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Stable Isotope Constraints on the Origin of Sulfur-Bearing Minerals in the Seawater Hydrothermal System of Surtsey Volcano, Iceland

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ABSTRACT

At mid-ocean ridges, seawater carrying SO_4 infiltrates the oceanic crust. However, hydrothermal fluid emissions from such systems predominantly contain H_2S. The absence of SO_4 may be explained by the reduction of seawater SO_4 to H_2S and/ or by the immediate precipitation of anhydrite upon temperature increase. These contrasting hypotheses highlight the need to explore sulfur cycling in the oceanic crust. Surtsey volcano, Iceland, offers an exceptionally well-constrained environment to study sulfur cycling in an exposed section of the oceanic crust. Here, anhydrite was measured for sulfur and oxygen isotope compositions to distinguish different sources of sulfur to the oceanic crust. Geochemical isotope modelling was used to (1) assess the major sources of sulfur to the system and (2) investigate hydrothermal processes (e.g., alteration, redox reactions) affecting isotope systematics of anhydrite at various temperatures. Comparison of model results with our dataset reveals that observed deviations in $\delta^{34}S$ and $\delta^{18}O$ of anhydrite from the original isotope composition of seawater SO_4 can be attributed to equilibrium isotope fractionation upon progressive seawater-rock alteration. Most of the sulfur derives from the seawater whereas the origin of oxygen changes from seawater- to a basalt-dominated source with progressive alteration. Reduction of SO_4 to sulfide was found to be limited below 150°C. Our modelling approach shows that low-temperature seafloor alteration may have the potential of significantly modifying the $\delta^{34}S$ value of the oceanic crust.

1. INTRODUCTION

The oceans play an important role in the global sulfur cycle. They provide both a sink and a source for atmospheric sulfur with sulfate (SO_4) being the most abundant sulfur species in seawater (~2714 ppm; Bruland, 1983). The sulfur isotope ($\delta^{34}S$) composition of seawater SO_4 (+21.24‰; Tostevin *et al.*, 2014) is controlled by: (1) river runoff ($\delta^{34}S$ = 0-10‰; Arthur, 2000), (2) volcanism and hydrothermal activity ($\delta^{34}S$ ~ 3‰; Arthur, 2000) and (3) deposition of evaporites ($\delta^{34}S$ = $\delta^{34}S$ of seawater) and sulfides ($\delta^{34}S_{pyrite}$ on average ~ -15‰) involving large isotope fractionation upon bacterial sulfate reduction (Walker, 1986). Circulation of seawater within the oceanic crust may lead to extensive chemical and isotopic modification of rocks and circulating fluids. For example, along mid-ocean ridges seawater with SO_4 infiltrates the oceanic crust. However, hydrothermal fluids emissions from such systems predominantly contain H_2S with a $\delta^{34}S$ value (-5 to +8‰; Shanks III *et al.*, 1995) and concentrations (270-900 ppm) much lower than seawater (Von Damm *et al.*, 1985). The absence of SO_4 in these vent fluids may be explained by: (1) reduction of seawater SO_4 to H_2S (Shanks III *et al.*, 1981; Mcduff and Edmond, 1982) and/or (2) precipitation of anhydrite upon temperature increase (Seyfried Jr. and Bischoff, 1979; Teagle *et al.*, 1998; Barker *et al.*, 2010). Recent geochemical and isotope modelling showed that reduction of SO_4 to sulfide is limited at low temperatures that are comparable to conditions of hydrothermal recharge zones at ocean ridge crests (Gunnarsson-Robin *et al.*, 2017). On the other hand, removal of SO_4 by anhydrite formation upon temperature increase in the oceanic crust would imply the occurrence of large anhydrite deposits in the altered oceanic crust (Alt, 2003; Mottl, 2003; Staudigel, 2014). Such deposits, however, are largely absent from samples of the crust (Alt *et al.*, 2003). Significant anhydrite deposits in the altered oceanic crust have been only reported from the Ocean Drilling Program (ODP) Hole 504B in the eastern Pacific and beneath the Trans-Atlantic Geotraverse (TAG) massive sulfide deposit on the Mid-Atlantic Ridge (Alt, 1995; Chiba *et al.*, 1998; Teagle *et al.*, 1998). The absence of anhydrite from crustal samples was explained by either retrograde solubility of anhydrite at lower temperature with cooling oceanic crust and/or lack of appropriate samples from the oceanic basement. To date, Hole 504B is the only basement hole that penetrates through a section of extrusive flows into the underlying sheeted dikes of the oceanic crust where anhydrite precipitation and preservation would be expected. Other basement holes are limited to crustal sections where anhydrite precipitation appears unlikely (Alt *et al.*, 2003). Thus, due to lack of data, it remains poorly understood whether seawater circulation within the oceanic crust permanently removes sulfur from the oceans or whether fluids containing sulfur return to the oceans with a modified chemical and isotopic signature.

Surtsey, a young oceanic island in the offshore SE-rift zone of Iceland, has a low-temperature seawater-dominated geothermal system that can be considered as an analogue to a geothermal aquifer hosted in the recharge zones at ocean ridge crests (Jakobsson and Moore, 1986). Water samples collected from boreholes achieved at Surtsey in 1979 and 2017 (Jakobsson and Moore, 1982; Jackson *et al.*, 2019) indicate >50% decrease in SO_4 water concentration compared to seawater (Jackson *et al.*, 2019). These results suggest >50% removal of seawater SO_4 during low-temperature seafloor alteration. This study aims to constrain the processes that affect chemical and isotopic composition of sulfate minerals (anhydrite) during seafloor alteration. Anhydrite was collected from cores from recently drilled boreholes at Surtsey (Jackson *et al.*, 2019; Weisenberger *et al.*, 2019). By coupling and determining sulfur ($\delta^{34}S$) and oxygen ($\delta^{18}O$) isotopes ratios of anhydrite, the major sources of oxygen and sulfur to the system (i.e. rock or seawater) are defined. Geochemical isotope modelling will be used to help to identify the processes (e.g., seawater-rock interaction and reduction) that may cause isotope variations during seafloor alteration. Findings of this study will demonstrate whether and how low-temperature seafloor alteration may play a role in the modification of the sulfur isotope composition of the altered oceanic crust.

2. GEOLOGICAL SETTING

The oceanic island of Surtsey forms part of the Vestmannaeyjar volcanic system off the south coast of Iceland (Fig. 1). The volcano grew from the seafloor during explosive and effusive eruptions from 1963 to 1967 (Thorarinsson *et al.*, 1964; Thors and Jakobsson, 1982; Jakobsson *et al.*, 2009). This activity produced approximately 1 km^3 of material which included basaltic tuff, tephra, intrusions and lava flows (Thorarinsson, 1967; Jakobsson and Moore, 1982; Schipper *et al.*, 2015). The hydrothermal system at Surtsey is hosted in the tephra and tuff deposits (Jakobsson and Moore, 1986). The heat in the hydrothermal system has been considered to be provided by intrusions formed from 1966 to 1967 (Jakobsson and Moore, 1982; Stefánsson *et al.*, 1985; Jakobsson and Moore, 1986; Jakobsson *et al.*, 2000). Borehole water temperatures range from ~50-140°C (Jackson *et al.*, 2019). Rapid alteration and consolidation of the basalt tephra produced palagonitic tuff and the formation of secondary minerals such as sulfates, carbonates, clays and zeolites (Jakobsson, 1978; Jakobsson and Moore, 1986). In 1979, a continuously cored borehole (SE-1) was drilled in Surtsey (Jakobsson and Moore, 1982) with a total depth of 181 m (Fig. 1) providing insights into the structure of the island and hydrothermal alteration of the tephra (Jakobsson and Moore, 1982; 1986). In 2017, three additional boreholes were acquired as part of the International Continental Scientific Drilling Program (ICDP) Surtsey Underwater volcanic System for Thermophiles, Alteration processes and INnovative concretes (SUSTAIN) project (Jackson *et al.*, 2019; Weisenberger *et al.*, 2019). Two vertical cored boreholes (SE-2a and SE-2b) were drilled to 152 and 192 m depth parallel to the SE-1 hole. A third cored borehole (SE-3) with a plunge of 55° and azimuth of 264° extended to a measured depth of 354 m beneath the Surtur I crater (Fig. 1).

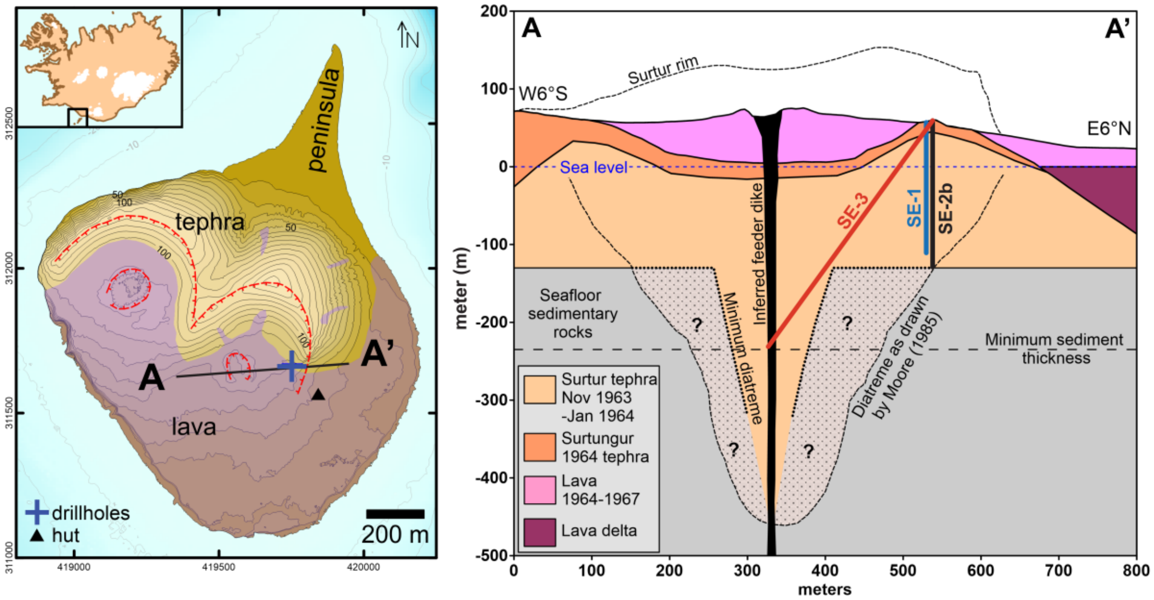

Figure 1: Location of the 1979 borehole, SE-1, and the 2017 boreholes, SE-2b and SE-3 at Surtsey, S Iceland. Maps and the schematic cross section of Surtsey are modified from Jackson et al. (2019).

3. METHODS

3.1 Sampling, Sample Processing and Analysis

Core sampling was carried out during the ICDP SUSTAIN field campaign in 2017 at Surtsey (Jackson *et al.*, 2019; Weisenberger *et al.*, 2019). The drill cores were retrieved to the surface within plastic liners. Approximately every 9 to 10 m, a ~10 cm long core segment was cut from the upper part of the third core section of the complete core run. Approximately 1/3 of each core segment from borehole SE-3 was subsequently crushed and anhydrite collected from the crushed rock. Samples from borehole SE-3 were selected because they contain anhydrite crystals that are sufficiently large for multiple isotope analyses. Anhydrite was embedded in epoxy along with the sulfate reference material, Anhydrite 1, used for oxygen and sulfur isotope analyses (Reuschel *et al.*, 2012). Each grain was analyzed for its chemical composition (Ca, S, Mg, Sr, Ba, Pb) using a JEOL JXA-8230 electron microprobe (EMP) equipped with a LaB6 electron emitter at the University of Iceland. Oxygen and sulfur isotope ratios were determined *in-situ* using a CAMECA-IMS 1280 SIMS facilities at the NordSIM laboratory of the Swedish Museum of Natural History in Stockholm. The isotope ratios for oxygen and sulfur are reported relative to VCDT (Cañon Diablo troilite) and VSMOW (Vienna standard mean ocean water), respectively, in standard delta notation.

3.2 Geochemical Isotope Modelling

Seawater-rock interaction modelling included conventional reaction path simulations where seawater was allowed to react with basaltic glass in steps. The stable or saturated secondary minerals in each step were allowed to precipitate (Stefánsson, 2010; Gysi and Stefánsson, 2011). The secondary minerals involved were those occurring in the hydrothermal system at Surtsey and included sulfate, carbonate, zeolites and clay minerals (Jakobsson and Moore, 1986). Sulfides (e.g., pyrite) were only included in the calculations for studying effects of reduction on isotope variations in anhydrite. Geochemical calculations were performed with the aid of the PHREEQC program using the wateq4f.dat database (Parkhurst and Appelo, 1999) and IsoGem (Stefánsson *et al.*, 2017). The thermodynamic database was updated to include modified equilibrium constants for anhydrite, calcite, clay minerals, zeolites and tobermorite (Johnson *et al.*, 1982; Neuhoff, 2000; Lothenbach *et al.*, 2008; Blanc *et al.*, 2010; Gysi and Stefánsson, 2011; Catalano, 2013). The values for the fractionation factors for mineral-H_2O pairs used in the calculations for $\delta^{18}O$ are based on fitting reported equilibrium fractionation factors to a smooth temperature function (Chiba et al., 1981; Zeebe, 2010; Kleine *et al.*, 2018 and references therein). The values of the sulfur fractionation factors for H_2S-SO_4^{2-}, HS^--SO_4^{2-}, anhydrite-SO_4^{2-} and pyrite-SO_4^{2-} were taken from Otake *et al.* (2008) and/or were calculated from reduced partition function ratios reported by Balan *et al.* (2014) and Eldridge *et al.* (2016). The aqueous species and minerals included in the calculations were H_2O, SO_4^{2-}, HS^-, H_2S, anhydrite, calcite, clay minerals, zeolites, pyrite and tobermorite. The chemical and isotopic compositions of basaltic glass were taken from Kaasalainen and Stefánsson (2012), Muehlenbachs and Clayton (1976) and Torssander (1989). The chemical composition of seawater was taken from Bruland (1983) whereas isotope values derived from Ólafsson and Riley (1978) and Tostevin *et al.* (2014).

4. RESULTS

4.1 Chemical and Isotope Composition of Anhydrite

The chemical and isotopic compositions of anhydrite collected from borehole SE-3 at Surtsey are graphically shown in Figure 2. Anhydrite was of pure anhydrite endmember ($CaSO_4$) composition. Minor impurities of Sr (0.08 to 0.25 wt.%) occurred occasionally. The $\delta^{34}S$ values of anhydrite were slightly lower than $\delta^{34}S$ of oceanic sulfate (+21.24‰; Tostevin *et al.*, 2014) and ranged from +18.4 to 20.8‰. In contrast, $\delta^{18}O$ values showed a large variability ranging from +5.5 to +12.9‰, thus differing from the seawater-SO_4 $\delta^{18}O$ value (+9.6‰; Kusakabe *et al.*, 1982).

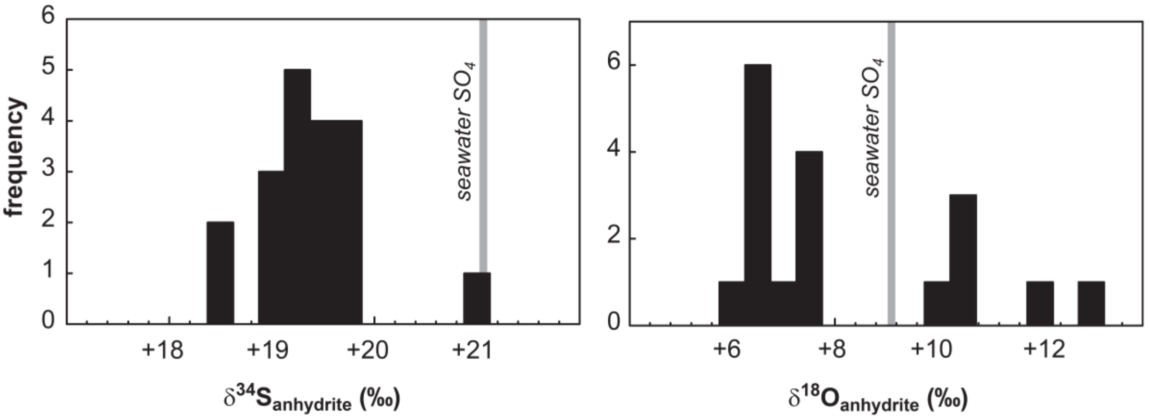

Figure 2: Isotope variations of anhydrite grains (n=19) from borehole SE-03 at Surtsey. The $\delta^{34}S$ and $\delta^{18}O$ values of seawater SO_4 are taken from Tostevin *et al.* (2014) and Kusakabe *et al.* (1982), respectively.

4.2 Geochemical Isotope Modelling

The results of the reaction path simulations between basaltic glass and seawater are shown in Figures 3 and 4. At low temperatures (≤100°C), the dominating secondary minerals forming at low reaction progress were Mg-Fe bearing clay minerals and zeolites (Fig. 3). With increasing reaction progress, calcite formed, followed by anhydrite and tobermorite. At 150°C, the modelled mineral sequence differed slightly. Anhydrite was found to become supersaturated in the geothermal water and was among the first minerals to form, followed by clay minerals and zeolite and eventually calcite and tobermorite (Fig. 3). The formation of secondary minerals was primarily dependent on the water pH at modelling temperature and extent of reaction (i.e., seawater-rock ratio). The formation of anhydrite was the primary process that limited sulfur mobility in the reacting seawater. This implies that the dominant source of sulfur and oxygen in anhydrite is seawater-SO_4. However, with progressive seawater-rock interaction, the residual fresh rock may provide an important source of both sulfur and oxygen (Fig. 4). Anhydrite may also form when seawater is heated to at least 120°C (Seyfried Jr. and Bischoff, 1979), where both Ca and SO_4 are solely of seawater origin. Equilibrium sulfur and oxygen isotope fractionation between anhydrite and seawater is positive (Chiba et al., 1981; Balan *et al.*, 2014; Eldridge *et al.*, 2016), resulting in the enrichment of the heavy isotope in the solid phase. Hence, heating of seawater from 0°C to 300°C and contemporaneous anhydrite precipitation from the residual water would lead to a progressive decrease in both $\delta^{34}S$ and $\delta^{18}O$ values of anhydrite. These eventually approach the seawater isotope values at high temperatures.

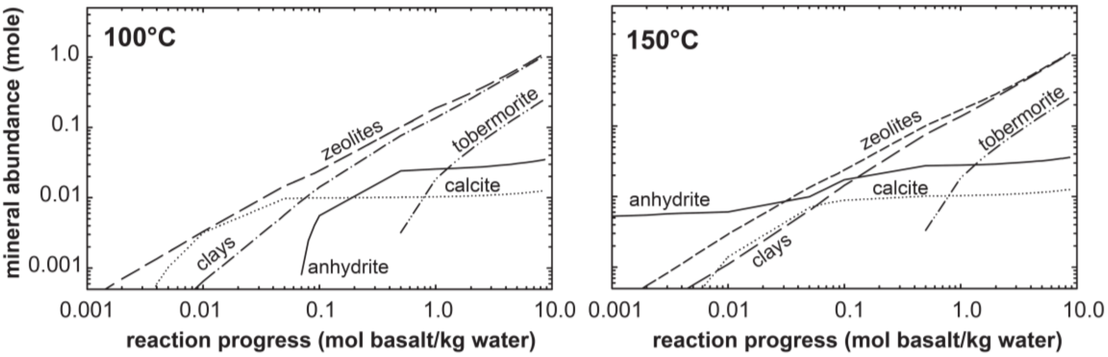

Figure 3: Calculated mineral abundances upon interaction of seawater with basaltic glass at 100°C and 150°C. The reaction path modelling was performed using the software PHREEQC (Parkhurst and Appelo, 1999).

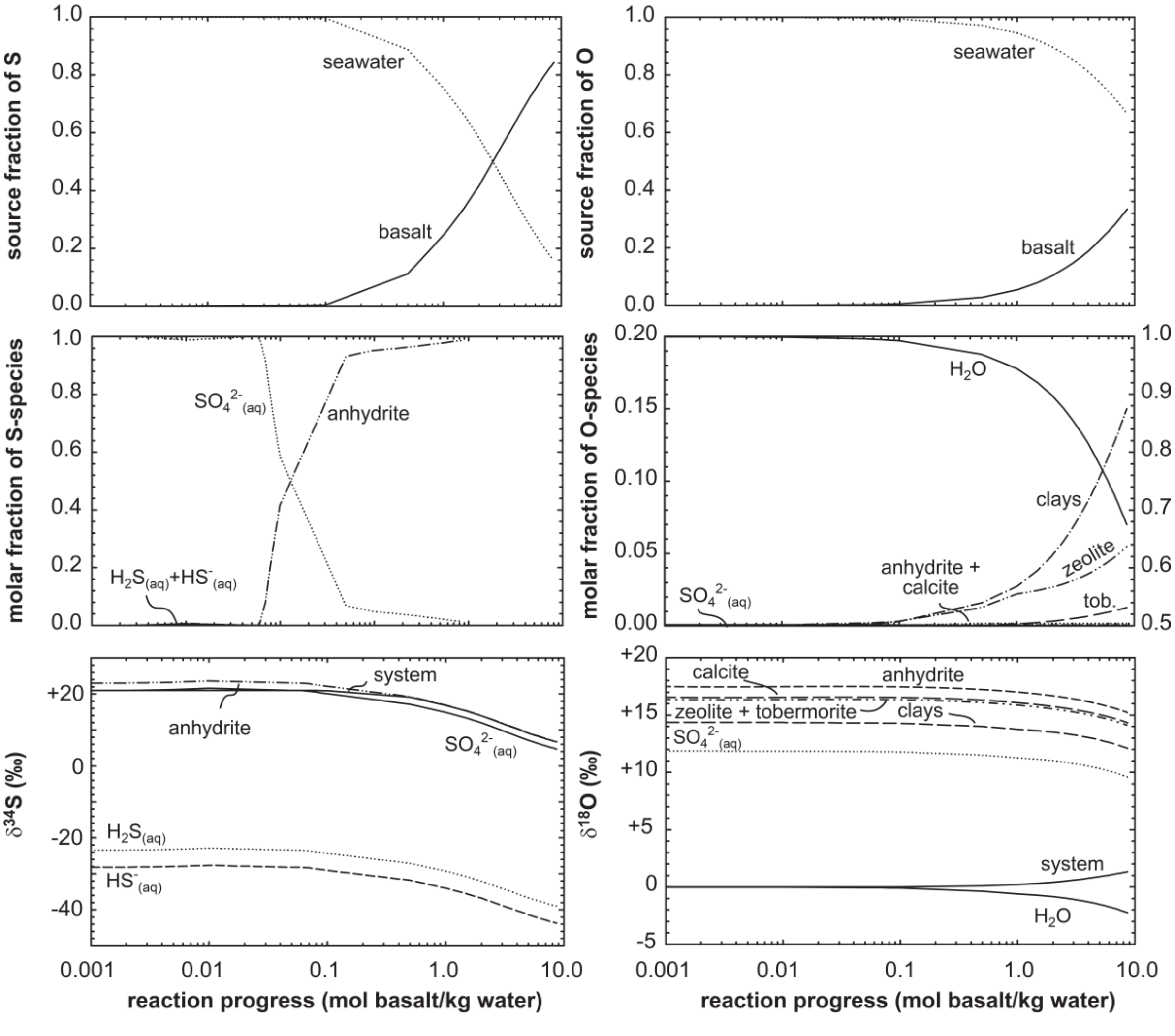

Figure 4: Results from geochemical isotope modelling at 100°C using PHREEQC (Parkhurst and Appelo, 1999) and IsoGem (Stefánsson *et al.*, 2017) showing the shift of sources of S and O in anhydrite from seawater-dominated to rock-dominated. With progressive water-rock interaction (i.e., high reaction progress or decreasing water-rock ratio) δ^{34}S and δ^{18}O values of anhydrite will approach the isotopic value of the rock.

5. DISCUSSION

5.1 Origin of SO_4 in Anhydrite

Comparison between modelled reaction pathways of progressive basalt alteration at varying temperatures showed that both δ^{34}S and δ^{18}O variations in anhydrite from Surtsey borehole SE-3 may derive from progressive seawater-rock interaction at 100-150°C (Fig. 5). Our model implies that observed isotope variations indicate that the seawater is the probable source of both the sulfur and the oxygen in the anhydrite. Deviations of δ^{34}S and δ^{18}O values from the isotope values of seawater-SO_4 can be attributed mainly to equilibrium isotope fractionation between the anhydrite and seawater at low temperature (100-150°C) upon progressive seawater-rock interaction. At 100-150°C, equilibrium sulfur isotope fractionation between seawater-SO_4 and anhydrite is very small (+1.5 to +2.0‰; Balan *et al.*, 2014; Eldridge *et al.*, 2016). Consequently, at high seawater-rock ratios (i.e., low reaction progress), the δ^{34}S values of the newly-formed anhydrite are close to those measured for seawater-SO_4 (+21.24‰; Tostevin *et al.*, 2014). However, with decreasing water-rock ratios (i.e., increasing reaction progress), the δ^{34}S of the precipitating anhydrite may approach a value as low as +4.5‰. This suggests that with progressive seawater-induced alteration the basalt with a δ^{34}S value ranging from -1.5 to +4.1‰ (Torssander, 1989) may provide a significant source of sulfur for the anhydrite. However, these low δ^{34}S values have not been observed at Surtsey, thus obviating the basaltic host rock as a potential source of sulfur for anhydrite in the young hydrothermal system. Furthermore, at 100-150°C, equilibrium O isotope fractionation between anhydrite and seawater ranges from +13.2‰ to +18.3‰ (Chiba et al., 1981). Thus, the δ^{18}O values of anhydrite forming at high seawater-rock ratios (+17.5 to +25.3‰) and low temperatures (≤100°C) are significantly more positive than δ^{18}O values of anhydrite (~+12.1 to +12.3‰) forming at elevated temperatures (~150°C). With increasing seawater-rock ratios, the δ^{18}O values of anhydrite are predicted to approach the δ^{18}O values of the reacting basalt (+5‰; Muehlenbachs and Clayton, 1976) and the basalt will eventually take over as a predominant source of oxygen to the system. As with sulfur, these low δ^{18}O values have not been observed in anhydrite from the hydrothermal system at Surtsey. This confirms that seawater is the major source of oxygen in anhydrite.

Reduction of dissolved SO_4 to H_2S upon seawater-rock interaction and subsequent precipitation of sulfur-bearing minerals from the residual water would lead to the δ^{34}S values of anhydrite becoming progressively more positive, eventually exceeding the δ^{34}S values of seawater-SO_4 (Kusakabe *et al.*, 1982; Gunnarsson-Robin *et al.*, 2017). At temperatures similar to those of the hydrothermal system at Surtsey (≤50-150°C), reduction processes would result in relatively positive δ^{34}S values of anhydrite ranging from +27 to +40‰. Such positive values have not been observed in anhydrite deriving from the SE-3 borehole at Surtsey. This implies that reduction processes are unlikely to cause isotope variations in the present sulfur-bearing minerals. This agrees with previous studies showing that reduction of dissolved SO_4 to sulfide is limited below 250°C (Ohmoto and Lasaga, 1982; Gunnarsson-Robin *et al.*, 2017).

Extending our comparison of modeled reaction pathways to δ^{34}S and δ^{18}O variations observed in anhydrite derived from ODP hole 504B demonstrates that δ^{34}S values become progressively less positive with depth (Teagle *et al.*, 1998). Our model confirms the interpretation of Teagle *et al.* (1998) that these values are the result of progressive seawater-basalt interaction at elevated temperatures. The sulfur in anhydrite is not only derived from seawater but also from oxidation of basaltic sulfide minerals. In contrast, δ^{34}S (> +21.7‰) and δ^{18}O values (> +7.0‰) observed in anhydrite precipitated beneath the active TAG hydrothermal mound are rather positive (Chiba *et al.*, 1998). Our model predicts that such isotope variations in anhydrite may be the result of heating of seawater to high temperatures (> 250°C) and contemporaneous anhydrite precipitation (Fig. 5).

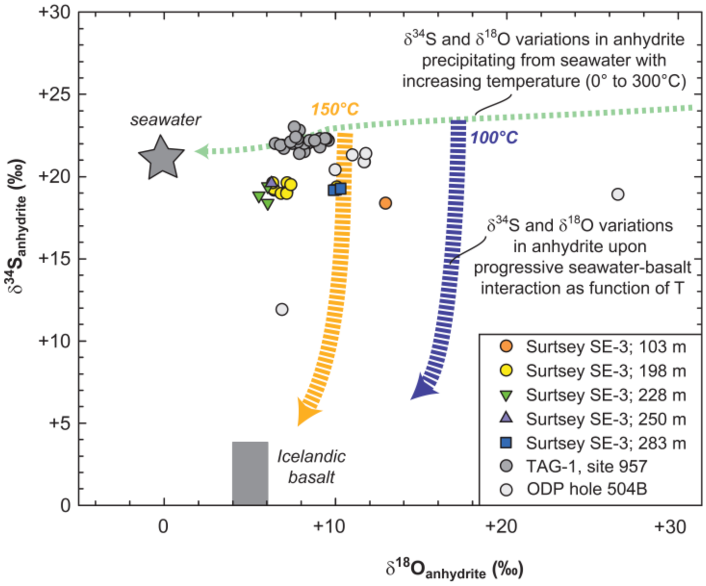

Figure 5: Comparison of δ^{34}S and δ^{18}O isotope values in anhydrite from borehole SE-3 at Surtsey (this study), TAG-1 (Chiba *et al.*, 1998) and ODP hole 504B (Teagle *et al.*, 1998) with modelled isotope variations in anhydrite upon seawater-basalt interaction and from precipitation of heated seawater. The δ^{34}S and δ^{18}O isotope values for Icelandic basalt are taken from Torssander (1989) and Muehlenbachs and Clayton (1976), respectively.

5.2 Implication for the Isotope Composition of the Altered Oceanic Crust

The amount of sulfur in the altered rock can be estimated from the molar abundance of sulfur-bearing minerals calculated by reaction path modelling (Fig. 3). Our modelling approach demonstrates that significant amounts of sulfur (up to 0.15 wt.%) may be added to basalt upon seawater-induced alteration. The sulfur content of the completely altered basalt is an order of magnitude larger than the initial sulfur content of fresh MOR basalt (~0.05 wt.%; Wallace and Carmichael, 1992). Assuming a production rate of the oceanic crust of 5.5×10^{15}g yr^{-1} (Bach *et al.*, 2003), the sulfur uptake of the oceanic crust upon anhydrite formation can be estimated to range from 2.0 to 2.6×10^{13} mol yr^{-1}. This sulfur flux is similar to calculated sulfur fluxes that are based on sulfur concentration measured in low-temperature geothermal aquifers in off-rift and flank ridge systems (Wheat and Mottl, 2000; Alt, 2003; Wheat and Fisher, 2008; Staudigel, 2014; Coogan and Gillis, 2018). Note, however, that our calculated sulfur flux is a maximum value as anhydrite formation most likely is not uniform throughout the oceanic crust. Nonetheless, the formation of anhydrite upon seafloor alteration in low-temperature geothermal aquifers of the oceanic crust could lead to a significant modification of the bulk δ^{34}S value of the upper oceanic crust to <2000 m depth. Low-temperature seawater-basalt interaction accompanied by anhydrite formation would shift the bulk δ^{34}S value of fresh basalt (-1.5 to +4.1‰; Torssander, 1989) to more positive values (+5.0 to +10‰). This would be due to the incorporation of seawater-derived SO_4, as heavy sulfur isotopes, for example, in the crystal lattice of the precipitating anhydrite.

6. CONCLUSION

Anhydrite was collected from a cored borehole at Surtsey volcano to study the effects of low-temperature seawater-basalt interaction on isotope variations in anhydrite. The anhydrite has a pure $CaSO_4$ endmember composition and displays δ^{34}S (18.4-20.8‰) and δ^{18}O (5.5-12.9‰) values that deviate slightly from the isotopic composition of seawater-SO_4. By coupling measured δ^{34}S and δ^{18}O values with geochemical reaction path modelling, the major sources of oxygen and sulfur in anhydrite is found to be seawater with minor input from the surrounding basaltic host rock. However, with progressive alteration, the principal source of sulfur and oxygen to the anhydrite may shift to the host basalt, thus explaining the departure of δ^{34}S and δ^{18}O values in the anhydrite from the isotopic values of seawater. The modelling approach was also used to calculate the amount of sulfur added to the basaltic rock through seawater-rock interaction. The results show that low-temperature seafloor alteration has the potential to significantly modify the δ^{34}S value of the Surtsey basalt, thus implying processes that make the oceanic crust isotopically more positive over time.

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