

### A Model for Sulfur Speciation and Sulfur Isotope Fractionation during Magmatic Degassing on Earth and Mars.

J. M. de Moor<sup>1,2</sup>, P. L. King<sup>1</sup>, Z.D. Sharp<sup>2</sup>, and T.P. Fischer<sup>2</sup>. <sup>1</sup>Institute of Meteoritics, MSC03 2050, 1 University of New Mexico, Albuquerque, NM87131 (mdemoor@unm.edu) <sup>2</sup>Department of Earth and Planetary Sciences, 1 University of New Mexico, Albuquerque, NM 87131.

**Introduction:** We present a model for S speciation and isotope fractionation in magmatic degassing that is applicable to terrestrial and martian magmas. The model calculates equilibrium proportions of H<sub>2</sub>S, S<sub>2</sub>, and SO<sub>2</sub> in magmatic gases, S<sup>2-</sup> and SO<sub>4</sub><sup>2-</sup> dissolved in melts, and the S isotope compositions of gases and melts at temperatures between 600°C and 1300°C and pressures between 0.01 bar and 10 kbar.

The model is tested by comparison to S isotope compositions measured in gases and rocks from a terrestrial basaltic volcano. We then apply the model to conditions of magmatic degassing on Mars to address: 1. The S gas species that are exsolved from martian magmas; 2. the potential modification of primary S isotope signatures in martian melts by magmatic degassing; and 3. the S isotope composition of the martian surface.

**Model Parameters:** The model input parameters are magmatic oxygen fugacity (fO<sub>2</sub>), temperature (T), pressure (P), and the mole fraction of water in the gas phase (XH<sub>2</sub>O). The model assumes chemical and isotopic equilibrium and that the fO<sub>2</sub> of the gas phase is buffered by that of the magma, which is reasonable for iron-rich magmas like those on Mars.

The proportions of S<sup>2-</sup> and SO<sub>4</sub><sup>2-</sup> dissolved in the melt are calculated from:

$$X = 1 / (1 + \exp(2.82 - 2.18fO_2)) \quad \text{eq. 1}$$

where X is the mole fraction of SO<sub>4</sub><sup>2-</sup>, and fO<sub>2</sub> is expressed in log units relative to the QFM buffer [1].

The proportions of SO<sub>2</sub>, H<sub>2</sub>S, and S<sub>2</sub> in the gas are assessed using the reactions:



The Gibbs free energy of equations 2 and 3 are calculated at T using thermodynamic data from [2], allowing calculation of equilibrium constants for both reactions (K<sub>1</sub> and K<sub>2</sub>, respectively) at T. A modified Redlich-Kwong equation of state from [3] is used to assess the fugacity coefficient for H<sub>2</sub>O at P and T. This allows application of:

$$fSO_2 / fH_2S = e^{\log K_1 + 1.5 \log(fO_2) - \log(\gamma_{H_2O}) - \log(X_{H_2O}) - \log P} \quad \text{eq.4}$$

from [4], which, together with:

$$fSO_2 / (fS_2)^{0.5} = K_2 / fO_2 \quad \text{eq.5}$$

allows calculation of the proportions of SO<sub>2</sub>, H<sub>2</sub>S, and S<sub>2</sub> (S species/total S) in the gas phase, assuming that the fugacity coefficients for the S gases do not change much with respect to each other as P and T change.

Equations for S isotope fractionation factors for SO<sub>4</sub><sup>2-</sup>-H<sub>2</sub>S and SO<sub>4</sub><sup>2-</sup>-S<sup>2-</sup> are taken from [5]. Equations for S isotope fractionation for SO<sub>2</sub>-H<sub>2</sub>S and SO<sub>2</sub>-S<sub>2</sub>, are derived from [6]. The fractionation factors for SO<sub>2</sub>-SO<sub>4</sub><sup>2-</sup>, SO<sub>2</sub>-S<sup>2-</sup>, H<sub>2</sub>S-S<sup>2-</sup>, S<sup>2-</sup>-SO<sub>4</sub><sup>2-</sup>, and S<sub>2</sub>-S<sup>2-</sup> can then be calculated following [7]. The equation determining the isotope fractionation between the bulk gas and bulk melt is modified

from [8] to include all species potentially present in the gas phase:

$$\begin{aligned} 1000 \ln \alpha_{gas-melt} = & \\ XA1000 \ln \alpha_{H_2S-SO_4^{2-}} + XB1000 \ln \alpha_{SO_2-SO_4^{2-}} + & \\ XC1000 \ln \alpha_{S_2-SO_4^{2-}} + YB1000 \ln \alpha_{SO_2-S^{2-}} + & \\ YA1000 \ln \alpha_{H_2S-S^{2-}} + YC1000 \ln \alpha_{S_2-S^{2-}} & \quad \text{eq.6} \end{aligned}$$

where X and Y are the mole fractions of SO<sub>4</sub><sup>2-</sup> and S<sup>2-</sup> in the melt, respectively, and A, B, and C are the mole fractions of H<sub>2</sub>S, SO<sub>2</sub>, and S<sub>2</sub> in the gas, respectively.

The evolution of the S isotope compositions of bulk melt and gas, and the species present in each are modeled for open and closed system degassing conditions following [9]. The isotope composition of a gas phase accumulated from open system degassing is also calculated.

#### Results:

*A Terrestrial Basaltic System.* Samples of gas and scoria were collected at Masaya (Central American Arc) to test the model. Masaya's magma is relatively oxidized at ΔQFM+2 [10] providing a good example of melt where most of the dissolved S exists as SO<sub>4</sub><sup>2-</sup> (eq.1). The S isotope compositions of the gas and scoria were reported by [11]. The initial S content of the melt was estimated by analyzing plagioclase hosted glass inclusions, which contain up to 240 ppm S. The degassed matrix glass contains ~20 ppm S, indicating that at least 90% of the initial S was lost to the gasphase (no sulfides are present).

The measured results are shown along with modeled degassing fractionation curves in Figure 1. An important result of this experiment is that the gas phase sampled at Masaya has an isotope composition reflecting that of an accumulated gas even though Masaya displays open system behavior. The initial isotope composition of the Masaya magma is modeled as +5.2‰ suggesting that the mantle source is affected by slab-derived fluids with high δ<sup>34</sup>S inherited from subducted seawater sulfate.

*Martian Magmas.* Martian magmas range in fO<sub>2</sub> from ~ΔQFM 0 to -3 [14, 15]. Sulfur dissolved in melts of these compositions will exist as S<sup>2-</sup>(eq.1). Figure 2 shows model results for S gas compositions in equilibrium with martian magmas with fO<sub>2</sub> of ΔQFM -3, -1.5, and 0, and P varied from 10 kbar to 0.01 bars. The results show that gases exsolved from martian magmas could have a wide range of compositions. H<sub>2</sub>S is favored at high P, S<sub>2</sub> is favored at low P and low fO<sub>2</sub>, and SO<sub>2</sub> is only favored at low P and high fO<sub>2</sub>. The results suggest that only the most oxidized martian magmas could produce substantial quantities of SO<sub>2</sub>.

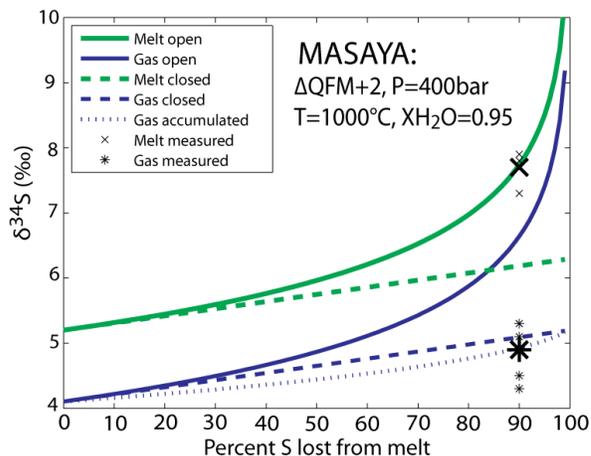
Isotope fractionation models for open system degassing at fO<sub>2</sub> and P conditions that favor S<sub>2</sub>, H<sub>2</sub>S, and SO<sub>2</sub>

are presented in Figure 3. A chondritic mantle value of  $\delta^{34}\text{S}$  0‰ is used as the initial isotope composition of martian magmas. Degassing fractionation is minimal in the case where  $\text{S}_2$  gas is dominant (Figure 3a). Minor evolution of the melt towards lower  $\delta^{34}\text{S}$  occurs when  $\text{H}_2\text{S}$  is dominant (Figure 3b). The melt can become significantly depleted in the heavy isotope when  $\text{SO}_2$  is the dominant S species in the gas (Figure 3c). In all cases, the bulk accumulated gas phase has a narrowly restricted S isotope composition of between  $\delta^{34}\text{S}$  0‰ and +2‰.

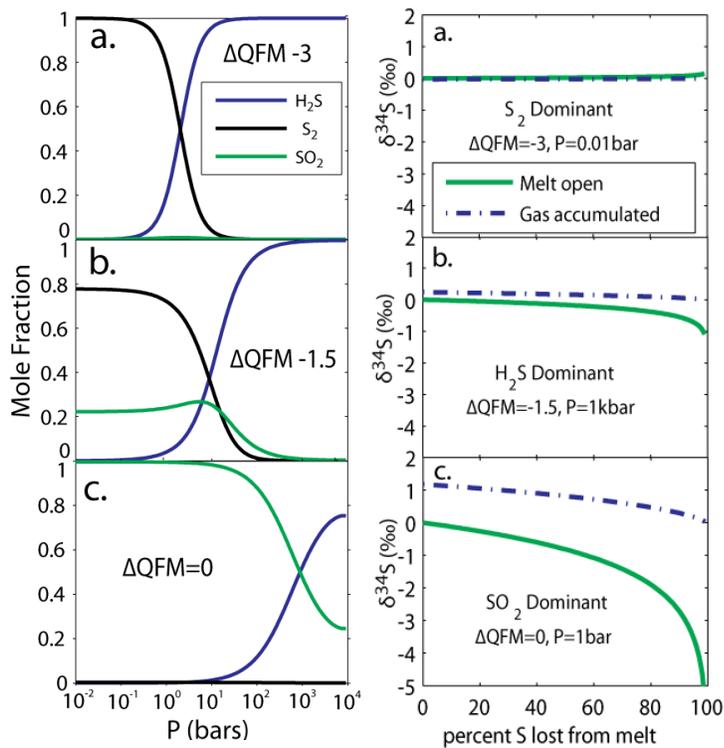
**Implications:** Our results suggest that  $\text{SO}_2$  is rarely the dominant magmatic S gas exsolved from martian magmas and is only favored at low pressure at the most oxidized conditions measured in martian meteorites. Furthermore, the model suggests that S isotope fractionation during martian magmatic degassing is minimal except where  $\text{SO}_2$  is the dominant gas species. Sulfides in Chassigny, Lafayette, and some Shergottites have  $-5\% < \delta^{34}\text{S} < 0\%$  [16] which could be explained by low P degassing fractionation at relatively high  $f\text{O}_2$  (i.e. where  $\text{SO}_2$  is dominant in the gas). The range of  $\delta^{34}\text{S}$  values measured in Nakhilites [16, 17] cannot be explained by degassing fractionation because the  $f\text{O}_2$  values for these meteorites would favor  $\text{H}_2\text{S}$  or  $\text{S}_2$  in the gas phase. The observed range in  $\delta^{34}\text{S}$  values could either be due to mantle inhomogeneity or assimilation of near-surface S. The model results suggest that gases exsolved from martian magmas had a narrow range in  $\delta^{34}\text{S}$  between 0‰ and +2‰, which should represent the bulk S isotope composition of the martian surface.

#### References:

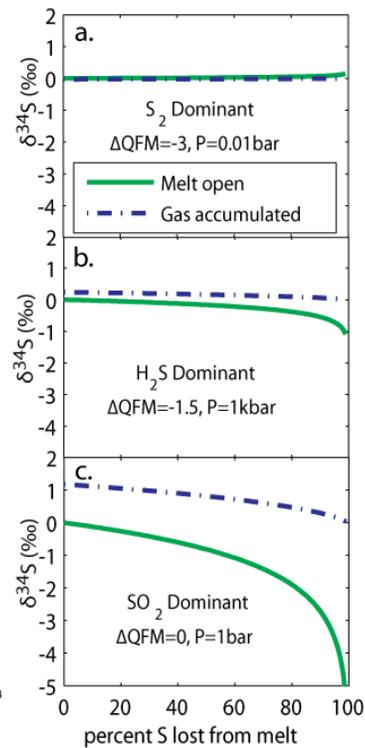
[1] Jugo P.J. et al. (2005) GCA, 69, 497-503. [2] Robie R.A. et al. (1995) USGS Bull., 2131. [3] Holland T. et al. (1991) Contrib. Min. Pet., 109, 265-273. [4] Gerlach T.M. et al. (1996) in C.G. Newhall and R.S. Punongbayan (Eds), Univ. Washington Press, 415-433. [5] Miyoshi T. et al. (1984) Geochim. Jour., 18, 75-84. [6] Richet P. et al. (1977) Ann. Rev. Earth Plan. Sci., 5, 65-110. [7] Sakai H. et al. (1982) GCA, 46, 729-738. [8] Mandeville C.W. et al. (2009) GCA, 73, 2978-3012. [9] Holloway J.R. et al. (1994) in M.R. Carroll and J.R. Holloway (Eds) MSA 187-230. [10] Mather T.A. et al. (2006) JGR, 111, D18205. [11] de Moor J.M. et al. (2010) Goldschmidt 2010 abstract. [12] Martin E. et al. (2007) Contrib. Min. Pet., 154, 559-573. [13] Burton M.R. et al. (2000) Geology, 28, 915-918. [14] Herd C.D.K. et al. (2002) GCA, 66, 2025-2036. [15] Peslier A.H. et al (2010) GCA, 74, 4543-4576. [16] Greenwood J.P. et al/ (2000) GCA, 64, 1121-1131. [17] Greenwood J.P. et al. (1997) GCA, 61, 4449-4453.



**Figure 1:** Comparison of S isotope compositions measured in gas and scoria at Masaya to model results. Large “X” and “\*” indicate average values of scoria and gas, respectively. The model inputs were  $T=1000^\circ\text{C}$  [12],  $f\text{O}_2=\Delta\text{QFM}+2$  [10], and  $\text{XH}_2\text{O} = 0.95$  [13].



**Figure 2.** Model results for S speciation for gas in equilibrium with martian magmas. Model inputs were  $T=1200^\circ\text{C}$  and  $\text{XH}_2\text{O} = 0.2$ .



**Figure 3.** S isotope degassing fractionation models for martian magmas. Model inputs were  $T=1200^\circ\text{C}$  and  $\text{XH}_2\text{O} = 0.2$ .