PARTITIONING OF HIGHLY SIDEROPHILE ELEMENTS BETWEEN SULFIDE-, METAL- AND SILICATE MELTS: THE EFFECTS OF CU AND NI AND IMPLICATIONS FOR PLANETARY DIFFERENTIATION E.S. Steenstra[1], S. Oudshoorn[2], J. Berndt[1], W. van Westrenen[2], S. Klemme[1], [1]Institute of Mineralogy, WWU Münster, Germany (esteenst@uni-muenster.de), [2] Faculty of Science, Vrije Universiteit, NL

Introduction: The depletions of highly siderophile elements (HSE) in planetary mantles provide fundamental insights into core formation processes and the nature and extent of the delivery of primitive meteoritic materials to the terrestrial planets [1−4]. Interpretation of these depletions requires insights into the variability of HSE partition coefficients between metal, sulfide and silicate melts during planetary differentiation. One aspect of HSE partitioning between sulfide liquid and silicate melt that is not well constrained are the potential effects of dissolved Ni and/or Cu in sulfide liquid. It has been shown that these elements may strongly affect the activities of many other siderophile and chalcophile elements, for example through the effects of Ni and Cu on O solubility in sulfide matte and Fe/S [e.g., 5]. Here, we constrain the effects of Ni and Cu on HSE activities in sulfide- and silicate melts by presenting a new experimental dataset consisting of >25 experiments at near-constant *P-T* conditions.

Approach: Sulfide, metal and silicate liquids were equilibrated with a primitive basaltic glass at 1 GPa and 1883 K using a Boyd and England-type piston cylinder presses at VU Amsterdam and WWU Münster. Capsules were loaded with a grounded primitive synthetic basalt [4] mixed with 25% metal powder (90% Fe, 10% Si) and sulfide powder composed of FeS powder plus 15−30% Cu and/or Ni and 5 wt.% Pd, Re and/or 10 wt.% Ir, Ru, Pt). The metallic Si was added to the starting mixture to sufficiently reduce the experimental fO_2 to prevent the formation of HSE nuggets in the silicate melt [e.g., 4]. Several experiments were also performed without added Fe metal for comparison purposes. Samples were chemically equilibrated at peak conditions for 60 to 90 min [4]. Experimental run products were embedded in epoxy, polished and analyzed using EPMA and LA-ICP-MS at WWU Münster. The LAICP-MS analyses of silicate melts were calibrated using the NIST 610 glass and ^{29}Si for Pd, Ag, Re, Pt, Au, the GSD-1G glass and ^{29}Si for Ir and a Ni sulfide and ^{56}Fe for Ru [7]. All metal and sulfide LA-ICP-MS analyses were calibrated using ^{56}Fe as an internal standard. We have previously shown 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 [4]. Finally, the LA-ICP-MS derived metal and/or sulfide contents (when needed) were corrected for matrix effects, if applicable, by using the results from ref. [4].

Results: Fig. 1 shows a typical run product. All experimental phases were found to the unzoned and chemically equilibrated, consistent with previous observations [e.g., 4]. The Ni and Cu contents of sulfide liquids were up to 24 and 29 wt.%, whereas for metal alloys it ranged between 2.5 and 23 wt.%, respectively.
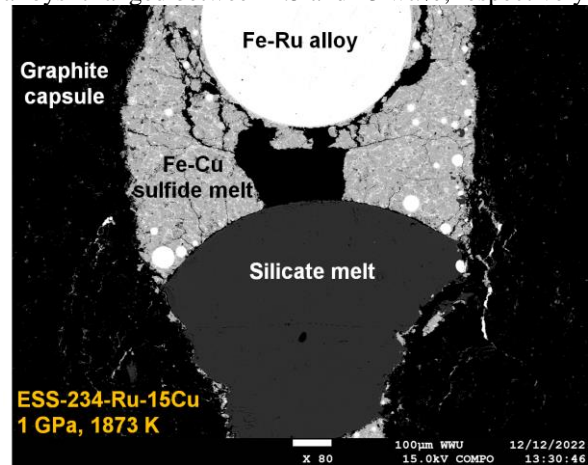

Fig. 1: BSE image of typical run product. The efficient separation of silicate melt, S-poor alloy and S-rich sulfide melt is clearly visible.
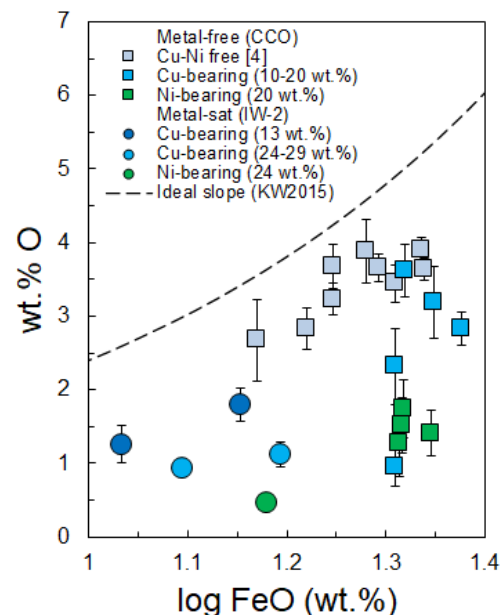

Fig. 2: O contents of sulfide matte as a function of log FeO (wt.%) of silicate melt. Ideal slope assuming constant FeO activity in silicate melt and sulfide matte is plotted for comparison purposes [5].

The effects of Cu and Ni. Variable FeO activity of both the sulfide and silicate melt, reflected by variable O in sulfide matte, exerts a key control on trace element partitioning [e.g., 4,5,7]. Fig. 2 shows the derived O contents for the sulfides mattes for metal-absent (corresponding to an approximate redox state close to the CCO buffer) and metal-saturated experiments (corresponding to a moderately reduced state of -2 to -1 log units below the iron-wüstite buffer). The O contents of sulfide liquids systematically decrease with increasing Ni and Cu content and with a decrease in oxygen fugacity (fO$_2$), in agreement with most previous studies [e.g., 4,5,8]. It should be noted ref. [5] did not observe a negative effect of Cu content on O solubility for Cu contents of <16 wt%. At higher Cu contents, we instead observe a clearly negative effect (Fig. 2)`[8]. Figure 3 shows the effects of variable Cu and Ni content of sulfide matte on D$^{sul-sil}$ Pt (where D$^{sul-sil}$ i is defined as the ratio between the concentration of element *i* in the sulfide liquid and silicate melt, respectively). The preliminary results show that D$^{sul-sil}$ Pt varies by 3.5 log units at a constant FeO content (Fig. 3). This implies that the variation in D$^{sul-sil}$ Pt in these experiments is solely due to variable Cu and Ni content and its effects on O solubility in sulfide matte and sulfide melt Fe/S. Our results show that other HSE are significantly affected by these variables as well [9].
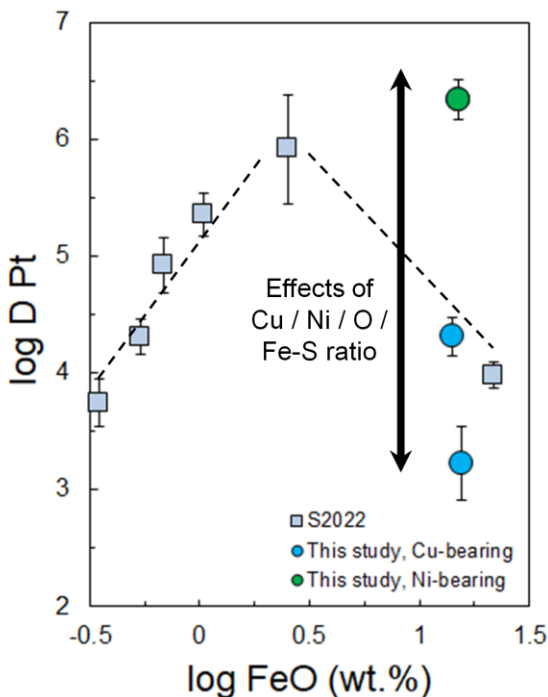
Implications and outlook: The analyzed experiments highlight the importance of both Cu and Ni in sulfide liquids for determining D$^{sul-sil}$ values. Additional experiments are currently performed to fully constrain the effects of Ni and Cu on HSE and Au, Ag partitioning between sulfide-, metal- and silicate liquids.

Given that terrestrial mantle sulfide inclusions can contain up to 40 at% Ni [e.g., ref. 10], the new results will then be used to assess the extent of HSE partitioning in Ni-rich sulfides within the terrestrial mantle. Other planetary mantles may contain Ni and/or Cu-bearing sulfide liquids as well and the potential effects of Ni and Cu on HSE partitioning will be incorporated in existing accretion and core formation models for these bodies. These parameterizations and the latter applications will be reported at the meeting.

References: [1] Day et al. (2012) *Nat. Geosci* [2] Dale et al. (2012) *Science* [3] Brenan et al. (2019) *Nat. Geosci* [4] Steenstra et al. (2022) *GCA* 336 [5] Kiseeva & Wood (2015) *EPSL* [6] Wohlgemuth-Ueberwasser et al. (2015) *JAAS* [7] Wood and Kiseeva (2015) *AM* [8] Fonseca et al. (2008) *GCA* 72 [9] Laurenz et al. (2016) *GCA* [10] Beyer et al. (2022) *CMP*

Fig. 3: Log D$^{sul-sil}$ Pt as a function of log FeO (wt.%) of silicate melt. Dashed line and light blue squares are data from ref. [4] plotted for comparison purposes [5].