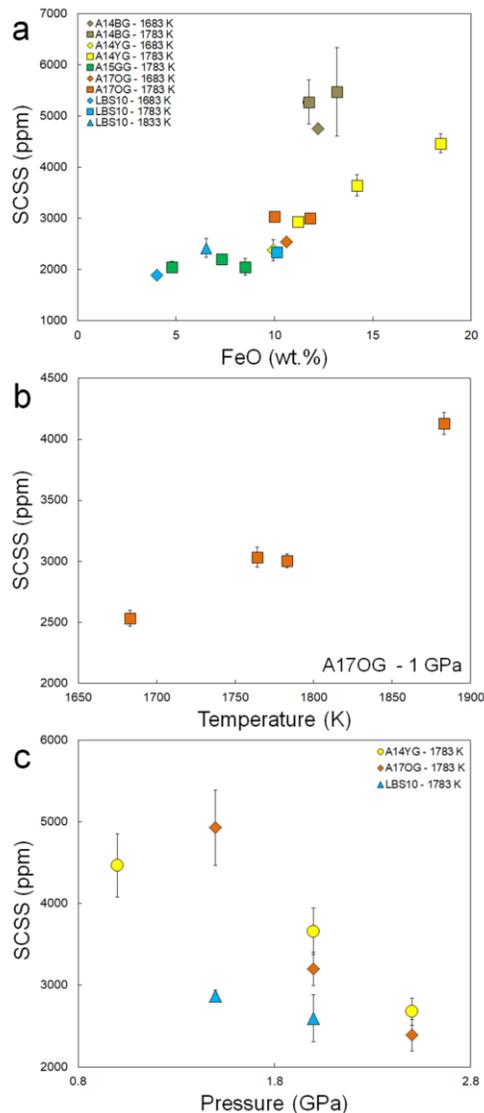


**EVIDENCE FOR A SULFUR-DEPLETED LUNAR INTERIOR FROM THE SOLUBILITY OF S IN LUNAR MELTS.** E.S Steenstra<sup>1,2</sup>, A.X. Seegers<sup>1</sup>, J. Eising<sup>1</sup>, B.G.J. Tomassen<sup>1</sup>, F.P.F. Webers<sup>1</sup>, J. Berndt<sup>3</sup>, S. Klemme<sup>3</sup>, S. Matveev<sup>4</sup>, W. van 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 <sup>4</sup> Faculty of Geosciences, Utrecht University, the Netherlands ([e.s.steenstra@vu.nl](mailto:e.s.steenstra@vu.nl))

**Introduction:** S is a volatile element and understanding its origin, abundance, and distribution in planetary interiors is important due to the effects of the S cycle on properties of planetary crusts and atmospheres. In case of the Moon, constraining S abundances in lunar reservoirs is important to constrain the early volatile budget of, and volatile fluxes in the Earth-Moon system [1-5]. One key aspect of the lunar sulfur cycle relates to the question: was the lunar interior ever saturated in sulfide minerals? Previous studies focused mostly on determination of the S content at sulfide saturation (SCSS) for terrestrial magmas, which have distinctly lower Fe and Ti contents relative to their lunar counterpart. Only few studies determined the SCSS for some lunar melts compositions [6-8]. Determination of the SCSS for low- and high-Ti melts over a wide  $P$ - $T$  and compositional range is required to assess if the source regions of lunar magmas sampled during the Apollo missions were sulfide saturated.

**Methods:** We quantified the SCSS for a suite of low- to high-Ti lunar melt compositions (A14 black and yellow glass, A15 green glass, A17 orange glass and a composition representative of late-stage lunar magma ocean (LMO) residual melt. The SCSS was determined as a function of  $P$  (1-2.5 GPa) and  $T$  (1683-1883 K) using a piston cylinder press at the VU high  $P$  laboratory. Sulfide mixtures consisted of FeS doped with 0.5 % of Se and Te. Experiments were predominantly conducted in C capsules within sealed Pt outer capsules. For these experiments, FeS powder was loaded in both the bottom and top of the C capsule to prevent significant Pt contamination [9]. Four experiments were performed in MgO capsules. Run durations varied between 30 – 120 minutes, shown to be sufficient to attain chemical equilibrium between sulfide-silicate [10]. Run products were measured for major elements with EPMA, whereas trace elements were measured with LA-ICP-MS at Münster University. The latter results were used to quantify the sulfide-silicate partitioning of 16 iron-loving elements, including Se, Te.

**Results:** Run products showed well-segregated sulfide blobs with a silicate melt that quenched to a heterogeneous-textured melt (high-MgO compositions) or a homogeneous glass. Some of the highest FeO-runs showed exsolved, minute FeS specks, consistent with sulfide saturation of the silicate melts [6]. Sulfides in most run products suffered no or very limited Pt contamination (<2 wt%).



**Fig. 1** SCSS versus (a) FeO at 1 GPa (b)  $T$  and (c)  $P$ .

Our new experimental data confirm previous observations of the increase of SCSS with FeO at > 5 wt% FeO and  $T$  and the decrease of SCSS with  $P$  [6,9] (Fig. 1).

Our new SCSS data is combined with previous data for high FeO (> 5 wt%) ( $N = 337$ ) silicate melts and regressed to the following equation to obtain a model for predicting SCSS for lunar melts [6,8,11]:

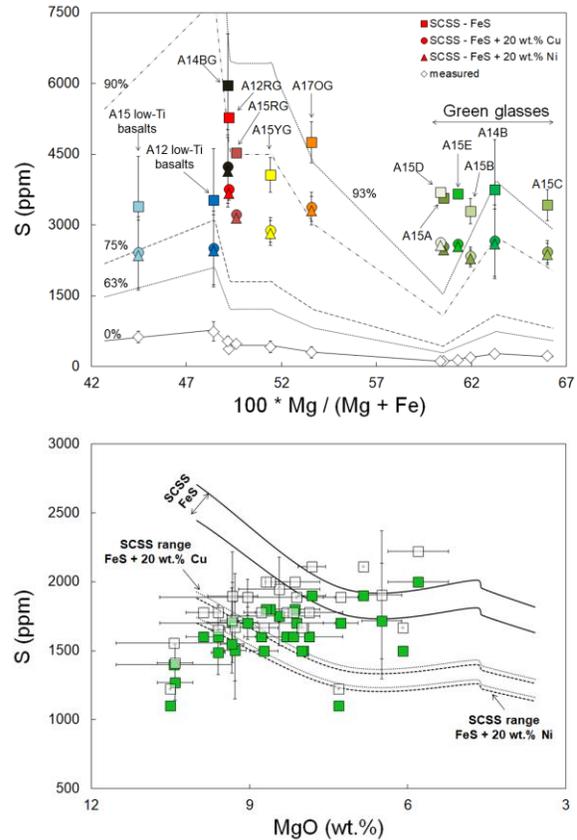
$$\ln[S]_{\text{SCSS}} (\text{ppm}) = A + \frac{B}{T} + \sum C_i X_i + D X_{\text{Fe}} X_{\text{Ti}} + E \frac{P}{T} + \ln X_{\text{FeS}}^{\text{sulfide}} + \frac{F}{T} (X_{\text{NiS}}^2 + X_{\text{NiS}} X_{\text{CuS}_{0.5}}) + \frac{G}{T} (X_{\text{CuS}_{0.5}}^2 + X_{\text{NiS}} X_{\text{CuS}_{0.5}}) + \frac{H}{T} (-X_{\text{NiS}} X_{\text{CuS}_{0.5}})$$

where  $A-H$  are regression coefficients,  $T$  is temperature,  $X_i$  are the molar fractions of cations Si, Al, Fe, Ca, Mg, Ti and  $P$  is pressure in GPa. Terms  $X_{\text{FeS}}^{\text{sulfide}}$ ,  $X_{\text{NiS}}$  and  $X_{\text{CuS}_{0.5}}$  are included to include the effects of sulfide composition on SCSS [11] and are defined as molar fraction ratios  $\text{Fe}/(\text{Fe} + \text{Ni} + \text{Cu})$ ,  $\text{Ni}/(\text{Ni} + \text{Fe} + \text{Cu})$  and  $\text{Cu}/(\text{Cu} + \text{Fe} + \text{Ni})$ , respectively. Our new model predicts the observed effects from Fig. (1) and the negative effects of Cu and Ni in sulfide on the SCSS.

We use this model to calculate the SCSS values for the various lunar low- and high-Ti melts at their proposed multiple saturation points. For (near)-primary melts (volcanic glasses and A12-A15 low-Ti basalts, the measured S abundances [4,12-14] can more or less be directly to calculated SCSS values. These results are shown in Fig. 2a. We find – even after correcting for the maximum extent of inferred degassing [4,13] – that measured S abundances for all of these samples are up to several thousand ppm lower than the predicted SCSS value. Although Cu or Ni-rich sulfides yield lower SCSS values, the existence of such sulfides in their source regions are excluded from low Cu and Ni contents in these samples [15,16].

For more evolved melts such as the A17 high-Ti basalts, calculated SCSS values cannot be directly determined with measured S contents due to the possible effects of fractional crystallization. We therefore modelled the SCSS along the liquid line of descent (LLD) determined for high-Ti basalt 70017 [17] (Fig. 2b). Note that this approach should be considered to yield a lower estimate for the SCSS, as the LLD was determined at 1 atm and associated lower  $T$ , relative to the inferred MSP's of the A17 high-Ti basalts. Most of the S contents fall below the modeled SCSS field for stoichiometric FeS, suggesting these basalts were not sulfide saturated, even when the maximum extent of degassing is assumed [4]. Some of the most evolved basalts could have been sulfide saturated, but this is highly dependent of the  $P$ - $T$  assumed for their formation.

**Discussion:** Our results provide solid evidence that the source regions of the volcanic glasses and low-Ti basalts were not sulfide saturated, unless the extent of S degassing has been underestimated by several orders of magnitude. However, such significant degassing is excluded from S isotope systematics of low and high-Ti basalts [4]. This shows that (highly) siderophile element depletions determined for the lunar mantle reflect a major sequence of metal segregation, i.e. core formation. Our results also provide additional evidence for the S-poor nature of the Moon [13] and its core [1,3]. It is also consistent with the observation that the lunar mantle depletions and ratios of S, Se, Te can be reconciled with formation of a S-poor lunar core in a fully molten Moon [2].



**Fig. 2** (a) Modelled SCSS values for stoichiometric FeS (squares), FeS + 20 wt% Cu (circles) and FeS + 20 wt% Ni (triangles) for the different (near)-primary melts considered. Vertical lines represent different degrees of degassing (b) Modelled SCSS values for A17 high-Ti basalts along LLD of 70017. Open squares represent measured values corrected for 10% degassing [4]. Basalt data from [4,14].

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