

**THE FATE OF SULFUR AND CHALCOPHILE ELEMENTS DURING CRYSTALLIZATION OF THE LUNAR MAGMA OCEAN.** E.S. Steenstra<sup>1,3</sup>, J. Berndt<sup>3</sup>, A. Rohrbach<sup>3</sup>, S. Klemme<sup>3</sup>, W. van Westrenen<sup>1</sup> <sup>1</sup>Vrije Universiteit Amsterdam, the Netherlands, <sup>2</sup>The Geophysical Laboratory, Washington D.C., United States, <sup>3</sup>Institute of Mineralogy, Münster University, Germany ([e.s.steenstra@vu.nl](mailto:e.s.steenstra@vu.nl))

**Introduction:** The distribution of S during differentiation of the Moon is key for understanding volatility-related processes [1], composition of the lunar core [2-5] and/or the occurrence and extent of sulfide saturation [4-6]. In turn, crystallization of sulfides during solidification of the Moon could strongly affect trace element abundances and ratios, including that of the (highly) siderophile elements. Although several workers have recently addressed the possibility of sulfide saturation of primitive lunar melts using S solubility and chalcophile element systematics [4-6], the distribution of S during lunar magma ocean (LMO) crystallization has never been experimentally assessed. To model the S concentration at sulfide saturation (SCSS) as a function of LMO crystallization, we performed high  $P$ - $T$  experiments in piston cylinder presses at VU Amsterdam and WWU Münster. We used a wide range of silicate melt and sulfide compositions to fully incorporate the effects of evolving composition on the SCSS.

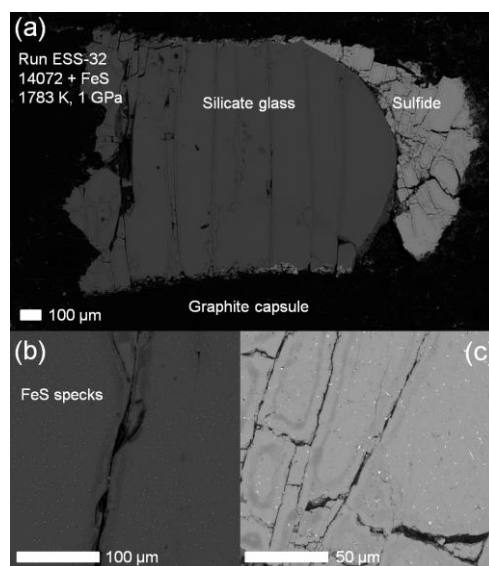
**Methods:** Sulfides and silicates were equilibrated at a constant  $P$  of 1 GPa and  $T$  between 1383–1883 K using piston cylinder presses at VU Amsterdam and WWU Münster. Silicates consisted of synthetic equivalents of lunar KREEP basalts (14072, 14276, 15386), high-Ti basalt 10017 and lunar granite 73255. Sulfide compositions consisted of FeS doped with 0.1 wt.% of P, V, Co, Ni, Cu, Zn, Ga, Ge, Se, Nb, Mo, Cd, Sn, Sb, Te, Ta, W, Pb, Bi. Synthetic silicate equivalents of 10017, 15386 and 73255 were additionally doped with 2000 ppm Li, Rb, Cs, Th and U using high-purity standard solutions. Run products were embedded in epoxy, polished and analyzed using EPMA and LA-ICP-MS at WWU Münster and Utrecht University. The LA-ICP-MS measured trace element compositions of sulfides were corrected for matrix effects using [7].

**Results:** Fig. 1 shows a typical experimental run product with quenched sulfide and silicate liquids. Typical sulfides have Fe/S ratio's close to stoichiometric FeS, with several wt% of O and <1 wt% of trace elements. Fig. 2 shows the measured SCSS values for the various silicate compositions, normalized to 1783 K using the  $T$  dependency from [4]. Measured sulfide compositions ranged between FeS to FeS + <60 and 34 wt% Cu and Ni, respectively. We observe that an increasing dilution of FeS with Cu and Ni results in lower SCSS values (Fig. 2) [4,8]. Using the approach of [4,5,8], we parameterized the SCSS as a function of  $P$ - $T$ -composition using data from this study and previous studies [4 and references therein] ( $N = 350$ ):

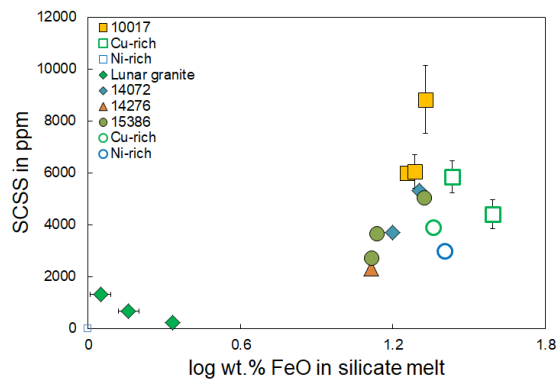
$$\ln[S]_{\text{SCSS}} (\text{ppm}) = A + \frac{B}{T} + \sum C_i X_i + D X_{\text{Fe}} X_{\text{Ti}} + E \frac{P}{T} + \ln X_{\text{FeS}}^{\text{sulfide}} + \frac{F}{T} (X_{\text{NiS}}^2 +$$

$$X_{\text{NiS}} X_{\text{CuS}_{0.5}}) + \frac{G}{T} (X_{\text{CuS}_{0.5}}^2 + X_{\text{NiS}} X_{\text{CuS}_{0.5}}) + \frac{H}{T} (-X_{\text{NiS}} X_{\text{CuS}_{0.5}})$$

where  $A$ - $H$  are regression coefficients,  $T$  is temperature,  $X_i$  are the molar fractions of cations Si, Al, Fe, Ca, Mg, Ti,  $T$  is temperature in K and  $P$  is pressure in GPa. Terms  $X_{\text{FeS}}^{\text{sulfide}}$ ,  $X_{\text{NiS}}$  and  $X_{\text{CuS}_{0.5}}$  relate to the effects of sulfide composition on SCSS and are defined as molar fraction ratios Fe/(Fe + Ni + Cu), Ni/(Ni + Fe + Cu) and Cu/(Cu + Fe + Ni), respectively [4,8].



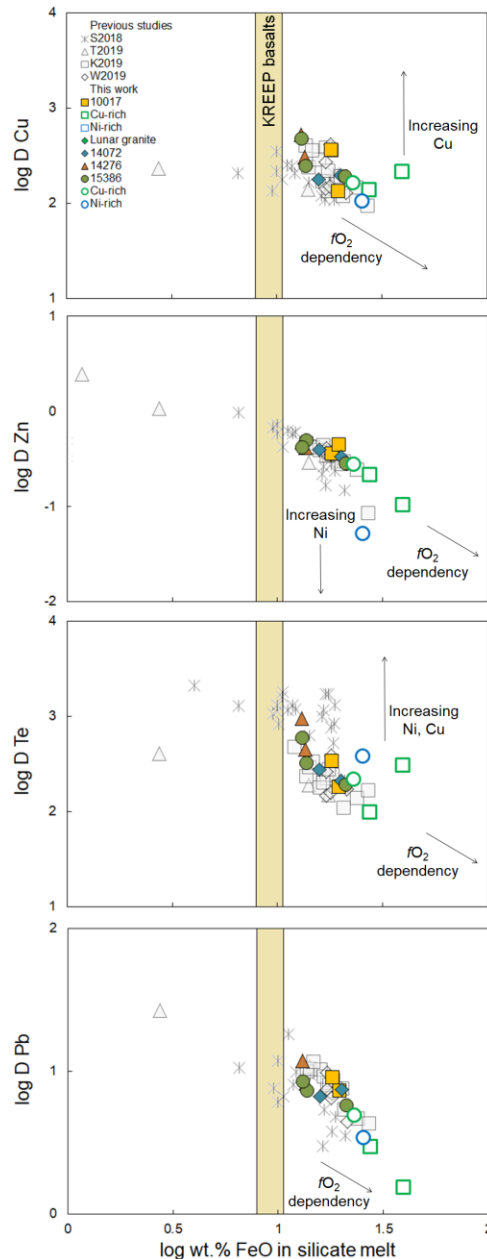
**Fig. 1:** Backscattered electron images of typical run product



**Fig. 2:** Summary of derived SCSS values for the various lunar compositions obtained at 1 GPa, normalized to 1783 K. Open symbols represent experiments performed with (Fe,Ni,Cu)S sulfide liquids.

New regressions are similar to our previous expression, confirming the robustness of the latter model [4]. We also studied the sulfide-silicate partitioning behavior of

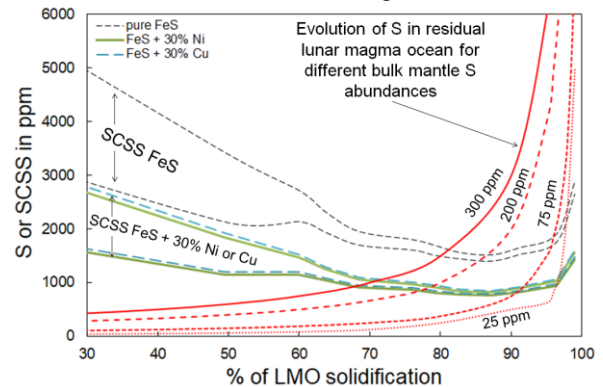
trace elements. Examples for Cu, Zn, Te and Pb are shown in Fig. 3. The results show that addition of Ni or Cu to the sulfide liquid has very different effects on  $D_{\text{sul/sil}}$  values of each element.



**Fig. 3:**  $D_{\text{sul/sil}}$  values from this study and [4,10-12] as a function of silicate melt FeO content. Values from [4] were corrected for matrix effects using the model of [7]. Horizontal bars represent the FeO range of KREEP basalts.

**Discussion:** We use our revised SCSS model to calculate the systematic variability of the SCSS as a function of LMO crystallization. For this purpose, we used the compositions and  $P$ - $T$  estimates for an anhydrous LMO [9] and explore FeS liquids and FeS liquids with 30% Ni or Cu, respectively. A wide range of

bulk silicate Moon (BSM) abundances of S are explored and we assume S behaves as a highly incompatible element in the absence of sulfides ( $D_{\text{min/melt}} = 0.001$ ). The results are shown in Fig. 4.



**Fig. 4:** Evolution of the SCSS as a function of LMO solidification for FeS and FeS + 30% Ni or 30% Cu liquids.

Our modeling results show that the SCSS decreases to about 85% of LMO solidification, after which it is increased due to a strong increase of the FeO content of the residual melt. We also observe that residual magma ocean liquids can only experience sulfide saturation from >70% of LMO solidification. This is dramatically increased with more plausible BSM S abundances (25-75 ppm) and FeS-like liquids (>90% of crystallization). A robust finding is that highly differentiated LMO liquids [13], such as (ur)KREEP, most likely experienced sulfide saturation. Given the chalcophile behavior of Pb (Fig. 3) this may (partly) explain the high  $^{238}\text{U}/^{204}\text{Pb}$  ( $\mu$ ) values of both the source of KREEP and the KREEP liquids themselves [14-15]. However, given the late occurrence of sulfide saturation during LMO crystallization it seems unlikely that lunar mantle siderophile and/or chalcophile element systematics were significantly affected by such processes [4,6].

**Conclusions:** Sulfides may have played an important role during LMO crystallization. We will perform additional SCSS and sulfide-silicate trace element modeling work for various LMO crystallization models. These results will be presented at the meeting.

**References:** [1] Wing and Farquhar (2015) *GCA* 170, 266 [2] Steenstra et al (2017) *AM* 102, 92 [3] Righter et al (2017) *EPSL* 463, 323 [4] Steenstra et al (2018) *GCA* 231, 130 [5] Ding et al (2018) *GCA* 222, 319 [6] Day (2018) *AM* 103, 1734 [7] Steenstra et al (2018) *JAAS*, in press [8] Smythe et al (2017) *AM* 102, 795 [9] Lin et al (2017) *EPSL* 471, 104 [10] Trautner et al (2019) *This meeting* [11] Kelderman et al (2019) *This meeting* [12] van Westrenen et al (2019) *This meeting* [13] Charlier et al (2018) *GCA* 234, 50 [14] Nemchin et al (2011) *GCA* 75, 2940 [15] Snape et al (2016) *EPSL* 451, 149