

THE FATE OF SULFUR DURING PARTIAL MELTING OF THE MANTLE AND FRACTIONAL CRYSTALLIZATION OF BASALTS – IMPLICATIONS FOR THE SULFUR GEOCHEMISTRY OF MARTIAN METEORITES AND DEGASSING FLUX OF SULFUR-RICH GASES FROM THE MARTIAN INTERIOR. S. Ding^{1*}, R. Dasgupta¹, C-T. A. Lee¹, M. Wadhwa², ¹sd35@rice.edu, Dept. Earth Science, Rice University, MS126, 6100 Main Street, Houston, TX 77005, USA, ²School of Earth and Space Exploration, Arizona State University, AZ, USA.

Introduction: Sulfur storage in and transport between reservoirs such as core, mantle, crust and atmosphere of Mars are tied to igneous processes. In particular, degassing of sulfur-rich gases could have been key in the warm early Mars atmosphere. To assess the degassing flux of sulfur from the mantle to the atmosphere, two steps are usually followed. (1) An assumption that the Martian mantle-derived basalts are sulfide saturated and thus experimental determination of S contents of high-FeO* basaltic melts at sulfide saturation (SCSS) provide a reasonable S-outflux [1, 2]. (2) To correct for the entrapment of sulfur in the Martian crust, the budget of magmatic S in the basaltic crust, approximated by S contents in Martian meteorites [3,4], is subtracted off. However, both of these steps rely on some untested assumptions. First, it is not considered whether sulfide, if present in the Martian mantle, can remain in the residue during partial melting; Second, most Martian meteorites contain cumulus minerals and some have experienced secondary alteration (weathering/impact effects), i.e., meteorite S budgets may not reflect true liquid concentrations. Further, though it is well known that both SCSS and S concentration changes in the evolving melt, no study has modeled the fate of sulfur during emplacement and crystallization of basalts into the Martian crust. Martian meteorites carry a record of mantle melting and subsequent differentiation history of Martian magmas. Investigation on S geochemistry of Martian meteorites in the context of generation and differentiation of primitive Martian basalts can thus provide an understanding in this regard.

In this study we determine S concentration of 7 Martian meteorites and model the behavior of S during both decompression melting of a model Martian mantle and isobaric crystallization of primary Martian magmas. Comparisons between new and existing data and modeled results suggest that (1) parental magmas of Martian meteorites might not be sulfide-saturated and only become sulfide-saturated after crystallization and (2) mixing between these differentiated sulfide-saturated basaltic melts and cumulus minerals with/without cumulate sulfides could explain the bulk sulfur contents in some Martian meteorites.

Methods: Bulk S contents of 7 Martian meteorites (the shergottites Los Angeles, Zagami, NWA 856,

NWA 1068, and Tissint, and the nakhlites NWA 998 and Nakhla) were measured using high mass-resolution solution ICP-MS following the method in [5]. Sulfur in the bulk rock fractions was dissolved and converted to the S⁶⁺ species in the form of SO₄²⁻ which is analyzed with the ThermoFinnigan Element 2 magnetic sector ICP-MS at Rice University. Further, we compiled the bulk S data of Martian meteorites from this study and previous studies. 32 Martian meteorites belonging to different lithology with available bulk rock mineralogy and composition are included. Cumulus fractions in each meteorite are calculated from mineral modes and densities.

We employed alphaMELTS [6] and SCSS parameterization from [2] to model variation of SCSS along the liquid line of descent (LLD) of a primary Martian basalt. Calculation was done for three starting composition and two different pressures. We also modeled SCSS change along isentropic decompression melting path of a model Martian mantle with two different potential temperature. We calculated dF/dP following [7] and approximated dT/dP and dX/dP using existing partial melting experimental data on model Martian mantle compositions [8,9].

Results: Within the analytical errors, the two different fractions each from NWA 856, NWA 1068 and NWA 998 yielded identical results. Therefore, the S concentrations reported here for these samples are the averages of the data for the two different fractions for each meteorite. Basaltic shergottites Los Angeles, Zagami and NWA 856 have S contents of 2865 ± 224 , 1954 ± 91 and 1584 ± 10 ppm, respectively. Olivine-phyric shergottites NWA 1068 and Tissint have S contents of 1280 ± 48 and 2120 ± 68 ppm. Clinopyroxenites Nakhla and NWA 998 yield the lowest S concentrations of 690 ± 60 and 253 ± 42 ppm S, respectively. Our measurements agree with the range of sulfur contents reported in previous studies of the martian meteorites [3,4]. It is noticeable that bulk sulfur concentration of basaltic shergottites and ol-phyric shergottites show more scatter ranging from <500 ppm to >2500 ppm compared to those of cumulates (e.g., nakhlites, Iherzolithic shergottites and ALH84001) which mostly cluster below 1000 ppm.

Discussion and Implications: Lack of correlation between bulk sulfur contents of Martian meteorites

(including this study and previous studies) and MgO or FeO_T concentration suggests that neither pure fractional crystallization nor sulfide-saturation alone can explain the bulk S contents in most of the Martian meteorites. On the contrary, a correlation between bulk S concentrations and the estimated fraction of liquid that the meteorites likely contain is observed. The correlation suggests that instead of degassing, cooling and crystallization of primary basalts may be important in S budget in Martian crust.

The bulk S of Martian meteorites is compared to the model evolution of S along LLD. And possible scenarios of S evolution during fractional crystallization in the crust are shown in Fig 1. Firstly, certain basaltic shergottites (Los Angeles and EETA79001B) are at or close to the model SCSS values derived at shallow crystallization, suggesting that at least some of the differentiated Martian basaltic magmas are sulfide saturated (liquid in scenario a and b, Fig. 1). Secondly, some cumulate Martian meteorites with or without trapped liquids (e.g., Iherzolitic shergottites) match, or are close to, the modeled S content in cumulates, which implies that significant quantity of S could originate in Martian crust as cumulus sulfides (cumulates in scenario a and b, Fig. 1). Thirdly, S contents of some basaltic and olivine-phyric shergottites, which contain a few to moderate cumulus minerals, can be obtained by mixing between sulfide saturated liquids or liquids with S concentration very close to SCSS and sulfide-free cumulates (scenario c and d in Fig 1). Another possible scenario is that primary magma of ol-phyric shergottites started sulfide undersaturated and these shergottitic liquid froze in before the melt becomes sulfide saturated (scenario e in Fig 1). Our model also implies that in order to reproduce the sulfide saturated differentiated melt and precipitate realistic amount of sulfide in the cumulates, it is likely necessary that Martian mantle-derived primitive magma was sulfide-undersaturated and became sulfide-saturated only during crystallization at a later stage.

To investigate the possibility of producing sulfide-undersaturated primitive magma, we modeled SCSS change along isentropic decompression melting path of a model Martian mantle. The calculation shows that within the plausible melting degree, a hot Martian mantle ($T_p \sim 1525$ °C) likely contains ≤ 1000 ppm S in order to produce sulfide undersaturated primitive magma while 700 ppm S is the upper limit to derive sulfide undersaturated primitive magmas from a cold mantle ($T_p \sim 1365$ °C).

The discussion above does not rule out sulfur degassing, but calls for caution in the estimation of the amount of S outgassing via young Martian basaltic volcanism. If meteorite sulfur data are any indication of the sulfur budget of ancient Martian crust, S-degassing

to the late Noachian and early Hesperian atmosphere could also be limited; instead, cumulates in the Martian crust could be an important inventory of magmatic sulfur as it may also be on Earth [10].

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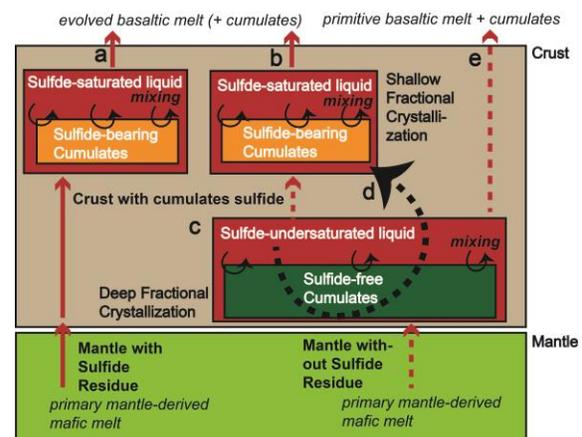


Fig. 1. Schematic of S evolution during fractional crystallization in the crust. (a) Emplaced mantle-derived mafic melt is sulfide-saturated. Sulfide is enriched in the cumulates and evolved basaltic liquid is sulfide-saturated. (b) and (c) Emplaced mantle-derived mafic melt is not sulfide saturated. Regardless of the depth of crystallization, the cumulates are initially sulfide-free. Because S becomes enriched as an incompatible element in such a sulfide-undersaturated liquid, the liquid eventually becomes sulfide-saturated and sulfide-bearing cumulates form. (d) Mixing between sulfide-free cumulates and sulfide-saturated liquid could be realized by open system magma chamber overturns. (e) Sulfide-undersaturated liquid with or without some sulfide-free cumulates froze in before the melt becomes sulfide saturated. Supply of sulfide-saturated liquid is represented by solid straight lines with arrows while that of sulfide-undersaturated liquid by dashed straight lines with arrows. Solid curved lines with arrows indicate liquid-cumulate mixing in a closed system while dashed curved line with arrow indicates liquid-cumulate mixing in an open system.