ALS Method S-ISTP01

Sulfur Isotope Analysis & Application

Sulfur (S) isotopes are commonly applied to studies of deposit genesis and for environmental fingerprinting of ore. The deposit genesis studies in turn inform exploration models, but sulfur isotopes also possess untapped potential for use as an exploration vectoring tool, and are a powerful addition to the exploration toolbox for many deposit types. ALS has partnered with the Queen's Facility for Isotope Research (QFIR) of Queen's University to offer sulfur isotope analysis by Continuous Flow-Elemental Analyser-Isotope Ratio Mass Spectrometry (CF-EA-IRMS).

How do S isotope compositions vary in nature?

Sulfur has four stable isotopes ^{32}S, ^{33}S, ^{34}S, and ^{36}S. From most to least abundant, ^{32}S accounts for 94.99% of sulfur, ^{34}S for 4.25%, ^{33}S for 0.75%, and ^{36}S for 0.01% [1]. For most applications in mineral exploration and environmental geochemistry, the analysis of only the most abundant isotopes, ^{32}S and ^{34}S, is required.

As variations in the ratio (R) $^{34}S/^{32}S$ are small, isotopic data are reported in $\delta^{34}S$ notation, which denotes the parts per thousand (permil or ‰) variation in the $^{34}S/^{32}S$ value of the sample relative to the international standard, Vienna Canyon Diablo Troilite (CDT):

$$\delta^{34}S\ (‰) = \left(\frac{R^{34/32}_{Sample}}{R^{34/32}_{CDT}} - 1 \right) + 1,000$$

The term 'isotope fractionation' refers to the relative partitioning of 'heavy' (^{34}S) and 'light' (^{32}S) isotopes between two coexisting phases in a natural system. Oxidation and reduction reactions are the greatest drivers of sulfur isotope fractionation on Earth [2]. Heavier isotopes tend to concentrate in the more oxidised state [3,4], so ^{34}S enrichment tends to increase from sulfide to elemental sulfur to sulfate [5]. It is the metabolism of sulfate-reducing bacteria (SRB) that produces the greatest sulfur isotope fractionations; organisms preferentially use the lighter (^{32}S) isotope for their metabolic processes, so sulfate reducing bacteria tend to leave residual dissolved sulfate enriched in ^{34}S due to their preference for ^{32}S-bearing sulfate [6]. Laboratory-based experiments have demonstrated sulfate reducing bacteria are capable of producing sulfur isotope fractionations of over 80‰ in residual dissolved sulfate [7]. The impact of sulfate reducing bacteria on the sulfur cycle is observed in the $\delta^{34}S$ of sedimentary sulfide and sulfate minerals, coal beds, various types of mineral deposit, and magmas that have interacted with crustal rocks (Fig.1) [2]. Although highly variable overall, the Earth has a bulk $\delta^{34}S$ of approximately 0‰, as do most meteorites (Fig.1) [2,5].

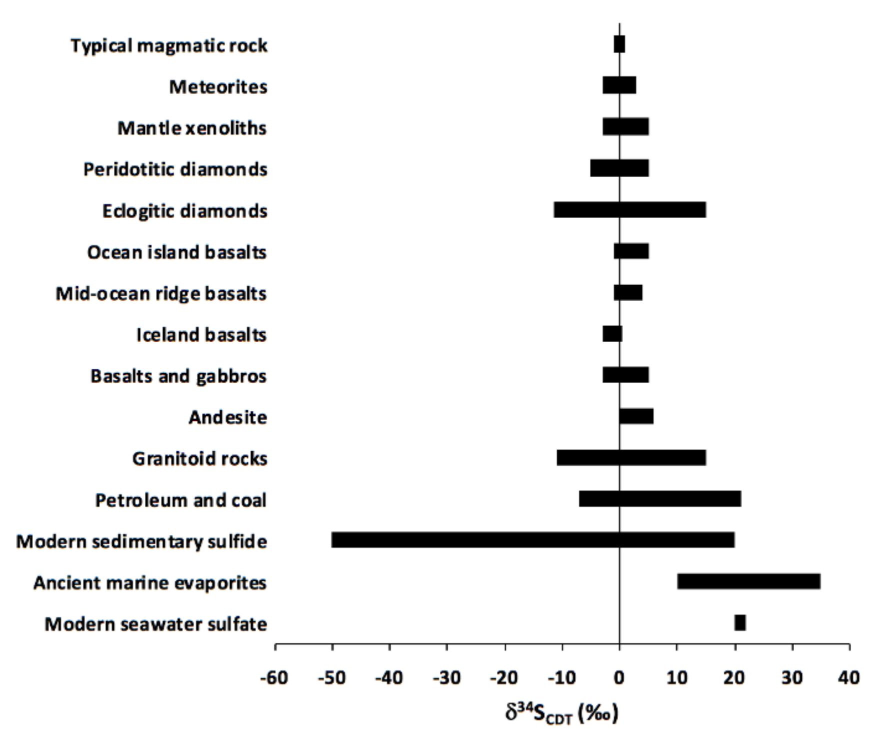

Fig.1 The range of $\delta^{34}S$ for sulfide minerals from meteorites, mantle xenoliths, diamonds, igneous rocks, and modern sediments, adapted after [2] and [5].

Applications of sulfur isotope geochemistry:

Using sulfur isotopes to indicate the primary mechanism of PGE mineralisation in magmatic sulfide deposits

In mineralisations related to mafic (basaltic) magmas, sulfur isotopes can be used to distinguish between sulfur-rich magmatic systems, in which copper and nickel are important resources, and sulfur-poor magmatic systems, in which platinum group elements (PGEs) are the target [5,8]. In sulfur-rich magmatic systems, δ^{34}S in sulfide minerals tend to be positive and highly variable, whereas in sulfur-poor magmatic systems (like the Merensky Reef of the Bushveld Igneous Complex), the δ^{34}S of magmatic sulfide minerals varies minimally, centering on the mantle value of approximately 0 to 2‰ [5]. Recently, sulfur isotope measurements performed at the QFIR labs combined with whole rock geochemistry were used to assess if the incorporation of non-magmatic sulfur-bearing rocks had played a significant role in platinum group element mineralisation in the northern limb of the Bushveld Igneous Complex [9]. The δ^{34}S of < 4‰ found below the main platinum group element reef in this study area are similar to the values documented for the Merensky Reef in the eastern and western limbs of the Bushveld Igneous Complex (~ 0 to 3.5‰), suggesting that the platinum group element mineralisation formed in a similar manner, without significant crustal contamination (δ^{34}S of typically 8 to 9‰, but up to 12‰) [9].

S isotopes as vectors for mineralisation

Although sulfur isotopes have a long history of application in ore deposit studies, they have been underused in mineral exploration. Past studies have demonstrated that variations in sulfur isotope ratios may help vector towards volcanogenic massive sulfide deposits [10], orogenic gold deposits [11], sedimentary exhalative deposits [12], and porphyry copper deposits [13,14]. For example, Roth (2002) documented sulfur isotopic zonation at Eskay Creek, with the sulfide minerals in and immediately around the deposit having the most positive values (up to about 5‰), and a systematic decrease in values (more biogenic) with increasing distance from the deposit (down to about -40‰) [10]. There are also several examples of sulfur isotopes in groundwater being effectively applied to mineral exploration [15–17].

Leybourne and Cameron found that dissolved sulfate concentrations are elevated in groundwaters near the Spence porphyry copper deposit, and δ^{34}S values are lower(~2‰) compared to upflow waters (> 4‰), consistent with the increasing influence of sulfur derived from the oxidation of copper-sulfide minerals within the deposit (Fig. 2) [16]. Most recently, Kidder et al. investigated the sulfur isotopic composition of groundwater sulfate as a vector for copper-molybdenum porphyry and exotic mineralisation buried under cover [15]. These analyses, conducted at QFIR, allowed the investigators to distinguish between multiple mixing endmembers to identify the sulfur sources in groundwater sulfate. Proximal to the porphyry system of the Picaron prospect (Atacama region, Chile), groundwater sulfate δ^{34}S tends to be lower (< 5‰), reflecting the oxidation of primary sulfide minerals [15]. A second endmember with a δ^{34}S of greater than

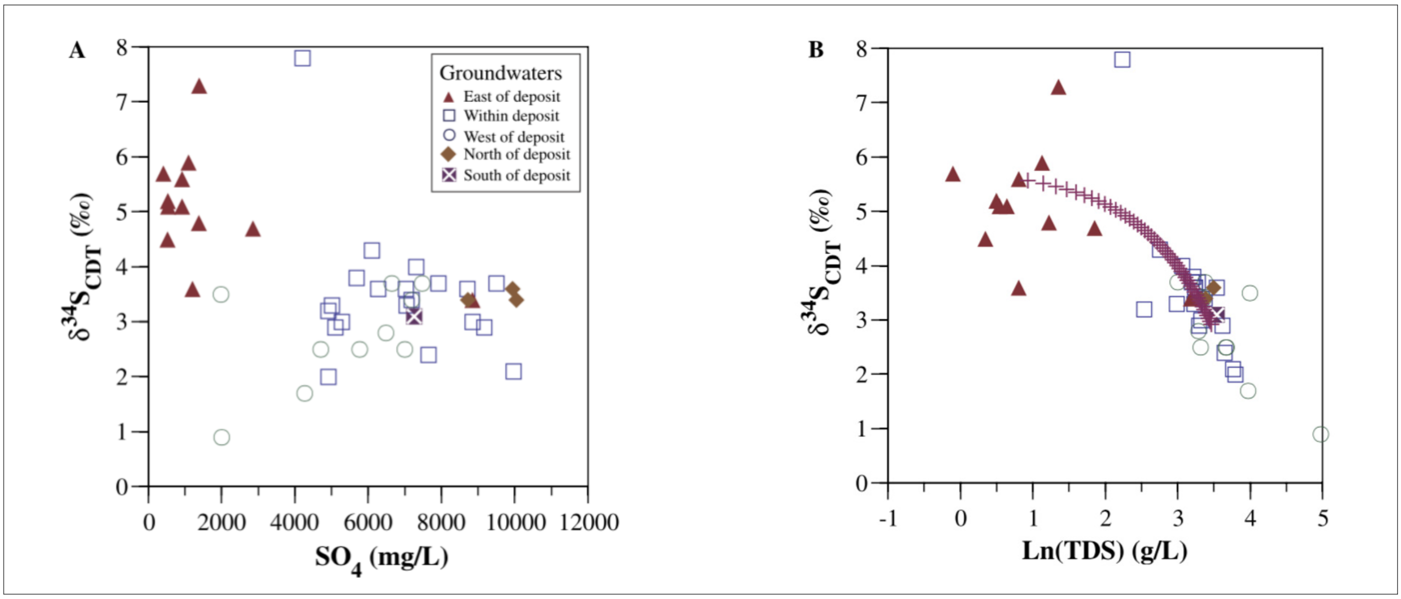

Fig.2 Plots of (A) SO$_4$ and (B) Ln total dissolved solids (TDS; salinity) vs. δ^{34}SCDT for groundwaters from in and around the Spence deposit, Chile. Tick marks (at 2% mixing intervals) show the effect of mixing between saline and dilute end-member groundwaters (from [16]).

8‰ is also present in the area and is likely related to the dissolution of soil gypsum derived from the redistribution of salar solutes [15]. As with in other investigations, a sulfate $\delta^{34}S$ of less than 5‰ is interpreted to correspond to a magmatic sulfur signature, and this can be useful for the use of groundwater sulfur isotopic compositions as a vector [16,18,19].

How are sulfur isotope compositions determined?

Sulfur isotope analyses are typically performed on pulverised whole rock, but mineral separates and microdrilling can also be used to isolate individual sulfate or sulfide minerals. For analysis, samples (between 0.2 mg and 40 mg, depending on sulfur content) are weighed into tin capsules. For sulfate minerals, such as barite, a catalyst (V_2O_5) is required; this is not necessary for sulfide minerals. Sulfur can also be measured from sulfate in waters but a step to precipitate the sulfate as barite is needed. To precipitate barite, waters are mixed with a $BaCl_2$-satured solution.

Sulfur isotope measurements are performed using a MAT 253 Stable Isotope Ratio Mass Spectrometer (Isomass Scientific Inc.) coupled to a Costech ECS 4010 Elemental Analyser (EA). Samples are dropped automatically into a 1000°C combustion reactor (filled with tungstic oxide on alumina and high-purity copper) and the sample and tin capsule react with oxygen and combust at temperatures of 1700 to 1800°C. The sample is broken down into its elemental components, N_2, CO_2, H_2O, and SO_2, with high-purity copper wires absorbing excess oxygen. The gases separate as they flow through the gas chromatographic (GC) column that is kept at a constant temperature. Gases are then ionised and subjected to a magnetic field that separates ions based on their mass-charge ratio (m/z) before measurement. Signals for the isotopes of SO_2, m/z 64 ($^{32}S^{16}O^{2+}$), 65 ($^{33}S^{16}O^{2+}$, $^{32}S^{17}O^{16}O^{+}$, $^{32}S^{17}O1^{6}O^{+}$), and 66 ($^{32}S^{18}O^{16}O^{+}$, $^{32}S^{16}O^{18}O^{+}$, $^{32}S^{17}O^{2+}$, $^{33}S^{17}O^{16}O^{+}$, $^{33}S^{16}O^{17}O^{+}$, $^{34}S^{16}O^{2+}$), are measured simultaneously. The integrated area of each peak relative to those of a SO_2 reference gas are used to determine the sulfur isotope ratio. The final data are expressed in δ notation as $\delta^{34}S$ (in units of ‰), and corrected by normalising the $^{34}S/^{32}S$ value of the sample to materials that have been thoroughly characterised against Vienna Canyon Diablo Troilite (CDT), including the in-house standards MRC and M6801, as well as certified reference material NBS127.

Protocols ensure both quality assurance and quality control for results by generating 10% analyses each of the following:

1. Certified reference materials and secondary standards
2. Random duplication of unknown samples
3. Blanks

Precision is based upon duplicate sample analyses and measurements are reproducible to 0.2‰. This quality assurance and control program provides the routine quality monitoring of both the measurements and the instrumentation.

What samples can be analysed for sulfur isotopes?

All samples that contain sulfur in measurable levels can be analysed for their isotopic composition, but the amount of material needed will depend on the percentage of sulfur present, therefore it is helpful to know the sulfur content to determine the optimal weight of sample for analysis. The lower the sulfur content, the greater the amount of material required. For example, pyrite (FeS_2, 53% sulfur) requires 0.2 mg of material, whereas mixed samples with minimal sulfur content may require up to 40 mg to provide sufficient sulfur for measurement. This information can be gained with analytical methods such as X-ray diffraction (XRD), X-ray fluorescence (XRF), multi-element methods, or induction furnace.

The table below details the volume of sample required for analysing the sulfur isotope composition of dissolved sulfate:

Sulfate Concentration (ppm)	Min Volume of Water Required (ml)
>50	35
Between 20 and 50	110
<20	500

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