Sulfur Isotope Fractionation During Basaltic Degassing

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We examine S degassing and S isotope fractionation at basaltic volcanoes using S isotope compositions of scoria and magmatic gases from three active basaltic volcanoes in contrasting tectonic settings: Masaya and Cerro Negro (Central American Arc), and Erta Ale (East African Rift). We present S contents and S speciation of gases and melt inclusions to constrain degassing conditions. An equilibrium isotope fractionation degassing model is used to assess the S systematics considering oxygen fugacity, temperature, and pressure of degassing.

Erta Ale is a reduced system at Δ QFM ~0 [1]. Pristine scoria from Erta Ale have an average $\delta^{34}S$ value of + 0.9 ± 0.3 ‰ (n = 5) and gas samples have $\delta^{34}S$ values of + 0.7 ‰ to -1.9 ‰, spanning the MORB range of + 0.3 ± 0.5 ‰ [2] and extending to lighter values. Synchrotron micro-X-ray Absorption Near Edge Spectroscopy (XANES) analysis of an olivine-hosted melt inclusion from Erta Ale indicates that S^{2-} is the dominant S species in the melt (rather than S^{6+}). High temperature (1086°C) fumarolic gas samples have SO_2 as the dominant S species. Significantly, the scoria are isotopically heavier than the gases, which is the opposite of that expected for equilibrium conditions between S^{2-} in the melt and SO_2 gas because at equilibrium the more oxidized S species retains the heavy isotope. We interpret the low $\delta^{34}S$ values of the gas to reflect a kinetic effect that occurs as S diffuses from the melt into the gas phase (on the bubble scale) that favours the transfer of the light isotope into the gas.

Gas and scoria samples from the oxidized arc volcanoes (Cerro Negro and Masaya; ~ΔQFM +2 [3]) have a range of $\delta^{34}S$ values from + 2.2 ‰ to + 9.3 ‰. Scoria are isotopically heavier than the gases by ~3 ‰ at Masaya and by ~5 ‰ at Cerro Negro. XANES analysis of an olivine hosted melt inclusion from Cerro Negro shows that S^{6+} is the dominant S species in the melt. The negative $\Delta^{34}S_{gas\text{-}melt}$ relationship observed at Masaya and Cerro Negro is consistent with degassing of SO_2 or H_2S from a melt containing S^{6+}. However, equilibrium modelling predicts that the gas should be isotopically lighter than the melt by only 1‰ to 1.7‰ for degassing between 1 bar and 4 kbar (higher degassing pressure favours H_2S over SO_2, resulting in larger fractionation between gas and S^{6+} in the melt). The large $\Delta^{34}S_{gas\text{-}melt}$ observed at Masaya and Cerro Negro can be explained by equilibrium fractionation in addition to a kinetic effect as observed at Erta Ale. In all three cases the compositions of the gases are isotopically lighter than predicted by equilibrium modelling by 2 ‰ to 4 ‰, suggesting a common kinetic effect that favours the transfer of the light isotope into the gas phase.

[1] Giggenbach and Le Guern (1976) *GCA* **40**, 25-30. [2] Sakai et al. (1984) *GCA* **48**, 2433-2441. [3] Mather et al. (2006) *JGR* **111**, D18.

Ex situ carbonate mineralization: a novel way to sequester CO_2 at the expense of saline wastewater

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In situ and ex situ technologies based on carbonate mineralization offer ways to insure the permanent and safe storage of this greenhouse gas. In our opinion, both anthropogenically produced CO_2, at a cement plant, for example, and saline wastewaters can be utilized as valuable resources. The brines recovered from desalination operations and produced water associated with oil and gas exploitation are promising sources of alkalis and alkaline earths needed in the carbonation process. Our ex situ approach involves the formation of hydrated carbonate minerals (e.g., nesquehonite, $MgCO_3{\cdot}3H_2O$) at room temperature through the reaction of gaseous CO_2 bubbling in Mg (7 g L^{-1}) wastewater, similar to what is commonly available industrially [1]. The reaction rate is rapid, with carbonate deposition in about ten minutes. We have demonstrated that the method can be efficiently applied to more concentrated solutions, up to 32 g L^{-1} of Mg. The efficiency of the carbonate mineralization process ranges between 65 and 80%, depending on the salinity of the solution [2]. The thermal behavior and structural stability of the nesquehonite precipitate suggest that it will remain stable at the temperature conditions that prevail at the Earth's surface, i.e., below 600 K, the threshold of periclase nucleation [3]. Moreover, our results indicate that if this mineral is left in contact with the simulated brine or heated, it can be expected to transform to other carbonates thermodynamically more stable, up to about 650 K, e.g., dypingite $[Mg_5(CO_3)_4(OH)_2{\cdot}5H_2O]$ and hydromagnesite $[Mg_5(CO_3)_4(OH)_2{\cdot}4H_2O]$. These experimental results also provide information about the fate of secondary carbonates that form in a CO_2 injection environment.

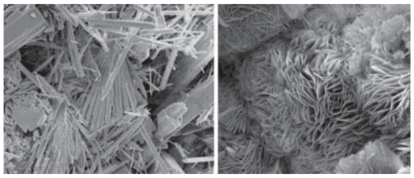

Figure 1: Nesquehonite (left), obtained by direct synthesis, and dypingite (right), obtained by transformation of early-formed carbonate.

The resulting carbonate precipitates formed in our approach can profitably be used in many applications, for example in the production of building materials. Our approach offers a complementary solution to CO_2 abatement in countries where the production of saline waste is significant.

[1] Ferrini *et al.* (2009) *Journal of Hazardous Materials* **168**, 832-837.
[2] Mignardi *et al.* (2011) *Journal of Hazardous Materials* **191**, 49-55.
[3] Ballirano *et al.* (2010) *Journal of Hazardous Materials* **178**, 522-528.