short timeframe through the application of scientific research to prospecting in the Gangdese metallogenic belt. The understanding of the deposit genesis evolved from its initial interpretation as a Sedex type deposit to that of a porphyry-skarn type deposit, and this has been the key to successful exploration of Jiama.

Exploration by the China National Gold Group in the vicinity of the Jiama mine and 81 ranch prospect, within the area of permits held by Tibet Huatailong Mining Development Co. Ltd, consisted of systematic field sampling, geological mapping, and drilling with geochemical analyses of samples. Our study examined the geochemistry of the Jiama copper polymetallic deposit, to explain the formation mechanism of the geochemical

anomalies, and combining this with information on the deposit genesis, to establish a geochemical exploration model and apply it to the exploration in the prospect area. Results obtained include the following:

(1) Identification of single-element geochemical anomalies for Cu, Mo, Pb, Zn, W, Sn, Ag, As, Sb, Bi, S, Li, Ni, Co, Sr, V, Ba, Be, Cr, Ga, Nb ,Y, Cd, Ce, Cs, Ge, In, La, Ta, Te, Th, Tl, U.

(2) Cluster analysis identification of five element associations at Jiama (As-Sb, Zn, Pb-W-Bi-Te-Ag-Se, Cu-S, and Mo) and four element associations in the 81 ranch prospect (Zn-Cd-In, S-Se, Mo, and Cu-Bi-Ag-Te). R-type factor analysis shows that peripheral element associations related to the mineralisation are factor F4 (S, Cu, Mo) at Jiama, and factors F7 (Li, Zn, S, Cu) and F8 (Mo, Sb, As) in the 81 ranch prospect.

(3) Development of a geochemical exploration model and delineation of three potential prospecting areas (A-type Mogulang, B-type Zhisuolang and C-type Xiangbeishan South) through analysis of the geochemical data, including profile and surface rock element distributions.

REE geochemical provinces in the world's largest REE deposit of Bayan Obo, China

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‘Green energy futures’ are driving unprecedented demand for rare earth elements (REE), and rekindling significant REE exploration activity worldwide. Only the single REE element La was analysed by the Regional Geochemistry - National Reconnaissance Programme (RGNR) in China, although the project has covered more than 7 million sq. kilometers in the past 30 years in China. The project provided limited information for finding REE deposits, and no regional geochemical data are available for the world's largest REE deposit of Bayan Obo, in Inner Mongolia, China. The China-Mongolia Geochemical Mapping project (CMGM) was carried out across the boundary regions at a density of one sample per 100 km^2 from 2006 to 2012 and 16 REE elements were analysed. Three significant geochemical provinces containing LREE enrichment were delineated. One of these coincides with and surrounds Bayan Obo and the other two provinces were delineated to the west of Bayan Obo. The rare earth distribution patterns of the anomalies are generally similar to those at Bayan Obo. However, there are significant differences in Eu anomalies between the new provinces and Bayan Obo. Samples from the new provinces show significant negative Eu anomalies while those from the Bayan Obo province shows only slightly negative Eu anomalies. The REE patterns at Bayan Obo imply that the anomalous source is from ore-bearing dolomitic rocks. In contrast, anomaly patterns in the two new provinces suggest that the REE are related to alkaline granitoids, which may have ore-bearing potential for a new class of REE deposits in this area.