



Desk study of earlier mine environment studies by utilizing isotope and geochemical methods

Applicability of O, H, S, Sr, Pb, B, Li, Mg and U isotopes and geochemical applications in environment studies

ERA-MIN – SUSMIN Project Milestone 5.1

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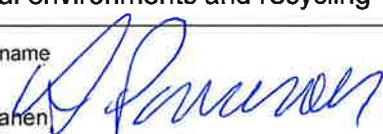
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Abstract Water is both a crucial resource for the mining industry, as well as the primary pathway for the spread of mining related contamination to the environment. Knowledge and characteriza- tion of hydrogeological parameters at a mine site are crucial for establishing baseline hydro- logical conditions and for predicting the release and transport of contamination related to mine drainage. This report provides a consolidation literature based information on how and why different geochemical and isotopic analytes may contribute to characterization of mine water-environment interactions. First the report describes the background information on the geochemical settings common to mine areas. Contaminant mobility is discussed in the context of how geochemical monitor- ing can be applied to understand mine water-environment interactions. Also a review of the principles of environmental isotope tracer applications as they relate to mine water-environ- ment interactions is presented. The report also concludes with a review of case studies demonstrating the application of the discussed principles and of isotope system applications.			
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Synopsis

Water is both a crucial resource for the mining industry, as well as the primary pathway for the spread of mining related contamination to the environment. Knowledge and characterization of hydrogeological parameters at a mine site are crucial for establishing baseline hydrological conditions and for predicting the release and transport of contamination related to mine drainage. This report provides a consolidation literature based information on how and why different geochemical and isotopic analytes may contribute to characterization of mine water-environment interactions.

The body of the review is divided into two sections:

Section 2 provides background information on the geochemical settings common to mine areas. Contaminant mobility is discussed in the context of how geochemical monitoring can be applied to understand mine water-environment interactions. General considerations for water monitoring and sample collection are provided, as well as example analytical procedures. This section concludes with a review of case studies demonstrating the application of the discussed principles.

Section 3 provides a review of the principles of environmental isotope tracer applications as they relate to mine water-environment interactions. This includes a summary of the theory behind the application and analytical methodology for 10 different isotope systems. It also includes, where available, case study examples of isotope system applications.

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1. INTRODUCTION

Because water is both, a crucial resource for the mining industry, as well as the primary pathway for the spread of mining related contamination to the environment, the main focus of this review is mine water-environment interactions. This report provides a literature based review of the key concepts behind geochemical and isotope methods which are either currently being employed, or which have potential for future incorporation in the study of mine water interactions with the environment.

Knowledge and characterization of hydrogeological parameters at a mine site are crucial for establishing baseline hydrological conditions and for predicting the release and transport of contamination related to mine drainage (Morton & Mekerck 1993, EPA 2003). Moreover, monitoring and modelling are essential for evaluating the effectiveness of water management and treatment procedures. Water management and treatment practices can subsequently be refined on the basis of site specific monitoring data.

Mine emissions and their interaction with surrounding water, soil and sediment are characterized through hydrogeochemical, hydrogeological and biological monitoring and modelling. Although the monitoring of mine emissions required by environmental permits commonly includes geochemical analyses of water, solute concentrations alone may not reveal the hydrological and chemical processes controlling the contaminant fluxes at a mine site. This is especially relevant at sites where factors such as multiple contaminant sources and complex hydrogeological conditions complicate interpretation of mine-environment interactions. Isotopes of water, as well as those of certain solutes typical to mine sites, facilitate additional characterization, both of water source and pathway, as well as physical, chemical, and biological processes that influence the mobility of contaminants in mine waters. Coupling major solute concentrations with isotopic analyses allows a more detailed evaluation of mine water-environment interactions than either approach on its own (Younger et al. 2002). Further, both isotope and geochemical analytical results can be applied in hydrogeochemical modelling for the prediction of chemical transformation and long-term impacts of mining at a study site and its surroundings.

Coupling geochemical characterization with isotopic tracer approaches provides a means to better understand a wide spectrum of mine water-environment interactions. However, to utilize multi-isotope and geochemical methods in addressing site specific questions requires basic knowledge spanning a wide range of geochemical and isotope theory. To help make integrated isotope and geochemical characterization more accessible, this report provides a consolidation of general geochemical and isotope theory as it relates to mine water- environment characterization studies.

2. Mine environments: geochemical setting

Mining has been conducted in Europe for over 10,000 years and mining practices have historically been associated with significant water and air pollution. Contaminants associated with mining emissions include metals (e.g. Al, Cr, Cu, Fe, Mn, Mo, Pb, Ni, Zn, V), metalloids (As, Sb), salts (e.g. sulphates), nutrients (nitrogen compounds) or organic compounds. To minimize the environmental impacts from these emissions requires a detailed understanding of both the source and propagation of contaminants at a specific site. Such understanding is applied in modern mining practices to guide the management of ongoing operations and the

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remediation of former mining sites (INAP 2009). Important concepts from the literature are summarized in the following section to provide background information on the geochemical controls of mining-derived contamination in the environment, with a focus on contamination in the hydrosphere. This section summarizes the primary sources of pollution associated with mining, reviews chemical and physical controls on mining derived contaminants in the hydrosphere, describes biogeochemical mechanisms of acid mine drainage, and includes select case studies that highlight the use of geochemical investigations at mine sites. Further information on the principles of mine water geochemistry and their applications can be found throughout the literature (e.g. Skousen & Ziemkiewicz 2005, Younger *et al.* 2002, ERMITE Consortium 2004, Kauppila *et al.* 2011, Kauppila *et al.* 2013).

2.1 Mine site pollutant sources

Most mining projects result in mining residues which are a significant source of pollutants. Mining residues include soil and rock removed to reach the ore deposit (waste rock/overburden material), the solid and liquid waste remaining after the separation of useful minerals from ore material (tailings and process water), and mine drainage resulting from water interacting with mineral surfaces exposed during mining.

Mining techniques are divided into two types of excavation: surface mining (open pits) and underground mining. Surface mining involves the removal of layer upon layer of overburden (natively vegetated areas or large quantities of waste rock) and underground mining consists of digging tunnels or galleries into the earth in order to obtain the ore. (Environmental Law Alliance Worldwide 2010, Kauppila *et al.* 2011). Waste rock is usually stored above ground in large waste piles or as backfill in open pits or inside underground mines (EPA 1997a). The size of the waste rocks ranges from small particles to boulders and the generated quantity can be enormous. In the mining industry, the quantity of overburden is much higher than the quantity of the mineral ore. As an example, the Environmental Law Alliance Worldwide (2010) states that if a proposed mining project involves the extraction of 100 million metric tons of mineral ore, it is almost certain the mining operations will generate more than one billion metric tons of waste rock. Waste rocks which are mineralogically and chemically inert may still act as a primary emissions source, leaching nitrogen compounds deposited through the use of explosives (Jermakka *et al.* 2015). Although waste rocks may contain significant levels of toxic substances, the content and the tendency to produce acid or neutral drainage are fairly low compared to tailings.

Tailings waste is produced through beneficiation, a process which involves the separation of important metals from uneconomic fraction and non-metallic material. The first step in beneficiation is crushing and milling the ore into small particles to facilitate the extraction of the desired resource. The next step may include physical and chemical separation using methods such as magnetic and electrostatic separation, flotation, solvent extraction, gravity concentration, amalgamation, precipitation and leaching. These processes can generate significant quantities of wastes, including the often contaminant laden semi-liquid tailings mixtures which are deposited in tailings ponds. The majority of mine tailings are disposed of in onsite impoundments (EPA 1997b). Chemical agents like cyanide, mercury or sulphuric acid, used by mining companies to separate valuable metals and minerals from the ore can represent a pollution source of primary concern. For example, mercury persists in the environment and can continue to leach into nearby water courses long after it is no longer being used in the industrial process (ARM 2004; SDWF 2009). The chemical tracers derived from the ore processing are described in more detail in section 2.2.2.

In addition to emissions, physical alteration of the land surface and subsurface can adversely impact the surrounding environment. Since mine sites are always part of a catchment area in

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the meteoric water circulation system, by changing the topography, all mines change the hydrological circumstances not only inside the mining area but also in the surrounding watershed (Salonen et al. 2014). In fact, the most common and widespread causes of water pollution by mining are impacts arising from the alteration of regional surface and groundwater flow paths, which in turn affects surface and groundwater quantities, runoff, soil moisture and evapotranspiration (Banks et al. 1997, Hedin 2003.). The changes in topographical and hydrological circumstances may also accelerate erosion, sedimentation, and subsidence. Erosion can be a major concern at hard rock mining sites because it may cause significant sediment loading to nearby water bodies, especially during severe storm periods. Further, sediments derived from mine sites may include natural and industrial contamination sources that pose a threat to aquatic organisms and human health. Besides erosion and sedimentation, mining subsidence (sinkholes and troughs) may occur as the result of underground mining. Subsidence can interrupt surface water and groundwater flow, impact farmland, and disrupt irrigation (EPA 1997a).

2.1.1 Mine water types

The ERMITE Consortium et al. (2004) definition for mine water is "all water emanating from active, abandoned or closed surface and underground mines", including draining from the dewatering adits, mine dewatering pumps, open pit mines and raw material handling facilities on the mine site. For water treatment and management purposes, mine waters are often classified according to their quality and potential for contamination, but characterizing helps also in assessing their environmental and toxicological effects. The mine waters can be classified as follows (modified from Banks et al. 1997, Younger et al. 2002):

Dewatering water: The precipitation and ground water seeping into open pits and underground mine. Needs to be pumped to surface to dewater the mine. Tends to contain residues of blasting agents (e.g. nitrogen compounds) and dissolved minerals and/or metals.

Drainage water: Surface or ground water which flows or has the potential to flow off the mine site that is diverted from other mine water fractions. Tends to have low mineralisation and low temperature.

Drill water: Water used in exploration drilling. Usually combined and collected with dewatering water.

Mill water: Water used to crush and grind ore, tend to contain dissolved minerals and/or metals. Usually combined and collected with process water.

Mine drainage and leachate: Seepage water which has trickled through solid mine wastes, waste rock sites and tailings dams. Tends to contain dissolved minerals, process chemicals, and metals. The geochemical characters of the flow path media define the quality of the mine drainage: acid producing/non-acid producing, neutral, alkaline, metallogenous and/or saline.

Mine effluent: Mining, mill, or process water which is treated before being discharged into surface water or circulated back to the process.

Mine water: Any surface or ground water present inside the mine site. Tend to have high mineralisation and warm temperature. Mineralisation usually increases with depth.

Process water: Water used in the mineral extraction, commonly contains process chemicals (e.g. SO_4 , Ca, K and C) as well as dissolved minerals and/or metals. Process water is treated before being discharged into surface water or circulated back to the process.

Service water: Water used for dust depression, cooling or workers needs.

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2.1.2 Mine drainage and AMD generation

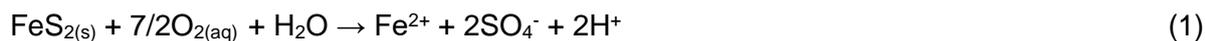
Mine drainage forms from water interactions with mineral surfaces exposed during mining. Subsequently, water sourced from mining impacted areas is commonly characterized by elevated concentrations of metals, nutrients, and altered pH values. Mine impacted drainage is classified by water quality as either acid mine drainage (AMD, often referred also as acid rock drainage ARD), neutral mine drainage (NMD) or saline drainage (SD). AMD is considered the largest environmental issue resulting from mining and forms when rocks that contain sulphide minerals, especially iron pyrite (FeS_2) are exposed to oxygen and water (INAP 2010). Although some sulphide-rich zones are surrounded by neutralizing minerals such as calcite and dolomites resulting in NMD and SD, metals and sulphate are still mobilized through oxidation (e.g. Ashton et al. 2001). Under certain conditions metals and sulphates may also be mobilized in the absence of oxidation processes to form NMD or SD (IIED 2002). While AMD has low pH and elevated metals concentrations, NMD is characterized by near neutral pH and elevated metals concentrations. Saline drainage also occurs at near neutral pH, has relatively low metal concentrations, and is characterized by high levels of dissolved sulphate, magnesium, and calcium ions in solution. The characteristics of the three types of mine drainage are summarized below (Table 1).

Table 1 Drainage characteristics (modified from INAP 2009).

Acid Rock Drainage	Neutral Mine Drainage	Saline Drainage
Low pH	Near neutral to alkaline pH	Neutral to alkaline pH
Moderate to elevated metals concentrations	Low to moderate metals concentration	Low metals concentrations, but may contain moderate iron
Elevated sulphate content	Low to moderate sulphate content	Moderate sulphate, magnesium and calcium content
Treatment measures include acid neutralization and removal of, metals and sulphate	Treatment measures include removal of metals and sometimes sulphate	Treatment measures include removal of sulphate and sometimes metal

Because AMD holds a prominent role as the greatest environmental challenge to the mining industry, and greatly influences metals mobility at many mine sites, additional consideration of the mechanisms and characteristics of this process is warranted. Pyrite is by far the dominant sulphide responsible for acid generation, but there are other metal sulphides (present in different ore deposits) that can contribute to acid generation, such as galena (lead sulphide, PbS), sphalerite (zinc sulphide, ZnS), chalcopyrite (iron-copper sulphide, CuFeS_2), and covellite (CuS) (EPA 1997b, Akcil & Koldas 2006). When sulphides in rock are exposed to atmospheric conditions (water and oxygen), sulphuric acid is formed (H_2SO_4), which can infiltrate from underground mines and waste rock piles into streams, rivers, and groundwater. Certain bacteria, for example *Thiobacillus ferrooxidans*, accelerate the oxidation and acidification process. Every sulphide mineral has a different oxidation rate, being subjected to a complex cycle of reactions during oxidations. The oxidation of pyrite in the presence of water to become dissolved iron, sulphate and hydrogen is depicted below (Singer and Stumm 1970).

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Oxidation of pyrite by ferric iron:



Oxidation of ferrous iron by oxygen:



Reaction rates are increased by bacterial activity

Precipitation of ferric iron:



Oxygen is important to maintain the rapid process of bacterial oxidation at pH values below 3.5. The type of bacteria necessary to catalyze oxidation depends on pH and the chemical and physical features of the soil and water (Ferguson and Erickson 1988). Other bacteria known to catalyze sulphide oxidation are presented in

Table 2.

Table 2 Sulphide ore bacteria with their growth conditions (modified from EPA 1994)

Bacteria	pH	Temp., °C	Aerobic
<i>Thiobacillus thioparus</i>	4.5-10	10-37	Y
<i>T. ferrooxidans</i>	0.5-6.0	15-25	Y
<i>T. thiooxidans</i>	0.5-6.0	10-37	Y
<i>T. neapolitanus</i>	3.0-8.5	8-37	Y
<i>T. denitrificans</i>	4.0-9.5	10-37	Y/N
<i>T. novellus</i>	5.0-9.2	25-35	Y
<i>T. intermedius</i>	1.9-7.0	25-35	Y
<i>T. perometabolis</i>	2.8-6.8	25-35	Y
<i>Sulfolobus acidocalderius</i>	2.0-5.0	55-85	Y
<i>Desulfovibrio desulfuricans</i>	5.0-9.0	10-45	N

Contamination originating from AMD is often persistent in the environment, leading to long term effects on surface and ground waters. The oxidation process of mined materials is quite rapid and can lead to a decrease in pH and subsequent increase in trace element mobility (e.g. Nieto et al. 2007). Since sulphuric acid will continue to be generated from sulphide bearing minerals as long as the rock is exposed to air and water, until the sulphides are completely leached out, this process can last hundreds, even thousands of years (SDWF 2009, INAP

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2009, Younger et al. 2002).

According to Gray (1997) the environmental effects of AMD are categorized as:

- chemical (e.g. increased acidity, increased soluble metals concentrations),
- physical (e.g. substrate modification, sedimentation, and turbidity),
- biological (e.g. behavioural, fertility modification, acute and chronic toxicity),
- ecological (niche loss, habitat disturbance, bioaccumulation and loss of food, elimination of sensitive species and reduced biodiversity, increased vulnerability)

Typically Fe and Al are the principal metals dissolved in association with sulphide oxidation. Metals such as Cu, Zn, Pb, Co, Cr, Mn, Cd, Ag or Au (and others) are also often found in ores rich in iron sulphide. These metals can also reach elevated concentrations in solution as the result of sulphide oxidation. Acid mine drainage can result in solution with pH below 2, can contain sulphate levels of 800-1,800 mg/L, copper levels up to 50 mg/L, iron levels up to 1,000 mg/L, lead levels up to 12 mg/L, zinc levels up to 1,700 mg/L and cadmium levels of several milligrams per litre, depending on the contents of the ore (World Bank Group 1998).

The mobilized metals can be leached from materials and carried downstream within a water-course (e.g. SDWF, 2009, Nordstrom 2011). In addition to the impact of low pH and elevated metals, at pH less than about 3.5 sulphide oxidation commonly results in the deposition of iron hydroxide ($\text{Fe}(\text{OH})_3$), a red-orange precipitate also known as “yellowboy” (Figure 1). Yellowboy can contaminate the surface of stream sediments and streambeds, destroying stream habitats (e.g. Jennings et al. 2008). Many abandoned mine sites include extremely large quantities of waste rock/overburden, hundreds of kilometres of underground galleries, and/or very large tailing ponds that can generate AMD and other contaminants from the mining processes.



Figure 1 Acid drainage leaching from a tailings dump (a); Acid drainage from underground mining (b) (photos © Lazăr Adina-Laura 2012)

2.2 Factors controlling contaminant transport in the hydrosphere

Mining impacts to water courses pose the greatest concern to the environment (Younger et al. 2002). The occurrence and concentration of contaminants depend primarily on the characteristics and composition of the ore deposit geology and mineralogy, the techniques and chemicals used in ore processing, the design of waste storage facilities and local conditions (e.g. climate, hydrological circumstances). Further the harm caused by these emissions depends

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not only on the total concentrations but, in particular, their toxicological properties and the form in which they occur (Kauppila et al. 2011). Therefore an understanding of element associations within major rock types can provide insight to which contaminants may be present at a given site even before mining operations begin at the site. Moreover, it is also important to understand the properties of mining wastes and processes occurring therein (e.g. Plumlee 1999, Kauppila et al. 2011).

As summarized by Nordstrom (2011), the mobility of contaminants from mining activities in water courses depend on the occurrence, abundance (total metal content), and reactivity of the contaminant in the host rock (also referred as geoavailability). The reactivity is related to the mineral's resistance to weathering, which in turn is dependent mineral properties (e.g. mineral type, grain size, texture), climatic factors, porosity and topographic relief (Smith and Huyck 1999). For example, rhomboidal pyrite is more readily chemically weathered than cubic pyrite, both of which are more rapidly weathered than iron oxides such as hematite. Further, as described already in Section 2.1.2, the abundance of pyrite in host rock commonly generates AMD leading to the release of metals, whereas abundant Ca and Na in host rocks buffer against acidification which may also release metals (e.g. Ashton et al. 2001)..

The mobility of a contaminant in a watercourse is dictated by site-specific hydrologic conditions as well as chemical processes present (e.g. Smith and Huyck 1999, Nordstrom 2011). The transport of contaminants in waterways is controlled by physical and chemical processes such as precipitation or co-precipitation through secondary mineral formation and sorption reactions, and remobilization through dissolution and ion exchange. These in turn are dependent on, for example, pH and redox conditions, solute concentrations, as well as the abundance of sorbent material. By changing the chemistry and oxidizing conditions of water and soil, anthropogenic and natural activities such as weathering and microbial processes may greatly affect the stability, mobility and toxicity of elements (e.g. Lottermoser 2010, Nordstrom 2011).

Additionally, contaminant mobility at a site often varies temporally with diel and seasonal conditions. For example, Fe photo-reduction may influence metals mobility on a diel cycle, while the "first flush" phenomenon may lead to a seasonal spike, and subsequent dilution of contaminant concentration (e.g. Dagenhart 1980, Nordstrom 2009, Gammons et al. 2015). In contrast, waterways that receive AMD and experience increasingly frequent periods of drought are likely to undergo a decline in water quality because of decreasing dilution from meteoric recharge (e.g. Nordstrom 2009). In cold climates or at high altitudes the temperature fluctuations, snow cover melt and frost are important factors controlling weathering and thus the release of contaminants from bedrock. Further, contaminant mobility in water, while partially an inherent property of the element, is also a function of site-specific conditions such as pH, solution composition (e.g. nature of suspended solids, other elements and compounds present), redox chemistry, temperature, water flow rates, and microbiology (e.g. Smith 2007, Wolkersdorfer 2008, Nordstrom 2011, Salonen et al. 2014).

Where metal rich AMD discharges into less acidic water bodies most metals tend to oxidise (e.g. Fe(II) and Mn(II)), hydrolyse, and precipitate from solution due to the relatively higher pH and redox potential in the receiving water (e.g. Stumm and Morgan 1996, Mosley et al. 2015). In the case of AMD, when the buffering capacity of the receiving water body is exceeded by the acidity of inputs, the water body becomes acidified. Apart from Fe(III) and some insoluble metals, most metal cations are more prone to stay in solution at acidic pHs (<4). Nordstrom (2011) provides relevant summaries of typical relationships in metals mobility in solution in relation to both pH (e.g. Al) and solution composition (e.g. Fe (III)).

Predicting the environmental impact of these mining residues requires an understanding of mineral–water interaction and characterization of the solid materials at the microscopic scale. Furthermore, the prediction requires characterization of mine waste potential to produce acid or neutral drainage containing potentially toxic metals. This entails evaluation of the ratio of

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primary sulphide to carbonate minerals within the waste, and trace element concentrations inherited from the ore deposit and mineral beneficiation processes (Kauppila et al. 2013, Technical Committee 2012). Mining waste characterization is crucial in planning waste management, including evaluating options for waste utilisation and selecting suitable methods for the closure and rehabilitation of the waste facilities. However, prediction of waste reactivity is challenging and the drainage water quality of the waste facility can be misjudged as the result of insufficient waste characterization.

There is a variety of both standardized and non-standardized methods available for mine waste characterisation. Characterization requirements and method selection depend on the geology of the deposit (e.g. ore type, mineralogy). More detailed discussions on mine waste characterisation methods can be found in Lottermoser (2010), Nordstrom (2011), Hudson-Edwards et al. (2011), Kauppila et al. (2013) Technical Committee (2012), and Karlsson & Punkkinen (2015).

2.2.1 Natural geochemical tracer application and interpretation

Mining activities alter water pathways and water-rock reactions which can often impart unique chemical characteristics to mine water relative to surrounding surface and groundwater sources. These natural geochemical tracers of mine water span a range of major ions, trace elements, rare earth elements, and precious metals in solution (e.g. Wolkersdorfer 2008, Wolkersdorfer et al. 2002, Sanden et al. 1997, Davis et al. 1998). Ideal natural geochemical tracers behave conservatively in solution, and occur at detectable and distinct concentrations within different end member water sources (Cook 2012). The chemical signature of mine water relative to surrounding natural waters is dependent on many site-specific variables such as regional geology, ore deposit characteristics, climate, the nature of water-rock interactions, and the physical properties of water, among others (Plumlee et al. 1999, Nordstrom et al. 2011). Plumlee et al. (1999) characterize the chemical composition of mine waters draining different ore deposits types across different geologic settings. An understanding of site conditions and likely geochemical conditions provides a basis for determining which analytes are likely to act as the most effective natural tracers at a given site.

The association of ions in solution with mineralogy specific to the host rock or ore body at a mine site can be used to distinguish mine water from background waters. For example, sulphate (SO_4) in solution may reflect weathering of sulphides common to a metal ore body, while Cu^{2+} or Zn^{2+} may provide insight to weathering of chalcopyrite or sphalerite, respectively. However, prior to basing quantitative mixing calculation on a specific species, it is important to consider the species' likely behaviour in solution (e.g. Younger et al. 2002, Schemel et al. 2006, Kalbus et al. 2006). Mining activities may release distinctly high concentrations of certain elements or species, but non-conservative behaviour can complicate mass balance and water mixing determinations. For example, arsenic (As), mobilized from minerals such as arsenopyrite, is commonly associated with gold mineralization, but is relatively reactive in solution. While quantitative mixing assessment is complicated by species that undergo reactive transport, the presence and distribution of such species can none-the-less provide qualitative insights to mixing, and guide more detailed quantitative approaches (Davis et al 1998). Further, an understanding of reactive pathways under site specific conditions can be applied to account for chemical speciation when evaluating water mixing and contaminant transport. Such evaluations are supported by widely used geochemical models such as PHREEQC (Parkhurst and Appelo 1999).

Conservative natural geochemical tracers can be applied in chemical mass balances to quantify water and solute fluxes between different water sources. Tracers for mass balance applications may include major or trace elements, depending on their abundance and reactivity.

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Because metal concentrations are commonly elevated in mine water, cations such as Ca^{2+} , Na^+ , Mg^{2+} , K^+ , Si^{4+} , and Mn^{2+} may provide effective mine water tracers (e.g. Bencala et al. 1987, Foos 1997, Cowie et al. 2014, Davis 1998). Similarly, SO_4 has also been applied as a mine water tracer due to its common occurrence at elevated concentrations in mine drainage (e.g. Bencala et al. 1987, Schemel et al. 2006, Engle et al. 2008). Trace elements which behave conservatively in solution, such as strontium, are also utilized to constrain water mixing (Cary et al. 2014). Additional mine water tracers span a range of metals and trace elements related to the mined ore or the surrounding geologic setting, which demonstrate relatively conservative behaviour in solution. For example, fluoride (F^-), exhibits relative conservative behaviour in solution and may become elevated in mine water through water-rock interactions during mining of fluoride containing minerals. In contrast, the halogens chlorine (Cl^-) and bromine (Br^-) do not commonly occur in rock forming minerals, but are also conservative in solution, and can therefore be used to isolate atmospheric or industrial end member inputs to hydrologic systems (Eby 2004). Rare earth elements (REEs) have also been utilized as tracers based on mineral associations to demonstrate mixing and stratifications of mine water from different metal ore mines (Wolkersdorfer 2002).

A common approach using natural geochemical tracers for characterizing waters from different sources is through comparison of the relative abundance of major cation and anion species in solutions. This is often done as a graphical depiction of ionic species across different samples using either Stiff or Piper diagrams. The Stiff diagram illustrates concentrations of major ionic species in two dimensions, depicting water composition as a two dimensional shape. The trilinear Piper diagram illustrates relative concentrations of major cation and anion species, as well as the combined ionic composition of waters. Major ionic species commonly compared between waters include the cations Ca^{2+} , Mg^{2+} , and Na^+ plus K^+ , and the anions HCO_3^- , Cl^- , and SO_4^{2-} . Comparison of major ions by graphical methods illustrates chemically disparate water sources, provides insight to mixing between source, can indicate non-conservative behaviour of major ions, and can be the basis for interpreting chemical influences (lithologic, atmospheric and anthropogenic) on water end members (Eby 2004, Foos 1997).

Temporal and spatial variation in solute concentrations influences the accuracy of geochemical tracer-based mixing determinations (Schemel et al. 2006, Bertrand et al. 2014, Kalbus et al. 2006). Schemel et al. (2006) recognized cross-stream spatial variability in solute concentration during evaluation of surface water mixing. To minimize uncertainty in tracer-based mixing determinations, they calculated mixing from median concentrations derived from measurements that spanned the observed solute gradient. In this way they accounted for spatial variability in solute mixing. In general, the most accurate mixing calculations are determined from methods that can account for variability at different spatial and temporal scales (Kalbus et al. 2006, Bertrand et al. 2014, Cook 2012).

2.2.2 Chemical tracers derived from ore processing and mining

Various industrial chemicals are utilized throughout the stages of mining and mineral beneficiation which may be incorporated in mine waters and inadvertently transported from the mine area. For example, blasting operations may impart high nitrate levels to mine runoff, while mineral beneficiation, metallurgical extraction and water treatment each entail a range of potential industrial chemicals that may be mobilized to the environment (Table 3). The remains of these chemicals (e.g. Na , K , Ca , or SO_4^{2-}) affect the quality of process effluent and mine runoff waters and can be used as chemical tracers to detect the migration of mine waters to the environment. Further, characterization of industrial chemical tracers supports assessment of mine water behaviour in the environment (mobility and attenuation) and its effects on receiving surface and groundwater systems.

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Table 3. Chemicals commonly used in blasting, ore processing, and water treatment (modified from McLemore 2008, Pöyry 2009, Lottermoser 2010)

Chemical	Chemical formula	Use
Ammonium nitrate	$N_2H_4O_3$	blasting agent
foaming chemical MIBC	$C_6H_{14}O$	foaming
Xanthate PAX	$C_5H_{11}OCS_2K$	foaming chemical
Sodium isobutyl xantate	$C_5H_{10}OS_2Na$	foaming chemical
Flocculent		thickening
Oxygen	O_2	autoclave (oxidaiton)
Hydrogen peroxide	H_2O_2	process water oxidation
Sodium hypochlorite	$NaClO$	process water oxidation
Potassium permanganate	$KMnO_4$	process water oxidation
Hydrated lime	$Ca(OH)_2$	neutralization/pH increase
Burnt lime	CaO	pH adjust
Nitric acid	HNO_3	acid wash
Lye	$NaOH$	pH adjust
Cyanide	CN	Gold extraction
Mercury	Hg	Gold extraction
Activated carbon		CIL-circle gold extraction
Copper sulphate	$CuSO_4$	foaming, cyanide elimination
Metabisulphite SMBS	$Na_2S_2O_5$	cyanide elimination
Ferrisulphate PIX	$Fe_2(SO_4)_3$	water treatment coagulent
Aluminum sulphate	$Al_2(SO_4)_3$	water treatment coagulent
Ferric chloride	$FeCl_2$	water treatment coagulent
Soda ash	Na_2CO_3	pH adjust
sulfuric acid	H_2SO_4	pH adjust
nitric acid	H_2NO_3	pH adjust
hydrochloric acid	HCl	pH adjust

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2.3 Geochemical sampling and monitoring

2.3.1 General Principles

The potential influence of mining operations on surface- and groundwaters can be monitored using biological indicators, such as plankton and benthic fauna, measuring chemical and physical parameters of the water and/or by studying aquatic sediments (Heikkinen et al. 2008). Water quality is determined from a combination of field measurements and laboratory analysis. Routine monitoring should include measures from outflow and discharge sites as well as background waters. In mining environment studies it is also often meaningful to sample downstream of discharge sites to assess mixing and dilution processes, as well as ecological impacts of mine influenced water in recipient water bodies. Such characterization may facilitate strategic discharge sites that enhance contaminant dilution and minimize the possible negative impacts of mine effluents.

To define reference background concentrations for the baseline evaluation for surface and ground water, it is advisable to sample one or more locations upstream. The selection of the sampling and monitoring sites is based on hydrogeological characteristics, as well as bedrock mineralogy to estimate the pathways and sources of the possible contaminants. Selection of background sampling points is critical, because the air emissions from a mine site may spread considerable distances, in cases over 5 km (Turunen et al. 2016).

The sampling interval is dependent on project objectives, and may range from daily to monthly, or be conducted after precipitation events or other environmental phenomena of interest. (e.g. USGS 2006, Kauppila et al. 2013 and Räsänen 2013) This enables better screening of possible perturbations in water quality.

Water quality is affected by several parameters, and for comprehensive knowledge of chemical reactions in water, the total chemical composition of waters including metals and metalloids, organic contaminants, nitrogen and phosphorus compounds, as well as other anions such as sulphate and chloride should be characterised. Total chemical composition of water allows detecting changes in water chemistry related to mining activities (Heikkinen et al. 2008).

Prior to the sample collection, consideration must be given to the type of sample containers, sampling equipment and acids needed for conserving the samples. Choosing the proper composition of sample containers, adequate sampling equipment and pre-treating methods will help to ensure that the quality control of sampling is maintained. For instance, glass is often the recommended container type because it is chemically inert with respect to most substances, whereas hazard substances may potentially leach plastics from plastic containers into the sample. However, some metals species will also adhere to the sides of glass containers in solutes. The analytical method requirements, sample matrix and contaminants determine the required sample container type and needed pre-treatment methods. An example list of an equipment for water sampling is given below (modified from Räsänen 2013):

- Coolers for transporting and storing the samples
- Sample containers:
 - plastic (HPDE or LPDE) bottles of varied volumes (1l, 0.5l, 100ml, 50ml), as defined by the laboratory for requested water sample analytes
- Disposable contamination-free plastic gloves
- Disposable unpowdered nitrile gloves
- Disposable syringes
- Filters, such as:
 - Three layered PVDF 0.45 µm GD/XP-filters, which include 20 µm and 5 µm

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- pre-filtering
 - Vacuum filters with 0.2 μm filter, that filters also colloidal Fe and Al
- Ionised water
- Disposable pipettes for sample preservation by acid addition
- Laboratory paper
- Acids for preservation of the water samples
- Samplers, such as:
 - Water Limnos sampler
 - Tube bailer
- Multi-detector device for measuring of physico-chemical parameters in conjunction with sampling

2.3.2 Sampling and pre-treatment

Since water chemistry changes according to time, depth and current, such variation must be taken into account when sampling. For instance, when taking water samples from a lake or other still water body it is advisable to take samples throughout the water-column from various depths as well as locations. Flowing-water sampling is optimally located in straight reaches and in mid-stream or a flowing part of the stream where the flow is uniform and water mixed throughout the cross section. Near the stream banks the water may be stagnant and exposed to evaporation or even pollution from the land, and no longer represent the overall concentrations or isotopic composition of the stream. For the same reason, the distance to confluence of two different running waters should be considered and sampling located far enough from confluence where waters are thoroughly mixed (e.g. USGS 2006, Kauppila et al. 2013 and Räsänen 2013). Surface water samples from, for example, rivers, lakes or ponds are taken by immersing the sample bottle to 5-10 cm of depth or with a sampler such as Limnos water sampler (Figure). During sampling, the underlying layers should not be disturbed, to prevent the release of particles from the bottom and mixing with the water. To avoid mixing of the sediments in shallow sampling locations, sample can be collected with syringe (Figure).



Figure 2. Pre-treating water samples in field. a) filtering with 0.45 μm GD/XP-filter, b) filtering with 0.2 μm vacuum filter c) acid conservation. (Photos © a) GTK, b) Turunen, K., c) GTK)

Groundwater samples are taken from existing wells by a sampler such as tube bailer (Figure). Prior sampling water volumes in groundwater wells are replaced by pumping. Collecting samples will be undertaken with new sampler at each sampling point. However, if the sampling will be performed regularly, the same sampler can be used again at same sampling location, providing it is stored properly without any possible contamination between samplings. To maintain the sample uniform for all different analysis, the water sample is usually taken into larger containers, from which it is divided into smaller subsamples. Each container will be rinsed 2-3 times with the samples prior sampling and sample division. This means, that the bottles for unfiltered samples are rinsed with unfiltered water and bottles for filtered samples

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are rinsed with filtered water. Rinse the bottle with a lid by shaking heavily, after which the rinse water is thrown away. For each sampling point, the filter and syringe will be replaced. Because mine waters are reactive and sample quality may change during the transport to laboratory, preserving water samples in low temperatures, low light, and through acid preservation hinders the possibility of chemical transformation. For instance, the pH generally decreases and redox potential increases after sampling, which results in precipitation of iron and/or aluminium through oxidation. This may also enhance the co-precipitation of other elements, which skews the distribution of total and dissolved concentrations of elements in water. Preventing post-sampling reactions is crucial, especially in case of elements such as Cd or As, of which even small concentrations pose a risk to human health and the environment. Required sample volumes and pre-treatment for different water analyses are described in Table 4, Section 2.3.4. (Heikkinen et al. 2008, Kauppila et al. 2013 and Räsänen 2013).

Sample collection should be conducted according to quality assurance protocol, including the collection of field blanks and duplicates, and be coupled with a statistically based sampling plan. Blanks (e.g. deionised water) are analysed to elucidate potential contamination during sampling and analyse procedures. The duplicate samples reflect the precision and repeatability of the sampling procedure. The blank and duplicate samples are collected at the same time and in the same location as field samples, and are treated (e.g. filtering and preserving) in the same way. For the evaluation of dissolved concentrations, the suspended solids are removed through filtering.



Figure 3. Water sampling images. a) bottle, b) pore water sample by a syringe, c) Lake water sample

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by a Limnos water sampler, d) groundwater sample by tube bailer. (Photos © a) Turunen, K., b) GTK, c) Turunen, K. d) GTK)

2.3.3 Monitoring

Laboratory analysis are often rather expensive and time consuming. Monitoring physico-chemical parameters of water is usually the most simple and effective way of identifying changes in the environment. Such monitoring provides a means of evaluating the performance of water management and treatment measures and can be used to guide sample site selection for additional analyses. Due to reactivity of the mine waters, Physico-chemical field data should also be collected concurrently with other sample collection.

Online monitoring at strategic points (e.g. crucial discharge points) allows mine operators to react quickly to rapid changes in water quality. An online monitoring system includes safety alarm features that warn of a sudden perturbations in water quality or quantity, thus enabling immediate follow-up sampling and analysis, which can be used to optimize water treatment systems and minimize adverse effects on recipient water systems. The parameters monitored in the field and technologies utilized depend on site specific conditions, but most commonly include water level, temperature (T), pH, electrical conductivity (EC), redox potential (Eh), dissolved oxygen (DO) and alkalinity. Most water quality parameters (e.g T, DO, pH, Redox, EC, NO₃, turbidity, water level) can be measured by portable multi-detector devices that are provided by several different companies (Figure 2).

Since most reactions of mine waters are **pH** dependent and it is rather easy and cheap to measure, pH may be the most common parameter measured at mine sites. pH is determined potentiometrically using a standard hydrogen electrode and a reference electrode in order to determine the concentration of hydrogen ions (Golterman et al. 1969).

Electrical conductivity depends mainly on the ion content of the water and thus it increases as ion concentration increases. Since natural waters usually have a rather low and constant range of EC, it can be used as a baseline to compare and detect influence of contaminant sources. As mine waters commonly exhibit elevated ion concentrations, EC is a useful parameter for monitoring the mixing of fresh water with mine influenced waters. However, reliable measurements are needed to understand contaminant sources and seasonal variation in mixing and dilution processes controlling the conductivity changes in the hydrological systems. For example, EC fluctuates depending on temperature and so the measured EC values at different temperatures need to be corrected corresponding to a standard temperature (Hayashi 2004). Furthermore, conductivity results should always be compared with other water quality parameters since it does not represent individual contaminants nor the overall state of the water (MEND, 2001).

The reactivity of mine waters is largely regulated by **oxidation-redox potential (ORP)**. Because redox conditions control the mobility and reactivity of elements such as iron, sulphur, nitrogen, carbon and many metallic elements, ORP acts as a significant control of contaminant release from mine sites. Redox reactions describe the exchange of electrons between reduced and oxidized species (Pourbaix 1966). The oxidation state of many solutes influences not only their mobility in solution, but also their toxicity (e.g. As, Sb, Cr). Furthermore, due to its role in solute mobility, redox potential is a key variable in selecting suitable water treatment technologies, and evaluating their performance. ORP is determined potentiometrically using an inert indicator electrode, usually made from gold or platinum, and a reference electrode (calomel or silver/silver chloride) (Nordström 2005). Once again it is important to keep in mind that redox potential indicates only processes occurring in solution, not individual contaminants nor the overall state of the water.

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Alkalinity is the sum effect of all bases (e.g. bicarbonates, carbonates and hydroxides) present in water that can neutralize acids, defined as the acid-neutralizing capacity of water. Without this acid-neutralizing capacity, any acidic pollution derived from mine site would cause an immediate change in the pH of the recipient water body. Thus alkalinity is one of the best measures of a water body's sensitivity to acid inputs (EPA 2015). The most common method for measuring alkalinity is the potentiometric titration technique, in which acid of defined concentration is continuously added to a water sample of known volume until the pH of the water reaches a specified endpoint (Figure 2). (MEND, 2001).



Figure 2. Water quality data collection images. a) determining alkalinity titrimetrically (sulphuric acid titration), b) measuring the the physico-chemical parameters by multi-detector device. (Photos © GTK)

Table 4 Analysis methods, sample volumes and pre-treatments for water samples to determine concentrations, speciation and related chemistry (modified from Kauppi et al. 2013 and Räisänen 2013).

Analysis	Volume of the sample	Pre-treatment
Multielement, ICP-OES/MS-ICP	100 ml	filtering with 0.45 µm GD/XP-filter or 0.2 µm vacuum filter, conserving with suprapur® HNO ₃ , 0.5 ml/100 ml
Multielement (acid-soluble), ICP-OES/MS-ICP	100 ml	conserving with suprapur® HNO ₃ , 0.5 ml/100 ml
Fe ²⁺ , spectrophotometric	100 ml	filtering with 0.45 µm GD/XP-filter or 0.2 µm vacuum filter, conserving with HCl 4 ml/100 ml
TOC, CHN-analyser	100 ml	conserving with H ₃ PO ₄ 1 ml/100 ml
DOC, CHN-analyser (142L)	100 ml	filtering with 0.45 µm GD/XP-filter or 0.2 µm vacuum filter, conserving with H ₃ PO ₄ 1 ml/100 ml
tot-N, ammonium	100 ml	no pre-treatment
Ion-chromatographic analysis of anions (SO ₄ , Cl, F), suspended solids, pH, spectrophotometric analysis of phosphate, alkalinity, NO ₃ , NO ₄	1 liter	no pre-treatment
Ecotoxicity (SFS-EN ISO 6341)	2 x 1 liter	filtering or no pre-treatment

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2.3.4 Analytical methods for geochemistry

Chemical analysis of mine water samples generally includes total and soluble metal and metalloid concentrations and anions. In addition, dissolved organic carbon (DOC), total organic carbon (TOC) and ferrous iron (Fe^{2+}) can be significant for estimation of water quality. The dissolved and total concentrations of cations in water can be measured by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES), Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), Inductively Coupled Plasma Mass Spectrometry (ICP-MS) or Atomic Adsorption Spectrometry (AAS). Anion concentrations are determined using ion chromatography. Organic contaminants are generally determined with gas- or liquid chromatographic methods, carbon through CHN-analyser and phosphate and Fe^{2+} by spectrometric methods (Heikkinen et al. 2008 and Kauppinen et al. 2013). Table 4 provides sample volumes and pre-treatment measures corresponding to different analytical techniques. Chemical analysis should also include quality assurance protocol to define analytical precision and accuracy.

2.4 Case studies on geochemical site characterization

The scientific literature is full of studies designed to understand the origin, transport and fate of contaminants released from mined and unmined areas, as well as studies designed to quantify the adverse effects of acid mine drainage on the environment (soil, water, aquatic habitats, etc). Previous studies include water and sediment chemistry, field and laboratory water column evaluations, field and laboratory sediment testing, benthic macroinvertebrate sampling for abundance and taxonomic richness, and model development to explain and predict impacts of acid mine drainage on various aquatic species. Select field-based geochemical studies relevant to the characterization of mine emissions are summarized below.

2.4.1 Dial variation in metals in Fisher Creek, Montana USA

In their work Parker et al. (2006) analysed dial variations in the concentrations of Fe(II), Fe(III), Cu, and Zn, during one day and compared the results with others taken one year earlier. The experiment was conducted in south central Montana, USA, on a river called Fisher Creek. Fisher Creek drains abandoned mine lands within the New World Mining District, located 10 km from the northeast corner of Yellowstone National Park. The area has polymetallic (Au–Ag–Cu–Pb–Zn) mineralization which occurs as hydrothermal veins, carbonate replacement bodies, skarns, and mineralized porphyry intrusions. The field experiment was composed of in-stream chambers (either transparent or opaque to light), filled with stream water and sediment, and placed in the stream to maintain the same temperature. Laboratory experiments included three phases: (1) equilibration of a Cu(II) and Zn(II) containing solution with Fisher Creek stream sediment (at a pH of 6.9 and different temperatures); (2) titration of Fisher Creek water from pH 3.1 to 7 (at four different isothermal conditions); and (3) analysis of the effects of temperature on the interaction of an Fe(II) containing solution with Fisher Creek stream sediment under non-oxidizing conditions. The results of in-stream experiments showed that dissolved concentrations of Cu and Zn were not influenced by daily photoperiod and temperature.

2.4.2 First flush

Nordstrom (2009) studied the effects of rainfall events on mine wastes and also on unmined mineralized areas, at three mine sites (both in, and outside the US). He concluded that rainfall

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events impact acid and metals loadings in receiving streams from both mine wastes, and un-mined mineralized areas. Gradual increased concentrations of metals occur during long dry spells and sudden large increases occur during the first flush.

2.4.3 Mining sourced metals in surface waters, Rosia Montana, Romania

The magnitude and environmental significance of metal (Cd, Cu, Pb, and Zn) concentrations in surface water and river channel sediment have been investigated by Bird et al. (2005) along a 140 km reach of the Rivers Abrud and Aries, and 9 tributaries affected by mining. The study area, Rosia Montana, in western Romania, is believed to be Europe's largest Au deposit. The River Aries catchment is underlain by a varied range of bedrock, including igneous, metamorphic and sedimentary assemblages. The speciation of sediment-bound metals was established using a 4-stage sequential extraction procedure (SEP) with four chemical phases: (1) exchangeable, (2) Fe/Mn oxides, (3) organic matter/sulphides and (4) residual. Sediment-bound Cd and Zn were found to be predominantly associated with the exchangeable phase of the sediment (9–74% and 6–65%, respectively), whilst Fe/Mn oxides (5–76%) and organic matter/sulphides (1–45%) generally accounted for the majority of Pb and Cu partitioning, respectively. Aries River was found to be less polluted than the Abrud River. Only Cu showed concentrations above guideline values, likely related to a porphyry Cu mineralization in the catchment. In general, river channel sediments were found to be more widely contaminated by heavy metals than surface waters.

Levei et al (2013) examined the potential environmental risk of tailings after precious and base metal ore processing, stored in seven impoundments located in the Aries river basin, Romania. Tailings were found to be highly contaminated with several hazardous/priority hazardous metals (As, Cu, Cd, Pb), fluoride and sulphate, and to pose potential contamination risk for soil, sediments, surface and groundwater. The ability of metals and ions to leach was attributed, proportionally, 61% to silicates, 11% to acidic minerals, 6% to organic matter, and 18% to the leachability of biogenic elements (Na, K, Cl⁻, NO₃⁻).

In a more recently study, Senila et al. (2015) analysed the metals content and bioavailability in the waters of Aries River catchment, Romania. The authors investigated the effectiveness of the DGT technique for the assessment of the bioavailable pool of metals in waters. Additionally, general physical-chemical indicators of water were determined. Very high total metal concentrations were found in the tributaries that drain the mining areas, but the influence of the polluted tributaries on the Aries River water quality was rather moderate, as a consequence of the relatively low tributary flow rate when compared to that of the Aries River. Using the DGT technique, the bioavailable metals fractions expressed as % of total dissolved metals concentrations were found to be 28–88% for Cu, 43–72% for Zn, 73–85% for Fe, and 33–70% for Mn.

2.4.4 Seepage water from sulphide mines in Finland

Heikkinen et al. (2009) studied the seepage water and drainage water geochemistry at two active sulphide mine tailings impoundments in Finland (the Hitura Ni mine and Luikonlahti Cu mine/talc processing plant) in order to assess the factors influencing tailings seepage quality and to identify constraints for water treatment. The physico-chemical parameters pH, EC, DO, redox, and alkalinity were collected with samples. Samples were analysed for dissolved major cations, trace metals, major anions, and total element concentrations. Changes in seepage water quality after equilibration with atmospheric conditions were also evaluated based on geochemical modelling.

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The results showed that, despite the similar operation times of the impoundments, effluent waters from the serpentine-rich, low sulphide Hitura tailings produced NMD with high Ni concentration, whereas seepage from the Luikonlahti high sulphide, multimetal tailings produced AMD with high concentrations of Zn, Ni, Cu, and Co. Even though tailings mineralogy clearly influenced seepage water quality, several other factors affecting the water quality were also identified. These included weathering of the tailings along the seepage flow path, process water input, and local hydrological settings. Geochemical modelling results showed that pH is increasing and some heavy metals are adsorbed to Fe precipitates after net alkaline waters equilibrated with the atmosphere. In the net acidic waters, pH decreased and no adsorption occurred. In order to decrease the SO_4^{2-} and metal loading (Fe, Ni and Mn), a combination of aerobic and anaerobic treatments were proposed for Hitura seepages. Continued monitoring of seepage quality was proposed at Luikonlahti instead of treatment, since the water quality was still adjusting to recent modifications to the tailings impoundment.

3. Isotope tracers in mine environments

While variations in the stable isotopes of H, O, and C have been widely used to understand the water and carbon cycles, relatively recent advances in analytical instrumentation have made it possible to precisely measure isotopic variations in numerous other elements that have a range of applications in environmental studies. Elements with stable isotopes subject to systematic partitioning (fractionation) in response to physical, chemical, or biological processes are particularly usefully in environmental studies. In the following sections the principles of select isotope systems will be described in the context of their current or potential future application in mine environment studies. As described by Sueker (2015), an understanding of the mechanisms of stable isotope fractionation can be utilized in mine environment studies for the following:

- support groundwater and surface water flow models;
 - assess sources of mine water recharge and discharge;
 - assess mining effects on groundwater and surface water connections;
 - assess potential effects on water supply to surrounding area;
- assess water-rock interactions;
- characterize fate and transport of mining related constituents (e.g., metals, sulphate, cyanide) in surface water and groundwater.

Isotopes of the following elements were selected for review on the basis of their proven or potential applicability to mine environment studies: O, H, S, Sr, Pb, B, Li, Mg, and U. Isotopes of O, H, Pb, S, Sr and U have been previously recognized for their applicability in mine environment studies (e.g. Faure & Mensing 2005, Tichomirowa et al. 2010, Eby 2004, Nordstrom et al. 2010). Furthermore, isotopes of B, Li, and Mg have potential applications to mine environment studies which have arisen through advances in analytical techniques and a concurrently increasing understanding of system dynamics. Where available, case studies are also presented to illustrate the application of select isotope systems within mine environment investigations.

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3.1 General stable isotope notation and principles for application

The following summary is intended to provide a basic framework for understanding and applying stable isotope as tracers, but assumes the reader already has a fundamental understanding of isotope geochemistry. A more detailed account on the principles of isotope geochemistry can be found from text books and review publications such as Wierderhold (2015), Clark & Fritz (1997), Kendall & McDonnell (1998), or Faure & Mensing (2005). Most stable isotope measurements are discussed using delta (δ) notation, by which the isotopic composition of a sample is expressed as parts per thousand (i.e. a per mil [‰] value) with respect to the isotopic composition of a known standard material. For example, a commonly used standard for the isotopes of oxygen and hydrogen in water is Vienna Standard Mean Ocean Water (VSMOW). The measured $^{18}\text{O}/^{16}\text{O}$ or $^2\text{H}/^1\text{H}$ composition of water is therefore reported with respect to VSMOW, and is calculated according to Equation 5.

$$\delta_{\text{sample}} (\text{‰}) = \left(\frac{R_{\text{sample}}}{R_{\text{VSMOW}}} - 1 \right) \times 1000 \quad (5)$$

Here R is the measured ratio of heavy to light isotopes of interest (e.g. $^{18}\text{O}/^{16}\text{O}$ or $^2\text{H}/^1\text{H}$) in both the sample and standard. For the elements discussed in the following sections, when isotopic composition is not expressed using δ notation, an explanation of alternate isotopic nomenclature is provided accordingly.

Stable isotopes provide a valuable tool for assessing fluxes of a specific element or compound of interest, or to identify the occurrence of physical, chemical, or biological processes in a certain environment (e.g. the occurrence of microbial reduction). In a scenario where water from two isotopically distinct sources mixes to a common pool, and the pool has not undergone process induced fractionation, these isotopes can be used to quantify source contributions to the pool following Equation 6, because water isotopes mix conservatively (Faure & Mensing 2005).

$$\delta_{\text{pool}} = [\delta_{\text{source1}} \times n] + [\delta_{\text{source2}} \times (1-n)] \quad (6)$$

where n is the percentage of O or H derived from source 1, and δ is the isotopic ratio ($^{18}\text{O}/^{16}\text{O}$ or $^2\text{H}/^1\text{H}$) expressed as a ‰ value relative to a known standard.

Because isotopes mix conservatively, other solutes with sufficient isotopic variation in nature may also be used to assess source and mixing to supplement water isotope data. The isotopic compositions solutes may also provide additional information on source and pathway not otherwise evident in water isotopes alone. When assessing source and mixing based on conservative solute isotopes, solute concentration in the different end members must be accounted for according to Equation 7.

$$\delta_{\text{pool}} = [\delta_{\text{source1}} \times n \times (S_1/P)] + [\delta^{87}\text{Sr}_{\text{source2}} \times (1-n) \times (S_2/P)] \quad (7)$$

where S_1 , S_2 and P is the concentration of solute in source 1, source 2, and the pooled water, respectively.

Because certain isotopes undergo predictable fractionation in response to specific environmental stimuli, variability in isotopic end members can provide insight to biological, chemical, or physical processes occurring within an environment. For example, biological process can be identified by $\delta^{34}\text{S}$, because ^{34}S becomes enriched in the sulphate species as the result of preferential microbial reduction of ^{32}S , while the progression of the physical process of evap-

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oration can be defined using $\delta^{18}\text{O}$ because ^{18}O is enriched in surface water through the preferential evaporation of ^{16}O . Systematic isotopic change induced by such processes can be characterized through field observations and experimentation using a fractionation factor (α), as defined by Equation 4. For practical purposes process induced fraction is also commonly discussed in terms of an enrichment factor (\mathcal{E}). For example, water evaporation under isotopic equilibrium at 25°C results in a 9.26‰ enrichment (\mathcal{E}) in the liquid relative to vapour state, such that $\alpha = 1.0093$ (Equation 8).

$$\alpha_{\nu}^l = \frac{R_l}{R_{\nu}} = \frac{\delta_l + 10^3}{\delta_{\nu} + 10^3} = \frac{\mathcal{E}_{l-\nu} + 1}{10^3} \quad (8)$$

where R_l is the isotopic ratio of the liquid and R_{ν} is the isotopic ratio of the vapour.

Progressive isotopic fractionation between two pools (e.g. water turning to vapour) results in a systematic change in the isotopic composition of each pool which can be described by the Rayleigh equations (Rayleigh 1896). Equation 9 relates the isotopic ratio of two pools with respect to the fraction of the element remaining in the original pool (f), and the process-specific fractionation factor.

$$R = R_0 * f^{(\alpha-1)} \quad (9)$$

where R is the isotopic ratio (e.g. $^{34}\text{S}/^{32}\text{S}$ or $^{18}\text{O}/^{16}\text{O}$) in pool 1 and R_0 is the isotopic ratio in pool 2.

Building from these concepts, mass balance calculations utilize isotopes to quantify exchanges between multiple pools, and can be applied to complex systems with many inputs and outputs. Equation 10 shows the conceptual application of chemical and isotopic compositions in a mass balance defining fluxes relative to a pool. Such mass balance assessments can be used to constrain information about fluxes or pools that are otherwise difficult to measure.

$$\sum(M_{input} * \delta_{input}) - \sum(M_{output} * \delta_{output}) = M_{pool} * \delta_{pool} \quad (10)$$

where M is the molar abundance of the solute of interest, δ is the isotopic ratio of that solute and input and output are the incoming and outgoing fluxes from a pool, respectively.

In this example, depending on the pool in question, there are likely numerous inputs and outputs that must be considered in the calculation.

Further information on the principles of isotope geochemistry and their applications can be found throughout the literature (e.g. Faure & Mensing 2005, Clark & Fritz 1997, Kendal & McDonnell 1998, Wierderhold 2015). The following discussion is intended to aid and promote the application of these isotope systems in mine environment studies by providing information from the literature on the principles and past applications of specific systems of interest.

3.2 Oxygen and Hydrogen in the hydrologic cycle

The heavy isotopes of the oxygen (^{18}O) and hydrogen (^2H , also known as deuterium) in water are prominent tools in environmental studies. To utilize water isotopes in an environmental study it is first necessary to understand controls on the isotopic composition of water throughout the hydrologic cycle. The most important changes in the isotopic composition of natural waters occur in the atmosphere and through the evaporation of surface waters (Dansgaard, 1964). Interaction of liquid water and water vapour is an essential influence on water isotope

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distribution throughout the global water cycle. The higher the isotopic mass of the water molecule (e.g. $H^{218}O$ compared to $H^{216}O$), the lower the vapour pressure (Friedman 1953). This leads to enrichment of heavier isotopes in the liquid phase, whereas lighter isotopes are enriched in the vapour phase. Therefore gas phase water that evaporates from liquid water is enriched in ^{16}O and 1H compared to the remaining liquid, which is in-turn relatively enriched in ^{18}O and 2H (D). Condensation of liquid water from water vapour reverses this process, by which the heavier molecule condenses first and thus rain is enriched in heavier isotopes relative to the cloud vapour.

Repeated rain events from a single atmospheric vapour mass result in progressive depletion of the ^{18}O and 2H within the vapour mass according to Equation 9, and drive the isotopic patterns of global precipitation. Global scale patterns of increasing isotopic depletion by precipitation occur from the equator towards the poles (the latitude effect), from coastal regions towards continental interiors (continental effect), and with increasing altitude (altitude effect) (Dansgaard 1964).

Because the equilibrium fractionation factors for water isotopes are temperature dependent predictable isotopic patterns also occur at a single location seasonally, whereby winter precipitation is more depleted in heavy isotopes (i.e. lighter) than summer precipitation (Rozanski et al. 1982). Seasonality also occurs in response to humidity during condensation and precipitation. While higher humidity facilitates isotopic equilibrium between vapour and condensate (e.g. rain drops), precipitation that occurs in low humidity is subject to evaporation and kinetic fractionation. Because large rain events induce greater humidity in the air column they are less impacted by this secondary kinetic fractionation. Accordingly, seasonal isotopic variability resulting from the amount of precipitation during a single event is called the amount effect (Dansgaard 1964).

Craig (1961) observed that the $\delta^{18}O$ and δD values of global precipitation are linearly related by Equation 11, which defines the Global Meteoric Water Line (GMWL).

$$\delta D = 8 \delta^{18}O + 10 \quad (11)$$

The GMWL has an $r^2 > 0.95$ which indicates that the fractionation of both O and H isotopes occurs in close association. Consequently, the two elements are usually discussed together. The slope and intercept of any Local Meteoric Water Line (LMWL), the line derived from precipitation collected from a particular site, can be significantly different from the GMWL. Deviation in the slope and intercept of LMWLs from that of the GMWL slope of 8 are caused by factors such as the origin of the vapour mass, evaporation during precipitation, and seasonality effects (Clark & Fritz 1997). Therefore site specific $\delta^{18}O$ and δD data are typically plotted with respect to a LMWL for discussion. Isotope data of precipitation from various locations across the globe are available from the IAEA/GNIP data base (IAEA/GNIP 2016).

Apart from precipitation, surface waters are preferentially depleted in lighter water molecules due to evaporation and are often enriched in heavy isotopes compared to the isotopic composition of rainwater from which they formed (Clark and Fritz 1997). The culmination of these processes label a meteoric water according to the environmental conditions to which it has been exposed.

Soil and groundwater generally reflect the weighted mean annual isotopic composition of precipitation, whereby the seasonal isotopic variability of precipitation is attenuated by mixing during water percolation through soil and bedrock. An exception to this may occur where waters from other sources (e.g. surface waters subject to evaporative enrichment) mix with groundwater (Clark & Fritz 1997, Zimmerman et al. 1967), or in aquifers with low specific yields and which exhibit large seasonal water table fluctuations (Kortelainen & Karhu 2004).

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3.2.1 Water isotope applications in mine site studies

The application of integrated stable hydrogen and oxygen isotopes at mine sites provides important information on:

- water origin;
- mixing phenomena, and;
- underground dynamics.

Possible sources of mine water recharge include:

- direct infiltration of precipitation and/or surface water via fractures or through historic mine openings;
- inflow of groundwater from regional aquifers;
- inflow of saline formation water or geothermal waters from depth.

Isotopic variability between meteoric water sources resulting from factors such as the altitude effect, seasonality, or precipitation vs surface water sources can be utilized to delineate groundwater origins. Additionally, Groundwater belonging to the meteoric cycle can be mixed with waters of different sources or origins, such as formation waters and geothermal fluids. Formation water may display distinct isotopic characteristics relative to meteoric waters (Frape & Fritz 1987). Formation water, a generic term mainly used to describe the water found during drilling operations below the cycling aquifer systems, undergoes isotopic fractionation as the result of extended contact with host rocks, often at elevated temperatures. Usually these interactions result in an increase of the $\delta^{18}\text{O}$ values of water, and a slight decrease of the δD values can occur in the presence of clays or through interactions with hydrocarbons (Clark & Fritz 1997, Kietäväinen et al. 2013).

Mixing phenomena can be studied using both $\delta^{18}\text{O}$ and δD values, as well as correlations between δD (used preferentially to $\delta^{18}\text{O}$ because it is less likely influenced by water-rock interactions) and salt content of waters (e.g. Blaga et al. 1984). In shallow, or low specific yield aquifers, where the seasonal isotopic fluctuation of precipitation may be evident in groundwater, analysis of groundwater water isotopes in conjunction with salt content relative to precipitation can also provide insight to recharge rate and pathways (Kortelainen & Karhu 2004, Clark & Fritz 1997, Zimmerman et al. 1967).

3.2.2 Water isotope sample collection and analysis considerations

A comprehensive description of sampling, laboratory water treatment and measuring techniques can be found in IAEA Guidelines series, Mook 2001, Clark & Fritz 1997, and elsewhere.

The main considerations for the collection, transport and storage of samples for the analysis of stable O and H are to sample fractionation. Sample handling fractionation can be induced by sample evaporation, isotope exchange with atmospheric moisture, or with the bottle material. Secondary evaporation during sample handling and storage alters the meaning of data. As described by Mook (2001), a 10% loss of sample to evaporation can result in isotope enrichment of about 10‰ in deuterium and 2‰ in ^{18}O .

High density polyethylene bottles (HDPE) are recommended for sample collection and storage and a 50 ml sample bottle is commonly used to collect sufficient volume for the combined analysis of both deuterium and $\delta^{18}\text{O}$. Prior to sampling the clean and dry sample bottle should be rinsed with sample water three times and the completely filled to leave no head space. If there is any concern regarding the air tight nature of the sample container, bottle caps can be sealed (e. g. using paraffin film) to avoid evaporation, and samples should be stored in the

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dark at approximately 5°C. Samples for isotopic analysis can be stored in HDPE bottles for up to a couple of months before fractionation through the walls of the sample bottle becomes a concern. The isotopic composition of water samples can be preserved for years, however, if stored in airtight glass containers (IAEA 2001).

In the field it is important to record GPS coordinates of the sampling points and to measure other physico-chemical parameters including water temperature, pH, electric conductivity, total dissolved solids (TDS), and dissolved oxygen, to aid interpretation. Water samples for chemical analyses (anions and cations) also provide valuable and necessary information as part of a comprehensive assessment.

The sampling strategy should include sample collection from potentially distinct isotopic sources that might interact with the water of interest (e.g. precipitation, surface water and groundwater). The sampling interval is dependent on project objectives, and may range from daily to monthly, or be conducted after precipitation events or other environmental phenomena of interest. Surface water sampling requires consideration to ensure representativeness. River and stream samples should be taken from mid-stream or a flowing part of the stream, while stagnant water near stream banks should be avoided as the water may show effects due to evaporation or pollution. When sampling after a confluence the degree of mixing between the two different running waters should be considered (e.g. sample far enough downstream that waters are thoroughly mixed). Samples from lakes and pit lakes should be collected from both the surface and from depth because isotopic variation likely occurs throughout the water-column. (IAEA 2001a)

3.2.2.1 Water isotope analysis by laser absorption spectroscopy

Recent innovation in instrumentation has facilitated direct isotopic measurement from water samples using laser absorption spectroscopy (Kerstel et al., 1999). These methods are based on the observation that an element's gas phase absorption of infrared light is related to its rovibrational transitions which can subsequently be used to characterize the isotopic species in the sample (IAEA 2001b, Dennis 2014). Commercially-available instruments for direct isotope analysis are manufactured by Los Gatos Research Inc. and Picarro Inc. The instruments of both manufacturers operate using different variations of cavity ring-down spectroscopy (CRDS). In CRDS absorption across wave length is measured with respect to time. Precision with, for example, the Los Gatos DLT-100 is in a range of 1‰ for δD and 0.2 ‰ for $\delta^{18}O$ (IAEA 2009).

Laser absorption spectroscopy has some advantages over the traditional isotope ratio mass spectrometry (IRMS) method. The instruments are usually easier to install and operate, have much lower initial and operational costs, require minimal maintenance and do not require compressed gasses. Portable CRDS instrument facilitate unmanned remote monitoring in the field.

Sample preparation for water isotope analysis by CRDS is minimal. However, some samples, like mine waters with low pH and/or high dissolved solids, may need to be purified prior to analysis. Water purification techniques must not cause changes to a sample's isotopic composition, or otherwise be conducted in a quantitative manner by which isotopic fractionation resulting from purification can be accounted for. Many laboratories distil water samples prior to analysis, which must be conducted in a quantitative fashion by which all of the sample water is recovered. Also during purification steps contact between ambient air and the water sample should be minimized to prevent influence of air vapour on the isotopic composition of the sample. Cryogenic distillation is the most common distillation method.

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3.2.2.2 *Water isotope analysis by isotope ratio mass spectrometry*

Isotope ratio mass spectrometry (IRMS) was developed to measure the isotopic mass ratios and compositions of natural samples with high precision (Brenna et al 1997). The first dual inlet, double collector gas-source mass spectrometer was developed by Alfred Nier in 1947 (Nier, 1947). Gas-source mass spectrometers are well suited for measuring light elements like H, C, N, O and S. Most modern systems use continuous flow sample injection (CF-IRMS) in which the samples and standards are carried into the mass spectrometer in a constant stream of helium gas, which reduces the required sample size and time taken for the measurement. Analysis by IRMS is time- and labour intensive, their initial- and operational costs are high, and they must be operated by experienced users.

To facilitate gas injection of a water sample for $\delta^{18}\text{O}$ analysis, the sample is brought to isotopic equilibrium with carbon dioxide, generally at 25.0 ± 0.2 °C, according to Equation 12. The isotopic ratio of CO_2 is analysed by IRMS and the temperature dependant fractionation factor is used to determine the $\delta^{18}\text{O}$ of the original water sample. (Epstein and Mayeda 1953).



$^2\text{H}/^1\text{H}$ analyses of water have historically been carried out on the hydrogen gas obtained by quantitative reduction of water. H_2 gas is generally produced by reducing the water at several hundred degrees Celsius with depleted uranium (Biegeleisen et al. 1952), zinc (Friedman 1953, Karhu 1997) or chromium (Cr^+) (Morrison et al. 2001).

In a more recent method the D/H ratio of a water sample can be transferred to H_2 by direct isotopic exchange catalyzed by platinum powder (Coplen et al. 1991, Wong & Clarke 2012, Mook et al. 1983, Lowe et al 1994), as described in Equation 13.



The equilibration technique is dependent upon chemical activities rather than concentrations. Consequently, the chemistry of the water sample must be known. After gas injection, the samples are accelerated toward a detector by stripping single electrons from the molecules. A magnet causes the accelerated ion beams flight path to curve according to the different masses of the ions. This forms a spectrum of molecular masses which can be used to quantify isotopes abundance in the sample (Figure 3).

3.2.2.3 *Reporting stable isotope abundance ratios for water*

As described previously, isotopic compositions are commonly reported in relation to a standard. In order to facilitate inter-laboratory comparison, common international standards are used. The most common modern international standard for oxygen and hydrogen stable-isotope variations in natural waters has been VSMOW (Vienna Standard Mean Ocean Water), though VSMOW2 is the current commercially available analogue to this standard. VSMOW corresponds to a hypothetical water with both oxygen and hydrogen ratios equal to the mean isotopic ratios of ocean water, originally defined by Craig (1961) as SMOW (IAEA 1995). Other common standards used for water isotopes include SLAP (Standard Light Antarctic Precipitation) obtained by melting of Antarctic ice, SLAP2, GISP (Greenland Ice Sheet Precipitation), NBS-1 (distilled Potomac River water supplied by the National Bureau of Standards, currently the National Institute of Standards and Technology), and NBS-1A (snow from Yellowstone Park) (IAEA 1981). At present, VSMOW2, SLAP2 and other reference standards are available from the IAEA Reference Products commercial web portal (<http://nucleus.iaea.org/rpst/>). In order to reduce operational cost, it is common that laboratories develop internal standards

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referenced against commercial international standards.

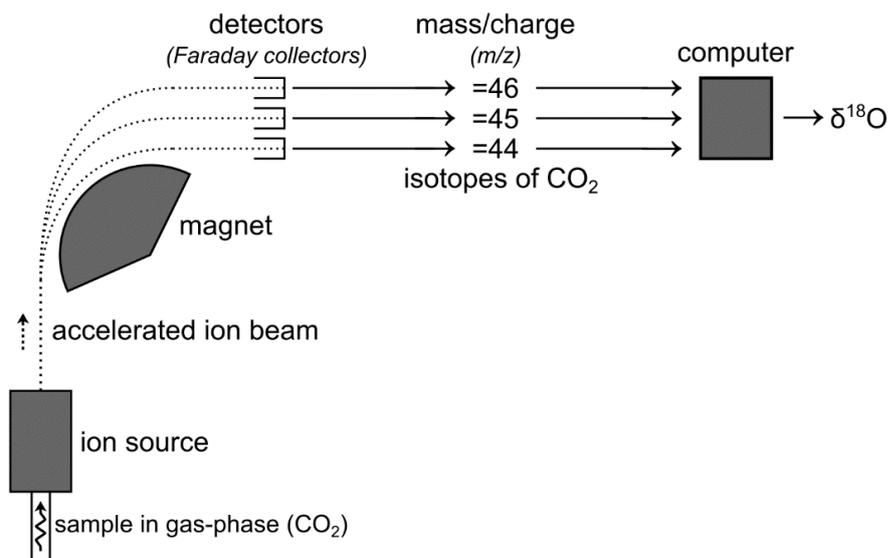


Figure 3 Simplified schematic of an IRMS used to analyse $\delta^{18}\text{O}$ of CO_2 .

3.2.3 Case Studies: Water isotopes ($\delta^{18}\text{O}$ and δD)

3.2.3.1 Identifying groundwater flow paths in bedrock fracture zones using stable isotopes of oxygen and hydrogen. Talvivaara mine, gypsum pond area, Northeastern Finland.

Talvivaara mine, located in North-eastern Finland near the municipality of Sotkamo and the city Kajaani (Figure 6). Isotope samples were analysed using cavity ring-down spectroscopy (Kittilä, 2015).

Similar distinct chemical and isotopic compositions were observed along the length of fracture zone 4 running NE-SW (seen in Figure 6). This was interpreted to mean that the particular fracture is well conducting and could possibly collect water from other fractures to transport it outside the mine area. At fracture zone 2, isotopic composition of the samples taken along the fracture was also strikingly uniform. This helped to verify that a hydraulic connection exists along the strike of the fracture. (Kittilä 2015). Based on geochemical analysis Pasanen et al. (2014) suggested that surface water from the large leakage at the gypsum ponds would be likely to enter the bedrock fractures and contaminate the groundwater system. However, the isotopic composition of groundwater collected from the bedrock fractures followed the local meteoric water line well, and did not indicate mixing with surface water samples, which consistently fell along an evaporation line (Figure 4). The notable exceptions are groundwater from the P4 well, which is a pumping well and believed to capture surface water from the adjacent Valkealampi pond, and R5, believed to be impacted by dammed surface water in the well vicinity (Figures 6 and 7). The lack of evidence for pond water-groundwater mixing elsewhere along bedrock fractures, despite elevated SO_4 concentrations in fracture zone 2, was interpreted to reflect the relative sensitivity of these two tracer methods (Kittilä 2015). Based on simple two part mixing models, a composition of up to 10% surface water within the precipitation derived groundwater would result in notable SO_4 concentration increase, but only a minor shift $\delta^{18}\text{O}$. Therefore the authors interpreted the lack of isotopic evidence for mixing to

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indicate that surface water infiltration to the bedrock fractures accounts for less than 10% of bedrock fracture water, and is smaller than previously anticipated (Kittilä 2015). However, long term monitoring is necessary in order to evaluate temporal variability in the system.

), produces nickel and in smaller quantities zinc, copper and cobalt. Mining operations began in 2008. Metals are extracted from finely ground ore by means of naturally occurring bacteria in a process called bioleaching (Riekkola-Vanhanen 2013). In November 2012 a leakage of acidic, metal-containing waste water was released from the gypsum ponds of the mine. The incident raised concerns that the contaminated water from the leak would enter the fractured bedrock, and that the fractures could transport the adverse substances outside the mining area (Kittilä 2015). Thus it was necessary to identify the potential flow routes of water through the fracture system and evaluate the risk of contaminants passing through them.

Bedrock fracturing is extensive in Finland and the fractures are often open, interconnected and well conducting. Bedrock fractures and their course, continuation and water content was roughly evaluated from geophysical data (gravimetric, magnetic, refraction seismic, electrical resistivity tomography and ground penetrating radar) by Eskelinen et al. (2013), Forss et al. (2013) and Pasanen et al. (2014). However, it was concluded that the geophysical data could not alone be reliably used to evaluate the flow directions and rates in the fractures, and so stable isotopes of oxygen and hydrogen were studied along with chemical characteristics to help identify the role and significance of each of the fractures in the system. In total 29 samples for chemical analysis and 39 samples for analysis of δD and $\delta^{18}O$ were collected. Samples were taken from springs, surface water sites, bedrock wells and shallow wells (Figure 6). Isotope samples were analysed using cavity ring-down spectroscopy (Kittilä, 2015).

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Figure 6). Isotope samples were analysed using cavity ring-down spectroscopy (Kittilä, 2015).

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. Location of the study area, sampling sites and major fractures. Modified from Kittilä (2015).

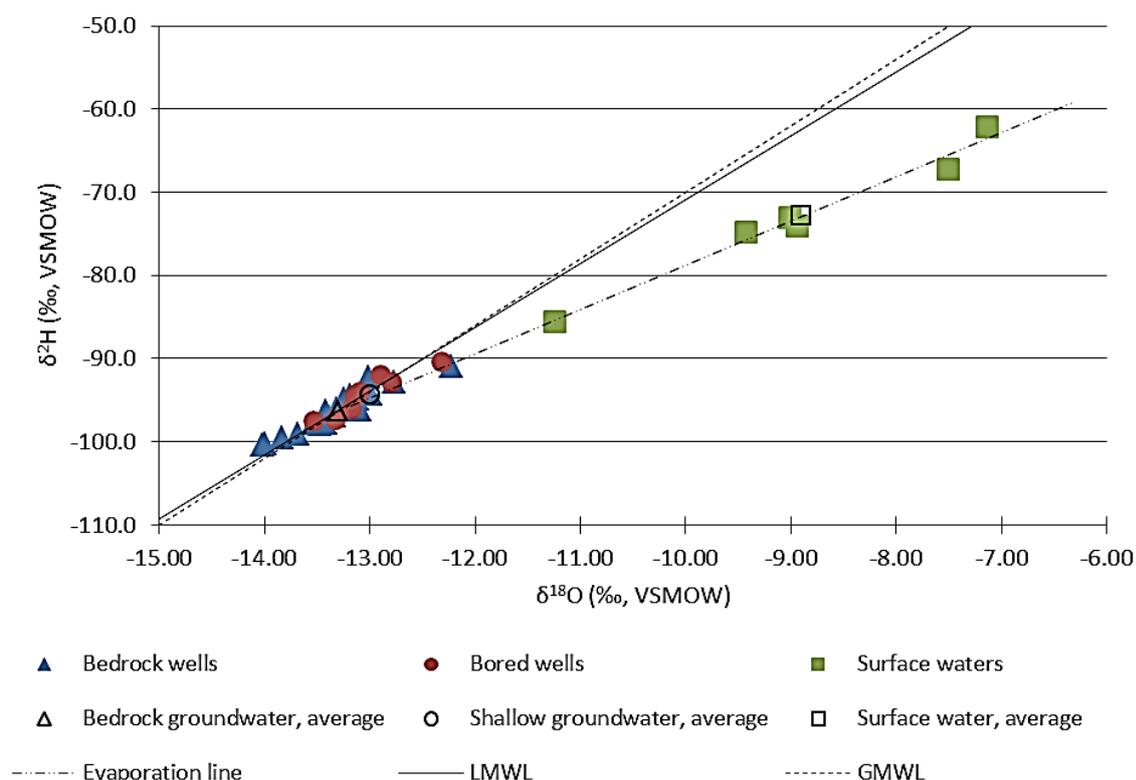


Figure 4 (from Kittilä 2015). Isotopic composition of the sampled waters. Surface water samples define a clear evaporation line. Global meteoric water line (GMWL) is from Craig (1961) and local meteoric water line (LMWL) from Kortelainen (2007).

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3.2.3.2 Baia Borșa mining district

Several studies have been performed on surface water and groundwater systems related to mining areas in the Carpathian Mountains of Romania (Blaga et al., 1981; Blaga et al., 1983a, 1983b; Blaga et al., 1984). Figure 5 shows the location of the Baia Borsa, Roșia Montană and Zlatna gold mining areas in the Apuseni Mountains, which have been impacted to varying degrees by historic mining. Production activity was abandoned in the Toroioga mine in 1999, and in the Gura Băii mine in 2007. The tailings dam, located at about 800 m altitude, is used to store waste generated by the processing plant. In March 2000, the Novăț pond dam (with a height of 26 m and a pond area of about 11 ha) failed as a result of intense rainfall in that period. Over 100,000 tons of tailings laden with Pb, Zn, Co and Cd were discharged into the Vaser Valley and then into the river Tisa. Following the rehabilitation, in November 2004, an effort to pump tailings water back into the pond was undertaken.

The Baia Borșa ore field corresponds to two mineralization events that overlap in the same area; the first one is represented by Caledonian metamorphosed volcanic hosted massive sulphide (VHMS) ores, and the second consists of Neogene epithermal ores. Most of the ore deposits (e. g. the Gura Băii, Măcârlău, and Colbu deposits) belong to the first group. The second group comprises the Toroioga filonian complex (Cu +/- Pb-Zn-Au complex ore).

Hydrologically, the different types of rocks behave differently. The schists are virtually dry due to a low level of fracturing and the plasticity of some minerals (e. g. graphite) which have closed water circulation paths, and act as impermeable layers between different levels of acid rocks or compact ore. Most underground water circulation is along the fault system or through mine openings.

Blaga et al. (1983a) incorporated hydrogen isotope composition (δD) and total salt content (Δd) in a study to distinguish source waters to the Novăț gallery. They collected mine water from galleries and surface running water over the course of one year. The total salt content was measured at 25 °C using a digital densimeter and is expressed in mg/l as the difference relative to standard distilled water. Table 5 summarizes the results from the different water sources.

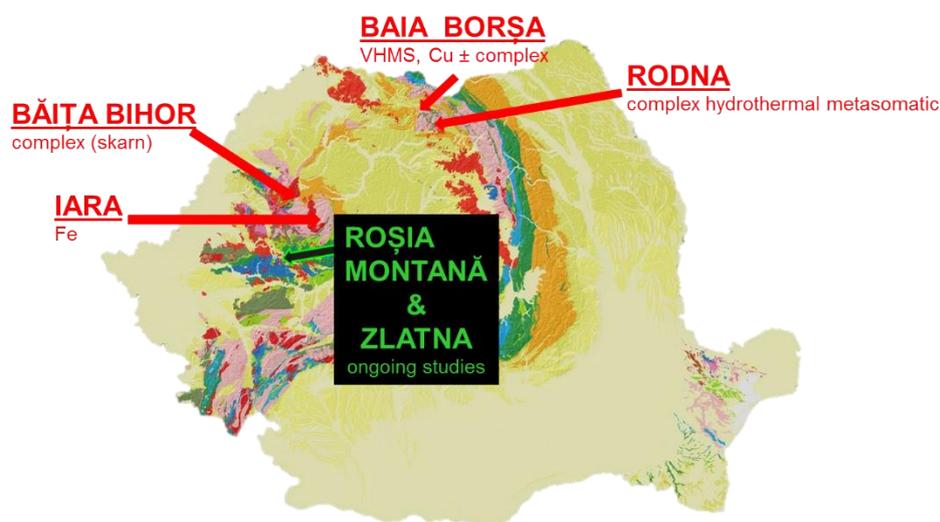
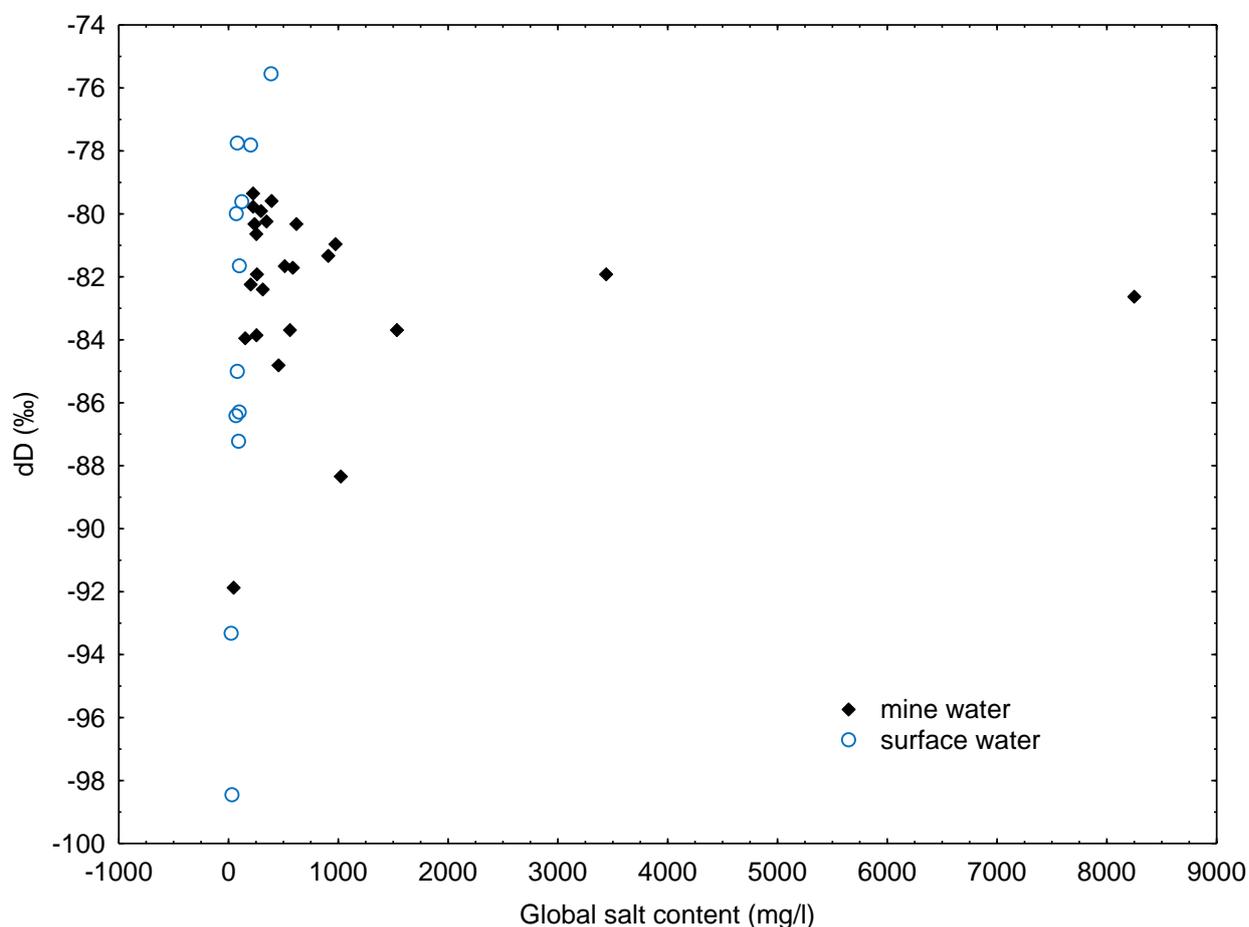


Figure 5 Surface water and groundwater related to mining areas. Case studies in the Carpathians (© Delia C. Papp, GIR).

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Table 5 Summary of the of δD (‰) values and total salt content (Δd) (mg/l) for different water sources from Baia Borşa mining district

		Min	Max	Mean	Std.Dev
All samples (no. of obs. 36)	δD (‰)	-98.45	-75.55	-82.92	4.54
	Δd (mg/l)	25.00	8249.40	650.00	1439.00
Mine water (no. of obs. 24)	δD (‰)	-91.87	-79.35	-82.38	2.90
	Δd (mg/l)	46.00	8249.40	918.77	1708.90
Surface water (no. of obs. 12)	δD (‰)	-98.45	-75.55	-84.09	6.80
	Δd (mg/l)	25.00	386.43	112.47	97.34



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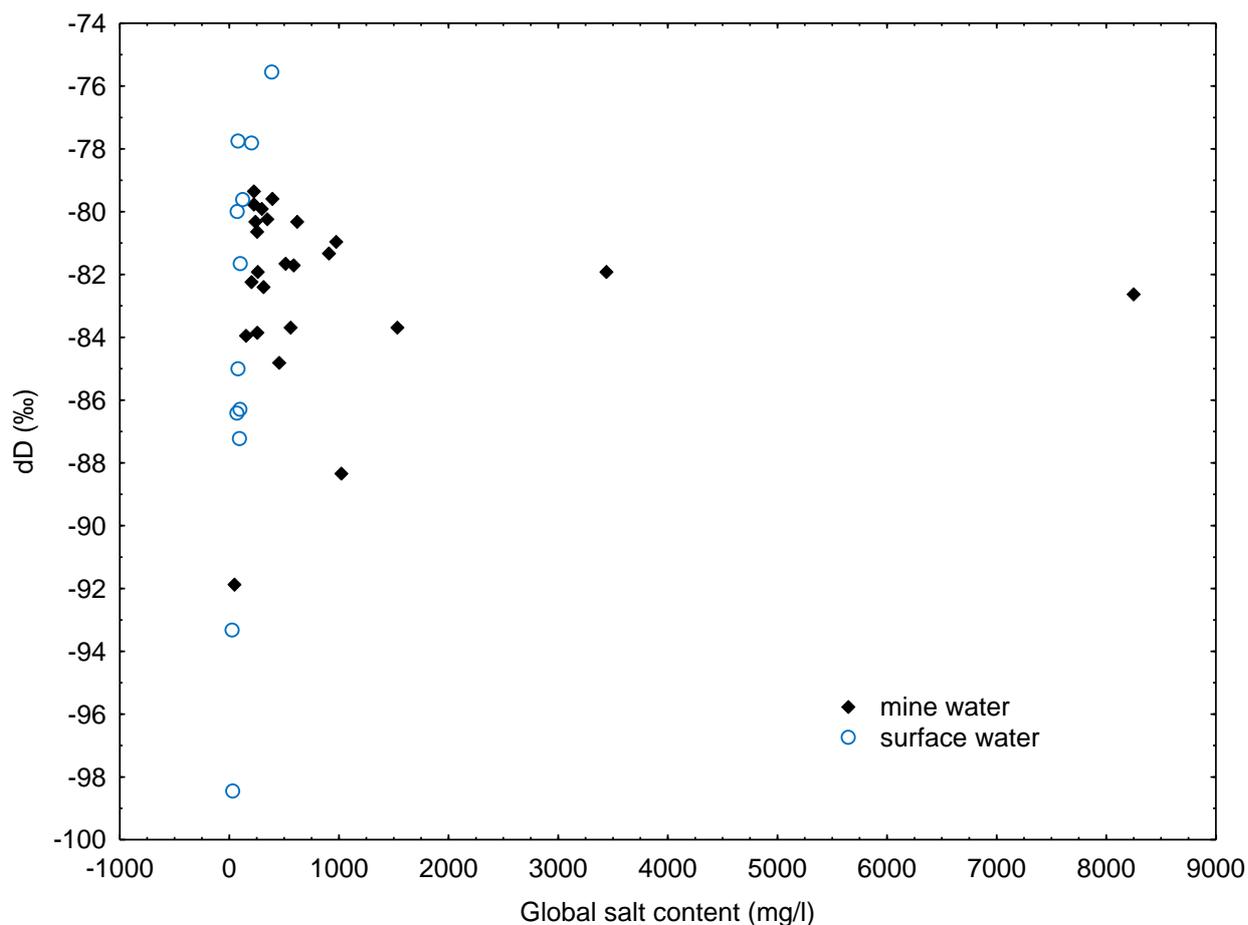


Figure 6 Scatter plot of the δD values and the total salt content for different water sources from Baia Borșa mining district (modified from Blaga et al 1983a).

Mine water displays δD values similar to those of the surface running water from the studied area. This, in combination with similar seasonal fluctuation in both Δd and δD between mine and surface waters, was interpreted to indicate mine water is of meteoric origin. However the total salt content varies significantly from one source to another. Some mine waters display similar Δd (mg/l) values to the surface water, but most are relatively elevated and a few are much higher (Figure 9). Occurrences of highly elevated total salt content is attributed to extensive underground circulation. Due to the evaporation during warm seasons, which causes enrichment both in deuterium and salts, a positive correlation between δD values and total salt content is expected for water of meteoric origin. For many water sources from Baia Borșa a low, or even negative correlation coefficient was obtained, indicating influence from phreatic water (Figure 7).

For mine water and surface water, several regression lines could be defined based on the δD values and the total salt content and were interpreted as mixing between different water sources to indicate flow path (Figure 8). For example, it was established that the water in the Novăț gallery resulted from the mixing between water from the Fractures I and II (Orz8) with the water type from Orz3 and G1300.

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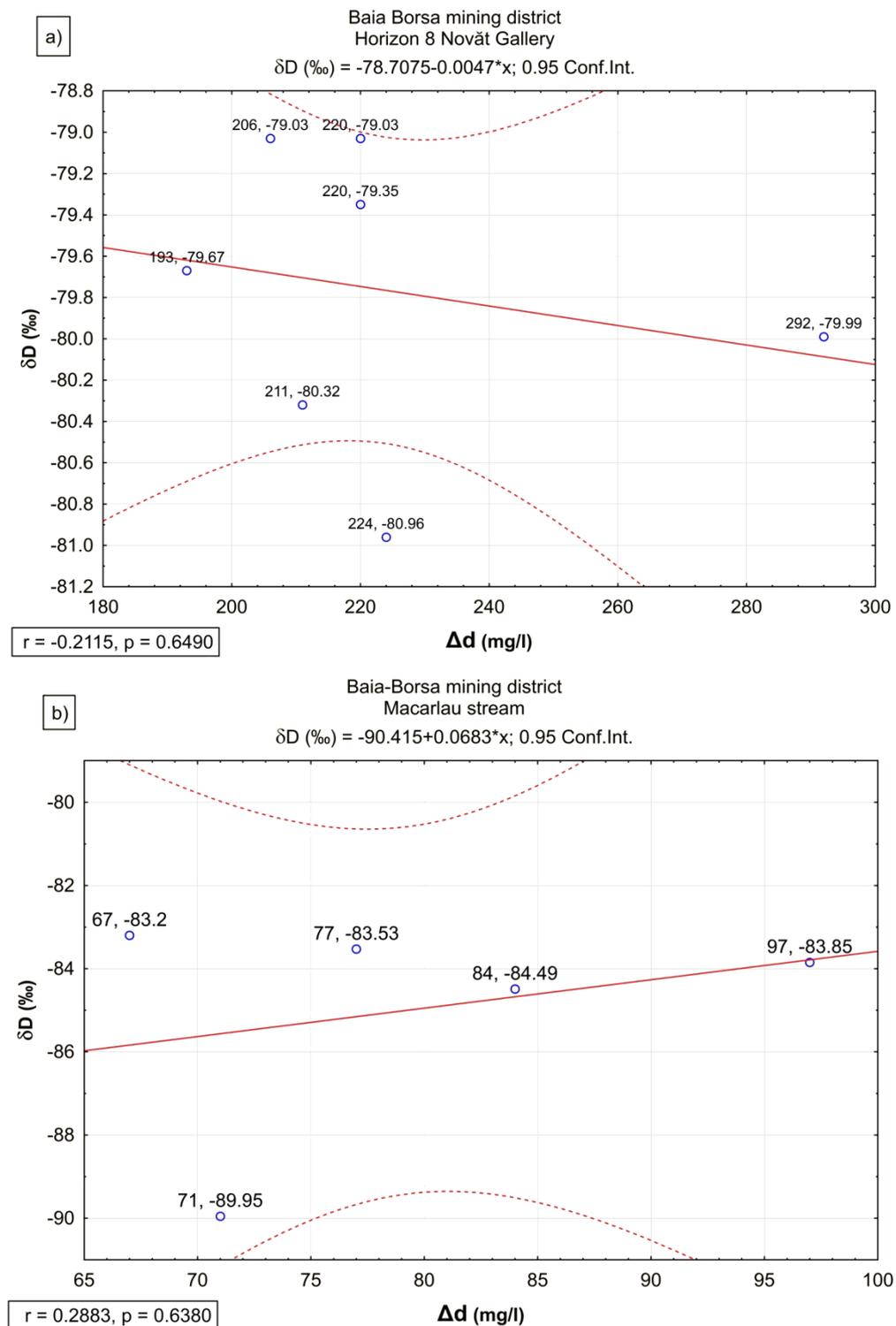


Figure 7 Correlation between δD values and total salt content for discrete mine and surface water sources in the Baia Borșa mining district: (a) Horizon 8 – Novăț Gallery; (b) Măcârlă stream (modified from Blaga et al 1983a). Solid lines show best fit regression, and dashed curves indicate 95% confidence interval.

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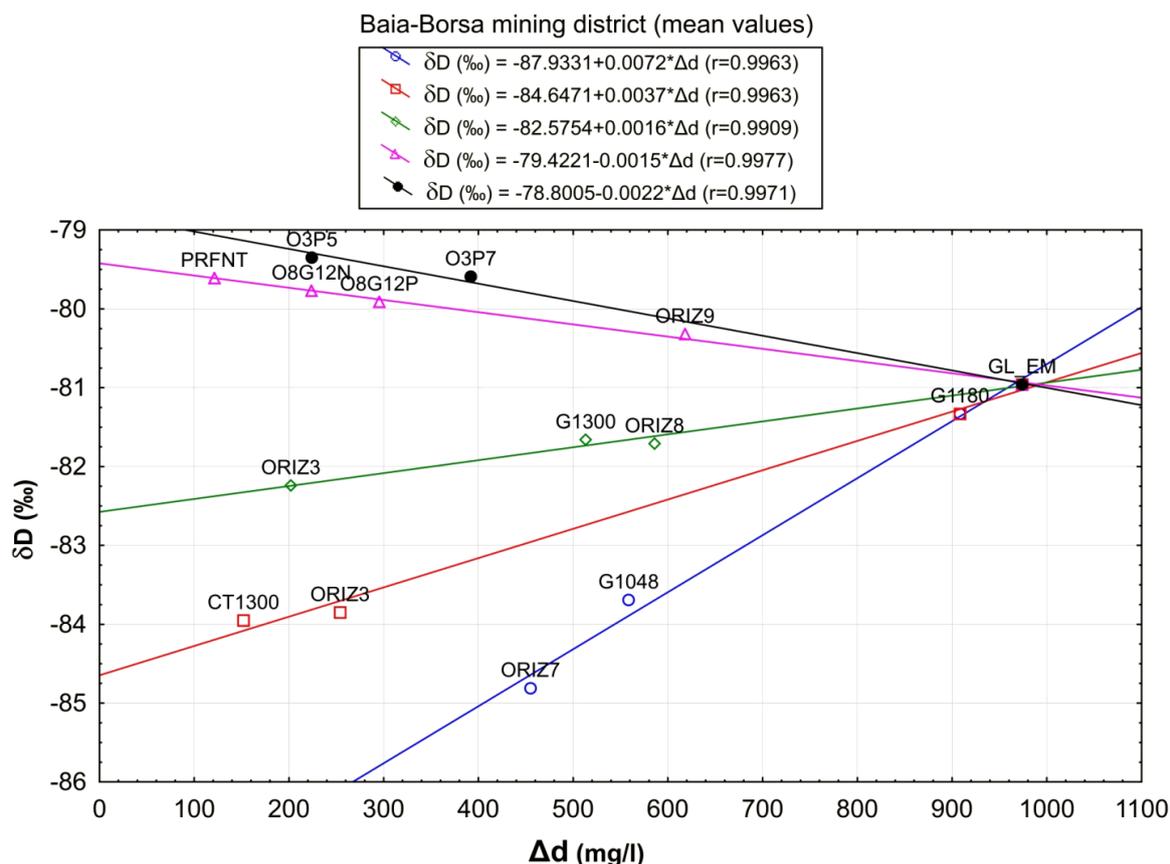


Figure 8 Regression lines defined by the δD values and total salt content for some water sources from the Baia Borsă mining district (modified from Blaga et al 1983a).

Both running water and mine water showed seasonal variation in δD values and total salt content, but the temporal sequence of minimum and maximum values in these parameters is unique at each source (Figure 9). Such temporal fluctuations are due to different infiltration patterns of the surface water and provide information on the underground flow rate. In surface water (Figure 9a, Figure 9b), a slight increase of δD and salt content occurs during warm seasons due to evaporation. During spring time both δD and salt content decrease due to snow melt. In Figure 9c, the δD and the salt content display minimum values in April and May due to the contribution of snow melt, followed by an increase in both parameters during warm seasons. This suggests rapid infiltration of the surface water and could indicate that infiltration fractures may remain active for a long period. In Figure 9d (mine water from the 6 Martie adit), the contribution of snow melt inputs occurs later in May and unlike other sites, δD and salt content do not fluctuate together. Additionally, the salt content is higher compared to other mine waters. Such findings are interpreted to indicate slower infiltration and/or long infiltration pathway. The main conclusions from combined physico-chemical and isotopic analysis of mine waters at Baia-Borsa are:

- mine water shows greater variation in total salt content than in the deuterium content compared to the local surface water;
- correlations between the δD values and total salt content show underground mixing phenomena between different water sources;
- seasonal variations in the δD values and the total salt content indicate a continuous refresh of mine water, though spatial differences in flow path and recharge rate are evident.

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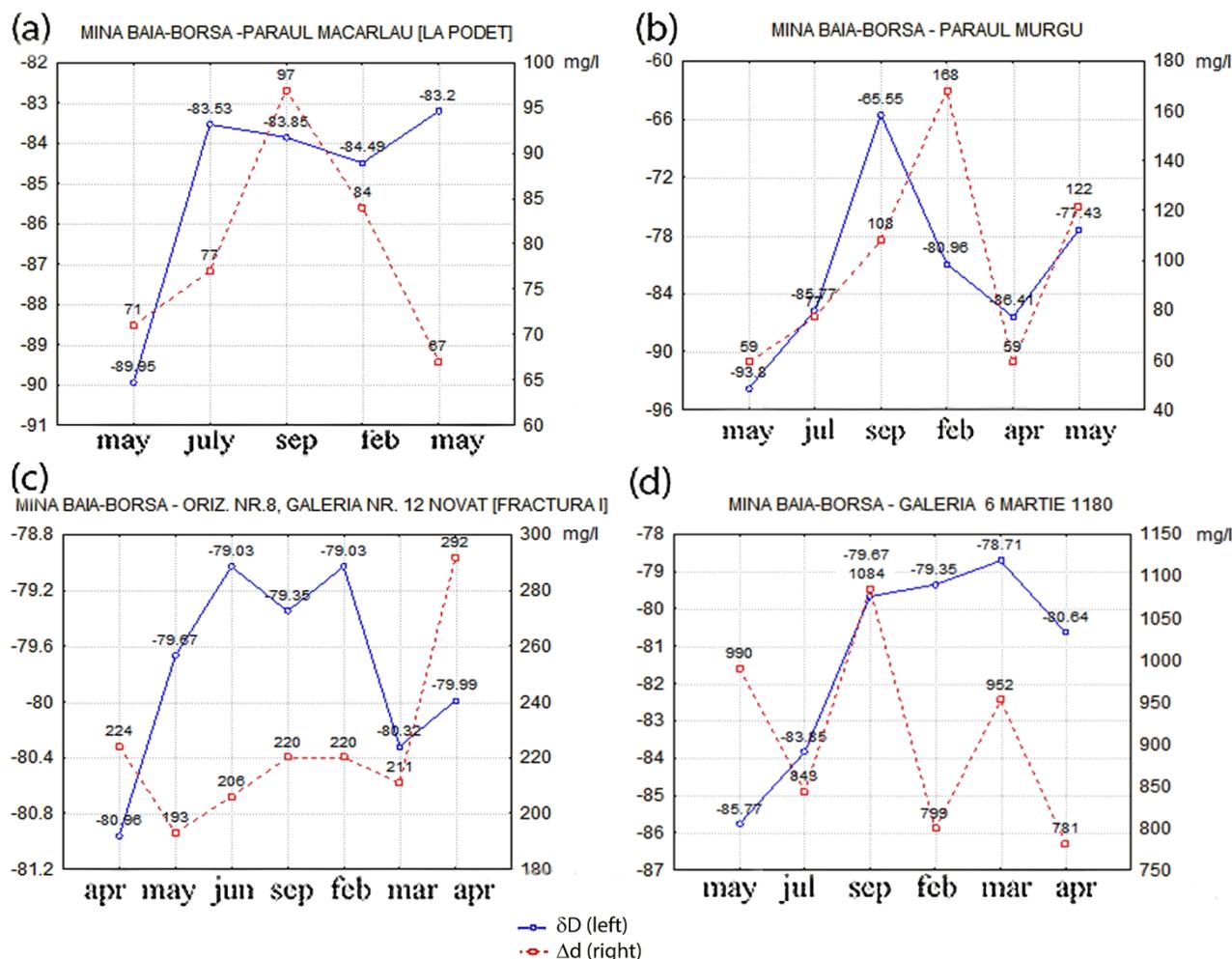


Figure 9 Seasonal variations of the δD values and total salt content for some water sources from the Baia Borșa mining district: (a) and (b) running waters; (c) and (d) mine waters (modified from Blaga et al 1983a).

3.3 Sulphur isotopes and mine environments

Sulphur (S) species are highly influential in acid rock drainage generation and exhibit measurable systematic variations in isotopic composition. Thus S isotopes have been utilized as tracers within mine water investigations (e.g. Taylor & Wheeler 1994, Knoller & Strauch 2002, Knoller et al. 2004, Edraki et al. 2005). The four stable isotopes of S are ^{32}S , ^{33}S , ^{34}S , and ^{36}S . These isotopes are subject to mass fractionation through chemical and biological processes (Faure & Mensing 2005). ^{32}S is the most abundant S isotope, comprising 95.04% of terrestrial S, followed by ^{34}S , at 4.20%. The ratio of $^{34}\text{S}/^{32}\text{S}$ (expressed as $\delta^{34}\text{S}$) is commonly used to evaluate mass dependant fractionation, as this comparison exploits the relatively large abundance of ^{34}S and its 6.2% difference in mass from ^{32}S . $\delta^{34}\text{S}$ is commonly expressed relative to the Canyon Diablo Troilite (CDT) standard derived from an iron meteorite and which has a $\delta^{34}\text{S}$ composition similar to terrestrial mafic rocks (e.g. Table 6) (Faure & Mensing 2005). Characteristic $\delta^{34}\text{S}$ values of different geologic materials are shown in Table 6. An understanding of the distribution of S isotope compositions and the mechanisms that drive isotope fractionation facilitate the use of $\delta^{34}\text{S}$ for assessing and allocating S sources to a given solution, as well as constraining mechanisms of solute mobility (e.g. Knoller & Strauch 2002, Edraki et al. 2005, Butler 2007, Nordstrom et al. 2010, Migaszewski et al. 2013).

Desk study of earlier mine environment studies by utilizing isotope and geochemical methods

Table 6 Approximate $\delta^{34}\text{S}_{\text{CDT}}$ characteristic of different geologic materials (adapted from Faure & Mensing 2005, Mitchell et al. 1998)

S Source	Approximate $\delta^{34}\text{S}$ (‰)
Modern marine sulphate	+20
Marine pyritic sulphide ¹	-27.5
Mafic igneous rocks ²	near 0
Felsic igneous rocks	+9 to -4
Petroleum	-8 to +32
Coal	-30 to +32.3

¹Average of reported values, while observed values range from -49.6 to +5.2 (Mitchell et al. 1998)

²The $\delta^{34}\text{S}_{\text{CDT}}$ is approximately equal to mafic igneous rocks. However, exceptions to this have been observed in ³⁴S enriched gabbro intrusions, indicating either changes in the isotopic composition of the earth's mantle, or fractionation within the magma (Faure & Mensing 2005).

3.3.1 Controls on S isotopes in solution

Fractionation of S isotopes can be induced by both kinetic and equilibrium processes. Equilibrium exchange occurs between sulphate and sulphides as a function of temperature and in general, ³⁴S enrichment follows S species oxidation state such that $\delta^{34}\text{S}$ is expected to decrease from $\text{SO}_4^{2-} > \text{SO}_3^{2-} > \text{S}_x^0 > \text{S}^2$ (Bachinski 1969, Faure & Mensing 2005, Hoefs 2009). Equilibrium exchange is also related to cation mass in coexisting sulphide species, such that heavier cations will bind ³²S more strongly, resulting in relative ³⁴S enrichment in compounds with lighter cations. For example, the $\delta^{34}\text{S}$ of coexisting minerals is expected to follow pyrite (FeS_2) > sphalerite (ZnS) > galena (PbS) (Sakai 1968, Bachinski 1969).

Kinetic fractionation during microbially mediated sulphate reduction is, however, the greatest source of isotopic variability in the S cycle (Faure & Mensing 2005, Canfield 2001). Under anaerobic conditions sulphur reducing bacteria metabolize sulphate during respiration to produce H_2S gas. During microbial sulphate reduction the S-O bond is preferentially broken among the lighter S isotopes resulting in ³²S enrichment in the reduced sulphur species and ³⁴S enrichment in the sulphate species (e.g. Faure & Mensing 2005, Seal 2006). An increase in $\delta^{34}\text{S}_{\text{SO}_4}$ in solution with decreasing SO_4 concentration is therefore characteristic of sulphur attenuation from solution through microbial reduction (Figure 10). S fraction attributed to microbially mediated reduction has been observed to range from 4-46‰ (Hoefs 2009, Seal 2006). Controls on the degree to which microbial reduction fractionates S are a continuing subject of research, though the magnitude of fractionation is generally anticipated to be inversely proportional to the rate of reduction, which is in-turn a function of temperature and sulphate concentration (Seal 2006, Hoefs 2009). Abiotic, temperature induced sulphate reduction, which may occur at temperatures as low as 100°C, may also fractionate S by 10 to 20‰ (Kiyosu & Krouse 1990).

Desk study of earlier mine environment studies by utilizing isotope and geochemical methods

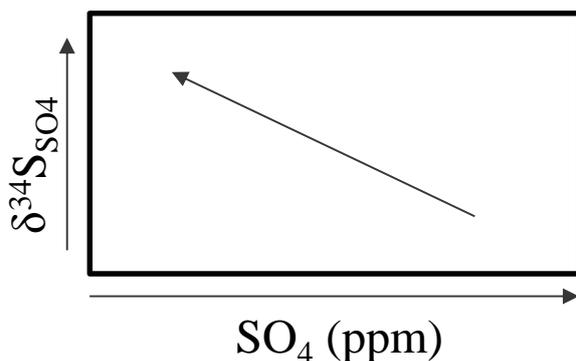


Figure 10 Schematic depicting relationship between $\delta^{34}\text{S}$ and SO_4 concentration in solution characteristic of microbial mediated sulphur reduction

S fractionation as the result of S reduction in a system with a finite sulphate supply will proceed as a Rayleigh distillation process (Equation 9) (Seal 2006). However, evidence of Rayleigh fractionation in a given system may be obscured by mixing between multiple sulphur sources (Equation 10), as well as the re-oxidation of relatively ^{34}S depleted secondary sulphide (Canfield 2001). The oxidation of mineral sulphide to sulphate induces little (plus or minus a few per mil) to no isotopic fractionation (Toran & Harris 1989, Taylor & Wheeler 1994), resulting from the quantitative oxidation of the sulphide (Seal 2006). Cyclical re-oxidation and reduction of S has been proposed as a mechanism to explain marine sulphide that is depleted by more than 70‰ relative to coexisting sulphates (Hoefs 2009).

To utilize S isotopes in a mass balance therefore requires consideration of potential sulphate sources (mineral weathering, anthropogenic and atmospheric sulphur inputs), as well as process related fractionation factors (sulphate reduction, redox cycling, and exchange reactions) (Nordstrom et al. 2010). Where the isotopic compositions of sulphate end members are constrained, comparison of $\delta^{34}\text{S}$ of aqueous sulphate ($\delta^{34}\text{S}_{\text{SO}_4}$) to sulphate concentration (SO_4) has been used to assess both sulphur source in solution, as well as processes influencing sulphur mobility (Edraki et al. 2005, Bernot et al. 2007, Junghans & Tichomirowa 2009, Migaszewski et al. 2013). Additional water quality data, chemistry parameters and isotope measurements are also commonly used in conjunction with sulphur isotope data to characterize potential end member sulphur sources and fractionating processes. Specifically, the isotopic composition of O in sulphate ($\delta^{18}\text{O}_{\text{SO}_4}$) is commonly used to compliment $\delta^{34}\text{S}_{\text{SO}_4}$ data to identify mixing, as variation in $\delta^{18}\text{O}$ may elucidate endmembers not evident from $\delta^{34}\text{S}_{\text{SO}_4}$ alone, and redox pathways (e.g. Knoller et al. 2004 Pellicori et al. 2005, Balci et al. 2007, Nordstrom et al. 2010).

3.3.2 S Sample collection and analysis considerations

Sample collection, preparation and analytical techniques vary widely for sulphur isotope studies, and are dependent, in part, on the sample medium and the desired sulphur compound(s) for analysis. For mine water studies, where characterization of sulphur source as well as process related fractionation is of interest, it is advantageous to collect samples from all potential sulphur end members for chemical and isotopic characterization. For example, to provide constraints on sulphur sources at a given mine site may require isotopic analysis of aqueous sulphate, primary sulphur bearing minerals, secondary sulphur minerals and precipitates, as well as any known industrial sulphur sources in the area (e.g. Edraki et al. 2005, Migaszewski et al. 2008, Junghans & Tichomirowa 2009). Water samples are typically collected following protocol conducive for anion analysis.

For isotopic analysis of sulphur in solid or aqueous media, the sulphur must first be extracted

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from the media. Sulphur extraction methods vary depending upon analytical technique. For environmental applications, the currently preferred analytical technique is by MC-ICP-MS, which has facilitated analysis of solutions with lower S concentration relative to the previously used gas source IRMS methods (Paris et al. 2013). Paris et al. (2013) introduced the MC-ICP-MS method by which high precision (reproducibility $2\sigma < 0.15\%$) could be attained from small sample size (5 to 40 nmol S). For isotopic analysis of S by MC-ICP-MS, solids are digested and sulphate is extracted from solution by ion chromatography. Paris et al. (2013) purified sulphur using the strong cationic resin AG50x8 (Bio-Rad). Hanousek et al. (2016) provides a variation on this approach in which sulphate separation was conducted using commercial anion exchange resin membranes (551642S, VWR).

3.3.3 Case Studies: S isotope tracer applications

Various applications of sulphur isotope tracer applications within mine site environmental investigations are illustrated in the following sections through the brief summary of different case studies. For additional details, please refer to the original studies and references there-in.

3.3.3.1 $\delta^{34}\text{S}$ and Site Mineralogy

Relationships between SO_4 concentrations and $\delta^{34}\text{S}$ were used to constrain the relative influence of different sulphur sources to solution in the mine-impacted Animas watershed in Colorado, USA through consideration of site specific mineral abundance, solubility, and dissolution rates (Nordstrom et al. 2010).

Water from streams, groundwater springs and mine adits was analysed for $\delta^{34}\text{S}$ of sulphate throughout the watershed. Additionally, the two mineral sources of sulphate with the lowest solubility in the watershed, pyrite (FeS_2) and gypsum ($\text{CaSO}_4 \cdot \text{H}_2\text{O}$), were analysed for $\delta^{34}\text{S}_{\text{CDT}}$. The authors found that gypsum was distinctly enriched in ^{34}S relative to pyrite, exhibiting $\delta^{34}\text{S}$ from +15 to +18 and -6.9 to +2.5, respectively. The enriched ^{34}S of gypsum indicated that the occurrence of this mineral was not a secondary product of acid drainage neutralization, but rather of hypogene origin. Additionally, it provided an isotopic tracer for characterizing waters impacted by these two sources of sulphur.

A comparison of dissolved calcium to sulphate concentrations in solution showed that samples with $\delta^{34}\text{S}$ compositions $> 4\%$ plotted near the 1:1 line representative of congruent gypsum dissolution, suggesting significant influence by gypsum dissolution in these waters. This stoichiometric relationship was used in conjunction with $\delta^{34}\text{S}$ to investigate the relationship between sulphur source and water quality (Figure 11). Where the calcium/sulphate molar ratio $[(\text{Ca})/(\text{SO}_4^{2-})]$ of waters was between 0.6 to 1.1, $\delta^{34}\text{S}$ was commonly $> 4\%$, suggesting waters with gypsum dominated sulphate origin. The pH in these waters ranged from 3-6. Where $(\text{Ca})/(\text{SO}_4^{2-})$ was 0.6, $\delta^{34}\text{S}$ was consistently $< 4\%$ and pH was < 4 , suggesting pyrite weathering was the dominant sulphate source in these waters. However, the occurrence of some samples with $\delta^{34}\text{S} < 4\%$ at elevated pH and $(\text{Ca})/(\text{SO}_4^{2-})$ indicated a third Ca source other than gypsum influencing the solute composition in these waters. The third Ca source was defined as calcite dissolution from an understanding of the regional geology and solute chemistry.

The consistency observed between the $(\text{Ca})/(\text{SO}_4^{2-})$ molar ratio, $\delta^{34}\text{S}$, and anticipated pH of different waters support the likelihood that sulphate concentrations are controlled by three processes across the water shed: weathering of pyrite, dissolution of gypsum/anhydrite, and dissolution of both gypsum/anhydrite as well as calcite. Because the other known sulphate minerals in the watershed, barite, alunite, and jarosite, occur at lower abundance and have lower solubility, it was inferred that these three processes act as the dominant controls on

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sulphate solubility in solution. The relative influence of each of these controls on sulphate concentration in solution at each sample site throughout the watershed could then be depicted through a comparison of $\delta^{34}\text{S}$ and $(\text{Ca}/\text{SO}_4^{2-})$ (Figure 12).

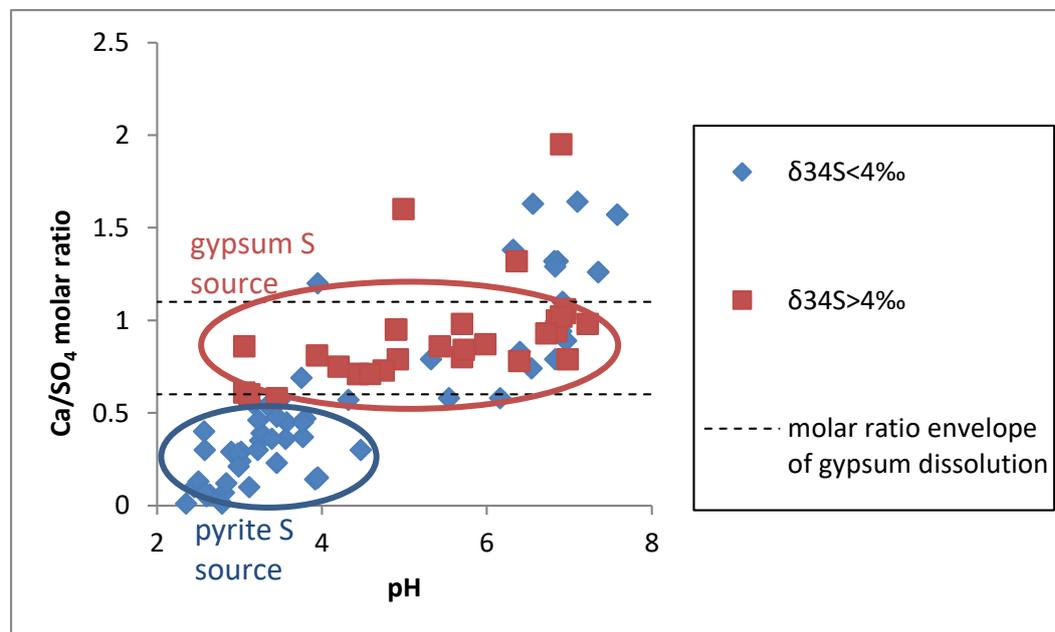


Figure 11 Comparison of Ca/SO_4 molar ratio against pH with consideration to $\delta^{34}\text{S}_{\text{SO}_4}$ for Animal River watershed samples (Adapted from Nordstrom et al. 2010).

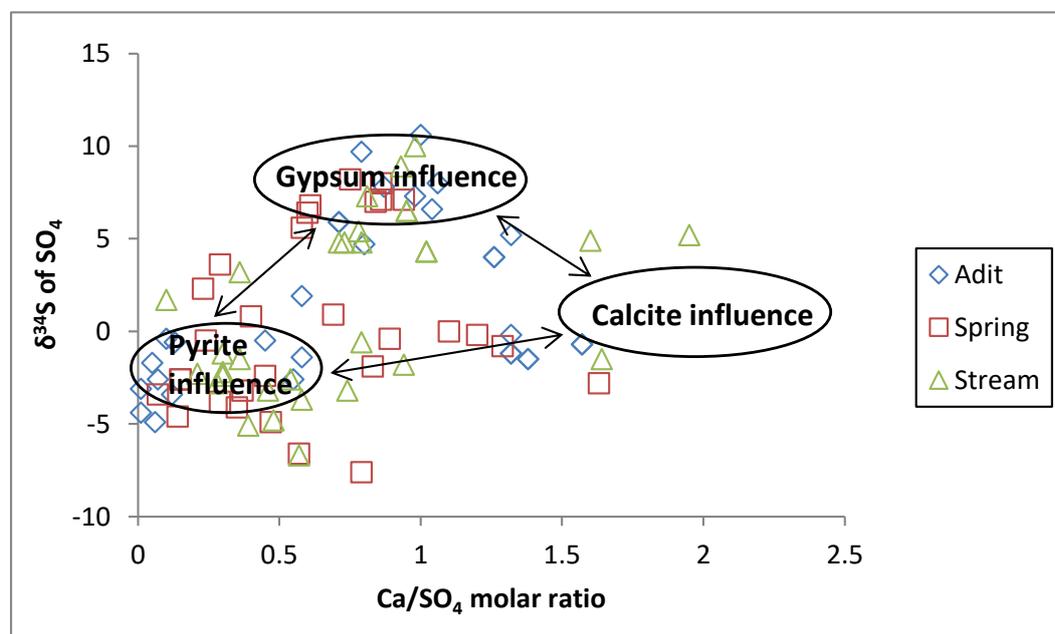


Figure 12 Arrows show hypothetical mixing between waters with different mineral controls on sulphate concentration.

In another case study example of sulphur isotopes used as a source tracer, Tichomirowa et al. (2010) identified the influence of an industrial sulphate source in addition mining related sulphate through a spatial comparison of $\delta^{34}\text{S}_{\text{SO}_4}$ against $1/(\text{SO}_4)$ across a site. Background water samples exhibited low sulphate concentrations and positive $\delta^{34}\text{S}$, while residual ore pore water had high sulphate concentration and low $\delta^{34}\text{S}$. These waters formed end members along

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which mine adit waters plotted, reflecting two part mixing between background water and mine impacted water (Figure 13). While water from an upper gallery also plotted along this mixing line, water sampled from lower galleries did not, suggesting a third sulphate source (Figure 13).

While water associated with the ore end member in Figure 13 generally exhibited elevated concentrations of Zn, Pb, Cu and Cd, the samples that did not plot on the ore-background water mixing line had notable concentrations of Cl, F, Na, Ca, and Pb. The differences in solute composition supported isotope data to suggest that historic industrial waste deposits act as the third source of isotopically distinct sulphate to site waters (Tichomirowa et al. 2010).

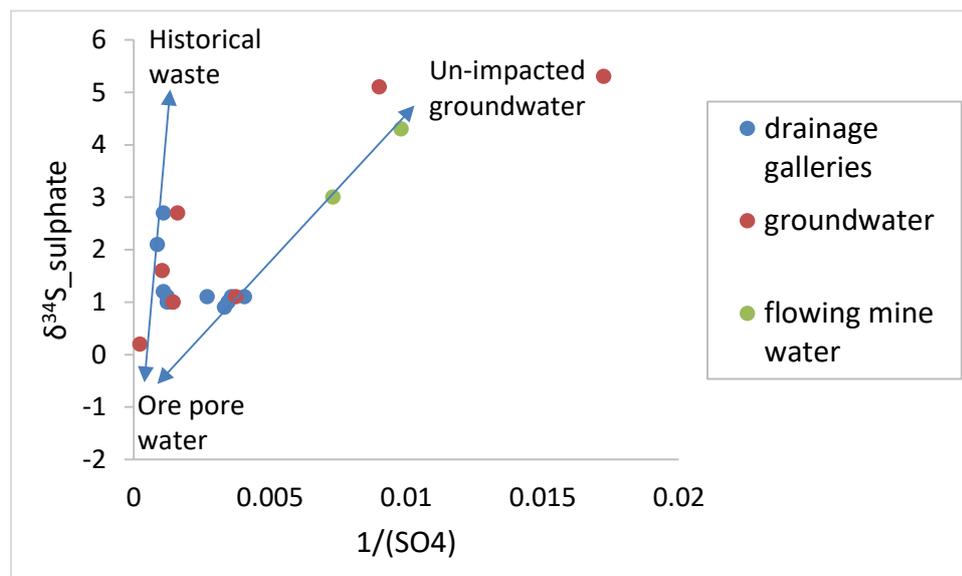


Figure 13 Two distinct mixing lines indicating distinct sources of sulphate to mine and groundwater (modified from Tichomirowa et al. 2010).

3.3.3.2 $\delta^{34}\text{S}$ and Atmospheric Sulphur Deposition

Sulphur inputs to the atmosphere can be diverse (e.g. anthropogenic, ocean aerosol, volcanogenic, biogenic) and vary both spatially and temporally (Nriagu & Coker 1978). However, because atmospheric sulphur deposition occurs primarily through precipitation, analysis of precipitation contemporary with sampling can be used to gain an approximate understanding of atmospheric sulphur inputs at a particular site (Faure & Mensing 2005). In the work described by Nordstrom et al. (2010), sulphur content in precipitation was negligible relative to the high concentrations in site waters, allowing precipitation influences to be ignored during the assessment of sulphate sources. Migaszewski et al. (2008) similarly identified negligible influence by precipitation on the $\delta^{34}\text{S}_{\text{SO}_4}$ in the water of a flooded open pit mine based on mass balance considerations. However, a control pond at their site, which was not influenced by pyrite oxidation, showed sulphate concentrations that reflected the $\delta^{34}\text{S}$ of local precipitation, which illustrates the potentially significant influence of precipitation on water $\delta^{34}\text{S}$. Clark and Fritz (1997) also recognize sulphur inputs from precipitation as a potentially significant influence to the isotopic composition of surface waters, soil water, or shallow groundwater. Sulphur inputs from precipitation are particularly relevant at sites where there is relatively little influence from mineral weathering, such as was observed in the control pond by Migaszewski et al. (2008).

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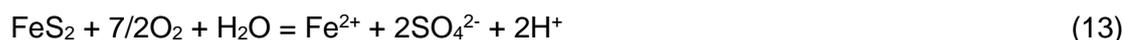
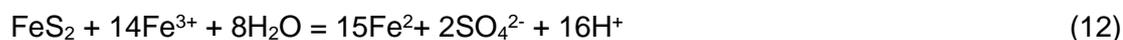
3.3.3.3 $\delta^{34}\text{S}$ and Oxidation-Reduction Processes in Solution

Influences from oxidation-reduction processes are particularly relevant in mine waters, wetlands, or other areas that may host both oxic and anoxic waters. In a flooded open pit mine in south central Poland Migaszewski et al. (2008) observed influences of both sulphate reduction and oxidation. The mine wall mineralogy included efflorescent sulphates that closely resembled the depleted $\delta^{34}\text{S}$ of the local pyrite. These sulphates were thus interpreted to result from the quantitative oxidation of the pyrite. The aqueous sulphate of mine water was enriched in ^{34}S relative to in-situ pyrite and efflorescent sulphates. Further, $^{34}\text{S}_{\text{SO}_4}$ enrichment increased with decreasing S concentration ($R^2 = 0.42$). Therefore, with consideration to mass balance, enrichment could not be attributed to an additional sulphate source, such as atmospheric sulphur deposition. The correlation in $\delta^{34}\text{S}_{\text{SO}_4}$ and $1/(\text{S})$ was subsequently interpreted as evidence of the progressive enrichment of $^{34}\text{S}_{\text{SO}_4}$ in solution through microbial reduction and removal of sulphate from the mine waters.

In the Dee River, near the Mount Morgan Au-Cu mine in Australia, Edraki et al. (2005) observed general similarity in aqueous $\delta^{34}\text{S}_{\text{SO}_4}$ and primary sulphide minerals, indicating aqueous sulphate in the river resulted from the quantitative oxidation of mining related sulphides. A correlation between $\delta^{34}\text{S}_{\text{SO}_4}$ and $1/(\text{S})$ in the downstream direction despite no evidence for fresh water dilution provided evidence for seasonal bacterial sulphate reduction in the stream as a mechanisms of sulphate attenuation (Edraki et al. 2005).

3.3.3.4 $\delta^{18}\text{O}$ of Sulphate

The contemporaneous evaluation of $\delta^{18}\text{O}_{\text{SO}_4}$ with $\delta^{34}\text{S}$ has the potential to strengthen sulphate source interpretations, as well as provide information on pyrite oxidation mechanisms. $\delta^{18}\text{O}_{\text{SO}_4}$ commonly exhibits greater variation between sulphate source end members such as precipitation, soil water and surface water than does $\delta^{18}\text{O}_{\text{SO}_4}$ (Mitchell et al. 1998). $\delta^{18}\text{O}_{\text{SO}_4}$ varies between sulphate sources due to large variation in $\delta^{18}\text{O}$ between molecular oxygen and water, microbial influence on the source of oxygen in sulphate (water or molecular oxygen), and the preservation of source oxygen signature in $\delta^{18}\text{O}_{\text{SO}_4}$ resulting from the low rate of oxygen isotope exchange between sulphate and water (Holt & Kumar 1991). Conversely, fractionation of sulphur during sulphide oxidation is relatively minor. Additionally, the traceable microbial influence on $\delta^{18}\text{O}_{\text{SO}_4}$ can provide insight to oxidation mechanisms (Taylor et al. 1984). Under abiotic conditions, ferric iron (Fe^{3+}) oxidizes pyrite at a significantly greater rate than molecular oxygen (O_2). During pyrite oxidation by Fe^{3+} , the oxygen in sulphate is derived solely from the water molecule, as shown in Equation 12. Conversely, the microbial mediated oxidation of pyrite by O_2 results in sulphate with oxygen derived primarily (87.5%) from O_2 , as shown in Equation 13.



This distinction in oxygen source is important because water is significantly depleted in ^{18}O ($\delta^{18}\text{O}$ ranging from approximately -50 to +10 ‰) relative to atmospheric O_2 (approximately +23.5‰). With consideration given to the source dependant fractionation of O during the formation of aqueous sulphate ($\epsilon = +4.1\text{‰}$ and -11.2‰ for H_2O and O_2 sources, respectively), the dominant oxidant source, and therefore mechanism for sulphate generation can be interpreted from $\delta^{18}\text{O}_{\text{SO}_4}$ (Taylor et al. 1984).

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As summarized from Nordstrom et al. (2010), interpreting $\delta^{18}\text{O}_{\text{SO}_4}$ can be complicated by the following variables:

- under highly acidic or high temperature conditions, isotopic equilibrium exchange of O between water and sulphate molecules in solution is accelerated
- mechanisms of microbial O exchange are not fully constrained
- the presence of unstable sulphoxyanions may impact oxygen isotope compositions
- $\delta^{18}\text{O}$ of water can vary temporally due to climate, mixing of water sources, or evaporation

3.4 Strontium isotopes and mine environments

Isotopic analysis of strontium (Sr) has been utilized across a range of studies applicable to mine water characterization, including evaluation of flow pathways, connectivity, water-rock/soil interactions (e.g. Shand et al. 2007, Shand et al. 2009, Tichomirowa et al. 2010), mineral weathering rates (Blum et al. 1993), salinity sources (Shand et al. 2009), and contaminant fate and transport (e.g. Cary et al. 2014, Khaska et al. 2015).

There are four stable isotopes of Sr, ^{88}Sr , ^{87}Sr , ^{86}Sr , and ^{84}Sr , which exist in nature at the relative abundances of 82.5%, 7.04%, 9.87%, and 0.56%, respectively (Dasch 1969). None of the isotopes of Sr are significantly fractionated by chemical or biological processes, but variation in Sr isotopic composition arises as the result of ongoing generation of ^{87}Sr through the beta decay of ^{87}Rb , which has a half-life of 4.9×10^{10} years. Therefore, while ^{88}Sr , ^{86}Sr , and ^{84}Sr occur in rocks at known relative abundances, variability in ^{87}Sr is dependent on the initial relative concentrations of Rb and Sr in a host rock, and the age of that rock. (Dasch, 1969, Palmer and Edmond 1992, Maurer et al. 2012).

The isotopic composition of Sr is commonly expressed as an absolute ratio of ^{87}Sr to ^{86}Sr , but can also be expressed using δ notation relative to sea water. A large range of Rb to Sr concentrations $[(\text{Rb})/(\text{Sr})]$ exists across different lithologies, from 0.06 in mafic rocks, to 1.7 in Ca-poor granites, resulting in the potential for high variability in ^{87}Sr abundance (Kendall and McDonnell 1992, Faure and Mensing 2005). Due to similar chemical properties with Ca, during mineral crystallization Sr occurs most abundantly in calcium rich minerals such as plagioclase, apatite, and calcium carbonate via lattice substitution for Ca^{2+} (Capo et al. 1998). Conversely, Rb, which has a similar radius and ionic charge to potassium (K^+), occurs most abundantly in K rich minerals such as micas and feldspar. In accordance with Bowen's reaction series, felsic rocks generated during late stage magma differentiation have greater relative $(\text{Rb})/(\text{Sr})$, lower Sr concentrations, and are enriched in ^{87}Sr relative to mafic rocks. (Kendall and McDonnell 1992, Clark and Fritz 1997).

Major variables that influence the isotopic composition of Sr in water from a given source include (Faure & Mensing 2005):

- Host rock mineralogy $((\text{Rb})/(\text{Sr})$ concentration)
- The relative susceptibility of Sr containing minerals to dissolution
- Exposure of Sr containing minerals to weathering
- Mixing of waters from different sources

Both dissolution kinetics and mineral exposure to weathering will influence solution $^{87}\text{Sr}/^{86}\text{Sr}$ composition. While the lithology present in water-rock interactions is a major control on the isotopic composition of strontium in solution, the $^{87}\text{Sr}/^{86}\text{Sr}$ composition of water generally does not reflect that found from whole rock analysis due to variability in $^{87}\text{Sr}/^{86}\text{Sr}$ among different minerals and incongruent mineral weathering. Variability in weathering rates between minerals within the same rock result in disproportionate influence from fast weathering minerals on the $^{87}\text{Sr}/^{86}\text{Sr}$ composition of a solution. According to Kendall and McDonnell (1998) and Shand et

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al. (2009), assessing the relationship between $^{87}\text{Sr}/^{86}\text{Sr}$ of solid phase and solution presents a persistent complexity in the interpretation of Sr isotopic data. While the $^{87}\text{Sr}/^{86}\text{Sr}$ composition of a water reflects mineral weathering inputs, anthropogenic inputs, and atmospheric aerosol deposition, it is not appreciably fractionated through physical, chemical or biological processes (Shand et al. 2009, Capo et al. 1998). For this reason $^{87}\text{Sr}/^{86}\text{Sr}$ is a commonly utilized tracer of water source, pathway and mixing (Shand et al. 2009).

3.4.1 Sr isotope tracer applications

Sr isotope composition has been applied, in combination with other geochemical data to characterize geochemical, hydrologic and hydrogeologic conditions of surface and groundwater sites. Sr isotopes can be applied to the study of mine waters as a means to characterize the geochemical evolution of site waters including flow paths, connectivity, mineral weathering rates, and end member delineation (e.g. Négrel et al. 2005, Shand et al. 2007, Shand et al. 2009, Tichomirowa et al. 2010, Cary et al. 2014). Limitations of Sr isotope methods arise when a predominant Sr source obscures the influence of mixing, or when end members are not isotopically distinguishable (Shand et al. 2009).

A common means of assessing end member mixing, potential flow path and connectivity is by plotting $^{87}\text{Sr}/^{86}\text{Sr}$ against Sr concentration [1(/Sr)]. Using this method, water source end members defined by disparate geochemical histories, for example groundwater and precipitation, can be established, and their relationship to water of undefined origin (e.g. surface water) can be identified. When samples plot between end members, relative contributions of source waters can be estimated. Conversely, if a sample does not plot between identified end members, additional influences to Sr isotope composition can be inferred. Figure 14 provides an illustration of groundwater mixing relationships as may be interpreted from Sr isotopic data. This end member approach can also be used to identify the nature and geographic distribution of hydraulic continuity between end member waters, or sources of salinity in water (Shand et al. 2009). Additionally, $^{87}\text{Sr}/^{86}\text{Sr}$ plotted against surface water flow rate can illustrate variability in source water under changing flow conditions (e.g. Shand et al. 2009, Wortberg 2015).

Variations of Sr isotopic fingerprinting include plotting $^{87}\text{Sr}/^{86}\text{Sr}$ against:

- concentrations of a contaminant of concern to define contaminant source and pathway (Cary et al. 2014, Khaska et al. 2015)
- other major cation concentrations, or cation/Sr ratios to distinguish lithologic and mineral controls
 - concentration of suspended Fe to illustrate Fe control on differences in $^{87}\text{Sr}/^{86}\text{Sr}$ signature across solute phases (Wortberg 2015)
 - Ca/Sr and Mg/Sr ratios to illustrate lithologic end-member controls (Négrel et al. 2005, Cary et al. 2014)
- $\delta^2\text{H}$ or $\delta^{18}\text{O}$ to show influence of an end member that has undergone evaporation (Kendall & McDonnell 1998, Khaska et al. 2015)

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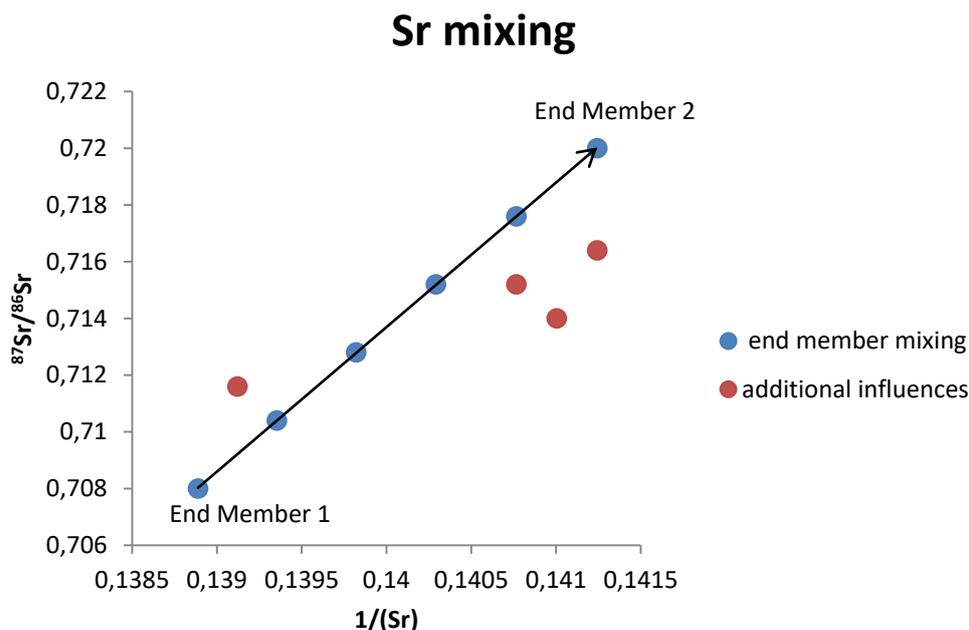


Figure 14 Illustration of linear mixing between two end members and data reflecting influences other than two part mixing (modified from Shand et al. 2007).

3.4.2 Sr sample collection and analysis considerations

The isotopic composition of Sr has been observed to depend on the colloidal particle size included in the sample (Wortburg 2015). Therefore, water filtration is an important consideration during sample collection, as it may lead to sample results that do not reflect the isotopic composition of total water. Commonly, water samples are collected in an acid washed, pre-rinsed sampling apparatus, and filtered to 0.2-0.45 μm into a polyethylene or HDPE sample container. The volume of sample required for a single analysis depends on the Sr concentration in the sample and analytical method specifics, and may range, for example, from 0.1 ml of high concentration solution to 30 ml of background sample (Mänttari 2016).

Solid samples are digested and Sr is extracted from solution using ion chromatography methods to facilitate isotopic analysis (e.g. Meynadier et al. 2006). Isotopic analysis of Sr is routinely conducted either using thermal ionization mass spectrometry (TIMS) or MC-ICP-MS. As little as a few nanograms Sr can be used for a single isotopic analysis, though to facilitate replicate analyses 0.4 to 1 μg purified Sr is preferred (Capo et al. 1998). Replicates that have $2\sigma \leq 0.003\%$ are considered acceptable high precision Sr isotope results, while $^{87}\text{Sr}/^{86}\text{Sr}$ ratios may be reported with precision down to the 6th decimal place (i.e. $\pm <0.00001$) using TIMS (Wortberg 2015). Mass bias induced during sample analysis can be corrected for by sample-standard bracketing using an international reference standard such as SRM-987 (Monna et al. 1998), or by defining a fractionation factor based on the known $^{86}\text{Sr}/^{88}\text{Sr}$ ratio of the samples (Capo et al. 1998).

3.4.3 Sr isotope Case Study

With regard to the application of Sr isotopes as a tool for tracing source waters in hydrological studies Wortberg (2015) investigated controls on the seasonal variability of $^{87}\text{Sr}/^{86}\text{Sr}$ observed

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in the Kalix River with a focus on the influence of suspended Fe phases. An important consideration when using Sr isotope data to interpret water sources in this catchment is the role of suspended Fe phases on Sr mobility. Fe precipitates act as strong scavengers of trace metals, and the Kalix River is characterized by high Fe concentration, with its suspended load being dominated by Fe-organic carbon (OC) aggregates. Further, the $^{87}\text{Sr}/^{86}\text{Sr}$ composition of Kalix river water samples correlates to the sample filter size [i.e. samples filtered to smaller size fractions have lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (Wortberg 2015)].

During springtime high flow, Fe suspended in river water is believed to be derived from complexes of Fe and organic carbon (Fe-OC) formed at the redox boundary in the riparian zone of forested areas of the Kalix river catchment. During base flow, suspended Fe is believed to be derived from Fe-oxyhydroxides which originate from wetland soils, and become coated in organic matter (Fe-OM) through adsorption. Wortberg (2015) hypothesized that the trends observed between $^{87}\text{Sr}/^{86}\text{Sr}$ and flow regime are related to the two distinct sources of Fe in the river suspended load.

Samples were collected from the Kalix River and the geochemically similar Råne River to compare isotopic variation in Sr between different catchments. The Råne river catchment consists of a greater proportion of wetlands, and was therefore anticipated to reveal less seasonal isotopic variability, reflecting a more singular source of recharge than the Kalix. Surface water samples were collected from the Kalix River from March to June of 2014 and from the Råne River from March to May 2014. Sample dates were selected to encompass the peak flow periods of each river. Water samples were analysed for major and trace ions, dissolved organic carbon, and Sr isotopes. Major and trace ions were analysed using Inductively Coupled Plasma Sector Field Mass Spectrophotometry (ICP-SFMS) with an accuracy of 5-15%. Samples for Sr isotope analysis were pre-filtered to 70 μm and then ultrafiltered to separate the suspended phase (>1 kDa) and the truly dissolved phase (<1 kDa) using a cellulose filter. Sr was extracted from dried samples using column chromatography methods and $^{87}\text{Sr}/^{86}\text{Sr}$ was analysed using TIMS with a long term reproducibility of ± 0.0000082 .

Wortberg (2015) found greater difference in the $^{87}\text{Sr}/^{86}\text{Sr}$ between the two catchments, and seasonally within each catchment, than was observed between the truly dissolved and suspended phases within a single catchment (Figure 15). However, both the Kalix and Råne Rivers showed small but significant difference (2σ) in $^{87}\text{Sr}/^{86}\text{Sr}$ between truly dissolved and suspended phases of Sr before and during spring flooding. After spring flooding in the Kalix River, the difference between $^{87}\text{Sr}/^{86}\text{Sr}$ was observed to diminish (Figure 15). Further, Sr concentrations in both rivers were much higher in the truly dissolved phase than the suspended phase before flooding. However, during spring flooding Sr concentrations in the truly dissolved phase decreased, while concentrations in the suspended phase remained constant, resulting in a greater influence from the suspended phase on the total river water $^{87}\text{Sr}/^{86}\text{Sr}$ (Figure 16).

Wortberg (2015) proposes the source of more radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ in the suspended relative to the truly dissolved phase in the Kalix River is driven by Fe in the suspended phase. This is supported by a strong correlation (R^2 of 0.97) in the difference between suspended and truly dissolved phase $^{87}\text{Sr}/^{86}\text{Sr}$ composition and the Fe concentration in suspended phase of the Kalix River (Figure 17). Wortberg (2015) proposes suspended phase Sr is mobilized with primarily Fe oxyhydroxides coated with OM from wetlands during base flow, ^{87}Sr enrich Fe-OC complexes are flushed from riparian zones during spring flooding indicating increased input of soil water relative to shallow groundwater during flooding. To fully explain the increase in $^{87}\text{Sr}/^{86}\text{Sr}$ during flooding, increased deep groundwater discharge to the river is also proposed.

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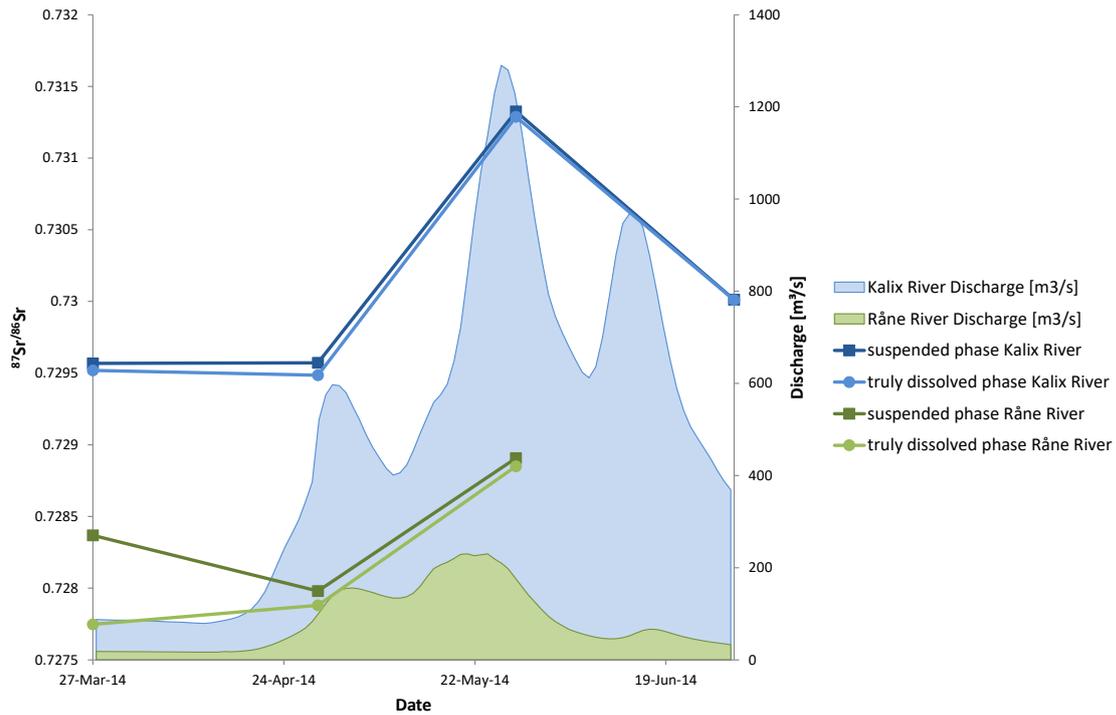


Figure 15 Comparison of $^{87}\text{Sr}/^{86}\text{Sr}$ in truly dissolved and suspended phases of the Kalix and Råne rivers in the context of river discharge (modified from Wortberg 2015).

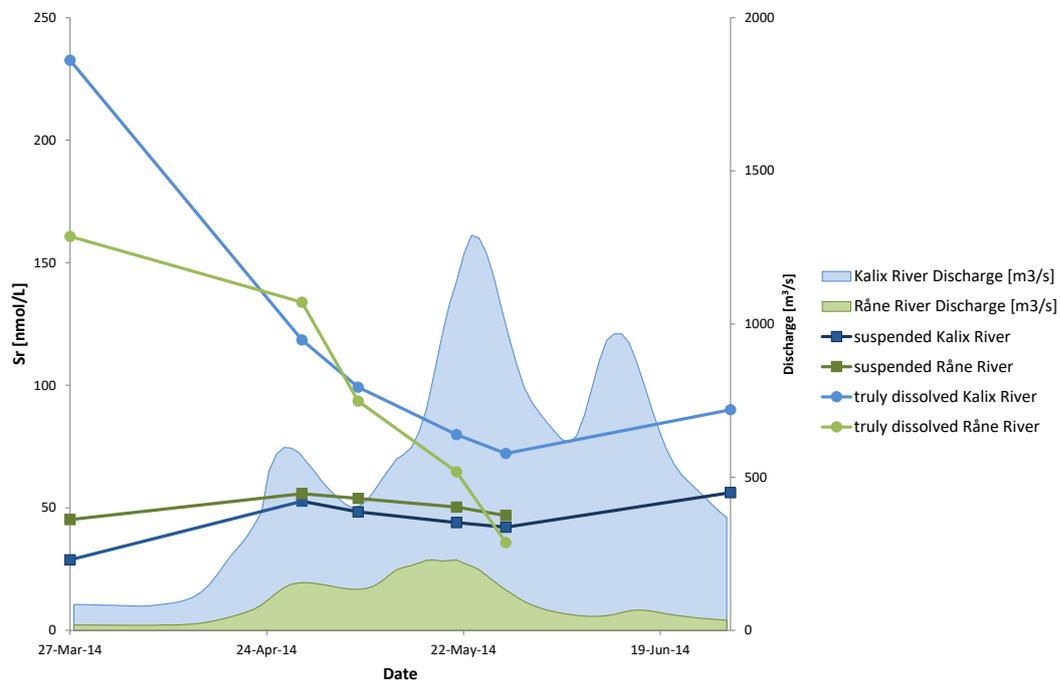


Figure 16 Comparison of Sr concentrations in the suspended and truly dissolved phase for both the Kalix and Råne Rivers in the context of discharge (modified from Wortberg 2015).

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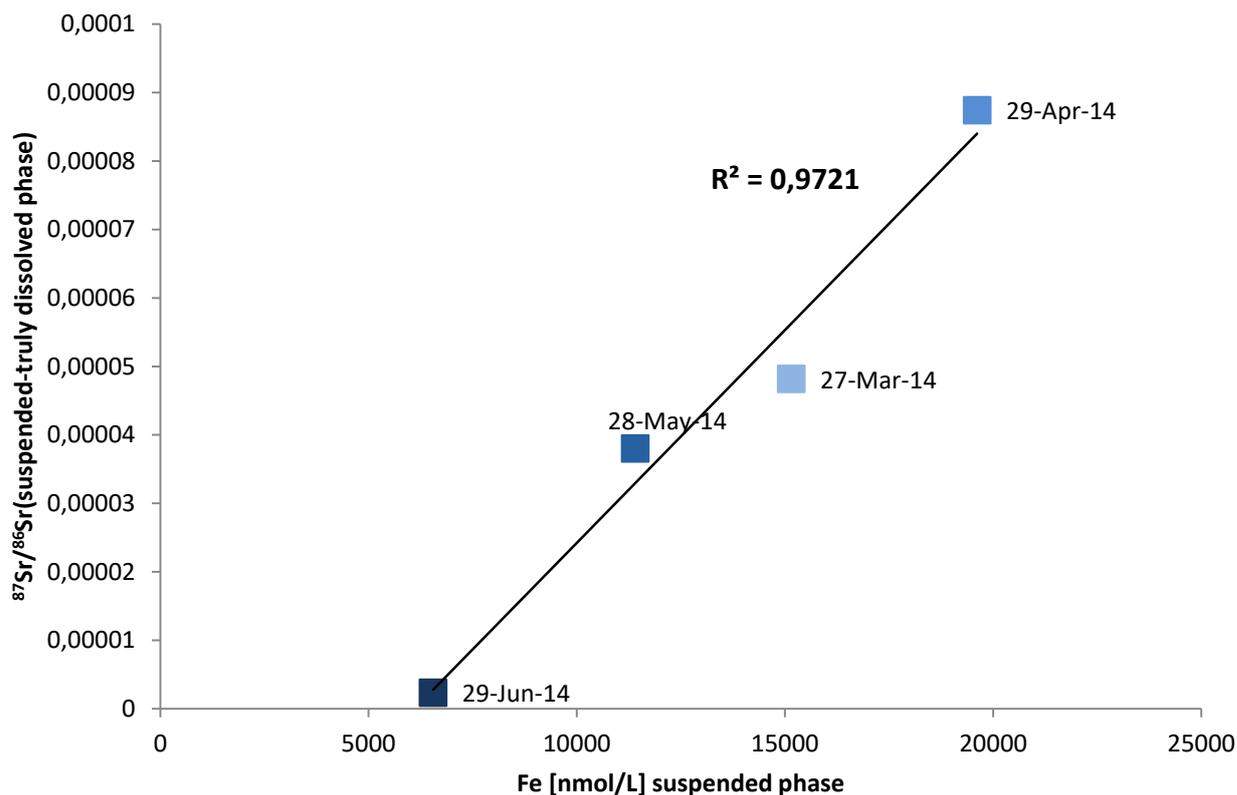


Figure 17 Correlation between the difference in $^{87}\text{Sr}/^{86}\text{Sr}$ from the suspended to dissolved phase with suspended phase Fe concentration in the Kalix River (modified from Wortberg 2015).

The lack of strong correlation between the difference in $^{87}\text{Sr}/^{86}\text{Sr}$ composition of suspended and truly dissolved phases to suspended phase Fe concentration in the Råne River suggests the influence of confounding variables such as DOC on Sr mobility in the Råne River suspended phase. High DOC in the Råne River during base flow results from a greater portion of wetland area discharging to the Råne.

This work illustrates the occurrence of $^{87}\text{Sr}/^{86}\text{Sr}$ composition between the truly dissolved (<1 kDa) and suspended phases of river water in two different boreal catchments. Further, an understanding for the discrepancy between suspended and truly dissolved phase $^{87}\text{Sr}/^{86}\text{Sr}$ was utilized to develop a conceptual model to explain temporal variation in river recharge flow paths.

3.5 Lead isotopes and mine environments

Lead (Pb) isotopes can be applied as tracers in mine site studies to determine the source of lead contamination in water, sediment, soil, and organics (Eby 2004). Additionally, though less commonly, Pb isotopes have been used for hydrogeologic evaluation of water source and flow path (e.g Erel et al. 1990, Kendall & McDonnell 1998, Lepitre et al. 2003, Heidel et al. 2007).

The four stable isotopes of Pb, ^{204}Pb , ^{206}Pb , ^{207}Pb , and ^{208}Pb , exist in nature in varying amounts. ^{204}Pb is the only primordial Pb isotope, while ^{206}Pb , ^{207}Pb , and ^{208}Pb are stable radiogenic daughter nuclides from the decay of ^{238}U , ^{235}U , and ^{232}Th , respectively. These three radiogenic parents have significantly different half-lives (i.e. the half-life of ^{238}U is 7.038×10^8 years, ^{235}U is 4.468×10^9 years, and ^{232}Th is 1.401×10^{10} years) (Eby 2004). Additionally, the initial concentration of Pb, and the ratios of (Pb)/(^{238}U), (Pb)/(^{235}U), and (Pb)/(^{232}Th) differ among

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minerals during formation. Subsequently, there are relatively large variations in the isotopic composition of Pb containing minerals, even within a single rock (Bird 2011).

The isotopic composition of Pb in a particular mineral is a function of the mineral's age and the initial parent/daughter concentrations upon crystallization (Bird 2011). Lead concentrations in igneous rocks are generally highest in feldspar rich granites and granodiorites, and lower in mafic and ultramafic lithologies. Radiogenic Pb is often associated with the presence of accessory minerals within a lithology. For example Th-rich monazite enriches in ^{208}Pb with time, while U-rich zircon will enrich in ^{206}Pb over time (Kendall & McDonnell 1998). Minerals such as Pb sulphides and feldspars, on the other hand, exclude U and Th during formation. Therefore, these minerals maintain a constant Pb isotopic composition over time, and exhibit a less radiogenic Pb signature (e.g. Lepitre et al 2003).

Because the relative abundances of ^{206}Pb , ^{207}Pb , and ^{208}Pb change with time, δ notation is not used for reporting. Alternatively, Pb isotope composition is commonly reported as a ratio, or decimal based on fractions of the in situ isotope abundances (e.g. Kendall & McDonnell 1998, Komarek et al. 2008). Lead isotopic composition is commonly discussed as a ratio of radiogenic Pb nuclides to primordial ^{204}Pb nuclides (e.g. $^{206}\text{Pb}/^{204}\text{Pb}$) in geologic and earth science investigations (Kendall & McDonnell 1998). Most geologic materials have Pb compositions that range from 14.0-30.0 $^{206}\text{Pb}/^{204}\text{Pb}$, 15.0-17.0 $^{207}\text{Pb}/^{204}\text{Pb}$, and from 35.0-50.0 $^{208}\text{Pb}/^{204}\text{Pb}$ (Bullen & Kendall 1998).

In environmental studies Pb isotopes are commonly presented and evaluated using only radiogenic nuclides, such as $^{206}\text{Pb}/^{207}\text{Pb}$ or $^{206}\text{Pb}/^{208}\text{Pb}$ (Komarek et al. 2008, Bird 2011). By eliminating ^{204}Pb , which occurs at lower abundance than the radiogenic lead isotopes, this approach reduces analytical error. Additionally, it precludes the need to correct data for interference from ^{204}Hg during analysis (Bird 2011). Further, comparing radiogenic nuclides can aid in assessment of source contribution by providing insight to the relative contributions of radioactive parent elements (Laptire et al. 2003).

3.5.1 Pb isotope applications

Lead isotopes provide a useful tracer, both for lead contamination in different environments, and in hydrologic tracer studies, because the differences in mass between different Pb isotopes are small and thus one isotope is not preferentially selected over another during mass-dependent processes. Therefore, similar to Sr isotopes, the isotopic signature of Pb from a particular source (e.g. an exploited ore deposit) may be used to characterize source contributions to different sinks in the environment independently of Pb concentration. Processes that cause Pb mobilization include anthropogenic activities such as mining, smelting, combustion, and other industrial processes.

Difficulties in the application of radiogenic Pb as a tracer arise since an ore deposit may have heterogeneous isotopic composition and incongruent weathering may lead to different mineral sources of Pb to solution over time. Isotopic heterogeneity is exacerbated by the occurrence of highly radiogenic Pb within accessory minerals. Further, anthropogenic contamination and the relative immobility of Pb in groundwater has the potential to complicate interpretation of Pb isotopes as tracers in solution (e.g. Veron et al., 1994, Nimz, 1998, Lepitre et al. 2003). However, where such sources of variability can be constrained, the distinct isotopic compositions that often occur within anthropogenic and accessory mineral Pb sources, in combination with concentration gradients resultant from low mobility in solution can also be utilized to evaluate Pb source and pathway (Veron et al., 1994, Nimz, 1998).

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3.5.1.1 *Pb sources in soils, sediments, solution, and organics*

The isotopic composition of lead present in soils, sediment, solution and organics can be used to provide insight to the relative influence of different Pb sources. In order to utilize Pb isotopes to delineate relative lead contribution from distinct sources, all potential sources of lead to the system must be defined and isotopically characterized (Komarek et al. 2008, Church et al. 2004, Lepitre et al. 2003). Komarek et al. (2008) provide a compilation of Pb isotope results from common lead sources reported globally. Lead within a study area may be derived from sources including catchment host rock lithologies, discrete ore deposits, surface anthropogenic deposits (e.g. industrial, agricultural, or mine site related), and atmospheric deposition. Additionally, the Pb source or sources of interest (e.g. an ore deposit related to local mining) must be relatively homogeneous and isotopically distinct from other sources (Church et al. 2004, Lepitre et al. 2003, Kendall & McDonnell 1998, Komarek et al. 2008). If these conditions are met, the relative contribution of Pb to the sampled medium can be determined from binary or multivariate isotope mixing models (e.g. Bird et al. 2010).

Importantly, anthropogenic Pb is primarily derived from Pb sulphide ore [e.g. galena (PbS)]. Because Pb sulphide ores exclude U and Th from their crystal structures during formation, they maintain a Pb isotope fingerprint dictated by their age of formation and melt composition, depleted in radiogenic nuclides relative to background lithologies (Bird 2010). Subsequently, a discrete source of anthropogenic Pb is often isotopically distinct from other ores and background lithologies (e.g. Renberg et al. 2002, Church et al. 2004, Bird 2011).

Lead isotopes are commonly utilized to distinguish lead sources in soils and fluvial sediments because Pb is relatively insoluble and therefore behaves conservatively in these media (Lap-tire et al. 2003, Kendall & McDonnell 1998). Under near neutral conditions, lead is quickly removed from solution by sorption to metal oxyhydroxides, or bound within organo-metallic complexes, where it is precipitated within sediment or immobilized within soils. This conservative tendency of Pb has been utilized to evaluate temporal trends in lead input to a system, which is applicable to mine site studies for defining pre-mining Pb accumulation at a site (e.g. Church et al. 2004, Renberg et al. 2002).

In addition to fluvial inputs, atmospheric deposition is an important source of lead in sediments and soils. Atmospheric lead is predominantly influenced by anthropogenic sources such as combustion of gasoline, combustion of coal, lead mining, and smelting of steel, base metals, and Pb (Eby 2004). For this reason Pb from atmospheric deposition is likely distinguishable from background lithogenic sources. Further, where Pb flux from the atmosphere can be constrained, Pb isotopes have been utilized to distinguish and quantify different anthropogenic sources of Pb (e.g. local smelting and regional pollution inputs) deposited to soils from the atmosphere (Ettler et al. 2004, Wen et al. 2015). Additionally, atmospheric lead signature provides a means for determining lead infiltration rates into soil profiles (Ettler et al. 2004, Wen et al. 2015).

Lead isotopes have been measured in a wide range of organic media to characterize Pb sources. For example, lead isotopes have been used to align elevated Pb concentrations in vegetation samples to specific Pb sources. Margui et al. (2006) observed similar isotopic Pb compositions in soils and vegetation that enabled allocation of the biotic Pb concentrations to different mine sites and background sources. Bioavailability of Pb has also been extrapolated from Pb mobility as determined using kinetic extraction techniques on soil sediments. After distinguishing labile and less labile portions of Pb in sediments, Camizuli et al. (2014) used Pb isotopes to identify Pb sources. Isotopic data showed a distinct mining impacted Pb signature between sites. However, the isotopic signature of labile and less labile pools of Pb within sites were indistinguishable, indicating that Pb from mining sources in these forest soils was no more mobile than Pb from background sources.

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Lead is only mobile in solution under low pH conditions, or within organo-metallic complexes where total organic carbon (TOC) concentrations are high (Kendall & McDonnell 1998). In most surface waters Pb concentrations are low (< 1 ppb), which poses an obstacle to the use of Pb as a tracer in solution (Kendall & McDonnell 1998). None-the-less, isotopic tracer studies of Pb in solutions have been employed to distinguish Pb source impact on water chemistry (e.g. Graham et al. 2006, Lepitre et al. 2003, Kurkjian et al. 2004). Due to low Pb concentrations, studies of Pb isotopes in solution generally entail special technical and methodological consideration for sample collection, handling, and preparation in order minimize sample contamination.

3.5.1.2 *Water flow-path studies*

Lead isotopes in solution may also be used to delineate flow paths within a catchment. Due to the relatively low concentrations of Pb in surface waters, Pb is not commonly applied as a solute tracer. However, it may be a useful tracer in catchments with low pH waters or high TOC, where Pb is more likely to be mobilized in solution. For example, in a scenario where Pb in shallow soil has a different source (e.g. anthropogenic waste) than Pb in deep soil (e.g. local mineral dissolution), shallow vs deep flow paths discharging to a water body may be distinguishable (Bird 2011, Kendall & McDonnell 1998). In such a case a binary isotopic mixing model could be applied to delineate shallow soil and deep groundwater flow paths, as described in Equation 8 (Kendall & McDonnell 1998).

When using solutes such as Pb to determine water source, it is important to recognize that solute chemistry is influenced by water residence time, flow path, mineral dissolution rates, cation exchange capacity, fluid mobility, and reaction kinetics in the catchment. Therefore, while under certain conditions Pb may provide insight to water flow paths, its non-conservative behaviour in solution warrants caution during data interpretation. Kendall & McDonnell (1998) recommend analyzing water isotopes in combination with solute tracers to verify hydrogeologic model assumptions and constrain flow path interpretations.

3.5.2 Pb isotope sample collection and analysis

Soil and sediment samples for isotopic Pb analysis are generally collected using polyethylene or polypropylene sampling tools into bags or boxes of a similar material. Measures such as minimizing atmospheric exposure and not using metal tools for sample collection should be taken to prevent Pb contamination during sampling and transport. Lepitre et al. (2003) provide a description of the measures taken to minimize water sample contamination, including sample container preparation and sample filtration. While cross contamination during filtration was a concern for Lepitre et al. (2003), other researchers have chosen not to filter water samples for Pb isotope analysis, as isotopic equilibrium between suspended particle surfaces and Pb in solution occurs rapidly (Kurkjian et al. 2004, Dunlap et al. 2000).

Analysis of Pb isotopes in solution has historically been conducted using TIMS. However, technological advances in mass spectrometry techniques have led to the use of MC-ICP-MS as the predominant analytical technique. Although MC-ICP-MS provides slightly diminished precision relative to TIMS, it MC-ICP-MS provides faster sample turn-around time. Table 7 provides example precisions achieved using different analytical techniques, as reported in the literature (modified from Bird 2011). During isotopic analysis of Pb by either TIMS or ICP-MS, mass bias effects during analysis must be corrected for. During isotopic analysis by TIMS, standard-sample bracketing, as described by Monna et al. (1998), is used to determine a fractionation correction factor. Mass fractionation in samples analysed by ICP-MS is identified by

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spiking samples with TI with known $^{203}\text{TI}/^{205}\text{TI}$, which is used to correct for fractionation accordingly.

Table 7 Summary of reported range of precision for different Pb isotope analytical methods (modified from Bird 2011)

Analytical Method	% relative standard deviation (RSD)
Thermal Ionization mass spectrometry (TIMS)	0.001-0.01
Inductively Couple Plasma quadrapole mass spectrometry (ICP-QMS)	0.01-0.98
High resolution/magnetic sector Inductively Couple Plasma mass spectrometry (HR/MS-ICP-MS)	0.04-0.2
Multi collector Inductively Couple Plasma mass spectrometry (MC-ICP-MS)	0.002-0.02
Glow discharge mass spectrometry (GDMS)	0.03

3.5.3 Pb and Sr Isotope Case Study

3.5.3.1 Introduction

Heidel et al. (2007) studied the origin and mixing processes of mine waters at the Himmelfahrt Fundgrube polymetallic sulphide ore deposit " in Freiberg Germany. The area has over 800 years of mining history with silver, lead, copper and zinc production. The mining operations ceased in 1969, after which the mine was flooded to a depth of about 227m below ground surface (bgs). Since the levels above the flooded parts are open to air and water, the sulphide ore continues to oxidise, resulting in acidic, high sulphate and trace metal-bearing mine water pollution in adjacent water systems. The mine belongs to one of the largest sulphide ore deposits in Europe, with mineralisation comprised mainly of the sulphide minerals galena (PbS), pyrite (FeS₂), sphalerite (ZnS), and arsenopyrite (FeAsS).

According to earlier oxygen and sulphur isotope studies, the sulphate in mine waters and culverts results primarily from groundwater and oxidized sulphide ores. However, to rule out any additional sources and assess the long-term changes in water chemistry Heidel et al (2007) investigated four major mine water types by means of lead and strontium isotope ratios and hydrochemical investigations between December 2005 and March 2006.

3.5.3.2 Sampling and analysis

Four major mine water types: waters from the flooded mine areas (flooding water), mine water accumulated in pools on the bottom of the galleries (pool water), groundwater flowing through Late Variscan mined ore and backfilled galleries (Late Variscan groundwater), and pore water from within Post Variscan mine areas that does not exhibit continuous flow (Post Variscan groundwater) were sampled in six different locations (Figure 18). In addition to mine water sampling sites, two background groundwater and surface water sites from River Freiburger Mulde about 10km upstream from the mine were sampled to compare the mine waters with the natural unaffected waters and to determine different lead and strontium sources in mine.

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Furthermore, the isotope compositions of different archived galena and carbonate samples taken from the mine were analysed. The water drains out to River Triebisch via culverts from 227m bgs. Lead and strontium isotope ratios were measured with thermal ionization mass spectrometry and the results were corrected using the international reference standards NBS 981 for Pb, and NBS-987 for Sr. The relative errors and average isotope ratios for the standards are presented in Table 8. In addition to Sr and Pb isotopes, the water samples were analysed for anion, cation, trace metal and strontium concentrations with precision between 5 and 10%. Water pH was measured on site. Bicarbonate was analysed by acidic titration with 0.01 N H₂SO₄ and sulphate by ion chromatography. Calcium and magnesium were analysed using flame-AAS and lead, strontium, iron and zinc either by ICP-OES or ETA-AAS, depending on the estimated concentration.

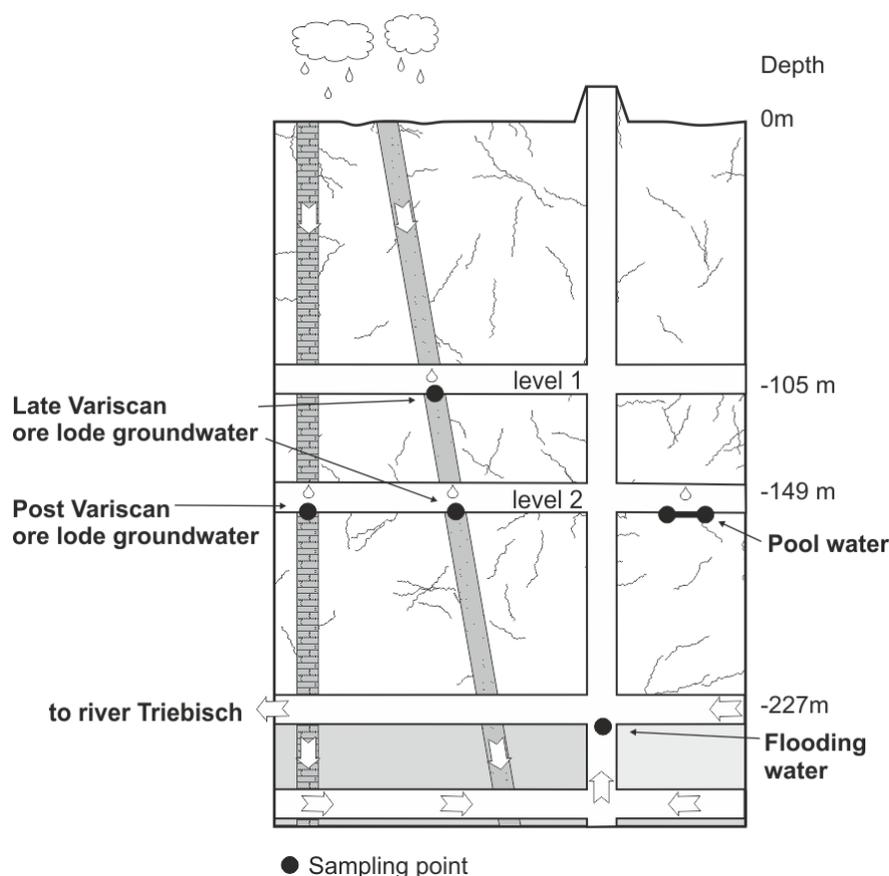


Figure 18 Profile of the mine and the sampling points in the Himmelfahrt Fundgrube mine. (Adapted from Heidel et al. 2007)

3.5.3.3 Results and discussion

According to hydrochemical investigations done by Heidel et al. (2007), the pool water had the lowest pH and the highest concentrations of sulphate, calcium, magnesium, iron, lead and zinc, which is due to sulphide oxidation and weathering of the host rock (Table 9). The groundwaters from the Late Variscan ore lode have relatively low sulphate, cation and trace metal content at 105m bgs, but the concentrations of sulphate, iron and lead increases and pH decreases at 149m bgs. The decreasing pH and addition of pore waters to the system explains the increasing ion concentrations. The flooding water and the groundwater from the Post Variscan ore lode differ from other mine waters, exhibiting higher strontium, lower lead content and the highest pH. Although the sulphate concentrations indicate sulphide oxidation, the high

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calcium, magnesium and strontium concentrations also indicate carbonate oxidation and thus buffering in these waters. Overall, the solute concentration differences between water types and mine levels can be characterised by different flow rates. Naturally, higher water volumes dilute solute concentrations, while lower flow allows for greater accumulation of solute in solution.

Table 8. The relative errors and average isotope ratios for the Pb and Sr standards used in the study.

	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$	$^{87}\text{Sr}/^{86}\text{Sr}$
Relative errors ($2\sigma_M$)	0.01-0.38%	0.01-0.37%	0.01-0.38%	0.003-0.03%
Average ratios of NBS 981 standard	16.9129 ± 0.0017	15.4616 ± 0.0019	36.646 ± 0.036	
Average ratios of NBS 987 standard				0.710289 ± 0.000046

The Pb isotope ratios of pool water samples were significantly higher compared to the ratios of other mine water samples (Figure 19). The Pb ratios of the pool water resembles Late Variscan galena which in turn has lower ratios than Post Variscan galena. According to hydrochemistry it seems that the flooding water and the groundwater from Post Variscan ore lode are affected by an additional lead source (Table 9). However, the Pb isotope ratios of the flooding water cannot not be distinguished from the groundwater of the Late Variscan ore lode. Moreover, the ratios of groundwater from the Post Variscan ore lode differs from them both, though they do not align with the ratios measured from Post Variscan galena. Despite repeated measurements, the Pb ratios of natural groundwater seem to have high relative errors and cannot be distinguished from any mine waters other than pool water, whereas natural surface waters differ significantly from all mine waters. Late Variscan Groundwater, Flooding water, and pool waters approximately fall on a mixing line between pool water, of which the dominant lead source is Late Variscan galena and 2) natural groundwater (Figure 19). Background surface water appears to be influenced by an unidentified third end member source of Pb (Figure 19). Natural groundwater Pb plots between the Standard European Lead Pollution (ESLP) and Petrol lines defined by Haack et al (1998), suggesting an anthropogenic source (Figure 20).

There are three possible end members for Sr: 1) flooding water, 2) pool water and 3) surface water (Figure 21). The Sr isotope ratios of pool water are significantly higher than the other waters and lie within the ratios of the host rock Grey Gneisses. The ratios also increase between December 2005 and March 2006 interpreted to result from increasing weathering rate of mica and K-feldspar due to decreasing pH. The ratios of groundwater from the Late Variscan ore lode lies between the highest ratios of the pool water and lower ratios of the flooding water and groundwater from the Post Variscan ore lode. The lower Sr ratios of flooding and Post Variscan ore lode groundwater might be explained by an additional Sr source from weathering carbonates. This is also supported by the relatively high pH, sulphate and strontium content of these waters (Table 9). Although the drainage area of the natural surface water consists of Grey Gneisses, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are a lot lower, suggesting an additional, possibly anthropogenic, Sr source.

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Table 9. The average chemical composition and standard deviations of water samples. n=10 for Late Variscan GW and flooding water samples, n=2 for pool and river water samples and n=1 for ground-water) (adapted from Heidel et al. 2007)

Sample	pH	SO ₄	HCO ⁻	Ca	Mg	Fe	Pb	Sr	Zn
Pool water	2.5±0.0	41000±2000	0	460±20	2300±200	5000±200	36±1	0.120±0.003	5700±200
Pool water	2.5±0.0	40000±2000	0	460±30	2200±200	5000±300	36±1	0.110±0.007	5800±200
Late Variscan GW 105m	5.7±0.2	96±9	3.4±0.3	32±1	8.9±0.4	0.039±0.041	0.043±0.015	0.120±0.004	1.7±0.1
Late Variscan GW 149m	3.9±0.1	113±17	0	33±2	9.3±0.6	0.500±0.249	0.690±0.260	0.120±0.004	4.4±1.4
Post Variscan GW	7.2	290	223	120	37	1.3	0.003	0.220	1.2
Flooding water	6.1±0.0	830±60	83.7±1.7	240±10	47±3	0.560±0.040	0.013±0.012	0.660±0.011	12±0.5
Groundwater	5.8	111	23.2	45	12	0.159	0.012	0.171	0.102
Surface water	7.7±0.3	37±7	35.4±1.2	20±2.8	4.9±0.4	0.169±0.094	0.008±0.002	0.101±0.003	0.010±0.003

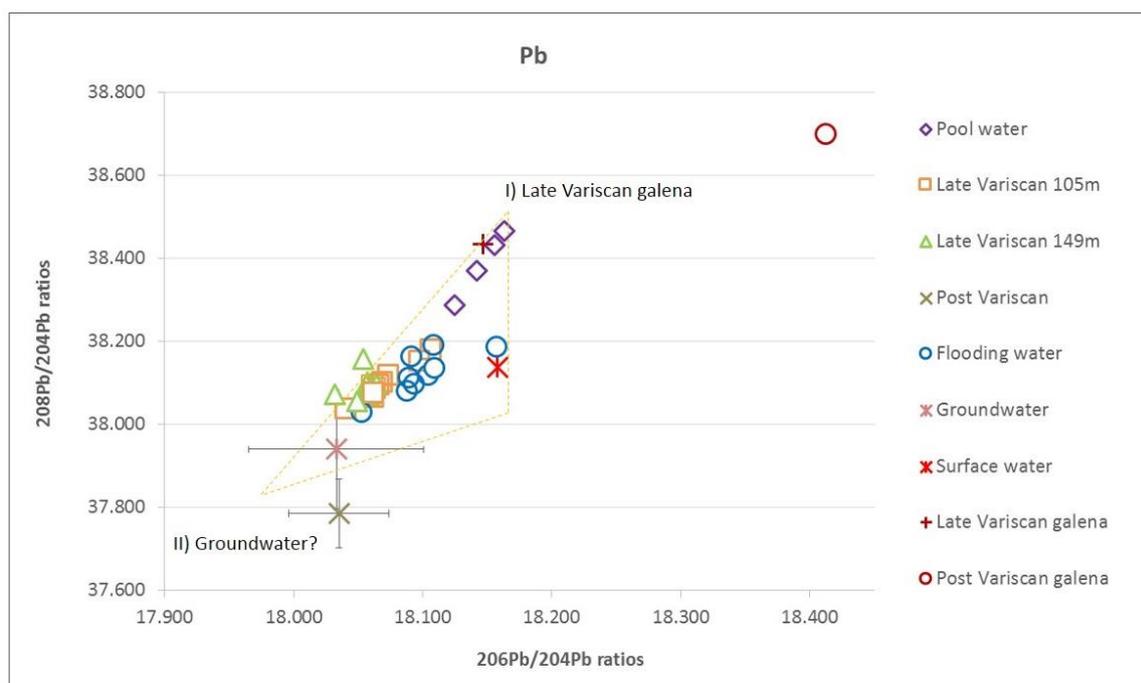


Figure 19 ²⁰⁸Pb/²⁰⁴Pb ratios vs. ²⁰⁶Pb/²⁰⁴Pb ratios of water samples and local galenas. The polygon indicates range potential Pb compositions based on proposed end members. The proposed Pb end members include (I) Late Variscan galena and (II) groundwater.

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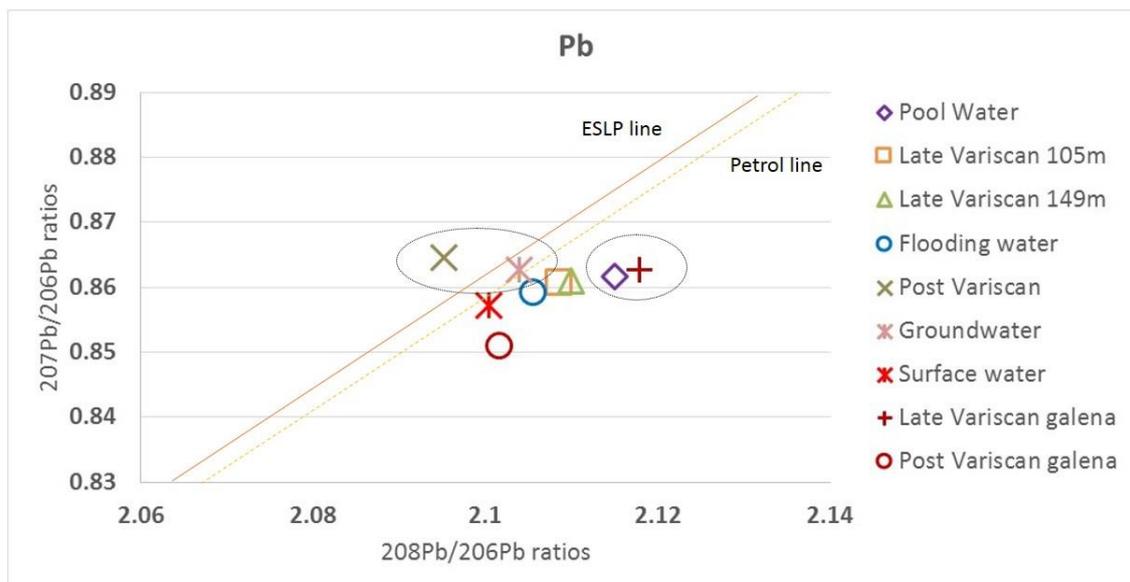


Figure 20 Average $^{207}\text{Pb}/^{206}\text{Pb}$ ratios vs. $^{208}\text{Pb}/^{206}\text{Pb}$ of water samples and local galenas. ESLP= the European Standard Lead Line and Petrol line indicate anthropogenic Pb sources.

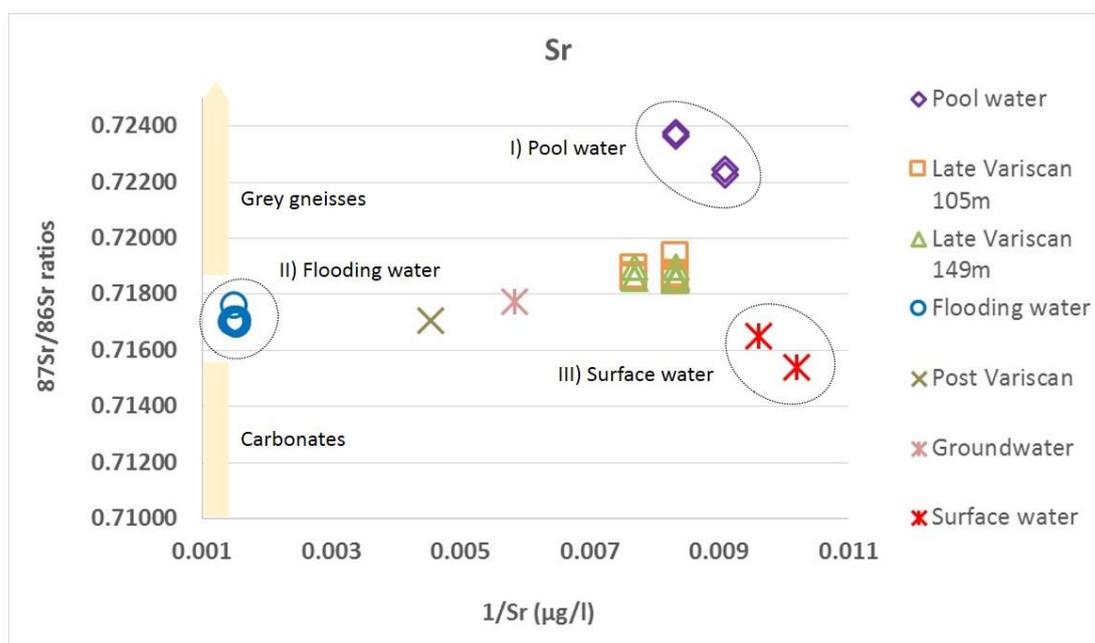


Figure 21 Measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratios vs. reciprocal Sr concentration and the Sr end members. The Sr isotopes ratios of local Carbonates and Grey gneisses are presented as yellow boxes on the left (Adapted from Heidel et al. 2007)

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3.5.3.4 Conclusions

The study of Heidel et al (2007) utilized Sr and Pb isotopes to reveal additional solute sources and mixing processes that were not previously identified from oxygen and sulphur isotope studies. As with sulphate in previous oxygen and sulphur isotope studies, Heidel et al. (2007) indicated at least two sources of lead in mine waters: oxidised sulphide ores (mainly Late Variscan galena) and anthropogenic lead from groundwater. Pb isotopes also indicated an additional lead source evident in surface water and one flooding water sample. Furthermore, in contrast to previous studies, strontium isotope composition along with hydrochemical parameters revealed the importance of gangue carbonates as an element source in flooded mine waters, which may also explain the third Pb source in flooding water. Other strontium sources were weathered host rock, Grey Gneisses, and anthropogenic inputs via groundwater. While the previous studies on oxygen and sulphur isotopes indicated increasing sulphide oxidation towards deeper levels of the mine, Heidel et al (2007) concluded that, since galena is the main sulphide controlling the Pb isotope ratios from weathered ore, but Late Variscan groundwater Pb reflects large influence from the background groundwater endmember, the increasing sulphate concentrations result from oxidation of host rock sulphide minerals other than galena.

3.6 Boron isotopes and mine environments

Boron (B) is a fluid mobile, lithophile element that exists in trace quantities in almost all crustal materials and which exhibits a wide range of isotopic compositions in terrestrial environments as the result of physical and chemical processes. Its isotopic variability combined with its water solubility make B a potentially useful tracer in hydrogeologic and environmental studies (Kendall et al. 2003, Lemarchand et al. 2007, Zhao & Liu 2010, Meredith et al. 2013). There are two stable isotopes of B, ^{10}B and ^{11}B , with relative terrestrial abundances of 19.8 and 80.2%, respectively. The isotopic composition of B is reported as $\delta^{11}\text{B}$ relative to a Boron standard (e.g. the National Bureau of Standards, Washington D.C., U.S.A. SRM 951, which is derived from mined borax).

Boron has a +3 oxidation state, but exhibits chemical behaviour more similar to C and Si than to congeners such as Al^{3+} (Faure & Mensing 2005, Kendall et al. 2003). Boron concentrations are relatively high in non-marine evaporates that contain Na, Ca or Mg, such as borax ($\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}$), it occurs roughly in correlation to silica content in clay-rich sedimentary rocks, and is low in mantle derived basalts. Tourmaline [$\text{H}_9\text{Al}_3(\text{BOH})_2\text{Si}_4\text{O}_{19}$] is the most ubiquitous carrier of B in igneous and metamorphic rocks. In nature boron occurs almost exclusively within one of the two oxyanions BO_3^{3-} or BO_4^{5-} . In solution, BO_3^{3-} forms trigonal boric acid ($\text{B}(\text{OH})_3$), while BO_4^{5-} forms tetrahedral complexes such as $\text{B}(\text{OH})_4^-$ (Faure & Mensing 2005).

Boron fractionation in solution is driven primarily by the equilibrium exchange reaction between these two species in which ^{11}B is more strongly bound in $\text{B}(\text{OH})_3$, while ^{10}B is preferentially exchanged to $\text{B}(\text{OH})_4^-$ (Equation 14) ($\epsilon_{\text{B}(\text{OH})_3-\text{B}(\text{OH})_4^-} = 19\text{‰}$ at 25°C) (Kakihana et al. 1977, Hoefs 2009).



The relative concentration of these two species in solution is pH dependant, with $\text{B}(\text{OH})_3$ being the dominant species in solution at $\text{pH} < 9$ (Palmer et al. 1987). Conversely, boron in the solid phase is generally within the tetrahedral ion. Boron undergoes pH dependant fraction through various water-rock/sediment interactions, including sorption to clays, humic acids, and Fe and

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Mn oxides by which the light isotope is enriched in the solid phase (Palmer et al. 1987, Lemarchand et al. 2005, Lemarchand et al. 2007). Variation in $\delta^{11}\text{B}$ in nature has been observed to range from approximately -50 to +70‰ (Faure & Mensing 2005, Hoefs 2009). Different media exhibit characteristic isotopic ranges (Figure 22 **Error! Reference source not found.**), and modern seawater is buffered to a $\delta^{11}\text{B}$ of approximately +40‰ (Faure & Mensing 2005).

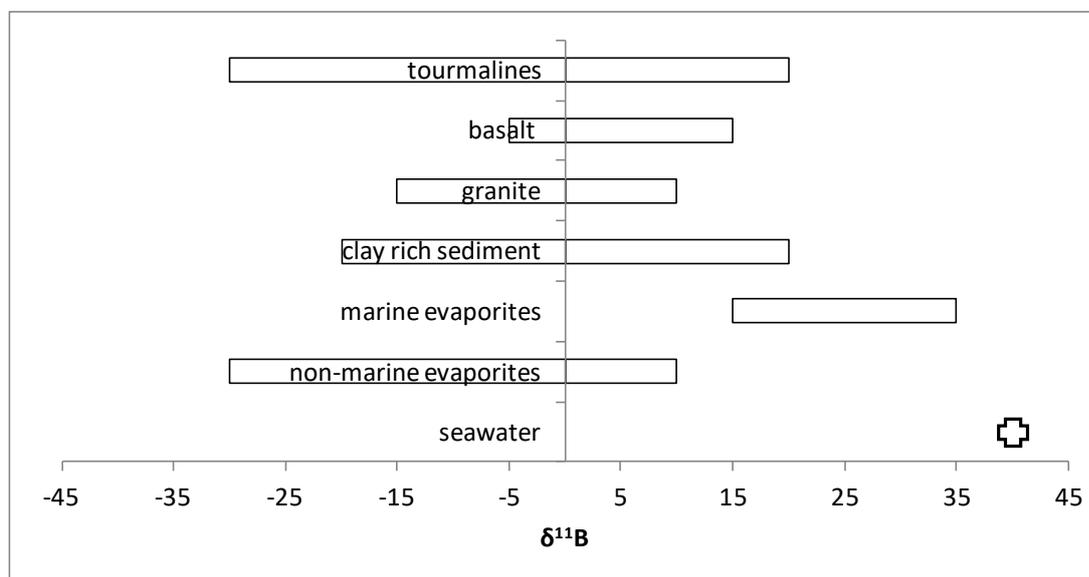


Figure 22 Range of observed $\delta^{11}\text{B}$ values in different media (modified from Faure & Mensing 2005, Hoefs 2009).

3.6.1 B isotope applications

B isotope studies facilitate insight into paleo-marine environment pH (Vengosh et al. 1991, Paris et al. 2010), provide insight into chemical weathering and geochemical evolution (Aggarwal et al. 2003, Lemarchand & Gaillardet 2006, Meredith et al. 2013), as a tracer of marine intrusion into groundwater systems (Phelps 2001, Hogan & Blum 2003, Chetelat et al. 2009), and as a tracer of anthropogenic contamination sources (Barth 1998, Chetelat & Gaillardet 2005, Petelet-Giraud et al. 2009).

Boron isotopes may serve as a particularly useful tracer of mine waters where B containing industrial chemicals are used for processing, or if the mined ore exhibits distinctive $\delta^{11}\text{B}$. Boron utilized in industrial chemicals is commonly mined from discrete non-marine evaporate deposits, and may subsequently exhibit an isotopic signature that is distinctive within a given catchment to facilitate B as an isotope tracer. For example, Barth (1998) reported that the B commonly utilized as a bleaching agent in European detergents is derived primarily from mines in California and Turkey, and is characterized by a $\delta^{11}\text{B}$ ranging from -5 to +3‰ SRM-951.

However, due to the potential for process related B fractionation, caution is warranted when using B as a simple tracer. Instances in which samples falls outside of defined end members have been interpreted to reflect non-conservative mixing behaviour (e.g. Hogan & Blum 2003, Meredith et al. 2013). Additionally, both B concentration and isotopic composition in precipitation may vary spatially and temporally, highlighting complexities to consider when designing a study to constrain isotopic end members (Petelet-Guiraud et al. 2010, Zhao & Liu 2010).

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3.6.2 B isotope sample collection and analysis

For mine site studies isotopic analysis of boron may be desirable in media including surface water, groundwater, precipitation, or solids. Sample collection and preservation is dependent on the study objectives and analytical technique. Water samples for isotopic analysis of B are generally filtered (to 0.2-0.45 μm) into precleaned HDPE or polypropylene sample bottles. Samples may or may not be acidified, depending on analytical technique.

Boron is extracted from solution by chromatography techniques, which may include multiple steps of sample purification. Amberlite IRA 743 resin is commonly used for B extraction, sometimes in successive purification steps (Lemarchand et al. 2002, Chetelat et al. 2009). Gaillardet et al. (2001) present a sublimation step to remove organics from potentially organic rich solutions. Lang et al. (2002) present a second purification step using Ion Exchange II anion resin and AG50 Wx8 cation resins. Solids can be processed for the homogenization of boron and dissolved for boron extraction following the methods which apply to solutions (Musashi et al. 1990, Tonarini et al. 1997, Chetelat et al. 2009).

Isotopic analysis of the purified B is commonly conducted by PTIMS (Nakamura et al. 1992), NTIMS (Hemming & Hanson 1994), or MC-ICP-MS (Lécuyer et al. 2002, Aggarwal et al. 2003). B isotope analysis has also been conducted using ion microprobe (Chaussidon & Albarede 1992), secondary ion mass spectrometry (SIMS) (Chaussidon et al. 1997) and laser ablation molecular isotopic spectrometry (Sarkar et al. 2014). Precision using TIMS and MC-ICP-MS typically ranges from 2σ 0.6-0.2‰ (Nakamura et al. 1992, Lécuyer et al. 2002, Aggarwal et al. 2003). The method presented by Aggarwal et al. 2003 appears to provide precision comparable to TIMS methods, with the added advantages of faster sample through put, and the capability of analysing smaller quantities of B.

3.7 Lithium isotopes and mine environments

There are two stable isotopes of Lithium (Li), ${}^6\text{Li}$ and ${}^7\text{Li}$, which exist in terrestrial environments at relative abundances of 7.59% and 92.41%, respectively (Roseman & Taylor 1998). The isotopic composition of Li is expressed using δ notation with respect to isotope reference material (e.g. L-SVEC), and can be expressed relative to ${}^6\text{Li}$, though is more commonly expressed as $\delta^7\text{Li}$. Due to the relatively large difference in mass of the Li isotopes (approximately 15%), Li undergoes mass fractionation as the result of certain physical and chemical processes, and its isotopic composition has been observed to vary by over 90‰ in natural media (Dellinger et al. 2014). While process related controls on Li fractionation are not fully constrained in natural systems, mineral dissolution, secondary mineral formation, and ion exchange reactions are particularly important sources of Li isotopic variation relevant to environmental studies. Lithium's large isotopic variability, single electron valence, and relative mobility in fluid make it a potentially useful tracer of chemical evolution at the earth's surface (Huh et al. 1998, Huh et al. 2001, Faure & Mensing 2005).

The isotopic composition of Li in sediments can provide insight to sediment provenance through the influences of incongruent mineral weathering (Dellinger et al. 2014). $\delta^7\text{Li}$ in solution, however, undergoes greater influence from silicate weathering processes, mineralization and cation exchange reactions than from Li source (e.g. host rock) composition (Dellinger et al. 2014, Wang et al. 2015, Millot et al. 2010, Négrel et al. 2010). The degree of Li fractionation between solid and solution phases is dependent on the nature of the solid phase, with general enrichment of ${}^7\text{Li}$ in solution relative to the solid phase (e.g. Huh et al. 1998, Hoefs 2009, Millot et al. 2010, Wang et al. 2015). Experimental results show the structural incorporation of Li into secondary minerals can induce up to 14‰ fractionation relative to solution (Anghel et al. 2002). Further, fractionation of up to 22‰ has been observed to result from Li sorption from

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solution to clay minerals and sediments (Zhang et al. 1998). Because the precipitation of Li from solution in weathering products is largely responsible for Li fractionation, Li isotope studies can provide insight to weathering environment, as well as the nature and duration of water-rock interactions (Hoefs 2009).

Millot et al. (2010) describe hydrologic controls on observed Li fractionation from bedrock to solution. In hydrologic regimes with short to moderate water residence times, solution becomes enriched in ^7Li as a function of secondary mineral formation through the preferential incorporation of ^6Li into minerals. In this kinetic reaction rate limited regime, the least fractionation is observed in high energy, low residence time environments that do not provide an opportunity for secondary mineral precipitation, while increasing fractionation is observed with increasing water residence times and progressive precipitation of secondary minerals. However, in lower energy environments with long water residence times (i.e. transport limited regimes), the isotopic composition of secondary minerals begins to approach equilibrium with solution, and the fractionation observed between solid and solution decreases with increased residence time (Bouchez et al. 2013, Wang et al. 2015). Subsequently, Li isotopes in solution may provide insight on contrasting hydrologic geochemical environments.

3.7.1 Li isotope applications

The following discussion is based on applications of Li isotopes as indicators of catchment scale variation in silicate weathering and secondary mineralization processes. Understanding of the spatial and temporal distribution of these processes may also be applicable to tracing the chemical evolution and impacts of mine waters in a hydrologic system. Further, Li isotopes may serve as a tracer of anthropogenic water pollution, as demonstrated by Négrel et al. (2010), who identified the impacts of Ca amended fertilizers strongly enriched in ^7Li in peat bog groundwater.

In order to evaluate the geochemical controls on Li isotopes within a specific sink (e.g. in solution), all potential Li sources must be considered. Significant sources of Li within a catchment may include silicate weathering, anthropogenic inputs, evaporite weathering, carbonate weathering, and atmospheric inputs. Millot et al. (2010) and Wang et al. (2015) illustrate the application of mass balances to account for these various lithium inputs at a catchment scale and to isolate the role of silicate weathering processes on the $\delta^7\text{Li}$ within the dissolved loads of studied rivers.

A source of difficulty when constraining lithium sources is defining elemental and isotopic compositions representative of mixed lithology catchment bedrock. The suspended sediment load has been used as a proxy representative of bulk catchment lithology, and has been found to have a Li isotopic compositions distinct from solution and within the range of crustal compositions reported in the literature (-3.5 to +7.5‰) (Dellinger et al. 2014, Wang et al. 2015). However, because suspended sediment is likely composed of not only sediment derived from the physical weathering (e.g. representative of bulk catchment lithology), but also products of ongoing chemical weathering, steps to further constrain characteristics of geogenic sources are recommended for improving methods to define source end members.

Lithium isotopic data in solution is often compared to the ratio of Li and Na concentrations $[(\text{Li})/(\text{Na})]$ to assess the progression of secondary mineral formation. Due to similar valence states, Li and Na enter solution approximately congruently during primary mineral dissolution. However, Li^+ has a greater affinity for cation replacement during secondary mineralization than Na^+ , which behaves conservatively in solution. Therefore, a comparison of Li^+ to Na^+ concentrations between source lithology and solution, after correcting for non-geogenic inputs such

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as atmospheric deposition, allows the progression of secondary mineral formation to be approximated. The relationship between Li and Na used to describe the role of secondary mineralization is shown in Equation 15, adapted from Wang et al. (2015).

$$Li_{(s2)} = 1 - (Li_{(aq)}/Na_{(aq)})/(Li_{(s1)}/Na_{(s1)}) \quad (15)$$

where $Li_{(s2)}$ is the concentration of Li lost from solution to secondary mineral formation, $Li_{(aq)}$ and $Na_{(aq)}$ describe concentrations of each ion in solution after correction for non-geogenic inputs, and $Li_{(s1)}$ and $Na_{(s1)}$ are an estimation of element concentrations in the geogenic source (e.g. catchment bedrock).

This estimate of mineral precipitation has been evaluated relative to δ^7Li in solution to provide insight to the isotopic fractionation of Li under different weathering environments (Millot et al. 2010, Wang et al. 2015).

Multiple steps are taken to constrain the weathering regime estimates provided by Equation 13. Corrections for non-geogenic Li sources and incongruent (Li)/(Na) inputs to solution must be made to accurately assess element mobility. For example, corrections for Na and Li inputs from precipitation, anthropogenic sources, evaporite dissolution and carbonate dissolution must be made. Based on an understanding of site geochemistry, corrections can be made for the occurrence of specific catchment lithologies that preferentially contribute to one of these two elements in solution, and which would otherwise breach the assumption of congruent dissolution. For example, if evaporites contribute significantly to Na concentrations but not Li concentrations in solution, variability in evaporite dissolution throughout a catchment is a source of incongruent Li/Na dissolution. Further, in granite catchments, Li rich biotite may be expected to weather at a different rate than Na rich plagioclase. Wang et al. (2015) and Millot et al. (2010) illustrate approaches to correct for such incongruent Li/Na sources.

Millot et al. (2010) utilize Li to distinguish kinetically rate limited and transport rate limited weathering environments. In the McKinzie river basin in Canada, catchments with long water resident times showed low Li/Na concentrations with only minor (approximately 13‰) δ^7Li enrichment relative to bedrock. This was interpreted to reflect the equilibration of Li isotopes between soil mineral and solution phases under sufficiently long water residence times. Drainages with shorter residence times showed solution substantially enriched in 7Li relative to bedrock, with relatively high Li/Na concentration. 7Li enrichment in solution would be anticipated to result from the preferential incorporation of 6Li into secondary minerals precipitated from solution. However, no discernible decrease in Li concentration relative to the more conservative Na^+ was observed in solution, as might be expected from secondary mineral precipitation. The change in isotopic composition without notable change in Li concentration was attributed to strong preferential adsorption of 6Li to Fe and Mn oxyhydroxides. Based on this interpretation, isotopic variation of Li in solution provides a notably more sensitive indicator of chemical weathering processes (in this case the precipitation of Fe and Mn oxyhydroxides) than element concentrations in solution.

The study above illustrates the potential for Li isotope application in mine site studies with respect to contaminant transport and attenuation mechanisms. Further work to constrain process controls on Li fraction could help facilitate such applications.

3.7.2 Li isotope sample collection and analysis

Water sampling for isotopic analysis of Li is conducted according to trace element sampling techniques. Samples are generally filtered into pre-cleaned polyethylene sample bottles and preserved with nitric acid. Collection of sediment and suspended solids for δ^7Li analysis is also

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common due to the important role fractionation between solid to dissolved phase plays on data interpretation. The suspended fraction can be recovered from a water filter when a sufficient volume of water has been filtered (Millot et al. 2010). To constrain the geogenic end member of Lithium sources at a catchment scale Dellinger et al. (2014) employ sediment profile sampling to account for isotopic variation of Li anticipated to occur across different sediment grain sizes, as recognized by Kiskáček et al. (2005).

Prior to Li isotope analysis solid samples are digested and Li is purified from solution using chromatography techniques and requires quantitative recovery to prevent fractionation (Tomascak et al. 1999, James & Palmer 2000, Hoefs 2009). Analysis of Li isotopes by MC-ICP-MS methods has facilitated higher precision than historically employed TIMS methods and subsequently led to increased utilization of these isotopes as environmental tracers (Tomascak et al. 1999, Hoefs 2009). MC-ICP-MS analytical techniques have been employed with precision ranging from approximately 1.1 to 0.05‰ (Tomascak et al. 1999, Dellinger et al. 2014). Instrumental fractionation is accounted for using standard-sample bracketing procedure during analysis, and by averaging repeated results of a single bracketed sample (Vanhaeck & Degryse 2012).

3.8 Magnesium isotopes and mine environments

Magnesium (Mg) is the 8th most abundant element in the earth's crust, and as a fluid mobile element is present throughout the hydrologic cycle. Three stable isotopes of Mg, ²⁴Mg (78.99%), ²⁵Mg (10.00%) and ²⁶Mg (11.01%) exist on earth (Rosmann & Taylor 1998). Variation in the relative abundance of Mg isotopes throughout terrestrial environments can be measured as the result of recent advances in mass spectrometer technologies, and provide a potentially valuable tracer of physical, chemical and biological processes in biogeochemical cycles (Young & Galy 2004).

Mg isotopic compositions are expressed using the δ notation with respect to a reference material (e.g. DSM-3 or CAM-1), and utilize the approximate 11% difference in mass between ²⁶Mg and ²⁴Mg. A variation of approximately 5‰ $\delta^{26}\text{Mg}$ is observed across different terrestrial environments with the lightest Mg observed in marine sediments and carbonates, and the heaviest in shale and soils (Figure 23). These isotopic variations are largely attributed to mass fractionation that occurs during silicate weathering and nutrient cycling processes. The isotopic composition of Mg is influenced by both biotic and abiotic processes, the specific mechanisms of which have been the focus of recent study (e.g. Young and Galy 2004, Tipper et al. 2006, 2010, 2012a & 2012b). As the controls on Mg isotopic fractionation become better understood, these isotopes may provide a tool for tracing biogeochemical processes with applicability to mine site characterization.

At a catchment scale Mg pools can be coarsely divided into bedrock, soil, soil exchangeable, vegetation and solution (Figure 23) (e.g. Bolou-Bi et al. 2012, Opfergelt et al. 2014). The isotopic composition of Mg within a pool is the combined result of isotopically distinct inputs, outputs, and fractionation associated with each flux. For example, if the Mg pool of interest is soil water, inputs may include primary mineral dissolution, secondary mineral dissolution, organic material decomposition, desorption from the soil's cation exchange pool, and atmospheric deposition (e.g. precipitation). Outputs from soil solution may include secondary mineral formation, adsorption within the soil cation exchange pool, biotic uptake, and leaching (to groundwater or surface water). Mixing models using Mg isotopes can aid in defining relative fluxes where inputs can be constrained to two or three end members (e.g. Equation 2). Similarly, isotopic information on fluxes within a system can be applied in a mass balance equation to constrain unknown fluxes within the Mg cycle (e.g. Equation 6).

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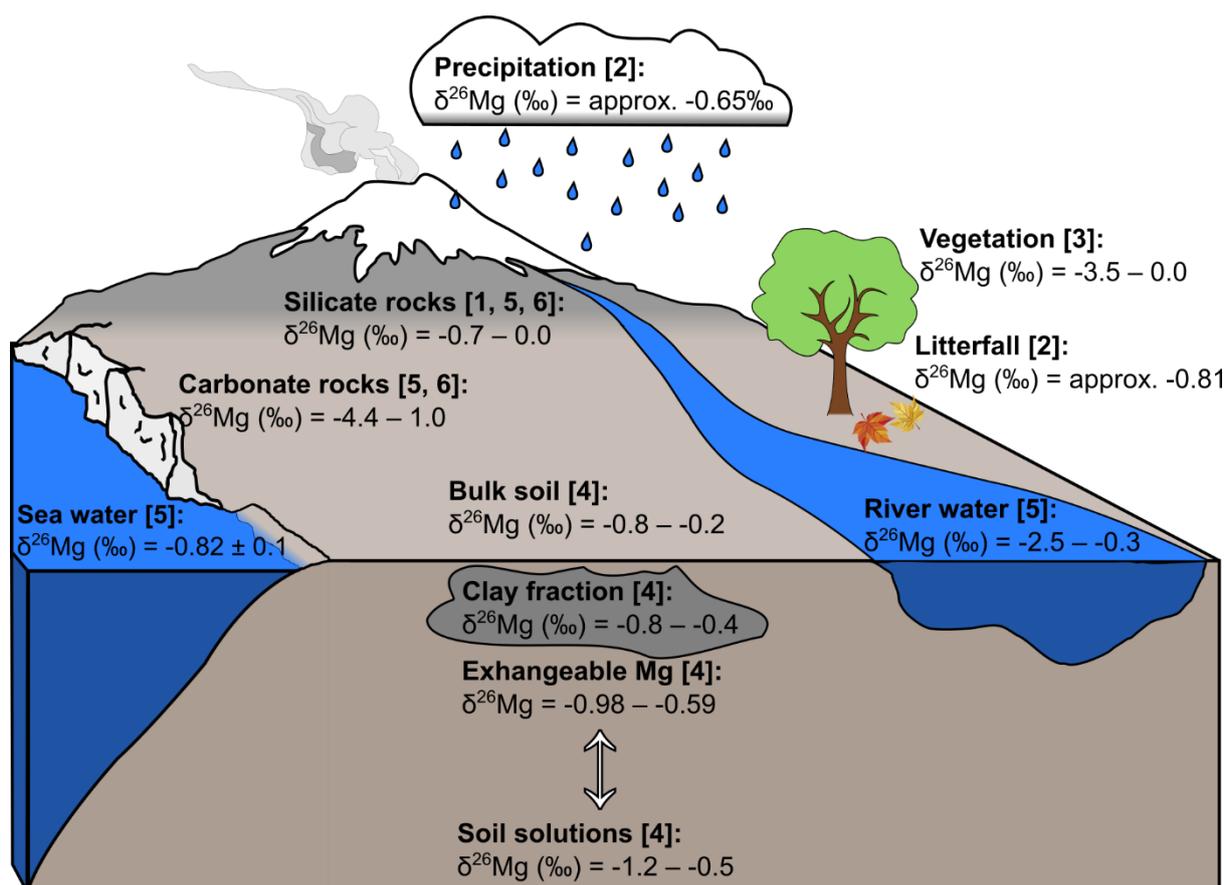


Figure 23 Generalized schematic of terrestrial Mg pools and fluxes ([1] Bizzarro et al. 2004, Teng et al. 2007 and Wiechert and Halliday 2007; [2] Bolou-Bi et al. 2012; [3] Galy et al. 2001, Black et al. 2006, Black et al. 2008 and Ra and Kitagawa 2007; [4] Opfergely et al. 2014; [5] Tipper et al. 2006 and [6] Young and Galy 2004).

3.8.1 Controls on Mg fractionation

The isotopic composition of Mg in soil and surface waters undergoes complex, site specific fractionating influences including preferential uptake of ^{26}Mg by vegetation, preferential incorporation of ^{26}Mg into secondary minerals, complex adsorption and desorption reactions, and potential incongruent mineral weathering. Surface waters are commonly observed to be depleted relative to catchment primary mineral Mg sources (i.e. bedrock) (Figure 23) (Bernot et al. 2008, Tipper et al. 2010, Bolou-Bi et al. 2010). This relationship has been attributed to the preferential incorporation of ^{26}Mg into weathering products during secondary mineralization (Tipper et al. 2012, Li et al. 2014). During secondary mineral formation ^{26}Mg is anticipated to be preferentially incorporated into crystal lattice octahedral sites as a function oxygen bond length, where heavier isotopes are found in greater abundance at shorter bond lengths (Li et al. 2014, Schauble 2004). Therefore, the isotopic influence of secondary mineral formation varies depending on the mineral formed. However, as discussed by Li et al. (2014), weathering products of Mg typically have shorter Mg to O bond lengths, which results in ^{26}Mg enrichment in secondary minerals relative to solution.

Cation exchange reactions have been attributed with complex influences on the ^{26}Mg of surface water and soil solution, and may be especially relevant in soils where Mg is not incorporated in the crystal structure of clays (e.g. kaolinites and illites). ^{26}Mg has been suggested to be both preferentially adsorbed to, and desorbed from soil cation exchange complexes (Huang et al. 2012, Opfergelt et al. 2014). Subsequently the cation exchange pool can be depleted or

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enriched in ^{26}Mg relative to primary minerals, depending on weathering conditions (Opfergelt et al. 2014).

Exceptions to the general observation of ^{26}Mg depletion in water relative to bedrock have been observed in Iceland (Pogge von Strandmann et al. 2008a). ^{26}Mg enriched stream waters were attributed to secondary carbonate formation in $\text{pH} > 10$ environments, which preferentially incorporate ^{24}Mg , and subsequently enrich effluent in ^{26}Mg . An alternate explanation proposed by Opfergelt et al. (2014) is the preferential desorption of ^{26}Mg from the soil exchange pool and subsequent leaching of heavy Mg to surface waters.

The incongruent dissolution of isotopically distinct primary minerals may also influence the isotopic composition of inputs to a system. This is not generally a concern for basalt, which does not incur perceptible Mg fractionation during mineral differentiation (Teng et al. 2010). However, Ryu et al. (2011) illustrate that preferential dissolution of chlorite from granite may contribute a Mg source to solution isotopically distinct from bulk rock.

Further, seasonal fluctuation in ^{26}Mg in solution has been observed in both soil and stream waters (Tipper et al. 2012, Bolou-Bi et al. 2012, Opfergelt et al. 2014). These fluctuations are largely attributed to seasonally variable soil hydrologic conditions, and suggest that soil water residence time and mobility markedly influences the ^{26}Mg of solution. Additionally, Opfergelt et al. (2014) observed that soil water in slow draining soils resembled the ^{26}Mg of the soil cation exchange pool, while waters in fast draining soils were consistently depleted in ^{26}Mg relative to the cation exchange pool. They explain this difference as the result of differing physical and chemical soil conditions, by which soil solution approached equilibrium with the cation exchange pool in the organic rich, low pH, slow draining soils. Conversely, in the quickly drained, less weathered soils, preferential adsorption of ^{26}Mg in the cation exchange pool resulted in the relative depletion of ^{26}Mg in soil solution (Opfergelt et al. 2014).

While the mechanisms of Mg fractionation are not fully defined, biotic uptake, secondary mineral formation, and cation exchange reactions are recognized as major fractionation inducing processes (e.g. Tipper et al. 2010, Li et al. 2014, Opfergelt et al. 2014). As the major Mg fractionation mechanisms are further constrained, Mg isotopes may provide a tool for distinguishing hydrological and geochemical site characteristics ranging from water residence times to controls on major ion sources and mobility in solution.

3.8.2 Mg isotope sample collection and analysis

Studies of low temperature Mg fractionation processes have targeted the various biosphere Mg pools. Sample matrices have included primary minerals in bedrock, bulk soils, clay fractions of soils, exchangeable Mg in soils, vegetation, precipitation, soil water, groundwater and surface water. Sample collection and preservation techniques are dependent on sample matrix. Generally, sampling for analysis of dissolved Mg isotopes in solution entails sample filtration and acidification using a clean, non-reactive sample bottles. Samples from soils, vegetation and bedrock should be collected using representative sampling techniques (e.g. composite sampling) (e.g. Bolou-Bi et al. 2012, Opfergelt et al. 2014).

Prior to isotopic analysis Mg must be extracted from the sample media at a high (nearly quantitative) recovery to ensure no isotopic fractionation during purification. For solid samples (soils, rock, organics) any organic matter is removed by pyrolysis and solids are digested in an $\text{HF}:\text{HNO}_3$ mixture to create a solution. Mg is separated from solution using ion chromatography methods. Wombacker et al. 2009 provides a commonly cited method for Mg purification using cation exchange resin AG50W-X8. Bolou-Bi et al. (2009) apply a sequential Mg sepa-

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ration process, using first AGMP1-X8 anion exchange resin to remove trace elements, followed by a two stage separation of major cations using AG50W-X12 cation exchange resin.

While early isotopic measurements of Mg were conducted using TIMS, the low precision (1 to 2‰) relative to variation in terrestrial environments (approximately 5‰) limited applications of Mg isotope studies (Hoefs 2009). Analytical advances using MC-ICP-MS have increased the precision of Mg isotopes analyses to less than 0.1‰ at 2σ (An & Huang 2014). Subsequently, Mg isotope studies became applicable to terrestrial environments.

Despite increased precision, accurate isotopic analysis of Mg remains a challenge, as illustrated by variable results for the reference material DSM-3, found by different major laboratory groups (An & Huang 2014, and references there in). Sources of analytical uncertainty in results have been attributed to sample preparation techniques, standard solution storage issues, and instrumentation mass bias (An & Huang 2014). An & Huang (2014) address these issues by providing a set of analytical technique guidelines for Mg isotope analysis using MC-ICP-MS. In this guidance they indicate the importance of standard-sample bracketing to correct for instrument mass bias and suggest DSM-3 or Cambridge-1 as the preferred Mg isotope standards.

3.9 Uranium isotopes and mine environments

There are three commonly occurring isotopes of Uranium (U), ^{238}U (99.27 %), ^{235}U (0.72 %), and ^{234}U (<0.01 %), all of which are radioactive. ^{238}U and ^{235}U are primordial isotopes, while ^{234}U is a radioactive daughter product within the ^{238}U to ^{206}Pb series, subsequent the two short lived intermediates ^{234}Th and ^{234}Pa . Uranium isotopes and their progeny have been applied in environmental studies as geochronometers, for contaminant source and transport studies, and can provide insight to geochemical evolution of hydrologic systems.

Uranium isotopes may be of particular use in mine site studies as a tracer of anthropogenic uranium sources, a proxy for the effectiveness of U remediation efforts, a tool for the assessment of hydrogeologic characteristics such as water flow path and residence time, and to provide insight to subsurface redox conditions (e.g. Robinson et al. 2004, Bopp et al. 2010, Ivanovich et al. 1991, Pogge von Strandmann et al. 2010). While there are many potential applications of U isotope series for environmental studies, the following sections will focus on the principles and applications of $^{234}\text{U}/^{238}\text{U}$ activity ratios and $^{238}\text{U}/^{235}\text{U}$ isotopic ratios. U-Th (thorium) and U-Ra (radium) systems can be applied in environmental studies as geochronometers to identify deposition dates and rates of change (van Calsteren & Thomas 2006). The following discussion focuses on U-U applications as tracers of anthropogenic pollutants and chemical processes relevant within mine site studies.

U occurs naturally in granite lithologies (4 to 10 $\mu\text{g/g}$) and accumulates in sedimentary rocks (on average 2 $\mu\text{g/g}$), with the most common U bearing minerals being uraninite (UO_2/UO_3), autunite [$\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 10\text{-}12\text{H}_2\text{O}$], brannerite (UTi_2O_6) and carnotite [$\text{K}_2(\text{UO}_2)_2(\text{VO}_4)2 \cdot 1\text{-}3\text{H}_2\text{O}$] (van Calsteren & Thomas 2006, Borylo 2013). Uranium mobility is largely related to its redox state. The commonly occurring redox states of U in natural environments are U^{+4} [U(IV)] and U^{+6} [U(VI)]. U(IV) exists in reducing conditions, is highly immobile, is precipitated from solution within secondary carbonate and phosphate minerals, and adsorbed to hydroxides and hydrated fluorides (Ivanovitch and Harmon 1992). U(VI) is the dominant species in oxygenated conditions and is relatively mobile in solution, generally as the uranyl ion (UO_2^{2+}), which complexes with carbonate, phosphate, and organic materials in solution (Ivanovitch and Harmon 1992). Adsorption of even soluble U(VI), especially in fine grained and organic sediments, can limit U mobility in solution.

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Due to variables such as U adsorption or dissolution, U concentrations in solution can change across short time periods (e.g. seasonally), which presents challenges to the use of U concentration as a measure of long term U mobility. U isotopes, while not influenced by mass fractionation to the degree of many lighter isotopes, have been observed to undergo systematic fractionation specifically related to changes in U oxidation state (e.g. Stirling et al. 2015, Ivanovitch and Harmon 1992). Therefore U isotopes can provide information on U mobility as a function of redox chemistry (Wang et al. 2015b, Bopp et al. 2010, Kendall and McDonnell 1998). Applications of $^{234}\text{U}/^{238}\text{U}$ and $^{238}\text{U}/^{235}\text{U}$ isotope systems within environmental studies are described further below.

3.9.1 $^{234}\text{U}/^{238}\text{U}$ disequilibrium applications

$^{234}\text{U}/^{238}\text{U}$ activity ratios (AR) have been utilized across a range of hydrologic, hydrogeologic and paleohydrologic studies that have relevance to mine-environment interactions. Applications have included delineating contaminant migration and flow pathways (Andersen et al. 2007, Ivanovich & Alexander 1987), characterizing groundwater circulation, (paleo)redox conditions and age (Suksi et al 2006, Drake et al. 2009, Ivanovich et al. 1991), as well as constraining physical and chemical weathering processes in river catchments and soils (Pogge von Strandmann et al., 2006, 2010, Chabaux 2011).

$^{234}\text{U}/^{238}\text{U}$ AR approaches secular equilibrium in closed mineral grains over time. Secular equilibrium occurs when the activity (the rate of decay multiplied by the number of atoms) of a parent and daughter nuclide is equal, and results from the daughter having a significantly shorter half-life than the parent isotope in a closed system (as occurs within a solid mineral) (Equation 16). When parent and daughter activities are expressed as a ratio, they equal 1 in secular equilibrium (Equation 17).

$$dN_B/dt = \lambda_A N_A - \lambda_B N_B = 0 \quad (16)$$

$$\lambda_A N_A / \lambda_B N_B = 1 \quad (17)$$

where λ is nuclide half-life, and N_A and N_B represent the number of atoms of the parent and daughter nuclides, respectively. λN is nuclide activity.

^{234}U has a half-life of 247,000 years, which is significantly shorter than that of ^{238}U , at 4.47×10^9 years, such that these nuclides reach secular equilibrium in a closed system in approximately 1.25 Ma. Subsequently, mineral grains older than 1.25 Ma often exhibit $^{234}\text{U}/^{238}\text{U}$ in secular equilibrium.

During congruent weathering of U bearing minerals U is therefore expected to enter solution in secular equilibrium (Porcelli & Swazenski 2003). However, deviation from secular equilibrium results from alpha recoil during the alpha particle decay of ^{238}U to ^{234}Th , in which the decaying nuclide recoils the atom's nucleus 10s to 100s of nm (Faure & Mensing 2005, Kramer & Genereux 1998, Kendall & McDonnell 1998). This recoil causes crystal lattice damage making the ^{234}U daughter nuclide more susceptible to weathering, oxidation and leaching. The recoil also has the potential to eject the daughter nuclide across phase boundaries into solution (Kigoshi 1971). These two processes result in solution exhibiting a greater $^{234}\text{U}/^{238}\text{U}$ activity ratio than its solid phase sources of U (Faure & Mensing 2005). Variability in a solution's activity ratio has been related to redox environments, water-rock contact time, and subsequently, weathering environment (Porcelli & Swarzenski 2003, Pogge von Strandmann et al. 2006).

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Under conditions of congruent weathering the equal dissolution of ^{234}U and ^{238}U lead to relatively high U concentration and $^{234}\text{U}/^{238}\text{U}$ AR in solution similar to the mineral source. Under reducing conditions where the less soluble U(IV) is the dominant species U concentration in solution decreases. However alpha recoil processes may propagate the selective dissolution of ^{234}U leading to high AR in solution. This low (U), high $^{234}\text{U}/^{238}\text{U}$ AR is characteristic of the redox boundary within an aquifer (Ivanovich et al. 1987 Porcelli & Swarzenski 2003). However, extended water-rock contact time facilitates equilibrium exchange between U in the solid and liquid phases such that the AR decreases towards 1 in deep, anoxic aquifer environments (Suksi et al 2006, Pogge von Strandmann et al. 2010). The predicted $^{234}\text{U}/^{238}\text{U}$ activity ratio in relationship to aquifer profile and U concentration is depicted schematically in Figure 24.

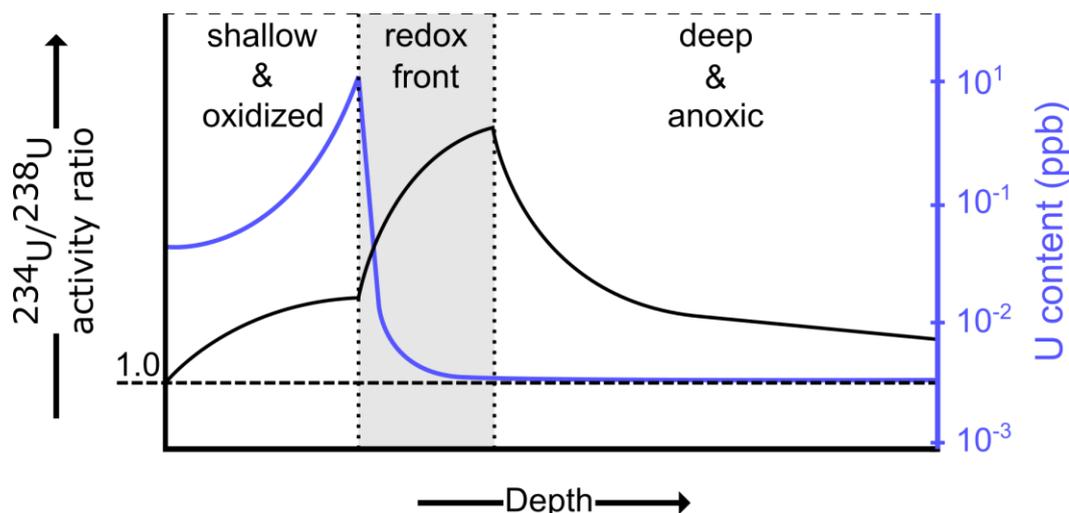


Figure 24 Schematic depiction of $^{234}\text{U}/^{238}\text{U}$ activity ratio and U concentration as a function of depth and redox environment in an aquifer. Residence time in this figure is assumed to increase in correlation with depth (adapted from Ivanovich et al. 1991).

3.9.2 $^{238}\text{U}/^{235}\text{U}$ as a “stable” tracer of oxidation-reduction

Historically, the relative abundance of ^{238}U to ^{235}U was believed to show no significant variation under the influence of natural processes, and was widely accepted to exist at a ratio of 137.88 [with the well-recognized, but isolated exception resulting from a fossil natural nuclear reactor in west Africa (e.g. Lancelot et al. 1975)]. However, measurable $^{238}\text{U}/^{235}\text{U}$ variation results from anthropogenic processes including ^{235}U enrichment and U burning within nuclear reactors (e.g. Christensen et al. 2004). As such, $^{238}\text{U}/^{235}\text{U}$ has historically been utilized as a tracer of anthropogenic U contamination. However, recent advances in analytical techniques have provided great enough analytical resolution to identify variation in $^{238}\text{U}/^{235}\text{U}$ as the result of natural processes as well. This natural variation has been the subject of recent work, both for corrections to U system geochronometers which assumed constant $^{238}\text{U}/^{235}\text{U}$ (Stirling et al. 2007), and as a tracer of the biogeochemical processes through which fractionation is induced (e.g. Wang et al. 2015a, Wang et al. 2015b, Stirling et al. 2007, 2015, Bopp et al. 2010).

Because the half-lives of ^{238}U and ^{235}U are much greater than the scale of the biogeochemical processes inducing fractionation, the influence of radioactive decay can be considered negligible and U can be applied using stable isotope methods to study the fractionating processes. Accordingly, $^{238}\text{U}/^{235}\text{U}$ can be reported as a δ value in relation to a known standard (e.g. IRMM U-A, CRM112a or CRM145 U metal standards). Through advances in MC-ICP-MS methods, systematic natural variations in $^{238}\text{U}/^{235}\text{U}$ of approximately 1‰ have been observed in both field and laboratory settings (Stirling et al. 2007, Bopp et al. 2010, Wang et al. 2015b, Stirling

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et al. 2015). The observed fractionation of $^{238}\text{U}/^{235}\text{U}$ is attributed the nuclear field shift effect, which occurs in the opposite direction, and to approximately 3 times the magnitude of the relatively negligible mass dependant fractionation of U (Bopp et al. 2010). Subsequently, contrary to what may be anticipated based on mass fractionation, ^{238}U is observed to be preferentially depleted in solution relative to solid phase.

Based on laboratory testing the systematic fractionation of $^{238}\text{U}/^{235}\text{U}$ is observed to result from the microbially mediated reduction of U(VI) to U(IV), while abiotic U reduction does not appear to induce measurable fractionation (Stirling et al. 2007, Stirling et al. 2015, Basu et al. 2014). Additionally, adsorption of U with no change in oxidation state is not expected to induce significant fractionation (Bopp et al. 2010, Shiel et al. 2013). Subsequently, $^{238}\text{U}/^{235}\text{U}$ has notable potential as a conservative tracer of redox conditions in groundwater. This is of particular relevance for monitoring the remediation of U in groundwater, which often entails microbial reduction to immobilize U in its reduced state. As a proxy for the effectiveness of U remediation, $^{238}\text{U}/^{235}\text{U}$ may prove more robust than the traditional use of U concentration measurements, which can be confounded by temporally variable solute dilution or adsorption reactions (Bopp et al. 2010).

3.9.3 U isotope sample collection and analysis

U isotopes can be analysed for environmental purposes across a range of media, including whole rock, soil, organic materials, soil water, groundwater and surface water. Further, comparison of isotopic composition between dissolved, suspended and solid U fractions is generally relevant in its application as a process tracer (e.g. Pogge von Strandmann et al. 2010). Due to the complex behaviour of U in solution, and the potential influence of phase change on isotopic composition, for analysis of dissolved U in solution samples should be filtered to the sub-micron level (e.g. 0.2 μm) and acidified (as noted by Dresel et al. 2002).

Prior to isotopic analysis solid samples are digested and U is generally purified from solution using ion chromatography methods (Bopp et al. 2009, Rademacher et al 2006, Turner et al. 2001, Luo et al. 1997). Isotopic compositions of U are analysed using either radiometric or mass spectrometry techniques (Luo et al. 1997, Borylo et al. 2013). Historically radiometric alpha spectrometry, in which alpha particle decay is measured through energy emissions, was the primary means for U isotope analysis. However, this method is best suited for isotopes with relatively short half-lives and/or high concentrations. Developments in mass spectrometry techniques, initially using TIMS, and more recently by MC-ICP-MS, have provided a more accurate means of U analysis suitable to environmental studies. As part of mass spectrometry methods samples are typically spiked with a tracer containing known isotopic or activity ratios of isotopes of similar mass to the analytes of interest (e.g. $^{228}\text{Th}/^{232}\text{U}$, or $^{233}\text{U}/^{236}\text{U}$) to account for instrument induced mass fractionation. Currently MC-ICP-MS methods provide the greatest analytical precision for the measurement of ^{234}U , ^{235}U , and ^{238}U , with uncertainties in $^{238}\text{U}/^{235}\text{U}$ commonly at or below 0.1‰ and uncertainties in $^{234}\text{U}/^{238}\text{U}$ activity below 0.1% (Luo et al. 1997, Turner et al. 2001).

3.9.4 Case Studies: $^{234}\text{U}/^{238}\text{U}$ applications

Ivanovich & Alexander 1987 utilized $^{234}\text{U}/^{238}\text{U}$ AR to study groundwater flow and mixing patterns throughout a regional groundwater system. In this study U concentrations were approximately an order of magnitude higher in unconfined aquifers than confined aquifers, while $^{234}\text{U}/^{238}\text{U}$ activity ratios were discernibly higher in the confined aquifers. U was subsequently used to classify groundwater end members of different age and origin, and to identify hydraulic

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connection between aquifers through a U based mixing model. Ivanovich et al. (1991) illustrated that groundwater flow rates within a single aquifer can also be reasonably modelled based on the isotopic evolution of U along a flow path when consideration is given to radioactive decay rates, nuclide sorption assuming first order kinetics, and alpha recoil ejection.

Pogge von Strandmann et al. (2006) analysed $^{234}\text{U}/^{238}\text{U}$ AR (as well as $\delta^7\text{Li}$) to delineate weathering regimes controlling dissolved loads across Icelandic rivers. In this study the greatest disequilibrium was observed near the origin of glacially fed river catchments, which they interpreted to reflect a high degree of mechanical weathering and subsequent high surface area/volume of grains. This mechanical weathering is suggested to facilitate preferential ^{234}U removal from mineral to solution (increasing $^{234}\text{U}/^{238}\text{U}$ activity ratios in solution) as the result of direct nuclide ejection across mineral grain boundaries during alpha recoil. Downstream from glacial river origins activity ratios decreased, approaching 1, which was interpreted to reflect increasing proportions of surface water derived from non-glacial (chemical weathering dominated) origins in the watershed. Conversely, in catchments not fed by glaciers, $^{234}\text{U}/^{238}\text{U}$ disequilibrium increased downstream, which was interpreted to indicate that the majority of physical weathering in non-glacial rivers occurs along the river course, as opposed to at its origins. In contrast, in basins where soil formation occurs, preferential ^{234}U leaching is believed to drive disequilibrium.

Pogge von Strandman et al. (2010) expand on the application of $^{234}\text{U}/^{238}\text{U}$ and $\delta^7\text{Li}$ to constrain weathering regimes by comparing the dissolved loads of streams from islands under different climactic conditions. In this work they utilized $\delta^7\text{Li}$ to constrain the source of variation in $^{234}\text{U}/^{238}\text{U}$ AR to alpha recoil ejection, as observed in physical weathering dominated regimes, or preferential ^{234}U leaching, indicative of a chemical weathering dominated regime. $\delta^7\text{Li}$ serves as a tracer of weathering, which under low chemical weathering conditions, becomes enriched in solution in correlation with increasing U disequilibrium. However, during rapid chemical weathering, the dissolution of ^6Li enriched clays results in little net Li fractionation between solid and dissolved phase (Figure 25).

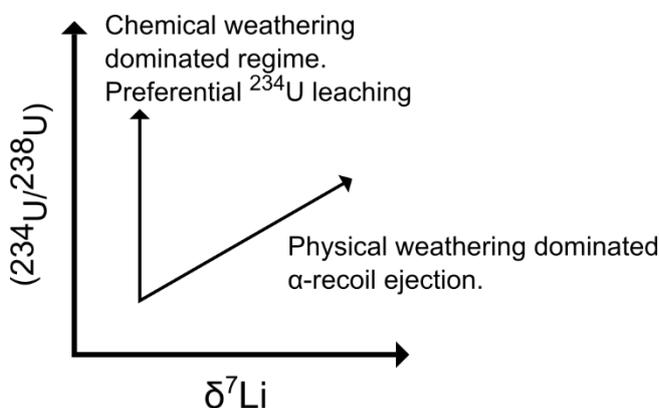


Figure 25 Projected relationship between $^{234}\text{U}/^{238}\text{U}$ and $\delta^7\text{Li}$ in surface water as a function of weathering environment (modified from Pogge von Strandmann et al. 2010).

4. Summary

This report provides a basic level of background information intended to help researchers more easily identify geochemical and isotopic tools for utilization in mine environment studies. While the content is intended to provide context for how and why different analytes may contribute to site characterization, it is by no means exhaustive. Additional, guidance specific to

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project design will be require beyond what is described here-in.

Approaches to geochemical characterization vary depending on site-specific data needs. Monitoring and sampling strategies should be developed with consideration to site-specific geochemical, hydrological, and hydrogeological setting, in addition to mine operating processes. Further, programs should be conducted according to quality assurance guidelines to ensure representative sampling of site waters. Hydrogeochemical characterization based on major ions can often be supplemented with analysis of trace elements related to an ore body or host rock assemblage (Plumlee 1999). Monitoring of physico-chemical parameters provides information fundamental to assessing the potential mobility and reactivity of contaminants in solution.

Isotopic characterization of $\delta^{18}\text{O}$ and δD in water provides insight to water source and pathway, especially where discrete water sources are influenced by evaporation, water-rock interaction, or are of different age. Water $\delta^{18}\text{O}$ and δD are commonly applied in mine water-environment studies to characterize flow regimes and surface water-groundwater interactions. However, to quantify mixing with $\delta^{18}\text{O}$ and δD requires sufficiently large isotopic differences in end members and/or large contributions from each end member. Isotopes of sulphur provide a means to quantify mixing, and in some cases, identify influences of bacterial sulphate reduction on sulphur mobility in solution. Sr and Pb isotopes provide conservative tracers of solute source, but require well characterized, isotopically discrete end members. Boron and Li fractionate in response to weathering processes and flow regime on a catchment scale, while Mg is uniquely fractionated by biotic uptake. Process induced fractionation limits the applicability of these isotope systems as source tracers to special circumstances, such as where a defined end member source exhibits an exceptional concentration or isotopic composition (e.g. Negrel et al. 2010, Hogan & Blum 2003). However, as ongoing work is completed to constrain fractionating processes, these systems may provide unique insight to mechanisms controlling solute mobility in mine water-environment studies. $^{234}\text{U}/^{238}\text{U}$ has been used as both a source and process tracer in groundwater at a regional scale (e.g. Ivanovich & Alexander 1987, Ivanovich et al. 1991). Further, $^{238}\text{U}/^{235}\text{U}$ shows promise as a tracer of biological reduction, and subsequently U mobility in solution (Stirling et al. 2007).

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