

The role of hydrogeochemistry in modern mineral exploration

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INTRODUCTION

Hydrogeochemistry has evolved substantially since its emergence about 80 years ago (Kidder et al. 2024). Over the same period, mineral exploration has been transformed by changing prospective terrains, economic pressures, new technologies, and demand for new critical minerals. Against a backdrop of rapid advances in data analytics and a widening disparity between exploration expenditure and discovery rates (Schodde 2025), what role can hydrogeochemistry play in modern mineral exploration and, in what scenarios?

Hydrogeochemistry is one of the few geochemical methods applicable from local (deposit) through to continental scale. Case studies worldwide demonstrate that anomalous dispersion halos (Fig. 1) can be detected in water for a wide range of metal(loid) deposits. More recently, interest has focused on its application for exploration beneath partial or complete (both transported or younger) cover sequences. As geochemists, our understanding of deposit-specific pathfinders is based on over 150 exploration hydrogeochemistry case studies (Kidder et al. 2024), predominantly focused on (i) gold deposits (Carlin and Orogenic: Grimes et al. 1995; Bowell 2001; Gray 2001; Reid et al. 2018, 2023b); (ii) porphyry deposits (Leybourne and Cameron 2008; Eppinger et al. 2012; Kelley and Graham 2021; Kidder et al. 2022a; Fig. 2); (iii) iron oxide copper gold deposits (IOCG: Kidder et al., 2022b; Mahan et al. 2023); (iv) volcanogenic massive sulphide deposits (VMS), carbonate-hosted deposits, non-sulphide base metal deposits, and sedimentary exhalative (SEDEX) deposits (Miller 1979; Kelley and Taylor 1997; Plumlee et al. 1997; Leybourne et al. 1998, 2002, 2003, 2009, 2022; Bowell 2014; Gault et al. 2015; Gray et al. 2016; Boni et al. 2025); and (v) uranium deposits (Deutscher et al. 1980; Earle and Drever 1983; Giblin and Snelling 1983; Noble et al. 2011). In addition to contaminant tracing, interpretations of bedrock geology using major element hydrogeochemistry and pH are also possible. In the Kelly Creek basin, the mapping of water chemical facies demonstrates a strong association of water with a Ca-Na-HCO₃-SO₄ signature associated with the Getchell Fault Zone (Bowell 2001), constraining water types to different bedrock lithologies.

Beyond the local scale, hydrogeochemistry has also been used in regional, pre-competitive, publicly funded surveys for environmental baseline and exploration reconnaissance purposes. The Australian Continental Hydrogeochemical Dataset initiative (Reid et al. 2023a) and European hydrogeochemical mapping program (Hájek et al. 2021) show the mapping potential of groundwater geochemistry. Lake and stream water geochemistry products include the National Uranium Resource Evaluation (NURE; Price 1976) in the United States, and the National Geochemical Reconnaissance datasets of the Geological Survey of Canada (McClenaghan et al. 2022). Further still, the advent of big data analytics is enabling global-scale mapping of water parameters (Batalla et al. 2026).

Ongoing interest in hydrogeochemistry has generally been linked to innovation in detection limits, analytical techniques, and the application of isotopes (Kyser et al. 2020). However, innovations to date haven't been sufficient to see broad application by mineral explorers. This lack of application by industry is likely due to perceived challenges of the sampling and interpretation techniques. Here, we present innovations from the preceding decade, highlighting innovative methods to improve sample collection, processing, and risk reduction. This article initiates an EXPLORE series on

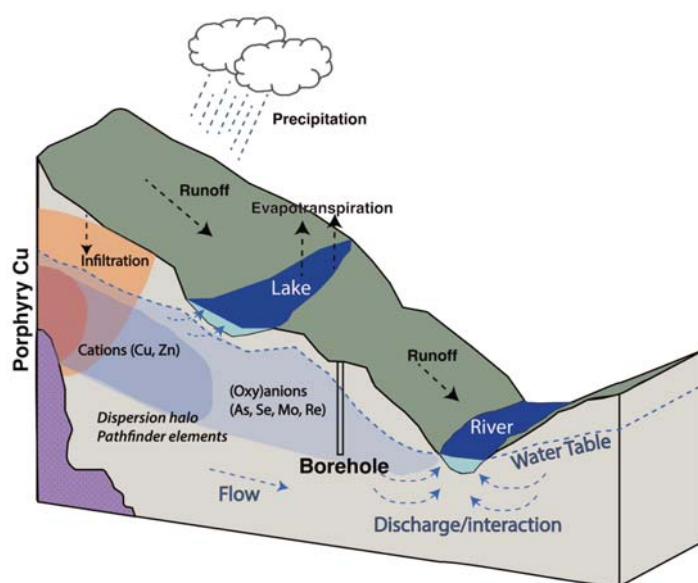


Fig. 1. Conceptual model for hydrogeochemical dispersion from a porphyry Cu-Mo deposit into lake, river and groundwaters, where it can be sampled as part of regional or local surveys. Metal dispersion in water can also be detected in waters collected from boreholes.

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water analysis approaches and techniques in federal and provincial laboratories.

CONVENTIONAL METHODS

Conventional water sampling methods typically use pumps, bailers, straddle-packer systems, or, specifically for surface waters, grab samples using a syringe (Fig. 3a) or a depth-controlled sampler (e.g. Kemmerer sampler: Fig. 3b). Regardless of the collection method, on-site filtration of samples (commonly at 0.45 μm) is required to minimize trace-element loss through adsorption onto colloids, also prevented by the acidification of cation samples with ultrapure nitric acid. Filtration can be done using vacuum flasks, Luer-Lock syringe filters (Fig. 2a), or in-line filter capsules attached to pump tubing (Gray et al. 2011). Pumping equipment for sampling continues to decrease in size, increasing the feasibility for use in exploration field programs. Handheld, peristaltic pump heads driven by rechargeable hand drills (Woessner 2007) are the lowest cost and smallest option for near-surface sampling of rivers and lakes, or shallow aquifers.

Separate aliquots are typically collected for cation analysis (filtered and acidified) and anion analysis (filtered and unacidified). Additional aliquots may be collected for stable isotopes, elemental speciation (e.g. Hg or Au), or ultra-trace pathfinders such as precious metals and PGEs. Detailed protocols for these various analytical workflows are provided in Leybourne and Cameron (2007), Sundaram et al. (2009), Gray et al. (2012) and Kidder et al. (2025).

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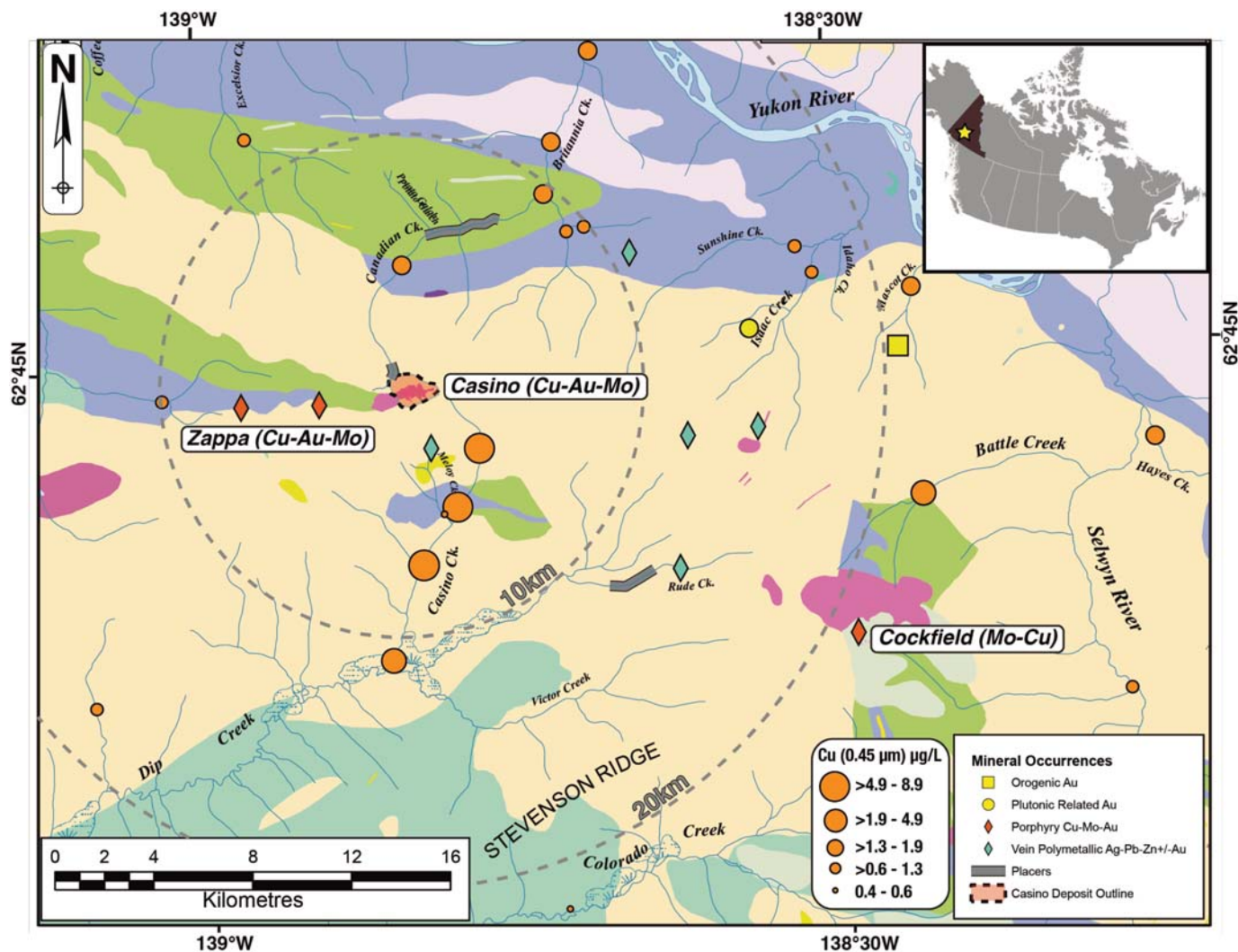


Fig. 2. Cu ($\mu\text{g/L}$) values of stream waters draining the Casino Cu-Au-Mo porphyry deposit, Yukon, Canada (modified from Kidder et al. 2022a).

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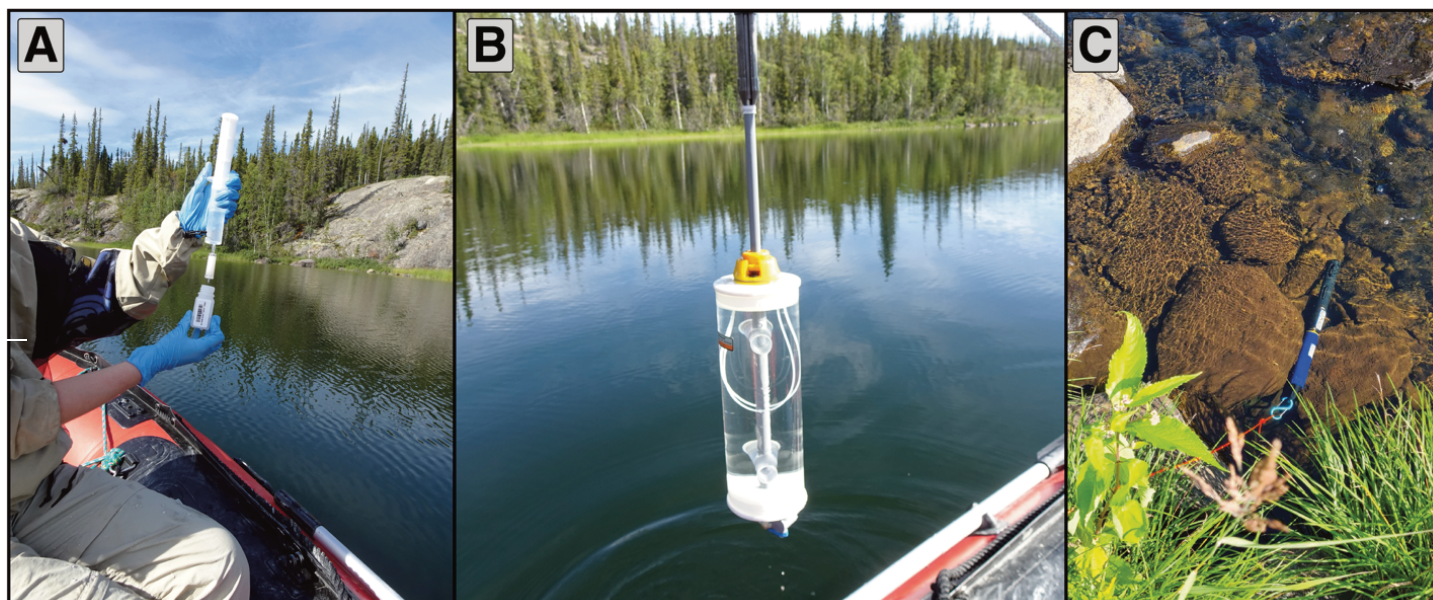


Fig. 3. (a) Syringe filtration into a 60 mL water bottle, (b) Kemmerer sampler used to collect water from the sediment-water interface at Rainy Lake, Northwest Territories, (c) multi-parameter probe deployed in a shallow stream to collect data.

A vital component of hydrogeochemical interpretation is the collection of physiochemical data (Barcelona et al. 1989; Sebol et al. 2007). These field parameters are best measured using a multiparameter probe (Fig. 3c) and commonly include water temperature, pH, conductivity, dissolved oxygen (DO), oxidation-reduction potential (ORP) and turbidity. Additional observations, including depth to water table for groundwater, permeability and porosity of host rocks, flow velocity and channel dimensions for surface water, odour, water colour, and presence of precipitates, should also be recorded. Field notes and site photographs are invaluable for geochemical data interpretation. For example, the presence of rusty or galvanized bore infrastructure can elevate Fe, Mn and Zn concentrations, especially in bailed water samples. In some regions, mobile applications support standardized metadata collection, such as the Fieldmark mobile application used in Australia (Crook et al. 2022).

A GROUNDWATER SAMPLING REVOLUTION

Groundwater geochemistry can generate pathfinder anomaly plumes typically of multiple-kilometre size (Leybourne and Cameron 2007). Redox conditions in deeper aquifers commonly promote the mobility of selected metal(loid)s, producing anomalies that strongly contrast with regional background values, often involving contrasting solubility and mobility between cations and (oxy)anions (Leybourne and Cameron 2007, 2008). One of the best examples of anomaly mapping using groundwaters is CSIRO's sampling of windmill boreholes on the Yilgarn Craton of Australia (Gray 2001; Gray et al. 2016), which effectively identified many known gold occurrences and producing deposits (Reid et al. 2023b). Historically, the costs of drilling to access water have been a barrier to collecting water samples in some regions. However, in many parts of the world, pre-existing human-made sources of groundwater are adequate for sampling. Established monitoring boreholes or public and private boreholes or wells (e.g. India Mark II hand-power water pumps) can be sampled at a sufficient density.

Fit-for-purpose drilling for hydrogeochemistry is constrained to methods that avoid the addition of drilling muds and chemical additives, which limits application largely to

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unconsolidated or weathered materials. Examples include reverse-circulation drilling (Kidder and Jones 2017), rotary methods (Barcelona et al. 1985), and, more recently, sonic drilling (Mohallel et al. 2025). In many settings, the logistics of mobilization, casing, and borehole development substantially increase the time and cost required for each borehole, reducing the efficacy of drilling for water in early stage, greenfields exploration.

The innovation of direct-push drilling (McCall et al. 2005) has the potential to revolutionize hydrogeochemical exploration and make it a mainstream geochemical tool. By advancing hollow rods through unconsolidated or weathered materials using rapid percussion, direct-push systems reduce the time required to complete boreholes. Water samples are commonly recovered during drilling with a peristaltic pump, removing the need for casing and well development (Maliva 2016). For greater depths or bedrock penetration, air-core systems may be required (Hofmann et al. 2010). Compared to other drilling methods, direct-push equipment can be vehicle-mounted or mobilized by planes or helicopters to reach remote or hard-to-access areas (Weger 1994).

Beyond reducing cost and drilling time, another evolving theme in direct-push drilling methods is depth-profile sampling (multiple samples at different depths) within a single borehole, allowing the development of three-dimensional hydrogeochemical models. Richard et al. (2026) demonstrate both multi-aquifer characterization, including physicochemical variation and vertical anomaly zonation at a gold deposit in the Abitibi (Canada).

The efficiency gains to both time and costs offered by direct-push drilling make high-density target testing increasingly practical and provide spatially resolved datasets that were previously difficult to obtain (Buskard 2022). In targeted programs, drill patterns can be tailored to the targeted deposit geometry and local hydrology, allowing sampling density to match expected footprints (Buskard et al. 2020).

HIGH-DENSITY, LOW-COST SURFACE SAMPLING TECHNIQUES

Reconnaissance surveys based on lake and river water geochemistry can assist with initial regional target generation and subsequent focusing that reduces property (tenement) size. However, site access has long constrained regional programs by increasing cost, extending field time, and, in some cases, exposing personnel to unnecessary risk. In most parts of the world, the costs associated with deploying helicopters for sampling programs are unsustainable.

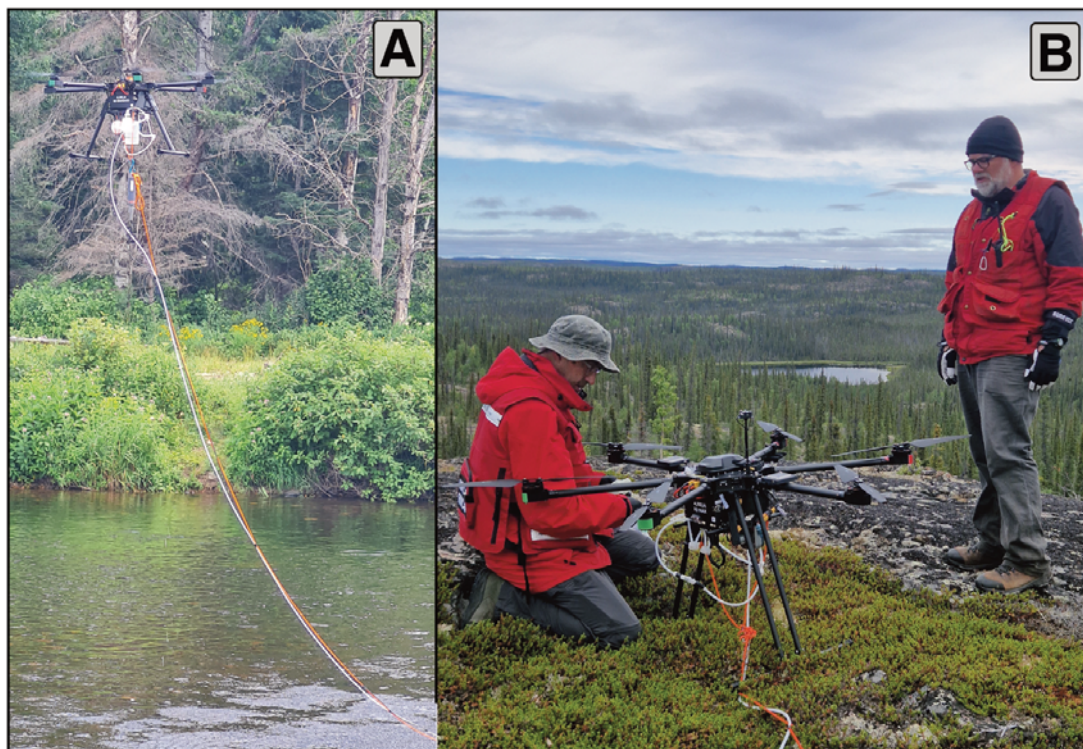
Rapid technological advances in drones, including hybrid (gasoline) fuel engines and low-latency satellite communications, have enabled long-range (10s km) and multiple-hour flight times. Deploying water sampling drones in place of helicopters has the potential benefit of massive cost reduction, making high-density sampling feasible at both local (deposit) and regional scales. The filtration required for exploration-grade data can be integrated using peristaltic pumps and in-line filter capsules (Kidder et al. 2024; Fig. 4a). Unfiltered samples have already been collected using grab-sampler payloads, mainly for lakes and mine pits (Terada et al. 2018; Castendyk et al. 2020) and, less commonly, rivers and streams (Detweiler et al. 2015; Smith 2015).

Recent changes in aviation regulations have also created frameworks for beyond-visual-line-of-sight (BVLOS) drone operations. Legislation for BVLOS is now in place in several major mineral jurisdictions, including Canada, the United States, parts of Europe and Australia, as well as parts of Africa. In most cases, these frameworks emphasize pilot certifi-

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Fig. 4. (a) A quadcopter drone hovers above a river surface as it pumps water upwards through the white LDPE tube. The drone is able to filter the water as it is collected at each sample site. **(b)** Regional-scale collection of surface water samples using an Aurelia X6 drone in the remote Arctic in Northwest Territories, Canada. The lake to be sampled is visible in the background.



cation and risk assessment. Long-range (10s of kms) BVLOS capability could reduce or eliminate the need for helicopter support for exploration and environmental water sampling, lowering operating costs for fuel and sampling consumables, and expanding the practicality of reconnaissance hydrogeochemistry (e.g. Fig. 4b).

IMPROVED TRACING AND SOURCE FINGERPRINTING USING STABLE ISOTOPES

One of the most rapidly developing areas of hydrogeochemistry is isotope geochemistry. Isotopic fractionation between solid and aqueous phases can generate predictable signatures in groundwater and surface water. These signatures provide a means to identify processes affecting water geochemistry and, for some metal(loid)s, to link anomalies to specific natural or anthropogenic sources.

The use of light stable isotopes (H, O, and C) for water characterization is well established and available commercially. These isotopes can constrain the sources of groundwater and surface water, hydrology and flow history, and water-rock interaction, as well as water evolution. Reactions between water and ore-related minerals are more effectively traced using isotopic systems of Pb, $\delta^{34}\text{S}$, or metal stable isotope systems, such as $\delta^{98}\text{Mo}$ (Fig. 5), $\delta^{65}\text{Cu}$, $\delta^{66}\text{Zn}$, and $\delta^{56}\text{Fe}$. More broadly, any element with two or more isotopes, or a radiogenic or cosmogenic isotope system, may be useful as tracers of fluid sources, metal provenance, and water-rock interaction processes (Kyser et al. 2020). Many deposit types and hydrological endmembers have now been characterized isotopically, providing a framework for routine application in hydrogeochemical exploration. The most advanced applications are currently for base-metal systems, including porphyry Cu (Leybourne and Cameron 2008; Kidder et al. 2021, 2024), VMS (Miller 1979; Kelley and Taylor 1997; Plumlee et al. 1997; Leybourne et al. 1998, 2002, 2003, 2009; Gray et al. 2014, 2016; Gault et al. 2015), and IOCG deposits (Kidder et al. 2022b; Mahan et al. 2023). Emerging

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work on $\delta^7\text{Li}$ and $\delta^{11}\text{B}$ also suggests potential use for Li exploration.

Porphyry systems can show distinct isotopic zonation (Fig. 5) associated with remobilization and enrichment of metals within the system. In addition, isotopic fractionation during sulphide oxidation and downstream adsorption of Cu can generate predictable gradients in $\delta^{65}\text{Cu}$ for both groundwater and stream waters (Mathur et al. 2013; Kidder et al. 2021, 2024). In alpine watersheds, the oxidation of Fe-bearing minerals has also been shown to result in distinctive fractionation in $\delta^{66}\text{Zn}$ and $\delta^{56}\text{Fe}$ (Borrok et al. 2008). The ability to distinguish metal sources in water is therefore a powerful tool for increasing confidence in targets generated using hydrogeochemical anomalies and reducing operational risks.

Historically, isotope geochemistry has not been widely used in mineral exploration because analyses were slow and expensive. Advances in MC-ICP-MS now allow measurement precision of approximately 0.001–0.002‰ (Yang 2009), while improvements in element separation and pre-concentration have reduced processing times and, ultimately, analytical cost (Kidder et al. 2020). Continued progress should support broader commercial adoption of these isotope systems for routine water samples and drive lower analytical costs. Furthermore, advances in quadrupole technologies (e.g. triple quadrupoles) are now advancing

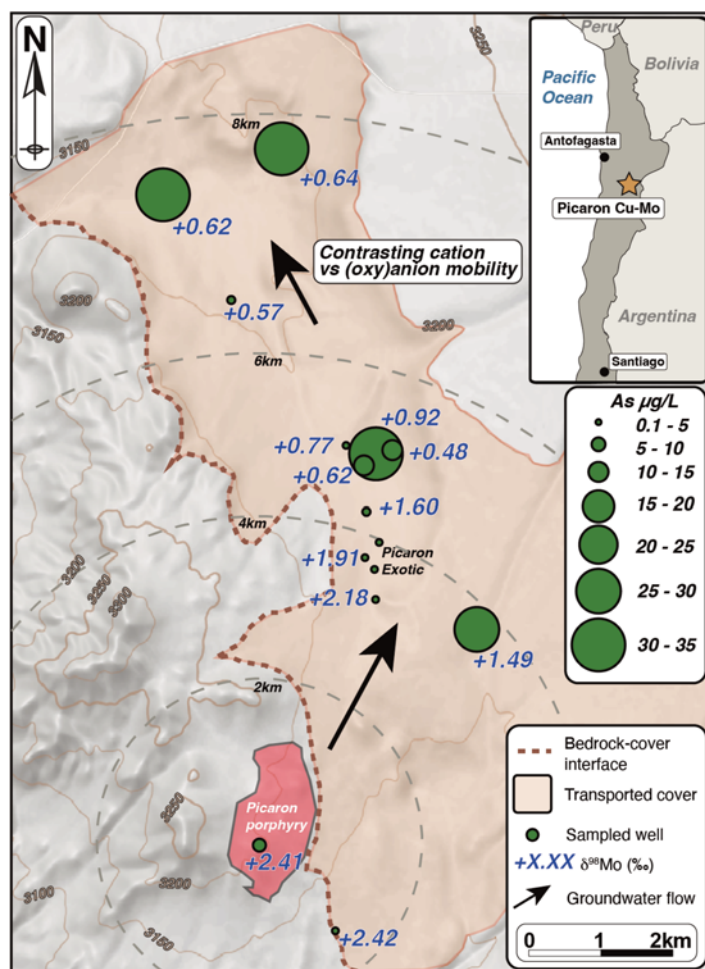


Fig. 5. As ($\mu\text{g/L}$) and $\delta^{98}\text{Mo}$ measurements of groundwaters draining the Picaron Cu-Mo porphyry deposit, Chile (modified from Kidder et al. 2021).

ing the possibility of low-cost, rapid, fit-for-purpose isotope analyses.

RAPID ANALYSIS AND REAL-TIME DECISION MAKING

An emerging advantage of hydrogeochemistry is the potential for time and cost savings through rapid field analysis using portable instruments (Fig. 6a) or mobile laboratories (Fig. 6b). This capability enables real-time decision making during field programs, which is uncommon for most other geochemical media.

Field-based water analysis can be performed using instruments that measure light intensity at specific wavelengths (e.g. photometers: Yehia and Heberlein 2015; Yehia et al. 2017, 2019) or across broader wavelength ranges such as UV and infrared (e.g. spectrophotometers: Zhang et al. 2013). These instruments are highly portable (Fig. 6a) but generally limited to a small number of analytes and much higher detection limits. Another option is X-ray fluorescence (XRF). Portable XRF has been applied to water analysis (Pearson et al. 2017; Kipnis et al. 2022) by concentrating approximately 10 mL of water onto a specifically designed filter membrane (Tiihonen et al. 2022). Reported detection limits for common pathfinders such as Mn, Ni, Cu, Zn, Pb, and U are generally $>10 \mu\text{g/L}$. Total XRF (TXRF)

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has also been used in field-laboratory settings (Alsecz et al. 2007; Grenier et al. 2013; Pelchat et al. 2013; Espinoza-Quiñones et al. 2015; Bonotto and Roveratti 2017), typically by drying 1 mL of sample on a carrier disk before analysis. Detection limits for TXRF are commonly $>5 \mu\text{g/L}$.

AUTOMATED WORKFLOWS

Hydrogeochemical interpretations are often centred around multivariate statistics along with thermodynamic modeling (e.g. PHREEQC, Parkhurst 1995; Parkhurst and Appelo 1999) of water chemistries to establish speciation or mineral saturation (Giblin 1994; Boyle 2003; Gilliss et al. 2004; Pirlo and Giblin 2004; Cameron and Leybourne 2005). The perception of workflow complexity is commonly considered a barrier to using hydrogeochemistry. The rapid evolution of machine learning in geochemistry is helping to automate these workflows. Hydrogeochemical studies have typically used tree-based (Nolan et al. 2015; Tesoriero et al. 2017; Lintern et al. 2018; Shen et al. 2020; Tut Haklidir et al. 2020; Stackelberg et al. 2021) and neural network (NN) (Rodriguez-Galiano et al. 2015) algorithms for both ground and surface water chemical interpretations. Most recently, machine learning models have been applied to groundwater datasets to predict aqueous concentrations of ore-related pathfinder elements (Xu et al. 2025), using random forests, gradient boosting, and neural network algorithms. As this data science revolution accelerates, rapid or automated workflows will likely become commonplace.



Fig. 6. (a) Field set up for rapid field analysis using a portable pXRF and spectrophotometer in the back of a vehicle, **(b)** water samples processed for ultrafiltration in a mobile laboratory set up in the back of a minivan.

CONCLUSIONS AND POTENTIAL IMPLICATIONS FOR MINERAL EXPLORATION

Exploration hydrogeochemistry continues to innovate within a rapidly evolving mineral exploration framework, and many of the perceived barriers to mainstream adoption in mineral exploration are being addressed.

Derisking targeting: Established and operationally ready isotopic systems are demonstrating an ability to identify hydrogeochemical processes and an ability to differentiate and identify metal(oid) sources. At the same time, detection limits for most pathfinder elements are commonly better than 0.005 ppb, providing confidence for exploration targeting based on hydrogeochemical anomalies.

Costs: Advances in sample analysis, particularly lower detection limits and in groundwater drilling methods, have greatly expanded the size of detectable plumes around mineral deposits while reducing the time and cost of collecting groundwater samples. Sampling equipment is also becoming smaller and more portable, making it easier to integrate into exploration workflows. As a result, both the costs and logistical demands of conducting exploration sampling, as

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well as the outcomes, are better aligned with large-scale exploration requirements. Dedicated, fit-for-purpose ground-water drilling programs are now viable, and surface water sampling has the potential to become automated soon. Water sampling can be a routine component of any stream sediment and lake sediment sampling program for very little added cost.

Interpretation: The rapid evolution of data analytics and machine learning is revolutionizing how we process and interpret our data. Studies are starting to show how machine learning can be applied to streamline hydrogeochemical interpretation and has the potential to simplify workflows.

Areas for improvement remain. A reemphasis on critical metal exploration in support of the greening and development of economies has highlighted a need to better understand the solubility and mobility of battery metals, including Co, Ni, Mn, Li, and REE, in water (Zhu et al. 2024). Future research should pivot to address this need. Similarly, element detection limits for field-based analysis are several orders of magnitude higher than comparable lab methods. Surface water sampling is potentially impacted by diurnal processes, which can influence survey design.

A lot of valuable data can be collected at very low cost. Explorers should be collecting physiochemical data measurements from water sources on exploration claims and tenements. Field-based, rapid analysis is another low-cost, dynamic fieldwork approach. Incorporating freely available pre-competitive (government) datasets into exploration workflows should also become standard practice.

Ultimately, at a time when mineral exploration predominantly focuses expenditure on brownfields prospects, hydrogeochemistry offers a tool to tackle challenges related to complex, high-risk (deep or covered), and early-stage prospects. Thus, hydrogeochemistry is a multi-scale area-reduction tool in reconnaissance exploration.

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