

SULFIDE LIQUID-SILICATE MELT FRACTIONATION OF HIGHLY SIDEROPHILE ELEMENTS AT HIGHLY REDUCED CONDITIONS: IMPLICATIONS FOR CORE FORMATION AND METEORITIC LATE VENEERS. E.S. Steenstra^{1,3}, J. Berndt³, S. Klemme³, W. van Westrenen², E.S. Bullock¹, A. Shahar¹, M. Walter¹ ¹The Geophysical Laboratory, Carnegie Institution for Science, Washington D.C., United States, ²VU Amsterdam, the Netherlands, ³Institute of Mineralogy, Münster University, Germany (esteenstra@carnegiescience.edu)

Introduction: Quantification of the distribution of highly siderophile elements (HSE; i.e., Ru, Rh, Pd, Re, Os, Ir, Pt) between metal- and sulfide melts during planetary differentiation is key for understanding core formation processes and the nature and extent of (a) meteoritic late veneer(s) [1–4]. Several lines of evidence point to the occurrence of highly reduced conditions in the solar system, e.g., during differentiation of the Earth and the aubrite parent body (AuPB) [5,6]. Previous experimental studies have shown that the sulfide-silicate partitioning behavior of trace elements becomes severely non-ideal at highly reduced conditions [7,8]. Further assessment of the suggested geochemical importance of sulfide liquids in Earth-forming differentiated and reduced impactors [9,10] and other reduced bodies like the AuPB [5] requires knowledge about the distribution of trace elements at such conditions. For most HSE, Au and Ag only mildly reducing sulfide liquid-silicate melt partitioning data are currently available, and it is unclear how their chalcophile behavior changes at very low fO_2 . This precludes a quantitative assessment of the potential HSE budget that can be delivered by large S-rich, differentiated impactors to the Earth [9,10]. In addition, it is unclear to what extent the HSE budget of aubrites [11] may be explained by sulfide liquid segregation [5] during AuPB differentiation. To address the above issues, we present new experimentally determined sulfide liquid-silicate melt distribution coefficients ($D^{\text{sul liq/sil melt}}$) of the HSE, Au and Ag as a function of fO_2 and corresponding variable FeO/S contents.

Methods: Sulfide- and Si-bearing metal liquids were equilibrated with a primitive basaltic glass at 1 GPa and 1700–1883 K using a Boyd and England-type piston cylinder press at VU Amsterdam and WWU Münster. Capsules were loaded with a grounded primitive synthetic basalt [8] and sulfide powder composed of stoichiometric FeS powder plus 5 wt.% Au, Ag, Pd or 10 wt.% Ir, Re, Pt). Various amounts of Fe-Si powder were added to systematically vary fO_2 and FeO/S contents of the silicate melts. Samples were chemically equilibrated at peak conditions for 180 to 20 min [8], depending on the target temperature. Experimental run products were embedded in epoxy, polished and analyzed using EPMA and LA-ICP-MS at the Geophysical Laboratory and WWU Münster, respectively. The LA-ICP-MS analyses of silicate melts were calibrated us-

ing the NIST 610 glass for Pd, Re, Pt, Au, Ag and the GSD-1G glass for Ir. Fig. 1 shows that this setup can be used to accurately determine HSE contents of silicate glasses to up to 1-3 ppb while using spot sizes of 110–130 μm .

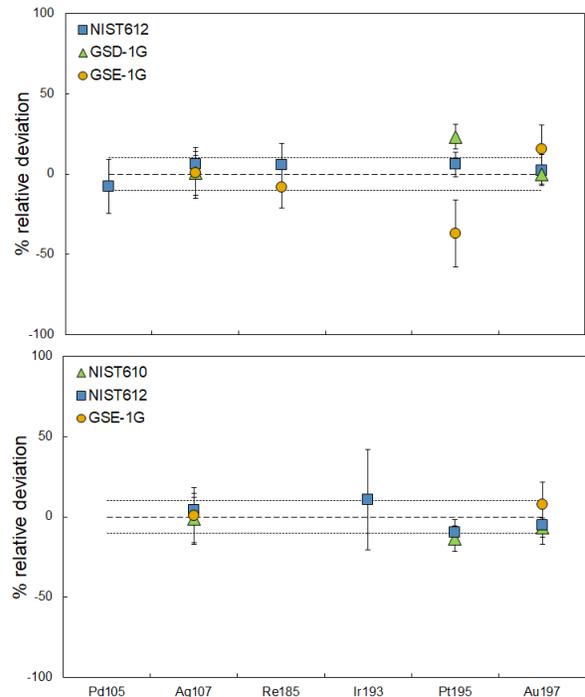


Fig. 1 Relative deviation of measured concentrations of HSE's, compared to preferred concentrations for the NIST 612, GSD-1G and GSE-1G reference materials [12]. LA-ICP-MS analyses were calibrated using NIST 610 as the internal reference material (upper panel; Pd, Re, Pt, Au) or GSD-1G (lower panel; Ir). Note the heterogeneous distribution of Pt in GSE-1G [12]. Solid lines represent 10% deviation.

Results: Fig. 2 shows a typical experimental run product. Sulfide liquids at moderately reduced conditions (i.e., CCO –1) have Fe/S close to stoichiometric FeS, with several wt.% O and <3.5 wt.% HSE. The S content at sulfide concentration (SCSS) ranged between 0.2 and 5 wt.%, depending on the redox state. Virtually all silicate melts have extremely low and relatively homogeneous HSE contents. No evidence for nano- or micro-nugget contamination was observed in the LA-ICP-MS spectra. This provides support for the hypothesis that the addition of metallic Si to the experiment reduces the formation of such nuggets [13] and that our experimental results are not affected by this potential issue.

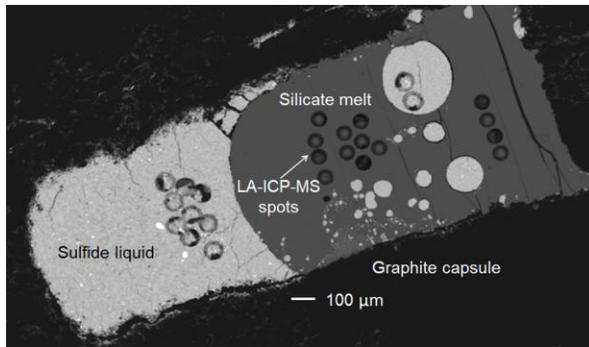


Fig. 2: Backscattered electron image of typical run product ESS-89

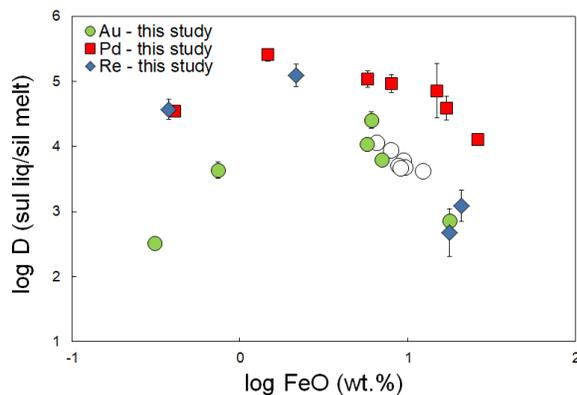


Fig. 3: $\log D^{\text{sul liq/sil melt}}$ of Au, Pd, Re as a function of FeO content of the silicate melt. Open circles are centrifuge experiments from [14]. Error bars represent propagated errors based on 2 SE uncertainties on elemental concentrations in sulfide liquids and silicate melts.

The new $D^{\text{sul liq/sil melt}}$ for some elements (Au, Pd, Re) are plotted as a function of FeO content of silicate melt in Figure 3. The results show at moderately reduced conditions (i.e., intermediate-high FeO contents) $D^{\text{sul liq/sil melt}}$ increases with decreasing FeO content of the silicate melt. At approximately 1-2 wt.% FeO in the silicate melt, all three elements behave increasingly less chalcophile with decreasing FeO contents. At low FeO (and high S) contents, the $D^{\text{sul liq/sil melt}}$ of Re, Pd and Au are (an) order(s) of magnitude lower, compared to moderate FeO contents (Fig. 3). Similar results are observed for Ir (not shown), whereas for the other HSE and Ag more experimental data are required. The non-ideal behavior of the HSE and Au is consistent with previous experimental results for other nominally (highly) chalcophile elements (e.g., Ni, Cu, Bi [7,8,11,14]). This behavior is most readily explained by their nominally chalcophile behavior: they will be more compatible in the silicate melt as the SCSS of the silicate melt increased at highly reduced conditions [7].

Discussion: The experimental results show that at low redox states (i.e., those appropriate for the AuPB, Mercury-like impactors) the HSE behave significantly

less chalcophile than that would be expected at such redox conditions if “ideal” behavior is assumed.

Once all experimental data are obtained, the sulfide liquid-silicate melt partitioning behavior of the HSE will be parameterized as a function of FeO and S content of the silicate melt and O content of the sulfide liquid using the approach of [8–10]:

$$\log D_M^{\text{sul liq-sil melt}} \approx A - \frac{n}{2} \log[\text{FeO}_{\text{sil melt}}(\text{wt.}\%)] + \varepsilon_{\text{MS}/n/2}^{\text{FeO}_{\text{sil liq}}} \log(1 - x_{\text{FeO}}^{\text{sil liq}}) + \frac{n}{2} \varepsilon_{\text{FeO}}^{\text{S}_{\text{sil melt}}} \log(1 - x_{\text{S}}^{\text{sil melt}}) \quad (1)$$

The results of the fitting procedure, as well as additional experimental results, will be reported at the meeting. We will also discuss the implications for (late) accretion of the HSE.

Conclusions: Experiments are currently performed to further assess the sulfide liquid-silicate melt partitioning of the HSE at reduced conditions. Our preliminary results show that incorporation of S-rich, reduced and differentiated impactors - under the assumption of highly efficient core-merging - could have delivered far more HSE to the proto-Earth than is currently assumed.

References: [1] Day et al. (2012) *Nat. Geosci.* [2] Dale et al. (2012) *Science* [3] Brenan et al. (2019) *Nat. Geosci.* [4] Riches et al. (2012) *EPSL* [5] Fogel et al. (2005) *GCA* [6] Rubie et al. (2015) *Icarus* [7] Wood & Kiseeva (2015) *Am. Min.* [8] Steenstra et al. (2020) *Icarus* [9] Wohlers & Wood (2015) *Nature* [10] Wohlers & Wood (2017) *GCA* [11] Van Acken et al. (2012) *GCA* [12] Jochum (2005) *GeoRem database* [13] Bennett et al. (2013) *GCA* [14] Brenan & Mungall (2014) *GCA* [15] Steenstra et al, under review. *GCA*