Salty Matters

John Warren - Monday April 30, 2018

Stable isotopes in evaporite systems: Part I - $\delta^{34}S$ (Sulphur)

Introduction

The sulphur isotopic composition of sulphate dissolved in modern seawater (SW), and their relation with the associated modern and ancient sulphate precipitates, has been studied for more than five decades. An understanding of the controlling factors is fundamental in any interpretation of the origin of modern and ancient sedimentary calcium sulphates.

So, we shall look at the significance of sulphur isotopes, first by reviewing what is known in terms of the isotopic evolution of marine sulphate salts across the evaporation series from gypsum to the bitterns, and then across a time perspective via the evolution of oceanic sulphate and sulphide signatures from the Archean to the present.

Sulphur isotopes across the bittern series

The accepted $\delta^{34}S$ value of modern seawater-derived calcium sulphate (gypsum) is + 20.0 ±0.2‰ (Sasaki, 1972; Zak et al., 1980 and references therein). This is a average value, based on numerous analyses across the range (+19.3 to +21.4‰). Notably, Rees et al. (1978) obtained a mean of +20.99 ± 0.09‰, using the SF_6 method, which has a better reproducibility than the conventional $S0_2$ method. Mediterranean seawater gave a $\delta^{34}S$ value of +20.5‰ (Nielsen, 1978).

Measured values in natural gypsum from seawater show initial precipitates have a $\delta^{34}S$ value slightly higher than that of its source brine (Figure 1). The highest isotope differential for gypsum naturally precipitated from seawater, as recorded in the literature, is +4.2‰ (Laguna Madre, Texas, U.S.A.; Thode, 1964). Most reported $\delta^{34}S_{gypsum\text{-}sw}$ differentials lie in range from 0 to + 2.4‰ (Ault and Kulp, 1959; Thode et al., 1961; Thode and Monster, 1965; Holser and Kaplan, 1966).

Prior to Raab and Spirto (Figure 1; 1991), laboratory experiment data on $\delta^{34}S_{gypsum\text{-}solution}$ are scarce, especially for solutions mimicking initial precipitation of gypsum from natural seawater and passing into halite saturation. Harrison (1956) measured a $\delta^{34}S_{gypsum\text{-}solution}$ value of ~ + 2‰ for gypsum precipitated from an artificial solution, that was saturated with respect to gypsum. Thode and Monster (1965) calculated a K-value [$(^{32}S/^{34}S)_{solution}$ / $(^{32}S/^{34}S)_{gypsum}$] of 1.00165 from a measured a $\delta^{34}S_{gypsum\text{-}solution}$ value of + 1.65‰ for a $CaSO_4.2H_2O$ -saturated solution, evaporated under reduced pressure and allowed to age and equilibrate for 24 months at room temperature. An experiment using natural seawater was carried out by Holser and Kaplan (1966), who sampled the products of evaporating seawater in a tank with continuous refilling (green circles in Figure 1). The results show "only a small difference between brine and gypsum precipitated" (Holser and Kaplan, 1966, p.97), resulting in a mean value of $\delta^{34}S_{gypsum\text{-}seawater}$ = +1.7‰ (+19.4 to +21.1‰). Harrison (1956) calculated from experimental vibrational frequencies for $S0_4$ in solution and in crystalline $CaSO_4.2H_2O$, a constant K = 1.001 for the reaction:

$$(Ca^{34}S0_4.2H_2O + {}^{32}SO_4)_{SOLID} = (Ca^{32}S0_4.2H_2O + {}^{34}SO_4)_{SOLUTION}$$

which means a 1‰ increase of $\delta^{34}S$ in the solid fraction. Nielsen (1978, p. 16-B-20), using Rayleigh-type fractionation curves indicates that, "... the gypsum/anhydrite of the sulphate facies should be slightly enriched in ^{34}S with respect to the unaffected seawater sulphate"

In the geological record the evaporites of the later Mg- and K-Mg- sulphate bittern facies are depleted in ^{34}S relative to the earlier, basal Ca-sulphates, as rseen in the geological record. Nielsen and Ricke (1964, p.582) give a mean value of +2‰ for the depletion in ^{34}S in later bittern evaporite sulphates relative to the basal Ca-sulphates in the Upper Permian Zechstein

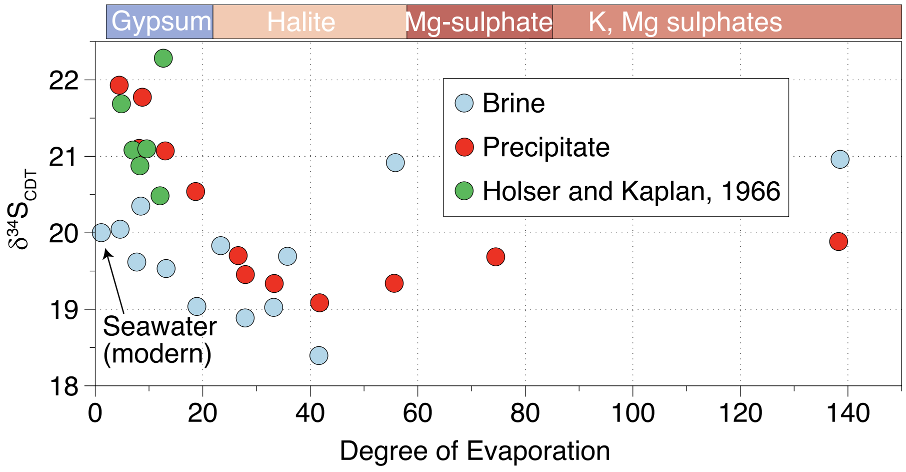

Figure 1. Sulphur-isotope composition of precipitates and of associated brines in the course of stepwise evaporation of seawater (blue and red circles respectively, after Raab and Spiro, 1991). The degree of evaporation is expressed in molal ratios of Cl^-, Mg^{++}, K^+ and Br. The mineral stability fields are defined according to the sequence of precipitates in the experiment, along with the chemical composition of the precipitates and associated brines.

Series (Hattorf and Reyershausen, Germany) whereas Holser and Kaplan (1966, pp. 116 and 117) give a value of -1.0±0.8‰ (their $\delta^{34}S_{\text{potash-magnesia facies sulphates}} - \delta^{34}S_{\text{gypsum/anhydrite facies}}$) for the Zechstein Basin (Germany) and -0.8±0.5‰ for the Upper Permian Delaware Basin (U.S.A.) evaporites (green circles in Figure 1).

Theoretical calculations of the behaviour of the sulphur isotopic fractionation during the late evaporation stages were made by Holser and Kaplan (1966, pp. 116 and 117, fig. 4) and by Nielsen (1978, p. 16-B-20, fig. 16-B-12) applying the Rayleigh distillation equation and using the same fractionation factor calculated from the initial gypsum (1.00165). Their curves are thus in a continuous line with those calculated for the Ca-sulphates. These show an increasing degree of depletion in ^{34}S in the sulphates precipitated in the course of the progressive evaporation in a closed basin, relative to the first Ca-sulphate precipitated, up to the end of the carnallite facies. They explain it by the continuous depletion in ^{34}S in the brines. Thus their calculated $\delta^{34}S_{\text{crystal-initial gypsum}}$ at the end of the halite facies is ~ -0.6‰, at the end of the Mg-sulphate facies -1.0‰, and at the beginning of the carnallite facies -3.8‰, and relative to the original seawater (their ^{34}SC) the differences are +1.0, +0.4 and -2.2‰, respectively. Nielsen (1978) also plotted an extrapolated fractionation curve for the residual brines in a closed reservoir, indicating that the brine is constantly depleted by 1.65‰ relative to the associated precipitate.

Prior to the laboratory work of Raab and Spiro (1991), no experimental data pertaining to the isotopic behaviour of sulphate sulphur in the late evaporative stages of seawater was available in the literature. Raab and Spiro evaporated seawater, stepwise and isothermally at 23.5°C, for 73 days, up to a degree of evaporation of 138x by H_2O weight. At various stages of evaporation the precipitate was totally removed from the brine and the brine was allowed to evaporate further. The sulfur isotopic compositions of the precipitates and related brines showed the following characteristics (Figure 1) where the initial δ^{34}S of the original seawater is +20‰. The δ^{34}S of both precipitates and associated brines decrease gradually across the gypsum field nd aup to the end of the halite field, where $\delta^{34}S_{\text{precipitate}}$ = + 19.09‰ and $\delta^{34}S_{\text{brine}}$ = + 18.40‰. The precipitates are always enriched in ^{34}S relative to the associated brines in these fields, but the enrichment becomes smaller towards the end of the halite field. A crossover, where the δ^{34}S value of the brines becomes higher than those of the precipitates, occurs at the beginning of the Mg-sulfate field. The $\delta^{34}S_{\text{precipitate}}$ increases from + 19.09‰ at the end of the halite field through +19.35‰ in the Mg-sulfate field to + 19.85‰ in the K-Mg-sulfate field, whereas the $\delta^{34}S_{\text{brine}}$ increased from +18.40‰, through +20.91‰ to +20.94‰, respectively.

This evolution implies different values of fractionation factors (α) for the minerals precipitated in the late halite, Mg-sulphate and K-Mg-sulphate fields, other than that for gypsum (1.00165). The value of $\alpha_{\text{precipitate-residual brine}}$ would then be very slightly >1 in the late halite field and >1 in the two later fields.

The experimental pattern of evolution of the δ^{34}S-values of the precipitates from their experiment is in good agreement with data for natural anhydrites interbedded in halites, where δ^{34}S-values are lower relative to basal gypsum (and secondary anhydrite), and of primary minerals of the Mg- and K-Mg-sulfate facies, reported in evaporitic sequences, such as those of the Delaware (U.S.A.) and of the Zechstein (Germany) basins and so can be used to better interpret a marine origin of the sulphate bitterns.

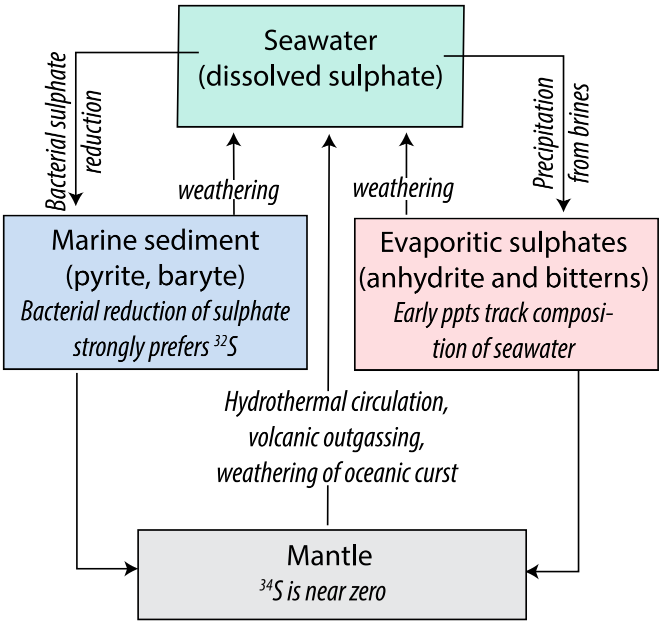
Seawater
(dissolved sulphate)
Bacterial sulphate reduction
weathering
weathering
Precipitation from brines
Marine sediment
(pyrite, baryte)
Bacterial reduction of sulphate strongly prefers ^{32}S
Evaporitic sulphates
(anhydrite and bitterns)
Early ppts track composition of seawater
Hydrothermal circulation,
volcanic outgassing,
weathering of oceanic curst
Mantle
^{34}S is near zero

Figure 2. The Sulphur Cycle

Ancient oceanic sulphate

The element sulphur is an important constituent of the Earth's exogenic cycle. During the sulphur cycle, ^{34}S is fractionated from ^{32}S, with the largest fractionation occurring during bacterial reduction of marine sulphate to sulphide. Isotopic fractionation is expressed as δ^{34}S, in a manner similar to that used for carbon isotopes and the longterm carbon curves related to the sulphur isotope curve across deep time (see next article). Sedimentary sulphates (mostly measured on anhydrite, but also baryte) typically are used to record the isotopic composition of sulphur in seawater (Figure 2). Mantle δ^{34}S is near 0‰, and bacterial reduction of sulphate to sulphides (mostly as pyrite) strongly prefers ^{32}S, thus reducing δ^{34}S in organic sulphides to negative values (≈ -18‰), so leaving oxidized sulphur species with approximately equivalent positive values (+17‰; Figure 3).

Historically, the sulphur cycle has been interpreted as being largely controlled by the biosphere and in particular by sulphate-reducing bacteria that inhabit shallow marine waters (Strauss, 1997). Typically, sulphur occurs in its oxidized form as dissolved sulphate in seawater or as evaporitic sulphate and in its reduced form as sedimentary pyrite. The isotopic compositions of both redox states are sensitive indicators for changes of the geological, marine geochemical or biological environments in the past (Figure 2). The isotope record of marine sedimentary sulphate through time has been used successfully to determine global variations of the composition of seawater sulphate.

The isotopic composition of sedimentary (biogenic) pyrite reflects geochemical conditions during its formation via bacterial sulphate reduction. Sedimentary pyrite is, thus, an important record of evolutionary (microbial) processes of life on Earth. Both time records (anhydrite and pyrite) have been combined in an isotope mass balance calculation, and changes in burial rates of oxidized vs. reduced sulphur can be determined (Strauss, 1997). This, in turn, yields important information for the overall exogenic cycle (i.e. the earth's oxygen budget as discussed in the next article).

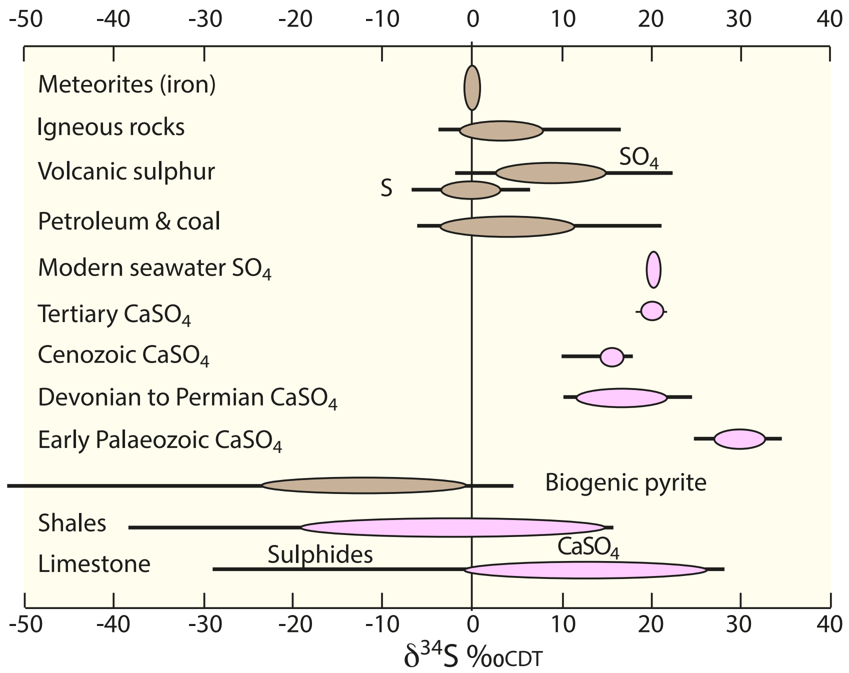

Figure 3. Overview of $\delta^{34}S_{CDT}$ values across the most common global sulphur sources, brown indicates a sulphide (mostly pyrite) measurement and pink indicates calcium sulphate.

And so, values preserved in ancient marine sulphate evaporites are part of the broader world sulphur cycle across deep time that includes movements in and out of marine sulphides (dominantly pyrite) and marine baryte precipitates (Figure 2). Values based on evaporitic $CaSO_4$ are consistent with the ranges seen in modern gypsum (Figure 3). A plot of ancient marine $CaSO_4$ evaporites shows the oxxidised sulphur curve for seawater has varied across time from +30‰ in the Cambrian, to around +10‰ in the Permian and that it increased irregularly in the Mesozoic to its present value of +20‰ (Figure 4). Oxygen values show much less variability and will be discussed in more detail in the next article in this series. Time-consistent variations are reflected in all major marine sulphate evaporite deposits and were most likely controlled by major input or removal of sulphides from the oceanic reservoirs during changes driven by longterm variations in tectonic activity and weathering rates.

Historically, simple removal of oceanic sulphate via an increase in the volume of megasulphate deposition in a saline giant was not thought to be accompanied by dramatic isotopic effects. Rather, variations within the global sulphur cycle were thought to be controlled by a redox balance with stored sulphides and organics in more reducing environments, which are also linked to the carbon cycle and the atmospheric oxygen budget.

In this scenario the oxidative part of the global sulphur cycle is largely governed by continental weathering (especially of marine black shale), riverine transport and evaporite deposition, while the reduced part of the sulphur cycle is controlled by levels of fixation of reduced sulphur-bearing compounds in the sediment column, mostly as pyrite via bacterial sulphate reduction (Figure 2.). The latter process preferentially removes isotopically light sulphur from seawater and so increases the $\delta^{34}S$ value in the ocean, and any consequent precipitate.

However, more recent work question aspects of this older sulphur cycle/pyrite/organics model. As just discussed, variations in $\delta^{34}S_{sulphate}$ across the Phanerozoic are traditionally interpreted to reflect changes in the total amount of sulphur buried as pyrite in ocean sediments — a parameter referred to as f_{pyr} and defined as (Hurtgen, 2012);

$$f_{pyr} = [(\text{pyrite } S_{burial})/(\text{pyrite } S_{burial} + \text{evaporite } S_{burial})].$$

However, Wortmann and Paytan (2012) conclude that the 5‰ negative $\delta^{34}S_{sulphate}$ shift in ~120-million-year-old rocks was caused by massive seawater sulphate removal, which

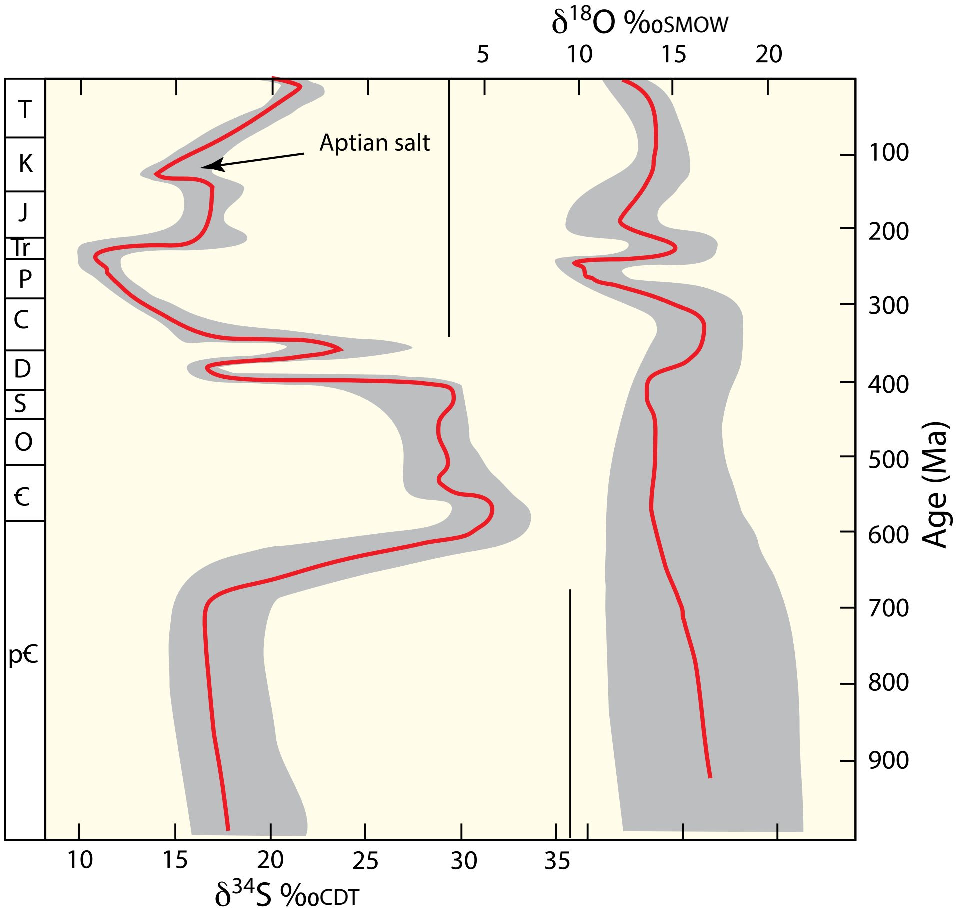

Figure 4. Sulphur and oxygen isotope age curves for marine sulphate evaporites. The heavy lines are the best estimates of $\delta^{34}S$ and $\delta^{18}O$ values of calcium sulphate minerals in equilibrium with world ocean sulphate at that time. Shaded areas are estimated uncertainty envelopes of these curves.

accompanied large-scale evaporite deposition during the opening of the South Atlantic Ocean (Figure 4). In their model, the negative $\delta^{34}S_{sulphate}$ shift is driven by lower pyrite burial rates that result from substantially reduced marine sulphate levels in the world ocean, tied to megasulphate precipitation. The authors attribute a 5‰ positive $\delta^{34}S_{sulphate}$ shift in the world's oceans about 50 million years ago to an abrupt increase in marine sulphate concentrations as a result of large-scale dissolution of freshly exposed evaporites; they argue that the higher sulphate concentrations in the ocean in turn led to more pyrite burial.

Likewise, Halevy et al. (2012) studied past sulphur fluxes to and from the ocean, but over a longer time-frame (the Phanerozoic). They quantified sulphate evaporite burial rates through time, then scaled these rates to obtain a global estimate of variation in sulphur flux. Their results indicate that sulphate burial rates were higher than previously estimated, but also greatly variable. When Halevy et al. (2012) integrated these improved evaporite burial fluxes with seawater sulphate concentration estimates and sulphur isotope constraints, their calculations implied that Phanerozoic f_{pyr} values (f_{pyr} = fraction of sulphur removed from the oceans as pyrite) were ~100% higher on average than previously recognized. These surprisingly high and constant pyrite burial outputs must have been balanced by equally high and constant inputs of sulphate to the ocean via sulphide oxidation (weathering). These relatively high and constant rates of pyrite weathering and burial over the Phanerozoic, as identified by Halevy et al. (2012, suggest that the consumption and production of oxygen via these processes played a larger role in regulating Phanerozoic atmospheric oxygen levels than previously recognized, perhaps by as much as 50%.

Both studies recognize the importance of episodic evaporite burial on the sulphur cycle, while Wortmann and Paytan (2012) clearly show that large-scale deposition and dissolution of sulphate evaporites over relatively short geologic time scales can have an enormous impact on marine sulphate concentrations, pyrite burial rates, and the carbon cycle and so probably play a more important role than previously recognised in regulating the chemistry of the ocean atmosphere system.

The ^{18}O content in seawater sulphate fluctuates less than sulphur values over geologic time (see next article for detailed discussion). The isotopic composition of sulphate minerals varied only slightly from the Neoproterozoic to the Palaeozoic decreasing from +17 to +14‰ (Figure 4). Values then rose during the Devonian to reach +17‰ during the Early Carboniferous (Mississippian). Values then fell to =+10‰ during the Permian, mimicked by a similar decline in sulphur values in the Late Permian to Early Triassic. Since the rise to +15‰ in the Early Triassic, values of marine sulphate minerals have remained close to +14‰ (add 3.5‰ to mineral determined value to give ambient seawater value). Overall, oxygen values show little correlation with marine sulphate variation and are perhaps are more controlled by sulphide weathering reactions.

What is also significant is that, given the now well established sulphur isotope age curve, a comparison of a measured $\delta^{34}S$ value from an anhydrite or gypsum of known geological age to the curve allows an interpretation of a possible marine origin to the salt. A value which differs from the marine signature does not necessarily mean a nonmarine origin, but, at the least, it does mean diagenetic reworking or, more likely, a groundwater-induced recycling of sulphate ions into a nonmarine saline lake (Pierre, 1988). Such oxygen and sulphur isotopic crossplots have been used to establish the continental (nonmarine) origin of the Eocene gypsum of the Paris Basin and the upper Miocene gypsum of the Granada basin, with sulphate derived from weathering of uplifted Mesozoic marine evaporites (Fontes and Letolle, 1976; Rouchy and Pierre, 1979; Pierre, 1982).

Sulphur is largely resistant to isotopic fractionation during burial alteration and transformation of gypsum to anhydrite (Figure 5; Worden et al., 1997). For example, primary marine stratigraphic sulphur isotope variation is preserved in anhydrites of the Permian Khuff Formation, despite subsequent dehydration to anhydrite during burial (≈1,000m) and initial precipitation as gypsum from Permian and Triassic seawater. Gypsum dehydration to anhydrite did not involve significant isotopic fractionation

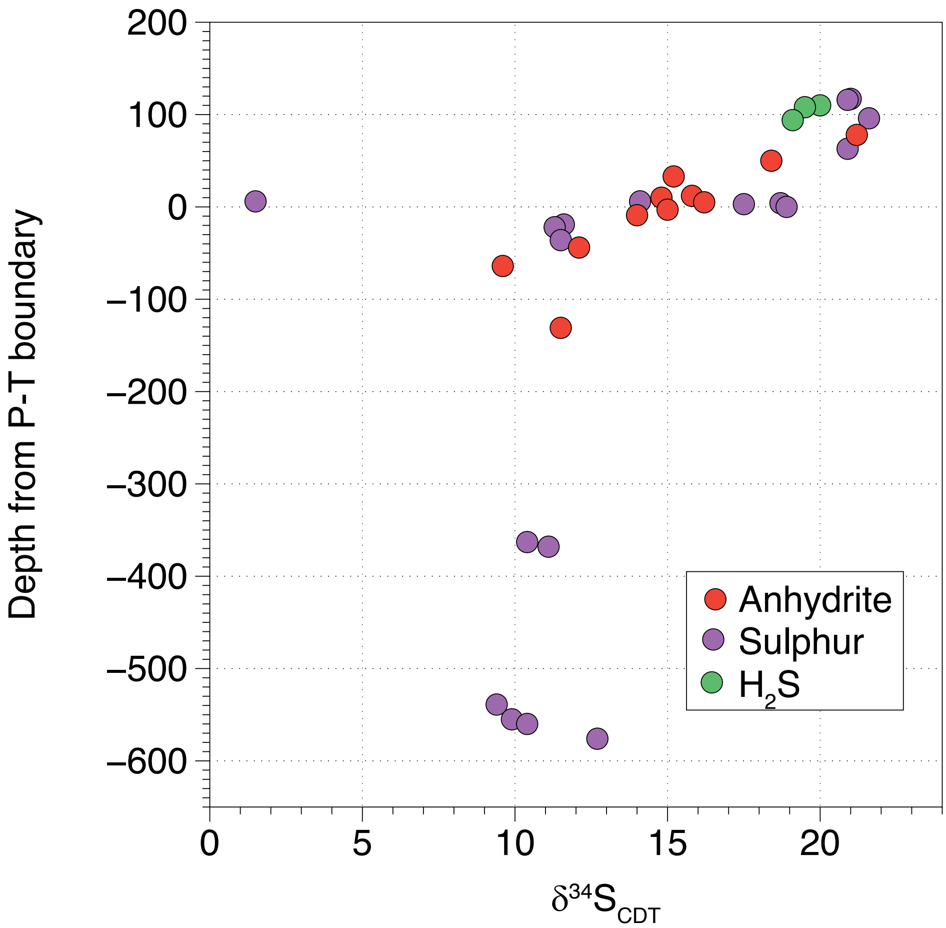

Figure 5. Depth of anhydrite, sulphur and H_2S samples relative to the Permo-Triassic border and their respective sulphur isotope compositions (after Worden et al., 1997).

or diagenetic redistribution of material in the subsurface. At depths greater than 4300 m, the same sulphur isotope variation across the Permian-Triassic boundary is still present in elemental sulphur and H_2S, both products of the reaction of anhydrite with hydrocarbons via thermochemical sulphate reduction (Figure 5). Clearly, thermochemical sulphate reduction did not lead to sulphur isotope fractionation. Worden et al. also argues that significant mass transfer has not occurred in the system, at least in the vicinity of the Permian-Triassic boundary, even though elemental sulphur and H_2S are both fluid phases at depths greater than 4300 m. Primary differences in sulphur isotopes have been preserved in the rocks and fluids, despite two major diagenetic overprints that converted the sulphur in the original gypsum into elemental sulphur and H_2S by 4300 m burial and the potentially mobile nature of some of the reaction products. That is, all reactions occurred must have occurred *in situ*; there was no significant sulphur isotope fractionation, and only negligible sulphur was added, subtracted, or moved internally within the system.

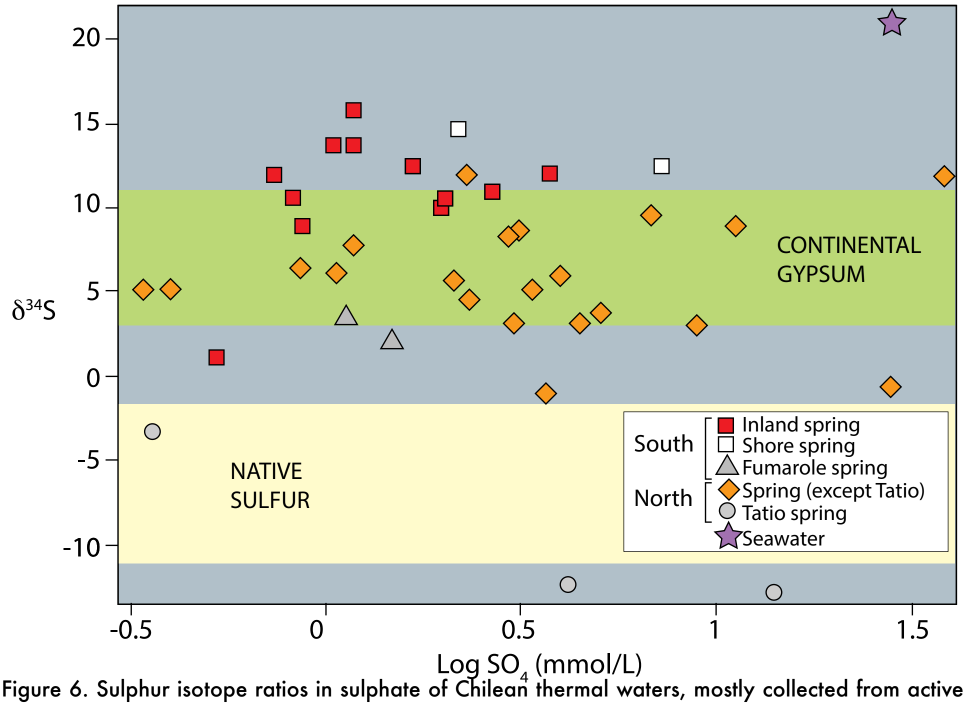

Figure 6. Sulphur isotope ratios in sulphate of Chilean thermal waters, mostly collected from active springs in the salars of northern and southern Chile (after Risacher et al., 2011).

The resistance to fractionation of sulphur isotopes in subsurface pore waters can also be utilised to determine the origin of saline thermal pore waters. In a study of sulphur isotopic compositions of waters in saline thermal springs, Risacher et al. (2011) came to the interesting conclusion that dissolution of continental sedimentary gypsum from the Tertiary-age Salt Cordillera was the dominant supplier of sulphate (Figure 6). The sulphate in the springs was not supplied by the reworking of volcanic sulphur in this active volcanic terrain. $\delta^{34}S$ values from 3 to 11‰ in continental gypsum and this also encompasses the range of $\delta^{34}S$ in pedogenic gypsum (5 to 8‰) and in most surface waters (3.4 to 7.4‰) including salt lakes (Rech et al., 2003). Frutos and Cisternas (2003) found isotope ratios ranging from 1.5 to 10.8‰ in five native sulphur samples. Figure 6 presents the sulphur isotope ratio of dissolved sulphate in thermal waters sampled by Risacher et al. (2011) and references therein. The $\delta^{34}S$ of sulphate in northern thermal springs is within the range of salt lakes waters and continental gypsum. In an earlier paper Risacher et al. (2003) showed that salar brines leak through bottom sediments and are recycled in the hydrologic system. Deep circulating thermal waters are dissolving continental gypsum in sedimentary layers below the volcanics associated with the present day salars. The exception to this observation is the sulphur in Tatio springs where Cortecci et al. (2005) proposed a deep-seated source for the sulphate, related to magma degassing (Figure 6).

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