Partitioning of Ru, Pd, Ag, Re, Pt, Ir and Au between sulfide-, metal- and silicate liquid at highly reduced conditions: implications for terrestrial accretion and aubrite parent body evolution

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13 Abstract: The abundances of highly siderophile elements (HSE) in planetary mantles and achondrites potentially provide important constraints on several 14 aspects of planet formation, including the nature and composition of late accreted 15 materials. Here, we experimentally and systematically assess the distribution of 16 the HSE between silicate melts, sulfide and/or metal liquids at the highly to 17 moderately reduced conditions thought to have characterized Earth accretion. The 18 results show that the chalcophile behavior of all elements, except for Re, is 19 strongly decreased at low FeO and/or high S concentrations in the silicate melt. 20 There are considerable differences between how FeO and/or S contents of the 21 silicate melt affect the D values of the various HSE, with the largest effects 22 observed for Pd, Pt, Ir and Au. If liquid metal is Si-rich and S-poor, the siderophile 23 behavior of the HSE mimics that in the presence of sulfide liquids, but with an offset 24 due to differences in HSE activities in metal and sulfide liquids. 25

Using our new experimental data, we quantify the relative effects of O in sulfide and S in silicate melt on the sulfide liquid-silicate melt partitioning behavior

of the HSE using a thermodynamic approach. The resulting expressions were used 28 to model the distribution of the HSE in highly reduced and differentiated EH- and 29 EL chondritic parent bodies and during differentiation of the aubrite parent body. 30 Our results show that even with their strongly decreased chalcophile and 31 siderophile behavior at highly reduced conditions, HSE abundances in the mantles 32 33 of these parent bodies remain extremely low. However, if such bodies accreted to Earth, any residual metal present in the parent body mantle and subsequently 34 retained in Earth's mantle would dramatically affect HSE abundances and produce 35 chondritic ratios, making it impossible to track the potential accretion of a large 36 reduced impactor to the BSE using HSE abundance systematics. In terms of the 37 aubrite parent body, our results confirm previous hypotheses related to the 38 importance of (un)differentiated core forming metals in establishing the HSE 39 contents of unbrecciated aubrites. Finally, our results confirm that sulfides are 40 likely a minor source of HSE abundances in aubrites, particularly for Re, consistent 41 with sample observations. 42

- 43 *Keywords:* late accretion, highly siderophile elements, core formation, sulfides, aubrites
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45 **1. Introduction**

The highly siderophile elements, which encompass the platinum group elements Ru, Rh, Pd, Os, Ir, Pt, as well as Re, Ag and Au, are key tracers of planetary evolution processes, including the addition of meteoritic materials to the Earth shortly (e.g., Brenan and McDonough, 2009; Dale et al., 2012; Day et al., 2012; Mann et al., 2012; Laurenz et al., 2016; Righter et al., 2018; Brenan et al., 2019; Zhu et al., 2019; Suer et al., 2021) or long

after its formation (e.g. Petrus et al., 2015). Recent experimental studies have highlighted 51 the anomalous behavior of many trace elements at highly reduced conditions in sulfide 52 liquid-saturated systems compared to moderately reduced or oxidized environments 53 (Wohlers and Wood, 2015, 2017; Wood and Kiseeva, 2015; Cartier et al., 2020, Steenstra 54 et al., 2020a,b). A key finding from these studies is that nominally chalcophile elements 55 56 behave increasingly less chalcophile at increasingly reduced conditions, or as the S content of the silicate melt increases and the FeO in silicate melt and O in sulfide liquid 57 decreases (Wood and Kiseeva, 2015). 58

Although the geochemical behavior of many elements are well constrained at such 59 conditions, the chalcophilic behavior of the HSE at highly reduced conditions remains 60 largely unconstrained. The HSE, which all exhibit highly chalcophilic behavior at slightly 61 reduced to oxidized conditions (e.g. Brenan et al., 2019 and references therein), could 62 behave significantly less chalcophilic with increasing S and decreasing FeO of the silicate 63 64 melt, as observed for other highly chalcophile elements (e.g. Ni, Cu, Bi; Wood and Kiseeva, 2015; Steenstra et al., 2020a). The distribution of the HSE between sulfide- and 65 silicate melts in highly reduced magmas may therefore be very different compared to that 66 67 for more oxidized systems such as the present-day terrestrial mantle. It is currently believed that the Earth as well as the aubrite parent body (AuPB) likely accreted at highly 68 69 reduced conditions at least for some portion of its growth (Javoy, 1995; Fogel, 2005; 70 Wade and Wood, 2005, 2016; Javoy et al., 2010; Dauphas, 2017; Münker et al., 2017; Greenwood et al., 2018a,b; Righter et al., 2018, 2020; Steenstra and van Westrenen, 71 2020). We recently assessed (Steenstra et al., 2020b) whether there is geochemical 72 73 evidence among moderately siderophile/chalcophile elements for late accretion of S-rich,

highly reduced impactors to the Earth, as proposed by Wohlers and Wood (2015, 2017)
based on Sm/Nd systematics. Although the modeled elemental abundances of
moderately chalcophile elements in highly reduced impactor mantles and the terrestrial
mantle were found to be inconsistent with such a scenario (Steenstra et al., 2020b), here
we focus on the HSE plus Re, Au and Ag, which generally have much lower volatilities
and much larger affinities for sulfide and /or metal liquids. These elements are therefore
particularly well-suited to further explore potential terrestrial accretion scenarios.

For aubrites, it has been proposed that their HSE abundances reflect a history of extensive post accretion processing events, which includes depletion by core formation, addition of a late veneer and/or core material mix-up during a potential breakup event of the aubrite parent body (AuPB) (Van Acken et al., 2012a). However, the extent to which aubrite HSE abundances may reflect metal- and/or sulfide segregation during differentiation of the HSE is not well constrained, and could affect estimates of potential HSE delivery to the AuPB.

Modeling the fate of HSE during (highly) reduced accretion requires quantitative 88 experimental constraints on the sulfide- and/or metal liquid-silicate melt distribution 89 90 behavior of these elements at appropriate conditions. To this end, fifty-one high P-T experiments were conducted in a piston cylinder apparatus to experimentally characterize 91 92 the partitioning behavior of Ru, Pd, Ag, Re, Ir, Pt and Au between sulfide-, metal- and 93 silicate melts at moderately to highly reduced conditions. These results were then used to obtain new parameterizations that allow for the prediction of their sulfide liquid - silicate 94 melt partition coefficients ($D_i^{Fe-S \, liq/sil \, melt}$) as a function of FeO and S content of the 95 silicate melt, and O content of the sulfide liquid. These parameterizations, are first used 96

to model the distribution of HSE abundances in highly reduced S-rich impactors accreted
to the Earth (Wohlers and Wood, 2015; 2017; Steenstra et al., 2020b). We subsequently
apply our data to study the nature of HSE depletions in aubrites and assess the role of
metal- and sulfide liquid segregation during AuPB differentiation.

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102 **2. Methods**

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2.1 Experimental approach

Experiments were performed in Bristol-type end-loaded piston cylinder presses (Boyd 104 and England, 1960) in the high-pressure laboratories of the Vrije Universiteit Amsterdam, 105 the Netherlands, and the University of Münster, Germany (Table 1). All experiments were 106 performed at a pressure of 1 GPa and at temperatures between 1718–1883 K using a ¹/₂ 107 inch talc-pyrex assembly (Van Kan Parker et al., 2011). The pressure calibration for this 108 assembly was based on the fayalite + quartz = ferrosillite and albite = jadeite + quartz 109 equilibria, the quartz-coesite transition and the MgCr₂O₄ + SiO₂ = Cr₂O₃ + MgSiO₃ 110 equilibria (Bose and Ganguly, 1995; Klemme and O'Neill, 1997; Van Kan Parker et al., 111 2011), with a corresponding pressure uncertainty of ~0.1 GPa. Experiments were 112 113 conducted using a combination of synthetic sulfide-, metal- and silicate powders. The silicate starting material was modeled after a primitive basaltic composition to facilitate 114 115 comparison of the results with previous studies (Steenstra et al., 2018, 2020a,b; Table 116 1).

117 Sulfide powders were prepared by adding various amounts of the HSE in the form of 118 high-purity (>99.9%) metal powders (Appendix section A.1). Generally only one HSE was 119 considered per experiment to prevent very high doping levels and resulting activity

changes. For some experiments performed with Ru and Au, 2 wt.% Ag was also added. 120 Variable amounts of Fe-Si powder were added to the experiments to systematically vary 121 the silicate melt FeO contents (and redox state) of the experiments (Table 1). Because 122 the (Fe-)Si-metal was sometimes fully consumed, in some of the experiments larger 123 amounts of (Fe-)Si metal were packed at the bottom of the graphite capsule to ensure a 124 125 highly reducing agent being present throughout the experiment,. The addition of Si should also reduce the formation of nanonuggets in guenched silicate melts (Bennett et al., 126 2014). All experiments were conducted in graphite capsules (3.5–5 mm long and 1.2–1.5 127 mm I.D.) that were machined from high-purity graphite rods. Temperatures were 128 controlled and monitored using a type D (97%W/3%Re - 75%W/25%Re) thermocouple 129 and a Eurotherm 2404 programmable controller. Samples were first pressurized to 0.5 130 GPa at room temperature. The samples were then gradually pressurized to the target 131 pressure of 1 GPa and they were simultaneously heated to 1083 and held at this 132 temperature for 20 to 60 min to reduce the porosity of the graphite capsules. Run times 133 at peak temperatures were 20-225 min, depending on peak temperature, based on 134 previous experimental assessments of the time required to achieve sulfide liquid-silicate 135 136 melt equilibrium (Kiseeva and Wood, 2013, 2015; Steenstra et al., 2018, 2020a,b). After the intended run durations (Table 1), the experimental charges were rapidly quenched, 137 embedded in epoxy and wet-polished using various grades of SiC sandpaper and Al-138 139 polishing powder. Samples were then carbon coated in preparation for compositional analyses. 140

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143 **2.2 Analytical approach**

The silicates, sulfides and metals in the experimental charges were analyzed for major 144 elements with JEOL JXA-8530F field emission electron probe microanalysers at the Earth 145 and Planets Laboratory, Carnegie Institution for Science and the University of Münster, 146 Germany (Tables 2, 3). Phases were analyzed using a defocused beam (5-15 µm), with 147 beam currents of 15–20 nA and an accelerating voltage of 15 kV. Measurement points 148 were set in lines and/or raster grids, depending on the available surface area of the 149 analyzed phases. Special care was taken to avoid analyses of areas close to the edge of 150 151 phases and/or surrounding capsule materials. Counting times were 10-30 s on peak and 5-15 seconds on each background. Analyses for sulfide liquids and silicate melts were 152 calibrated on well-characterized natural and synthetic micro-analytical reference 153 materials. The reader is referred to Steenstra et al. (2020c) for additional information 154 related to the conditions of EPMA analyses. 155

Trace element concentrations in guenched sulfide liquids, silicate melts and/or metals 156 were determined using laser ablation inductively coupled plasma mass spectrometry (LA-157 ICP-MS) at the University of Münster. The LA-ICP-MS analyses were performed using a 158 159 193 nm ArF excimer laser (Analyte G2, Photon Machines) with a repetition rate of 10 Hz and energy of $\sim 3-4$ J/cm² throughout the entire session and beam sizes ranging between 160 25–130 µm. The following masses were monitored: ²⁴Mg, ²⁹Si, ⁴³Ca, ⁴⁷Ti, ⁴⁹Ti, ⁵¹V, ⁵³Cr, 161 ⁵⁵Mn, ⁵⁶Fe, ⁵⁹Co, ⁶⁰Ni, ⁶¹Ni, ⁶³Cu, ⁶⁵Cu, ⁶⁶Zn, ⁶⁹Ga, ⁷¹Ga, ⁷³Ge, ⁷⁵As, ⁷⁷Se, ⁹⁵Mo, ¹⁰¹Ru, 162 ¹⁰⁵Pd, ¹⁰⁷Ag, ¹¹¹Cd, ¹¹⁵In, ¹¹⁸Sn, ¹²¹Sb, ¹²⁵Te, ¹⁸²W, ¹⁸⁵Re, ¹⁹³Ir, ¹⁹⁵Pt, ¹⁹⁷Au, ²⁰⁵Tl, ²⁰⁸Pb 163 and ²⁰⁹Bi. The NIST 610 glass was used as an external reference material for analyses 164 165 of Pd, Ag, Au, Re and Pt bearing experiments (Jochum et al., 2005a) due to nonavailability of other matrix-matched reference materials (i.e., in case of sulfides and metal
 alloys). Although only the HSE and Au, Ag are of interest for this particular study, most of
 the aforementioned were observed to be well-above detection limits and the data was
 thus reported as it may be beneficial for other researchers.

In case of Ir and Ru-doped experiments, glass reference materials GSD-1G (Ir, 170 171 Jochum et al., 2005b) and a Cu sulfide (Ru, Wohlgemuth-Ueberwasser et al., 2007) were used for calibrating LA-ICP-MS analyses. The concentrations of the other elements of 172 interest (e.g. Cu) within these same experiments were obtained with NIST-610 for 173 consistency with the other experiments.. In all cases, the Si (silicate melts) and Fe 174 abundances (sulfide liquids and/or metals) measured by electron microprobe were used 175 as internal standards. The LA-ICP-MS data was reduced using GLITTER software (van 176 Achterbergh et al., 2001, Griffin et al., 2008) and included monitoring and/or identification 177 of heterogeneities (e.g., sulfide inclusions in the silicate melt and vice-versa, nano-178 nuggets) or spatial compositional variations in the exposed section through the run 179 products. 180

The USGS glass reference materials BIR-1G, BCR-2G, GSE-1G, NIST 612 and/or 181 182 GSD-1G were analyzed every ~20-25 spots to assess the analytical accuracy and precision of measured trace element concentrations in the silicates, sulfides and/or 183 metals (Table S.2). These results show that the measured abundances of the elements 184 185 of interest are generally within (error of) 10% deviation relative to preferred concentrations in NIST 612, GSD-1G and GSE-1G (Jochum et al., 2005a,b). An exception is Pt in GSE-186 1G, for which we obtain lower concentrations (20±6 ppm), relative to preferred values (30 187 188 ppm; marked as *uncertain* in the GeoRem database). The concentrations of Ru measured

for NIST 610 are within error with published values, whereas for NIST 612 they are slightly
lower than published values.

The use of the NIST 610 or GSD-1G glass as a reference material for sulfides and 191 metals may result in discrepancies due to the use of non-matrix-matched standards 192 (Steenstra et al., 2019, 2020c). We assessed these potential matrix effects. It was found 193 194 that the sulfide abundances of refractory PGE Ru and Pt are consistently overestimated using ns-LA-ICP-MS and glass external reference materials, whereas abundances of the 195 more volatile element Ag are underestimated, in agreement with our previous work 196 197 (Steenstra et al., 2020c). In most cases EPMA-derived data for these elements was found to be sufficient. However, in the rare cases where LA-ICP-MS data for sulfides was 198 required, D values (Table 1) were based on LA-ICP-MS sulfide abundances that were 199 corrected using newly derived fractionation indices (Fig. S.1). 200

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202 **3. RESULTS**

3.1 Run products, oxygen fugacity and approach to a steady-state

Run products were characterized by well-segregated sulfide liquid and/or metal blobs imbedded in a silicate glass (Fig. 1a,c,e,f). The quenched silicate melts often contained small (i.e., sub-micron) FeS specks that are considered to have formed upon quenching from the silicate melt (e.g. Boujibar et al., 2014; Ding et al., 2018; Fig. 1c). Detailed investigation of the LA-ICP-MS spectra showed that these specks do not contain the highly chalcophile elements in appreciable quantities (see section 3.2), consistent with their proposed formation upon rapid quenching of the silicate melt (Boujibar et al., 2014). The sulfides generally showed smaller-scale (\sim 10–20 µm) quench heterogeneities whereas the Fe-Si metal usually quenched to a homogenous metal blob (Fig. 1).

The elements Ag, Pd, Pt and Au are known to readily dissolve up to very high 213 concentrations in sulfide liquid at the redox conditions of our experiments (Fonseca et al., 214 2009; Mungall and Brenan, 2014), requiring no assessment of the origin of Au, Pd, Pt, 215 216 Au-rich phases in the sulfide melt except for Fe-rich melt blobs. For Pt-bearing runs, sulfide liquids also showed rosette-shaped textures, indicative of a guench origin 217 (Fonseca et al., 2009). The sulfide liquids in experimental run products containing Ru 218 were often characterized by the presence of Fe metal globules in the sulfide liquid as well 219 as dendritic quenched Ru-rich phases. The latter are interpreted to represent Ru exsolved 220 upon guenching and **not** stable Ru-Fe alloy during the experiment before guenching 221 (Andrews and Brenan, 2002), and so were included in calculating Ru bulk contents of the 222 sulfide liquids. Iridium-bearing sulfide liquids were characterized by the presence of stable 223 Ir-Fe alloy crystals, whereas runs with high Ir contents such as ESS-152 also contained 224 rosette-shaped Ir textures, again indicative of a quench origin (Fig. 1d). The latter were 225 included in calculating Ir contents of the sulfide liquids, whereas the Ir-Fe alloy crystals 226 227 are considered to be a distinct phase stable at high temperature and were therefore not included (Mungall and Brenan, 2014). The solubility of Re in sulfide liquid was observed 228 to be very low (several 100 ppm), consistent with previous observations (e.g. Fonseca et 229 230 al., 2007). Finally, it should be noted that the C concentrations in the experimental silicateand sulfide melts must be low, on the order of <100-200 ppm for highly reduced silicate 231 232 melts (Li et al., 2017) and ~0.2–0.3 wt.% for FeS-rich sulfide liquids (Zhang et al., 2018).

Fe-Si liquid may dissolve up to several wt.% C and this rapidly decreases with increasing Si content of the metal liquid (Table S.4; Steenstra et al., 2020d and references therein). Oxygen fugacity (fO_2) was defined relative to the iron-wüstite buffer, or ΔIW :

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$$\Delta IW = 2 \log \left(\frac{a_{\text{FeO}}^{\text{silicate}}}{a_{\text{Fe}}^{\text{metal}}}\right) = 2 \log \left(\frac{x_{\text{FeO}}^{\text{silicate}}}{x_{\text{Fe}}^{\text{metal}}}\right) + 2 \log \left(\frac{\gamma_{\text{FeO}}^{\text{silicate}}}{\gamma_{\text{Fe}}^{\text{metal}}}\right)$$
(1)

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where $a_{\text{FeO}}^{\text{silicate}}$ and $a_{\text{Fe}}^{\text{metal}}$ are the activities of FeO and Fe in the silicate and metallic melt, 239 respectively. The activity coefficient of Fe in the metal ($\gamma_{\rm Fe}^{\rm metal}$) was calculated using the 240 online metal activity calculator (Wade and Wood, 2005). Term $\gamma_{\rm Fe}^{\rm metal}$ was calculated 241 without explicitly taking into account the effect of dissolved HSE on $\gamma_{\rm Fe}^{\rm metal}$ due to a lack 242 of appropriate interaction coefficients at the experimental P-T conditions. The activity 243 coefficient of FeO in the silicate melt ($\gamma_{\rm FeO}^{\rm silicate}$) was assumed to be unity, which is for most 244 experiments considered here a reasonable assumption given previous results for S-free 245 and S-rich systems (see Fig. 2 in both Steenstra et al., 2020a,d). The fO₂ of the 246 experiments varied between $\Delta IW+2$ to as low as $\Delta IW -4$ in runs where it could be 247 calculated (Table 1). Some experiments with higher S contents of the silicate melt for 248 which fO₂ could not be calculated probably experienced significantly more reducing 249 250 conditions, perhaps as low as $\Delta IW-6$ to $\Delta IW-8$, based on previous studies (e.g. Steenstra et al., 2020a,d). For the experiments that were conducted in the absence of (Fe-)Si metal, 251 252 the fO_2 was considered close to the C–CO₂ buffer, i.e. Δ FMQ–1 or Δ IW+2 as expected for graphite capsules (Kiseeva and Wood, 2013; Szumila et al., 2019). As in previous 253 254 sulfide-metal-silicate partitioning studies we did not have any direct control over the 255 fO₂/fS₂ ratio (e.g. Kiseeva and Wood, 2013, 2015; Wohlers and Wood 2015, 2017), which

is required for incorporating directly the effect of oxygen fugacity on derived sulfide-256 silicate partition coefficients (see Supplementary Information file section A.2 for a detailed 257 discussion). Despite long run-durations at high temperatures, the added Fe-Si metal was 258 not always fully consumed during the experiment with Fe-Si or Si metal accumulated at 259 the bottom of some of the experimental charges. For these experiments, the Fe-Si metal 260 261 was specifically added in larger quantities at the bottom of the capsule, to provide a sustainable reducing agent throughout the experiment (Table 1). This melt was generally 262 not in direct contact with the silicate melt, but rather with the FeS liquid that sank to the 263 264 bottom during the experiment. In these experiments the FeS layer occasionally formed a boundary layer between the silicate melt and the Fe-Si liquid. This prevented full 265 equilibration between the silicate melt and Fe-Si liquid, probably due to slower chemical 266 diffusivities in FeS liquid. Therefore, the recorded fO_2 in these experiments are 267 higher/more oxidizing than would be expected for a melt in direct contact with Fe-Si liquid 268 (Table 1). In all analyses only the phases that were in direct contact with the melt were 269 analyzed. Finally, it should be noted that any uncertainties in experimental fO_2 will not 270 affect the results or the models presented here, as our applied approach is essentially 271 272 independent of fO₂/fS₂, unless very large valence transitions occur for the elements of interest, which is not expected as discussed below. 273

Our experiments were held at peak conditions for at least 50 min at 1718–1733 K and >20 min at 1883 K (Table 1), but in almost all cases much longer. We previously showed with a time series that for comparable experiments steady state was approached within 30 min at 1783 K for a wide range of trace elements with very different diffusion rates (Steenstra et al., 2018). The approach to a steady state is likely much faster as implied from the results of Kiseeva and Wood (2013), who demonstrated equilibrium for
a wide range of elements within 30 min at 1673 K for comparable experimental set-ups.
Given the much longer run durations for almost all experiments, in conjunction with the
usually much higher temperatures, we conclude that steady state was achieved in all of
our experiments.

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3.2 Potential issue of micro-/nanonuggets in silicate melts

Interpretation of previous experimental results of HSE partitioning between sulfide-, 286 metal- and silicate melts has often been hampered by the presence of micro/nano-287 nuggets in the silicate melts (see Malavergne et al., 2016 for an extensive literature 288 review). Bennett et al. (2014) proposed that in the case of Pt the addition of metallic Si to 289 the experimental starting composition prevents the formation of nanonuggets as a result 290 of the rapid initial decrease in fO₂ and the corresponding lower initial Pt concentrations in 291 the silicate melt. Given these results, we therefore added metallic Si to the majority of the 292 experiments. The apparent absence of micro-/nanonuggets in almost all experimental 293 silicate melts discussed here is consistent with the results for Pt of Bennett et al. (2014) 294 295 and suggests this approach works for all of the other HSE's as well (Fig. S.2). It should also be noted that the absolute D values reported here (see sections 3.3, 3.4) are 296 297 comparable to or higher than values obtained for centrifuge experiments at comparable 298 *P-T-f*O₂ (Mungall and Brenan, 2014; see sections 3.3 and 3.4). This provides further evidence that our reported silicate melt HSE concentrations are not affected by inclusion 299 300 of nanonuggets.

302 **3.3 Distribution of HSE between FeS liquids and reduced silicate melts**

The most reduced silicate melts contained up to 5.6 wt.% S at 0.51 wt.% FeO, comparable 303 with observations for other trace element poor sulfide-silicate systems (e.g., Malavergne 304 et al., 2014; Namur et al., 2014; Wohlers and Wood, 2017; Boujibar et al., 2019; Steenstra 305 et al., 2020a,d; Table S.2). The variation in and magnitude of concentrations of Ru, Re, 306 307 Pt, and Ir measured in the sulfide liquids at different redox states are generally consistent with the results of previous experimental studies describing their solubility as a function 308 of fO₂ (e.g. Fonseca et al., 2007, 2009, 2011). The HSE contents of the sulfide liquids 309 ranged between several ppm to several 100 ppm for elements with sulfide melt solubilities 310 that vary strongly with fO₂ (Re, Ir, Pt) whereas other elements such as Ru, Pd and Au can 311 dissolve in sulfide liquids at concentrations up to several wt.% (Table S.3). The Fonseca 312 et al. (2007, 2009, 2011) studies found that the solubilities of Re, Pt and Ir are strongly 313 affected by dissolved O in the sulfide liquid. Indeed, Ir contents of sulfide liquids are much 314 lower for highly reduced runs in which sulfide liquids have very low O contents (0.1–0.4 315 wt.%), compared to more oxidized, metal-absent experiments (fO₂ near the CCO buffer) 316 in which sulfide liquids can contain up to 4–6 wt.% O. Finally, the C contents of the sulfide 317 318 liquids are expected to be on the order of <0.2-0.3 wt.% (Zhang et al., 2018) and therefore will unlikely have a measurable effect on sulfide liquid – silicate melt partition coefficients. 319 320 To quantify the distribution of the HSE between sulfide liquids and silicate melts we considered the sulfide liquid / silicate melt partition coefficient or $\ D_M^{Fe-S\,liq/sil\,melt}$: 321

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$$D_{M}^{\text{Fe-S liq/sil melt}} = \frac{\text{weight concentration of element } M \text{ in Fe-S liquid}}{\text{weight concentration of element } M \text{ in silicate melt}}$$
 (2)

Figures 2 and 3 show the newly derived log $D_M^{Fe-S \, liq/sil \, melt}$ values of the HSE as a 324 function of silicate melt FeO and S contents, respectively, in conjunction with data from 325 previous results at higher FeO contents (Kiseeva and Wood, 2013; Mungall and Brenan, 326 2014; Lauren et al., 2016; Brenan et al., 2019, Table 2). The results confirm our initial 327 hypothesis that the HSE generally show similar behavior as other nominally highly 328 chalcophile elements such as Ni and Cu (Wood and Kiseeva, 2015; Steenstra et al., 329 2020a,b). Their chalcophile behavior is strongly affected by FeO content and/or 330 increasing S content of the silicate melt and/or O content of the sulfide liquids (Kiseeva 331 and Wood, 2013, 2015; Wood and Kiseeva, 2015; Steenstra et al., 2020a,b). 332

For most elements $D_{M}^{Fe-S \, liq/sil \, melt}$ shows a parabolic dependency on FeO contents 333 of the silicate melt. From high FeO contents to intermediate FeO contents (~3-4 wt.%) of 334 the silicate melt, $D_M^{Fe-S \, liq/sil \, melt}$ of most elements increases. This is most likely a 335 combined result of decreased O content of the sulfide liquid and decreased S content of 336 the silicate melt, which is expected from thermodynamic models for such systems 337 (Kiseeva and Wood, 2013, 2015; Wohlers and Wood, 2017). From silicate melt FeO 338 contents lower than ~3-4 wt.%, $D_M^{Fe-S \, liq/sil \, melt}$ values generally decrease with decreasing 339 FeO content, which correlates with an increase of S abundance in the silicate melt. The 340 partitioning behavior of the HSE is thus most readily explained by the fact that chalcophile 341 elements are more compatible in S-rich silicate melts compared to S-poor silicate melts 342 343 (Wood and Kiseeva, 2015; Wohlers and Wood, 2017).

For all considered elements (Ru, Pd, Ag, Ir, Pt, Au) except Re, our results show that these elements behave similarly chalcophile at very low FeO contents (<0.5 wt.% FeO) and higher FeO contents (>10 wt.% FeO) (Fig. 2, 3). The results for other trace elements which were occasionally present in the experimental run products (Ti, V, Cr,
Mn, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Mo, Cd, In, Sn, Sb, Te, W, Tl, Pb and Bi) are
consistent with previously measured D values for these elements (Steenstra et al.,
2020a,b).

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352 **3.4 Distribution of HSE between Fe-Si liquids and reduced silicate melts**

Our new results can also be used to study the partitioning of Ru, Pd, Re, Pt, Ir and Au between Si-rich and S-poor metal, and S-rich silicate melts at highly reduced conditions. To quantify the distribution of the HSE between Fe(-Si) liquids and silicate melts we considered the Fe(-Si) liquid – silicate melt partition coefficient or $D_M^{Fe(-Si)liq/sil melt}$ (Table 3):

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$$D_{M}^{Fe(-Si)liq/silmelt} = \frac{weight concentration of element M in Fe(-Si)liquid}{weight concentration of element M in silicate melt}$$
 (3)

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A comparison of the metal liquid/silicate melt with the sulfide liquid/silicate melt partition 360 coefficients for the same experiments as a function of FeO content (Fig. 4) shows that 361 $D_{M}^{\text{Fe-S liq/sil melt}}$ of Re, Pt and Ir are consistently lower than their $D_{M}^{\text{Fe(-Si)liq/sil melt}}$ values, 362 ranging from 2 log units to 1.5 log units lower for Ir and Pt, 1.5 to 0.5 for Ru and up to 3-363 5 log units lower for Re. The values are comparable for Pd and Au, with Au only showing 364 a slight preference for metal liquids at moderately reduced conditions (Fig. 4). Ru, Re, Pt 365 and Ir are always more siderophile than chalcophile, independent of silicate melt FeO 366 content or fO_2 . This is consistent with the observations of Laurenz et al. (2016) who 367 described negative effects of S on their activities in Fe-rich alloys. The results for Au at 368

moderately reduced conditions are consistent with the proposed negative S effects on Au
 activity in metal alloys (e.g. Bennet et al., 2016).

The experimental Fe(-Si) alloys also contain C as a result of graphite saturation, 371 which could affect the activities of the HSE (Chabot et al., 2006; Mann et al., 2012). Mann 372 et al. (2012) observed from comparison of their C-free metal-silicate partitioning data for 373 374 Pt with C-saturated Pt data from the literature that C decreases the siderophile behavior of Pt. Similar negative effects of C on siderophile element activities have been reported 375 for almost all siderophile elements (e.g., Crockett et al., 2017). As the amount of C rapidly 376 decreases with increasing Si content of the alloy (e.g., Steenstra et al., 2020d), 377 D_{Pt}^{Fe(-Si)liq/sil melt}, and likely for other HSE, will relatively increase due to lower C contents. 378 However, increasing Si content of the metal will also decrease their metal-silicate 379 partitioning behavior (Righter et al., 2018). The effect of increasing Si on D is likely much 380 more substantial than the effects of decreasing C, yielding the observed parabolic 381 dependencies of $D_{HSE}^{Fe(-Si) liq/sil melt}$ with FeO of the silicate melt (Fig. 4). 382

Another notable feature is that the $D_M^{Fe(-Si)liq/sil melt}$ values of all HSE show very similar 383 behavior to their $D_M^{Fe-S \, liq/sil \, melt}$ behavior as a function of FeO, which in the case of Pt is 384 consistent with the observations of Médard et al. (2015) and Righter et al. (2018) for S-385 386 free systems at comparable fO₂ conditions. However, from comparison of our results of Pd and Pt with the S-free results obtained by Righter et al. (2018), a significant offset is 387 observed between $D_M^{Fe(-Si)liq/silmelt}$ at low FeO contents. This is a result of the strongly 388 negative effects of dissolved S on silicate melt FeO activity, as previously discussed in 389 390 detail in Wohlers and Wood (2017) and Steenstra et al. (2020a). This results in a different slope of $D_M^{Fe(-Si)liq/silmelt}$ values at FeO contents of approximately <1 wt.%. 391

392 **3.5 New thermodynamic models describing the sulfide liquid - silicate melt**

393

partitioning behavior of HSE during reduced accretion

To quantitatively describe the variation of $D_{HSE}^{Fe-S \, liq-sil \, melt}$ as a function of both FeO and S content of the silicate melt and O content of the sulfide liquid at constant *P-T*, we considered the approach developed by Wohlers and Wood (2017):

397

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

$$(4)$$

400

where *A* is a constant and *n* is defined as the valence of element M. Term $x_{FeO}^{Fe-S liq}$ is the mole fraction of FeO in the Fe-S liquid and $x_{S}^{sil melt}$ is the mole fraction of S in the silicate melt. Terms $\varepsilon_{MS_{n/2}}^{FeO_{Fe-S liq}}$ and $\varepsilon_{FeO}^{S_{sil melt}}$ are epsilon parameters and incorporate the interactions between Fe-O and the trace elements in Fe-S liquid and S-FeO in the silicate melt (Wohlers and Wood, 2017). The thermodynamic background and justification of Eq. (3) to treat the partitioning data is provided in detail in Supplementary Information file section A.3.

The approach outlined above requires accurate knowledge of the valence state(s) of the elements of interest and assumes that a single valence state of the element of interest dominates throughout the fO_2 range considered. Otherwise, this approach is independent of fO_2 . Previous experimental results generally proposed a 1+ valence state of Au in reduced silicate melts (Brenan et al., 2005; Li and Audetat, 2013; Sullivan et al., 2018), which we also assume (Table 4). Previous experimental sulfide liquid-silicate melt

partitioning results for Ag obtained at approximately $\triangle CCO -1$ suggests that Ag also 414 predominantly exists as Aq1+ (Kiseeva and Wood, 2015). For Pd, Laurenz et al. (2010, 415 2013) used experimental solubility data to argue for a monovalent valence state (Pd¹⁺) at 416 fO_2 lower than $\sim \Delta FMQ = 0$, consistent with the metal-silicate partitioning results of Mann 417 et al. (2012). We therefore assumed a 1+ valence state for Pd. For Ru, we assume Ru²⁺ 418 for all our experiments, as suggested to be prevalent below $\Delta IW + 2.5$ (Brenan et al., 2012) 419 and references therein; Mann et al., 2012). Bennett al. (2014) and Médard et al. (2015) 420 proposed on the base of inclusion-free Pt-solubility data that Pt should exist as Pt⁰ and/or 421 422 Pt⁻ or potentially as Pt-silicides. To illustrate the potential effects of valence assumptions on derived predictive models for Pt the experimental results were also fitted while 423 assuming Pt⁺. Rhenium is expected to be primarily dissolved as Re⁴⁺ in reduced (i.e. 424 $<\Delta$ IW +0.5) silicate melts, whereas at higher fO₂ beyond the realm of our experimental 425 dataset Re⁶⁺ becomes increasingly more prevalent (Ertel et al., 2001; Feng and Li, 2019). 426 Bennett and Brenan (2013) proposed the potential presence of Re¹⁺ or Re²⁺ based on 427 the shallower-than-expected slope of Re solubility versus fO₂ in metal-silicate systems, 428 consistent with the results of Mann et al. (2012). We therefore provide regressions for 429 Re^{1+} , Re^{4+} and Re^{6+} , covering the full range of potential uncertainties on log $D_{Re}^{Fe-S \, liq/sil \, melt}$ 430 arising from valence assumptions. For Ir, we assumed a 3+ valence state (Fonseca et al., 431 2011 and references therein). It should be noted that the effects of fO₂ uncertainties on 432 the exact valence states of all elements except Re are small compared to the dramatic 433 effects of variable FeO and S content of the silicate/sulfide melt (Fig. 3, 4). 434

The newly derived $D_{HSE}^{Fe-S \, liq/sil \, melt}$ values, obtained at 1 GPa within a narrow temperature range (1720–1883 K), were parameterized to Eq. 3. The individual

uncertainties on the partition coefficients and fitting parameters were not weighed in the 437 fit, but these are generally very small and incorporation of these would not affect the 438 results significantly. Due to the size of the experimental dataset, fit parameters were 439 considered to be statistically significant if p < 0.15. Multiple linear regressions were 440 performed using the RegressIt® excel add-on. Table 4 lists the fitting parameters. Fit 441 442 results were found to be best for Pd, Ag, Re, Ir, Pt and to a lesser extent Au. The poorer fit for Au could be due to its known complex dependencies on silicate melt composition 443 and fO_2 and/or fS_2 (Li et al., 2019). Due to the very limited number of data points available 444 for Au at highly reduced conditions this cannot yet be fully resolved. Fitting results for Ru 445 were found to be unsatisfactory overall, independent of assumed valence states, which 446 is likely due to the limited size of the dataset (N = 6). In terms of Pt and Re, experimental 447 results were best reproduced while assuming a -1 and 2+ valence state, respectively. 448 From the fitting results it is clear that Pd, Ir and Pt are most strongly affected by dissolved 449 S in the silicate melt, whereas the effects of O in the sulfide liquid are most pronounced 450 for Re (Table 4). The large effects of S in silicate melt on the activities of Pd are consistent 451 with the experimental observations of Laurenz et al. (2013). 452

The new fit parameters allow for calculating $D_{HSE}^{Fe-S \, liq/sil \, melt}$ as a function of silicate melt FeO and/or S content of the silicate melt, as well as O content of the sulfide, at fO_2 conditions ranging from the CCO buffer to well below the iron-wüstite buffer (~ ΔIW –7 to -8). It should be noted that there is no direct incorporation of the potential effects of other silicate melt compositional parameters on the activities of the elements of interest. Previous studies that were focused on non-FeO or S-related melt compositional effects on the activities of Pd and Pt suggests relatively limited effects of variable SiO₂ within a range of 20 wt.% SiO₂ (Borisov and Danyushevsky, 2011) compared to the large observed effects of S and FeO in the silicate and/or sulfide melt. It is thus unlikely that extrapolation of our experimental data to slightly less evolved compositions would underor overestimate $D_{HSE}^{Fe-S liq/sil melt}$ values.

The new parameterizations from Table 4 can thus be used to model HSE partitioning between FeS liquid and silicate melt at lunar and Martian upper mantle conditions, as well as in achondritic parent bodies, in addition to highly reduced planets. Figure S.2 provides a comparison between measured and modeled values.

468

469 **4. DISCUSSION**

470 4.1 Sulfide liquid – silicate melt fractionation of HSE at highly reduced 471 conditions

HSE abundance ratios are commonly used to interpret the nature of terrestrial late 472 accretion (e.g., Becker et al., 2006; Walker et al., 2015; Laurenz et al., 2016; Rubie et al., 473 2016). For example, chondritic Re/Os and Pt/Ir in conjunction with the supra-chondritic 474 Ru/Ir and Pd/Ir of abyssal peridotites, some mantle lherzolites and reconstructed primitive 475 upper mantle and Bulk Silicate Earth (BSE) has been suggested to indicate a late veneer 476 component and/or (an) igneous fractionation process(es), for example sulfide liquid 477 saturation or potentially Fe⁰ exsolution from the terrestrial magma ocean (Rehkamper et 478 al., 1999; Becker et al., 2006; Laurenz et al., 2016; Rubie et al., 2016; Armstrong et al., 479 2019). 480

Using our new models, we can assess the direction of HSE elemental fractionation by
 silicate melt – sulfide liquid differentiation at highly reduced conditions and compare these

observations with moderately to slightly reduced conditions (Fig. 5). We focus here 483 specifically on the HSE most commonly used in geochemical studies (Pd, Re, Ir, Pt; 484 Becker et al., 2006; Walker et al., 2015; Laurenz et al., 2016; Rubie et al., 2016). Platinum 485 generally behaves more chalcophilic than Ir, except at high FeO contents. The lowest 486 (sub-chondritic) predicted Pt/Ir ratios of the coexisting sulfide-saturated silicate melt are 487 488 observed at very low FeO contents of the silicate melt. Platinum also displays more chalcophilic behavior than Pd and Re in sulfide-saturated silicate melts that have >1 wt.% 489 FeO with the corresponding co-existing Si-poor Fe metal liquids (except for Pd at high 490 491 FeO contents; > 16 wt.% FeO). At highly reduced conditions and low FeO silicate melt contents (0.8–1.5 wt.% FeO), Re and to a lesser extent Pd behave significantly more 492 chalcophilic than Pt (Fig. 5). Palladium and Re behave only more chalcophilic than Ir at 493 highly reduced conditions (<0.6–1 wt.% FeO of the silicate melt, in the presence of Si-494 rich Fe metal liquids), whereas Pd behaves more chalcophilic then Re at FeO contents 495 exceeding >0.6-1 wt.% FeO. 496

Altogether, these results confirm that due to the interplay of the effects of S and FeO in silicate melt and sulfide liquid, the HSE show different relative chalcophilic behavior at highly reduced conditions. In the next sections we use this behavior to provide new constraints on highly reduced accretion processes.

501

502 **4.2 Distribution of HSE in highly reduced impactors accreting to Earth**

Accretion of the Earth has been proposed to involve highly reduced impactor(s) based on
the observed mantle abundances of nominally lithophile, refractory elements such as Nb,
Ta, U and Th (e.g. Münker et al., 2017, Wohlers and Wood, 2015, 2017) as well as from

oxygen isotope systematics (Greenwood et al., 2018a,b). Although Huang et al. (2020) 506 recently proposed that Nb - Ta systematics of the terrestrial mantle could also have been 507 established at more oxidizing conditions, isotopic similarities of various other refractory 508 elements (Ca, Dauphas et al., 2014; Mo, Burkhardt et al., 2011; O, Clayton et al., 1984; 509 Cr. Mougel et al., 2017) between the bulk Earth and enstatite chondrites also suggests 510 511 that a highly reduced component was involved in the accretion of the Earth. It has been proposed that such a signature could have been established through accretion of a single 512 highly reduced impactor upon formation of the Moon (e.g. Wade and Wood 2016). 513

Our new experimental results and parameterizations can be used to explore the 514 delivery potential of Ru, Pd, Re, Pt, Ir and Au to the growing Earth in such a scenario. As 515 in Steenstra et al. (2020b), first we explore core-mantle differentiation in two model bulk 516 impactor compositions: EH- and EL chondrite, with HSE concentrations for these 517 meteorite suites taken from Newsom (1995) and Alexander (2019). For each of these two 518 519 bulk compositions, we considered three end-member impactor structures in terms of core mass (all percentages in mass %): (a) a metal-free structure with a 15% FeS liquid core; 520 (b) a structure with a 30% core consisting of a 15% Fe-Si liquid inner core and a 15% 521 522 FeS liquid outer core; (c) a structure with a 65% core consisting of a 50% Fe-Si liquid inner core and a 15% FeS liquid outer core. The considered core masses and relative 523 524 core compositions encompass the full range of estimated core compositions of the 525 terrestrial planets in our solar system. The impactor mass was assumed to be fixed at 20% of the Earth's mass (Wohlers and Wood, 2015, 2017). Impactor mantle S 526 527 abundances of 1 and 3 wt.% were considered which encompass previously derived 528 aubrite vitrophyre abundances of S. The silicate melt FeO contents calculated for a

reduced silicate impactor mantle containing 1 and 3 wt. % S varies between ~0.4–0.65
wt.% FeO, respectively (Steenstra et al., 2020b, this study).

Incorporation of a 20 mass% impactor would yield S contents of the terrestrial core 531 that are within a realistic range (<3.8 wt.% S, e.g., Wohlers and Wood, 2017). The 532 considered FeO and S range captures most variation of the chalcophile and/or siderophile 533 534 behavior of the HSE at highly reduced conditions without extrapolation beyond the experimentally calibrated database. As the amount of Si in the core-forming metal liquid 535 determines the FeO and S contents of the co-existing mantle-forming silicate melt, we 536 used the previously experimentally determined relationships between Si in metal liquid, 537 O in sulfide liquid and FeO and S in silicate melt from Steenstra et al. (2020b), which are 538 based on low element doping levels. Bulk D values of the HSE during differentiation of 539 highly reduced impactors were calculated using the described modal abundances of FeS 540 and Fe-Si liquid for each of the three scenarios. 541

542

4.3 Implications for HSE abundances in the terrestrial mantle

In the first modeling scenario merging of the impactor core and proto-Earth core is 544 545 assumed to be instantaneous and completely efficient (e.g., Wohlers and Wood, 2017), although this may not necessarily be the case (e.g., Zube et al., 2019; Cambioni et al., 546 547 2021). For purposes of comparison, calculations were also performed for EH and EL impactor mantles with 0.3% mass of trapped metal. The $D_{HSE}^{Fe-S liq/sil melt}$ were calculated 548 for each scenario using Eq. (4) and the fit parameters listed in Table 4. For Ru, we 549 considered the experimentally measured $D_{HSE}^{Fe-S \, liq/sil \, melt}$ values that were obtained 550 closest to the modeled parameter space. Because our data does not allow for determining 551

Si interaction parameters of all the HSE considered, we used the highly consistent offsets between $D_{HSE}^{Fe-S \, liq/sil \, melt}$ and $D_{M}^{Fe(-Si)liq/sil \, melt}$ (Fig. 4) at highly reduced conditions (i.e. at 0.40 and 0.65 wt.% FeO corresponding to 3 and 1 wt.% S, respectively, see section 4.2) to calculate the expected $D_{M}^{Fe(-Si)liq/sil \, melt}$ values. These D values were used to calculate the abundance of the elements of interest in the core and mantle, respectively, using the following mass balance approach:

558

559
$$C_{\text{impactor mantle}}^{M} = \frac{C_{\text{bulk impactor}}^{M}}{\left[x_{\text{impactor mantle}} + (1 - x_{\text{impactor mantle}}) * \text{bulk } D_{M}^{\text{core/mantle}}\right]}$$
 (5)
560

Finally, we did not consider the potential *P*-*T* effects on HSE partitioning (e.g. Laurenz et al., 2016) due to a lack of data at the appropriate highly reduced conditions. We consider this reasonable given the very large effects of variable S and FeO content that are expected to mostly dominate the *P*-*T* effects on partitioning when extrapolating D values to the core-mantle *P*-*T* conditions relevant for the modeled impactors.

The HSE contents of the terrestrial mantle prior to impactor accretion are not precisely 566 known and depend on many variables including core composition, fO₂ during accretion, 567 potential sulfide liquid immiscibility and/or metal-segregation efficiency (e.g. Laurenz et 568 al., 2016; Rubie et al., 2016; Righter et al., 2018). We therefore assumed that the HSE 569 content of the terrestrial mantle prior to impactor accretion was completely depleted in 570 HSE and that the present-day BSE budget was completely dominated by a late veneer 571 contribution through accretion of large differentiated impactors. It is thus important to 572 573 emphasize that the calculated HSE abundances for the terrestrial mantle in the next section are lower limits – because any residual HSE present in the proto-Earth mantle 574

following early accretion of the Earth but prior to large impactor accretion would have to 575 be added to this estimate. The present-day BSE budget for the HSE was taken from 576 Wang et al. (2018). Their approach is based on the key assumption that HSE abundance 577 estimates for Earth's upper mantle can be reliably used to infer or model the whole mantle 578 composition. Evidence for global-scale homogeneity of the terrestrial mantle is provided 579 580 by geophysical observations of subducting slabs that penetrate the 660 km discontinuity as well as deep mantle plumes (as summarized by Lyubetskaya and Korenaga, 2007a,b 581 and references therein). However, it is also clear that significant chemical heterogeneities 582 exist in the terrestrial mantle, which could reflect initial accretion processes, protracted 583 terrestrial accretion or crustal recycling (e.g., Puchtel et al., 2018 and references therein). 584 As this can as of yet not be fully resolved, the modeled HSE concentrations and ratios in 585 this study could be simply reassessed in light of new, key constraints on the origin and 586 extent of terrestrial mantle heterogeneities. 587

Figure 6 shows the calculated HSE abundances in an EH- or EL chondritic impactor 588 mantle for the different core compositions considered. The calculations show that in two 589 scenarios (a 30 and 65 mass% core) the abundances of all considered HSE (Ru, Pd, Re, 590 591 Pt, Ir) in impactor mantles are (close to) negligible compared to BSE abundances, despite their significantly reduced chalcophile- and siderophile behavior at highly reduced 592 conditions. Even at very low degrees of impactor core mixing with the target mantle (i.e., 593 594 0.3 %) any "primordial impactor mantle" signature would have been fully overprinted. In addition, such impactor core addition to the proto-Earth mantle would fully account for the 595 level of present-day BSE HSE abundances, including that of a commonly proposed late 596 597 veneer (e.g., Wang and Becker, 2013). This makes it impossible, in terms of HSE

abundances, to differentiate between addition of small, undifferentiated impactors and
addition of very large, differentiated impactors. For these two scenarios, however, delivery
of Ag and Au to the proto-Earth would have been significant (Fig. 6).

The accretion of a highly reduced metal-free differentiated impactor with only a 15 601 mass % FeS liquid core yields HSE ratios that are more consistent with present-day BSE 602 603 values (Fig. 7). Due to the strongly decreased chalcophile behavior of Pt, Ir and to a lesser extent Pd in conjunction with the assumed absence of Fe-Si metal, the modeled impactor-604 mantle abundances approach in some cases present-day BSE values (Ag, Au and in 605 some cases Ir and Pt). Although some of the present-day BSE HSE ratios can be 606 reproduced in such a scenario for both a EH or EL chondritic impactor, for example in 607 case of accretion of an impactor with a 1 wt.% S bearing mantle, the net HSE abundances 608 delivered during such an event are generally one to several orders of magnitude too low. 609 Any degree of metal liquid present would profoundly affect the HSE budget of its mantle 610 and overprint any differentiation signature. 611

It should be noted that some fraction of the initial HSE may have remained in the 612 proto-Earth mantle after the initial stages of core formation as a result of (i) the 613 614 significantly decreased siderophile behavior of the HSE due to dissolved Si in the coreforming liquid (e.g. Righter et al., 2018, this study) or extreme P-T conditions (Suer et al., 615 616 2021), (ii) through accretion of oxidized material throughout terrestrial accretion (Rubie et 617 al., 2016) or (iii) less efficient metal segregation. In such a scenario, the present-day HSE primitive mantle abundances may in theory be (partly) reconciled by a combination of 618 both the "primitive" terrestrial HSE budget and the HSE delivered by (a) large 619 620 differentiated impactor(s). However, it is also evident that in such a scenario the HSE

elemental budget would likely be overwhelmed by the initial proto-Earth HSE budget and any later large impactor contribution to the Earth would be easily obscured (Fig. 6).

As previously discussed, P-T effects on partitioning within the relatively small (20%) 623 Earth mass) differentiated impactors were not considered. Pressure effects on Pd, Ru 624 and Ir partitioning between sulfide and silicate melts are relatively small (Laurenz et al., 625 626 2016), whereas for metal liquid - silicate melt systems they are more significant, especially for Ir (Mann et al., 2012). Temperature effects are significant for both metal- and sulfide 627 liquid – silicate melt partitioning of Ru, Ir, Pt and potentially other elements (Laurenz et 628 629 al., 2016; Suer et al., 2021). Increased P-T would decrease both the siderophile and chalcophile tendencies of all of the HSE. Our modeled impactor mantle abundances 630 should therefore be considered minimum values. This would not change the overall 631 conclusion that any residual metal in the impactor mantle would fully overprint any core-632 mantle differentiation signature in the impactor. 633

Our data therefore neither support nor reject the hypothesis of an up to 20 mass % highly reduced impactor being accreted to the Earth (Wohlers and Wood, 2015, 2017), for example during a Moon-forming impact (Wade and Wood, 2016). Given the results for other chalcophile and/or siderophile elements (Laurenz et al., 2016; Rubie et al., 2016; Steenstra et al., 2020b; Suer et al., 2021), it seems more likely that the chalcophile elements predominantly reflect the segregation of sulfide liquid during terrestrial magma ocean evolution combined with a late veneer.

Suer et al. (2021) recently proposed from laser-heated diamond-anvil cell metalsilicate partitioning experiments, obtained at 40 to 110 GPa, that Pt abundances would likely be relatively enriched in the BSE following core formation. Given comparable

temperature effects on metal-silicate HSE partitioning obtained at lower pressures (Mann 644 et al., 2012), their abundances in the early terrestrial magma ocean are also likely similarly 645 high. A subsequent removal of excess Pt, and potentially other HSE, for example due to 646 sulfide liquid segregation (Laurenz et al., 2016; Rubie et al., 2016) or iron exsolution 647 (Armstrong et al., 2019), is thus required to explain this discrepancy, with the present-day 648 649 HSE abundance systematics of the terrestrial mantle predominantly reflecting a late veneer. Finally, it cannot be excluded that this 'sulfide matte" (O'Neill, 1991) may have 650 been (partly) derived from accretion of a S-rich reduced impactor (Wade and Wood, 651 652 2016).

653

4.4 Application to aubrite parent body (AuPB) differentiation

Aubrites are a suite of highly reduced meteorites of which basaltic vitrophyres have very 655 low FeO (0.15–0.26 wt. %) contents and high S contents (up to 2.6 wt.%) (Fogel, 2005). 656 They are derived from a parent body that accreted and differentiated very early in the 657 history of the solar system (4564–4562 Ma), based on ⁵³Mn-⁵³Cr systematics 658 (Shukolyukov and Lugmair, 2004). This implies that the aubrite parent body likely 659 660 underwent a magma ocean stage (e.g., Keil, 2010) due to heat produced by decay of short-lived radiogenic isotope systems, during which metal- and sulfide liquid phases 661 (partly) segregated. Aubrites are characterized by an overall depletion of various volatile, 662 663 chalcophile and siderophile elements (Zn, Cd, In, Se, Te, TI) (Biswas et al., 1980, Wolf et al., 1983) as well as the HSE (e.g. Van Acken et al., 2012a). The high abundance of 664 sulfide phases strongly suggests aubrites were sulfide-saturated during igneous 665 666 differentiation, consistent with chalcophile element abundances in the Peña Blanca

Spring meteorite that points to segregation of 6 wt.% sulfide liquid during differentiation of the AuPB (Lodders, 1993). Fractionation of metal and sulfide of (a) parental melt(s) has also been suggested to explain relatively low metal and sulfide fractionations in some aubrites (Fogel, 2005). Alternatively, it could also be the result of sulfide mobilization during energetic and disruptive impact processes (e.g., D'Orazio et al., 2009).

We recently investigated the potential of moderately siderophile and chalcophile element storage in the AuPB Fe-Si core and sulfide liquid, respectively, but found that for most elements core formation and/or sulfide liquid segregation cannot explain their low abundances in aubrites (Steenstra and van Westrenen, 2020; Steenstra et al., 2020b). We now use our experimental results to provide more constraints on the nature of HSE abundances in aubrites.

Previous workers reported highly variable HSE abundances for both unbrecciated and 678 brecciated aubrites (Keil, 2010 and references therein; Van Acken et al., 2012a). Figure 679 7 shows measured bulk aubrite HSE abundances (taken from Van Acken et al., 2012a) 680 and calculated AuPB mantle abundances while assuming an EH or EL chondritic bulk 681 composition for the AuPB. Comparison between modeled mantle abundances and HSE 682 683 concentrations of non-breccia aubrites (LAP 03719, Mt. Egerton, Shallowater; solid lines in Fig. 7) shows that HSE abundances are significantly and consistently enriched in these 684 samples, with differences between calculated and measured abundances of up to 5 log 685 686 units (Re). Although some of the brecciated aubrites contain foreign metal-bearing clasts, and it is unclear when they were precisely added to these samples, non-brecciated 687 aubrites have similar or even higher bulk HSE abundances (Van Acken et al., 2012a). 688 689 This confirms that the variable amounts of metal are likely relicts of inefficient accretion

processes during accretion of the AuPB, as the metal analyzed in several aubrites has chondritic trace element abundances (Casanova et al., 1993; Van Acken et al., 2012b). Alternatively, they represent primitive core-forming materials mixed with the AuPB mantle during a catastrophic break-up event (Keil, 1989). A catastrophic break-up of the AuPB may also explain the very low volatile siderophile and volatile chalcophile element contents, which are generally difficult to fully reconcile with core formation processes (Steenstra and van Westrenen, 2020; Steenstra et al., 2020b).

Our results are consistent with the hypothesis of Van Acken et al. (2012a) that states 697 that approximately >0.1 % of (un)differentiated metal would be required to reproduce the 698 HSE abundances of aubrites, independent of the considered bulk composition. For 699 unbrecciated aubrites Mt. Egerton and Shallowater this may be as high as 20 % (Fig. 7). 700 We therefore conclude that any initial core formation depletion signature of HSE 701 abundances would be heavily if not fully overprinted by residual metal in the AuPB mantle. 702 Finally, our results are also consistent with the hypothesis that metal phases are the 703 dominant HSE carriers in bulk aubrites (Van Acken et al., 2012a), with sulfides playing a 704 lesser (Ru, Ir, Pt) or minor (Re) role in sequestering HSE's (Fig. 2-4; Casanova et al., 705 706 1993; Van Acken et al., 2012b).

707

708 CONCLUSIONS

The Earth and the aubrite parent body likely accreted at moderately to highly reduced conditions. In the case of Earth, a (highly) reduced component could have been added by accretion of a single or several larger differentiated Mercury- or AuPB-like bodies. To assess the potential distribution of the HSE during accretion of such components, we

obtained a new experimental dataset describing the chalcophilic and siderophilic behavior 713 of Ru, Pd, Ag, Re, Pt, Ir and Au at highly reduced conditions. Their sulfide liquid – silicate 714 melt and metal liquid partition coefficients were studied as a function of FeO and S content 715 of the silicate melt, as well as O content of the sulfide liquid. Using newly derived 716 parameterizations describing the sulfide liquid – silicate melt partitioning behavior of these 717 718 elements, we modeled their behavior during highly reduced accretion of EH- and EL chondritic impactors for a wide range of core formation scenarios. Our results show that, 719 despite the strongly decreased chalcophile and siderophile behavior of the HSE at highly 720 721 reduced conditions, their concentrations in differentiated impactor mantles are so low that metal- and sulfide-free silicate impactor mantle would be a negligible source for the 722 majority of the HSE, for most considered accretion models. Any small degree of impactor 723 core contribution to the BSE or the impactor mantle would overprint any primordial 724 terrestrial mantle signature. 725

Application of our results to accretion of the aubrite parent body confirms that the highly elevated HSE abundances in unbrecciated aubrites are most readily explained by the incorporation of minor to high degrees of primitive, largely unfractionated core forming materials in the AuPB mantle (Van Acken et al., 2012a), potentially during the catastrophic break-up of the AuPB.

731

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740

741 FIGURE CAPTIONS

742

Fig. 1: Backscattered electron images of typical experimental run products. Panel (a, b) show the lower and upper part of run ESS-153, respectively, with silicate glass and Rubearing metal blobs and FeS liquid. Note the well-segregated nature of each phase. Panel (c) shows a close up of run ESS-151 with FeS specks that formed upon quenching (Boujibar et al., 2014). Panel (d) depicts a close up of the dendritic quench texture of Ir in sulfide liquid, as observed for Pt and Ru as well. Also note the Ir-Fe alloy crystals that are morphologically distinctly different from the quench phases.

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Fig. 2: Sulfide liquid-silicate melt partition coefficients of Ru, Pd, Ag, Re as a function of 751 the logarithm of the FeO and S contents (in wt.%) of the silicate melt (left and right panels, 752 respectively). Vertical error bars are propagated errors based on 2 SE of EPMA and/or 753 LA-ICP-MS concentrations. Sulfide liquid / silicate melt D values of previous studies are 754 755 plotted for comparison purposes (KW13 = Kiseeva and Wood, 2013, obtained at 1673 K, 1.5 GPa; MB14 = Mungall and Brenan, 2014; L16 = Laurenz et al., 2016; B19 = Brenan 756 et al., 2019). Dashed lines without arrows are modeled dependencies (see section 3.5). 757 758 Dashed lines indicated with arrows qualitatively indicate direction of change from more oxidized to reduced conditions and were added for clarity. 759

Fig. 3: Sulfide liquid-silicate melt partition coefficients of Ir, Pt and Au as a function of the 761 logarithm of the FeO contents (in wt.%) of the silicate melt. Vertical error bars are 762 propagated errors based on 2 SE of EPMA and/or LA-ICP-MS concentrations. Sulfide 763 liquid / silicate melt D values of previous studies are plotted for comparison purposes 764 (KW13 = Kiseeva and Wood, 2013; MB14 = Mungall and Brenan, 2014; L16 = Laurenz 765 et al., 2016; B19 = Brenan et al., 2019). Dashed lines without arrows are modeled 766 dependencies (see section 3.5). Dashed lines indicated with arrows gualitatively 767 indicate direction of change from more oxidized to reduced conditions and were added 768 769 for clarity.

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Fig. 4: Metal liquid-silicate melt partition coefficients of Ru, Pd, Re, Ir, Pt and Au from this 771 study and previous studies (BM09 = Brenan and McDonough (2009), obtained at ΔIW = 772 -0.4 to +2.5; T = 2273-2588 K, P = 2 GPa for Au-rich (>95.5 wt.% Au) alloys, S-free; M12 773 = Mann et al. (2012), obtained at $\Delta IW = -1.5$ to +1.6, T = 2423–2773 K, P = 3.5–18 GPa, 774 S-free; M15 = Médard et al. (2015), obtained at ΔIW = -0.9 to -0.1, T = 1820-1873 K, P 775 = 0.5–1.2 GPa, S-free; B16 = Bennett et al. (2016), obtained at $\Delta IW = +1$ to +1.4, T = 776 1723–2278 K, P = 0.1 MPa to 15 GPa, S-free; L16 = Laurenz et al. (2016), obtained at 777 $\Delta IW = -1.5$ to -0.5, T = 2473 K, P = 11 GPa, S-bearing; R18 = Righter et al. (2018), 778 obtained at $\Delta IW = -7.8$ to -1.8, T = 1873 K, P = 1 GPa, S-free; B19 = Brenan et al. (2019), 779 obtained at $\Delta IW = -1.3$ to -0.7, T= 1673 K, P = 0.1 MPa, S-poor (approx.10 wt.% S) 780 sulfide liquids). 781

Fig. 5: Modeled ratios of sulfide liquid-silicate melt partition coefficients as a function of 783 FeO content of the silicate melt. Sulfide liquid – silicate melt partition coefficients were 784 calculated using Eq. (4) in conjunction with the fit parameters listed in Table 4 for the 785 various experimentally measured FeO and S contents of the silicate and/or sulfide liquid. 786 Indicated with vertical arrows are the expected signs of the variation of elemental ratios 787 788 of the co-existing sulfide liquid-saturated silicate melt for a given FeO content of the silicate melt. The vertical dashed lines indicate the transition from the sign of the variation 789 of elemental ratios. 790

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Fig. 6: Comparison between calculated impactor mantle, bulk impactor (Newsom, 1995; 792 Alexander, 2019) and present-day HSE mantle abundances (Wang et al., 2018). Impactor 793 mantle abundances were calculated considering an EH or EL chondritic bulk composition; 794 HSE abundances taken from Newsom, 1995; Alexander, 2019) and three different end-795 member core masses and core compositions (a 15 mass % FeS liquid core, a 30 mass 796 % core consisting of a 15 mass % Fe-Si metal liquid inner core and a 15 mass % FeS 797 liquid outer core and a 65 mass % core consisting of a 50 mass % Fe-Si liquid metal inner 798 799 core and a 15% FeS liquid outer core. Bulk D values during impactor differentiation were calculated using a mantle S content of 1 or 3 % with corresponding silicate melt FeO 800 contents of 0.65 and 0.43 wt.%, respectively (see text for details). Plotted for comparison 801 802 purposes are impactor mantle abundances that reflect incorporation of 0.3% core-forming metal and the present-day BSE abundances and ratios (Wang et al., 2018). 803

Fig. 7 Comparison between bulk aubrite HSE abundances (upper panels) and ratios 805 (lower panels) and calculated AuPB mantle HSE abundances and ratios. The AuPB 806 mantle abundances were calculated considering two bulk AuPB compositions (EH or EL 807 chondritic; values taken from Newsom, 1995; Alexander, 2019) and three different end-808 member core masses and core compositions (a 15 mass % FeS liquid core, a 30 mass 809 % core consisting of a 15 mass % Fe-Si metal liquid inner core and a 15 mass % FeS 810 liquid outer core and a 65 mass % core consisting of a 50 mass % Fe-Si liquid metal inner 811 core and a 15% FeS liquid outer core. Bulk D values were calculated using a mantle S 812 content of 3 % and a corresponding silicate melt FeO content of 0.43 wt.% (see text for 813 details). Plotted for comparison purposes are the AuPB mantle abundances that reflect 814 incorporation of 0.3 and 20 mass % residual metal in the AuPb mantle, in a scenario of 815 highly inefficient metal-silicate segregation and/or catastrophic break-up of the AuPB. 816 Lines represent bulk aubrite abundances (dashed lines indicate brecciated samples; 817 ALHA78113, ALH 84007, ALH 84008, ALH 84009, Aubres, Bishopville, Bustee, Khor 818 Temiki, LAR 04316; solid lines indicate data for unbrecciated aubrites; LAP 03719 819 (classified as an anomalous aubrite), Mt. Egerton, Shallowater; all data from Van Acken 820 821 et al., 2012a).

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1144 Figure 1









1154 Figure 5









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Run	<i>Т</i> (К)	t (min)	Starting material composition ^a	Phases ^b	log FeO (wt.%)	SCSS (ppm)	fO2 (∆IW)
Au (+Ag)							
ESS-90a	1883	60	30% GG + 40% Fe-S A + 30% Fe ₅₅ Si ₄₅	GI, Fe-S, Fe-Si	-0.13(1)	8750(89)	-
ESS-90b	1883	60	25% GG + 50% Fe-S A + 25% Fe ₅₅ Si ₄₅	GI, Fe-S, Fe-Si	0.755(3)	1939(41)	-
ESS-91	1883	30	40% GG + 60% Fe-S A	GI, Fe-S	1.247(2)	4878(319)	+2
ESS-98	1883	60	30% GG + 40% Fe-S A + 30% Fe ₅₅ Si ₄₅	GI, Fe-S, Fe-Si	0.909(1)	1639(30)	-
ESS-100	1883	30	20% GG + 30% Fe-S A + 50% Fe ₅₅ Si ₄₅	GI, Fe-S, Fe-Si	0.860(2)	2014(62)	-
ESS-110	1883	135	30% GG + 30% Fe-S A + 40% Fe ₅₅ Si ₄₅	GI, imm. Fe-S-Fe-Si met	-0.32(2)	27713(287)	-3.46
ESS-123	1883	60	50% GG + 25% Fe-S B + 25% Fe ₁₀₀	GI, imm. Fe-S-Fe met	1.549(1)	7869(318)	-0.08
ESS-124	1883	65	40% GG + 40% Fe-S B + 20% Fe ₄₀ Si ₆₀	GI, Fe-S, Fe-Si	1.047(1)	1984(27)	_
ESS-125-1	1883	70	35% GG + 25% Fe-S B + 40% Fe ₅₅ Si ₄₅	GI, Fe-S, Fe-Si	-0.37(1)	16934(174)	_
ESS-125-2	1883	70	35% GG + 25% Fe-S B + 40% Fe ₅₅ Si ₄₅	GI, imm. Fe-S-Fe-Si met	-0.21(1)	8120(189)	-3.62
ESS-134	1883	100	70% GG + 30% Fe-S B	GI, Fe-S	1.283(1)	4733(135)	+2
ESS-135	1883	120	40% GG + 30% Fe-S B + 30% Fe ₄₀ Si ₆₀	GI, Fe-S, Fe-Si	-0.30(2)	55783(121)	_
Pd							
ESS-94	1718	50	40% GG + 60% Fe-S C	GI, OI, Fe-S	1.173(5)	2559(64)	+2
ESS-95	1820	30	40% GG + 40% Fe-S C + 20% Fe ₅₅ Si ₄₅	GI, Fe-S, Fe-Si	-0.39(1)	21729(239)	_
ESS-96	1783	30	40% GG + 50% Fe-S C + 10% Fe ₅₅ Si ₄₅	GI, Fe-S, Fe-Si	1.233(2)	2569(44)	_
ESS-97	1733	50	30% GG + 30% Fe-S C + 40% Fe ₅₅ Si ₄₅	GI, Fe-S, Fe-Si	0.938(3)	1341(66)	_
ESS-99	1883	30	30% GG + 35% Fe-S C + 35% Fe ₅₅ Si ₄₅	GI, Fe-S, Fe-Si	0.869(3)	2019(75)	_
ESS-102	1883	30	60% GG + 40% Fe-S C	GI, Fe-S	1.309(1)	5777(37)	+2
ESS-108	1883	103	30% GG + 35% Fe-S C + 35% Fe ₅₅ Si ₄₅	GI, Fe-S, Fe-Si	0.282(3)	2751(38)	_
ESS-121	1883	60	30% GG + 35% Fe-S C + 35% Fe ₄₀ Si ₆₀	GI, Fe-S, Fe-Si	1.128(5)	2288(53)	_
ESS-122	1883	80	40% GG + 30% Fe-S C + 30% Fe ₁₀₀	GI, imm. Fe-S-Fe met	1.62(1)	13711(3220)	+0.14
ESS-151	1883	115	40% GG + 30% Fe-S C + 20% Fe100 + 10% Si100	GI, imm. Fe-S-Fe met	0.585(1)	1665(26)	-2.00
Re							
ESS-93	1883	30	50% GG + 50% Fe-S D	GI, Fe-S	1.247(2)	3919(155)	+2
ESS-103	1883	20	30% GG + 35% Fe-S D + 35% Fe ₅₅ Si ₄₅	GI, imm. Fe-S- Fe-Si met	0.423(2)	2618(43)	-2.32
ESS-104	1883	30	60% GG + 40% Fe-S D	GI, Fe-S	1.293(1)	5130(179)	+2
ESS-107	1883	120	30% GG + 30% Fe-S D + 40% Fe ₅₅ Si ₄₅	GI, Fe-S, Fe-Si	-0.27(2)	10019(113)	_
ESS-127	1883	70	33% GG + 33% Fe-S D + 34% Fe ₄₀ Si ₆₀	GI, imm. Fe-S-Fe-Si met	-0.08(5)	31158(195)	-3.03
ESS-128	1883	70	33% GG + 33% Fe-S D + 34% Fe ₁₀₀	GI, imm. Fe-S-Fe met	1.467(1)	6346(81)	-0.12
Ir							
ESS-109	1883	110	50% GG + 40% Fe-S E + 10% Fe ₅₅ Si ₄₅	GI, imm. Fe-S-Fe met	0.096(5)	4020(40)	-3.04
ESS-111	1883	45	60% GG + 40% Fe-S E	GI, Fe-S	1.336(1)	5991 (289)	+2
ESS-114	1883	120	35% GG + 25% Fe-S E + 40% Fe ₅₅ Si ₄₅	GI, imm. Fe-S-Fe-Si met	-0.12(1)	7092(88)	-3.46
ESS-119	1883	120	50% GG + 30% Fe-S E + 25% Fe ₅₅ Si ₄₅	GI, imm. Fe-S-Fe met	0.03(1)	5052(39)	-3.15
ESS-129	1883	80	40% GG + 30% Fe-S E + 30% Fe ₄₀ Si ₆₀	GI, imm. Fe-S-Fe-Si met	-0.21(1)	9594(239)	-3.40
ESS-130	1883	100	40% GG + 30% Fe-S E + 30% Fe ₁₀₀	GI, imm. Fe-S-Fe met	1.573(2)	10015(641)	+0.10
ESS-132	1883	110	40% GG + 20% Fe-S E + 20% Fe ₄₀ Si ₆₀	Gl, imm. Fe-S-Fe met	0.032(S)	3888(3¥)	-2.99

Table 1 Summary of experimental run conditions. All experiments were performed at 1 GPa in graphite capsules.

ESS-146	1883	90	40% GG + 25% Fe-S E + 35% Si ₁₀₀	GI, imm. Fe-S-Fe-Si met	-0.40(2)	13470(175)	-3.91
ESS-152	1883	110	35% GG + 35% Fe-S E + 10% Fe ₁₀₀ + 20% Si ₁₀₀	GI, Fe-S, Fe-Si	0.30(1)	3268(57)	_
Pt							
ESS-112	1883	120	50% GG + 25% Fe-S F + 25% Fe ₅₅ Si ₄₅	Gl, imm. Fe-S-Fe met	0.402(3)	2286(28)	-2.35
ESS-113	1883	120	60% GG + 40% Fe-S F	GI, Fe-S	1.339(1)	5819(202)	+2
ESS-120	1883	80	50% GG + 25% Fe-S F + 25% Fe ₅₅ Si ₄₅	GI, imm. Fe-S-Fe met	0.017(5)	3769(80)	-3.02
ESS-126	1883	55	30% GG + 30% Fe-S F + 40% Fe ₄₀ Si ₆₀	GI, imm. Fe-S-Fe-Si met	-0.16(1)	5977(115)	-3.39
ESS-143	1883	150	40% GG + 30% Fe-S F + 30% Fe ₄₀ Si ₆₀	GI, imm. Fe-S-Fe-Si met	-0.27(1)	9733(127)	-3.67
ESS-144	1883	120	40% GG + 40% Fe-S F + 20% Fe ₁₀₀	GI, imm. Fe-S-Fe met	1.550(1)	8363(307)	-0.03
ESS-149	1883	130	33% GG + 33% Fe-S F + 33% Si100	GI, imm. Fe-S-Fe-Si met, qtz	-0.46(1)	25919(135)	-3.94
ESS-150	1883	80	40% GG + 30% Fe-S F + 30% Fe ₁₀₀	GI, imm. Fe-S-Fe met	1.61(1)	13744(2263)	+0.12
Ru (+Ag)							
ESS-136	1883	70	40% GG + 30% Fe-S G + 10% Fe ₄₀ Si ₆₀ + 20% Fe ₁₀₀	GI, imm. Fe-S, Fe met	0.037(10)	5649(248)	-3.00
ESS-139	1883	150	40% GG + 30% Fe-S G + 30% Fe ₅₅ Si ₄₅	GI, imm. Fe-S, Fe-Si met	-0.37(1)	19521(174)	-3.43
ESS-141	1883	80	65% GG + 35% Fe-S G	GI, Fe-S	1.220(1)	3956(57)	+2
ESS-142	1883	120	40% GG + 40% Fe-S G + 20% Fe ₄₀ Si ₆₀	GI, imm. Fe-S-Fe met	1.273(1)	3085(50)	-0.67
ESS-145	1883	225	40% GG + 40% Fe-S G + 20% Fe ₄₀ Si ₆₀	GI, imm. Fe-S-Fe-Si met	-0.37(1)	40763(115)	-3.08
ESS-153	1883	90	40% GG + 30% Fe-S G + 15% Fe ₁₀₀ + 15% Si ₁₀₀	GI, imm. Fe-S-Fe-Si met	-0.22(1)	9497(108)	-3.44

 $\frac{1163}{1164}$ 1165 1166 ^a GG = primitive basalt (see Steenstra et al., 2020a). Letters A, B, C, etc. defines metal composition: Fe-S A = FeS + 5 wt.% Au, Fe-S B = FeS + 5 wt.% Au + 2 wt.% Ag; Fe-S C = FeS + 5 wt.% Pd , Fe-S D = FeS + 10% Re, Fe-S E = FeS + trace elements + 10 wt.% Ir (see Steenstra et al., 2020a), Fe-S F = FeS + trace elements + 10% Pt (see Steenstra et al., 2020a), Fe-S G = FeS + 10 wt.% Ru + 2 wt.% Ag; Fe-S = Fe-S liquid, Fe = Fe = Net, Fe-S = Fe-S i met, unr. Fe-S = unreacted Fe-Si metal at bottom of capsule which was not in direct contact with the measured silicate melts. For these samples I_Q^2 could often not be measured directly as there was no Fe(-Si) metal liquid in direct contact with the silicate melt.

1167	Table 2 Summary of experimentally determined sulfide liquid - silicate melt partition
1168	coefficients

	Ru	Pd	Ag	Re	Ir	Pt	Au
Au. Aa							
ESS-90a	_	_	_	-	_	_	5459(1733)
ESS-90b	_	_	_	_	_	_	14333(3394)
ESS-91	_	_	_	_	_	_	767(434)
ESS-98	_	_	_	_	_	_	5652(923)
ESS-100	_	_	_	_	_	_	22583(4790)
ESS-110	_	_	_	_	_	_	287(81)
ESS-123	_	_	48(17)	_	_	_	569(187)
ESS-124	_	_	79(26)*	_	_	_	13626(1816)
ESS-125-1	_	_	105(26)	_	_	_	748(542)
ESS-125-2	_	_	461(204)	_	_	_	7305(1751)
ESS-134	_	_	77(28)	_	_	_	245(176)
ESS-135	_		40(14)	_			361(128)
Pd			40(14)				301(120)
FSS-04	_	$7.16x10^{4}(5.32x10^{4})$	_	_	_	_	_
ESS 05		$2.47 \times 10^4 (6.43 \times 10^3)$					
ESS 06	-	$3.47 \times 10^{-10} (0.43 \times 10^{-10})$	-	- 7669(6364)	_	-	-
ESS 07	-	3.00×10^4 (9.01 $\times10^3$)	-	7008(0304)	_	-	-
ESS-97	-	$3.00 \times 10^{-10} (0.91 \times 10^{-1})$	_	-	_	-	-
E33-99	-	$9.67 \times 10^4 (5.00 \times 10^3)$	_	-	_	-	-
ESS-102	-	2.50×10^{-1} (5.20×10 ⁻¹)	_	-	-	-	-
ESS-108	-	$2.53 \times 10^{\circ} (6.74 \times 10^{\circ})$	-	-	_	-	-
ESS-121	-	2.59X10 ⁺ (1.46X10 ⁺)	-	5177(4227)	-	-	-
ESS-122	-	1/42(/21)	-	-	-	-	-
ESS-151	-	8.46x10 [°] (3.20x10 [°])	-	-	-	-	-
Re				- / - / - / -)			
ESS-93	-	-	-	516(348)	-	-	-
ESS-103	-	-	-	9.38x10 ⁴ (2.72x10 ⁴)*	-	-	-
ESS-104	-	-	-	286(114)	_	-	-
ESS-107	-	-	-	34964(22051)*	_	-	-
ESS-127	-	-	-	69121(50798)*	_	-	-
ESS-128	-	-	-	123(77)*	-	-	-
lr							
ESS-109	-	-	-	-	2.37x10 ⁵ (1.26x10 ⁵)	-	-
ESS-111	-	-	-	-	8.20x10 ⁴ (4.44x10 ⁴)*	-	-
ESS-114	-	-	-	-	1.95x10 ⁵ (1.01x10 ⁵)	-	-
ESS-119	-	-	-	-	4.04x10 ⁵ (2.39x10 ⁵)	-	-
ESS-129	-	-	-	-	1.58x10⁵ (9.97x10⁴)	-	-
ESS-130	-	-	-	-	1.45x10 ⁴ (9.03x10 ³)	-	-
ESS-132	-	-	-	-	1.84x10⁵ (7.85x10⁴)	-	-
ESS-146	-	-	-	-	4.91x10 ⁴ (1.57x10 ⁴)	-	-
ESS-152	-	-	-	-	1.13x10 ⁶ (1.05x10 ⁶)	_	-
Pt							
ESS-112	-	_	_	-	_	8.19x10 ⁵ (1.03x10 ⁵)*	-
ESS-113	-	_	_	-	_	9533(2364)*	-
ESS-120	_	_	_	_	_	2.26x10 ⁵ (8.89x10 ⁴)	_
ESS-126	_	_	_	_	_	8.42x10 ⁴ (4.18x10 ⁴)*	_
ESS-143	_	_	_	_	_	2.03x10 ⁴ (6.80x10 ³)	_
ESS-144	_	_	_	_	_	6658(1910)*	_
ESS-149	-	-	_	-	-	5566(2454)	_
ESS-150	_	_	_	_	_	2938(2154)	_
Ru, Ag							
ESS-136	6.26x10 ⁶ (4.43x10 ⁶)	-	320(150)	-	-	-	_
ESS-139	7.27x10 ⁵ (5.06x10 ⁵)	_	129(27)	_	_	_	_
ESS-141	1.56x10 ⁶ (6.88x10 ⁵)	_	150(29)	_	_	_	_
ESS-142	$1.10 \times 10^5 (6.16 \times 10^4)$	_	99(24)	_	_	_	_
ESS-145	6.01x10 ⁵ (2.98x10 ⁵)	_	105(34)	_	_	_	_
ESS-153	1.07x10 ⁶ (3.12x10 ⁵)	_	251(52)	_	_	_	_
			- ()				

^a D values for Au, Pd, Ir, Pt, were based on EPMA-derived concentrations of the sulfide liquid, unless otherwise stated (*). For Re, only runs ESS-104 and ESS-127 were based on EPMA-derived Re concentrations of the sulfide liquid. For Pt, runs ESS-112, ESS-113, ESS-126 and ESS-144 were based on LA-ICP-MS derived Pt sulfide liquid abundances. The LA-ICP-MS derived sulfide liquid abundances of Ru, Ag and Pt were corrected according to the fractionation indices shown in Fig. S.1.

-		Ru	Pd	Re	Ir	Pt	Au
	Au, Ag						
	ESS-110 ESS-123	-	-	-	-	-	1116(61) 5438(1314
	ESS-125-2	-	_	_	_	_) 3784(574)
	Pd		0700(404)				
	ESS-122 ESS-151	_	2720(494) 5.07x10 ⁵ (1.81x10 ⁵)	_	_	_	_
	Re		3.07×10 (1.01×10)				
	ESS-103	-	-	4.33x10 ⁷ (1.24x10 ⁷)	-	-	-
	ESS-127	-	-	$2.62 \times 10^7 (1.12 \times 10^7)$	-	-	_
	LSS-120	-	-	1.22X10 [°] (1.04X10 [°])	-	-	_
	ESS-109	-	-	-	3.57x10 ⁷ (1.42x10 ⁷)	-	-
	ESS-114	-	-	-	$3.71 \times 10^7 (1.26 \times 10^7)$	-	_
	ESS-119 ESS-129	-	_	_	$9.83X10^{\circ}$ (4.45X10^{\circ}) 3.02x10 ⁷ (6.03x10 ⁶)	-	_
	ESS-130	_	_	_	6.62x10 ⁶ (9.80x10 ⁵)	_	_
	ESS-132	-	-	-	2.09x10 ⁷ (3.84x10 ⁶)	-	-
	ESS-146	-	-	-	7.15x10 ⁶ (4.47x10 ⁵)	-	-
	ESS-112	_	_	_	-	$1.68 \times 10^7 (1.04 \times 10^7)$	_
	ESS-120	-	-	_	_	6.73x10 ⁶ (1.68x10 ⁶)	_
	ESS-126	-	-	-	-	2.04x10 ⁶ (4.90x10 ⁵)	_
	ESS-143 ESS-144	-	_	_	_	$1.04 \times 10^{\circ} (2.34 \times 10^{\circ})$ 7 87 × 10 ⁵ (1.25 × 10 ⁵)	_
	ESS-149	_	_	_	_	2.98x10 ⁵ (7.67x10 ⁴)	_
	ESS-150	-	-	-	-	1.68x10⁵ (9.03x10⁴́)	_
	Ru, Ag	2 022406 (7 002405)**					
	ESS-130 ESS-139	$3.02 \times 10^{6} (1.20 \times 10^{6})$	_	_	-	-	_
	ESS-142	1.79x10 ⁷ (7.30x10 ⁶)	-	_	_	-	_
	ESS-145	5.51x10 ⁶ (8.34x10 ⁵)	-	-	-	-	_
<u> </u>	ESS-153	3.10x10' (5.85x10°)		-	-	-	_
11	/6 °AILL 77	values were based	on EPMA-derived	concentrations of t	he sulfide liquid **A	nomalous	
11	78						
11	70 79						
11	80						
11	81						
11	82						
11	83						
11	84						
11	85						
11	86						
11	87						
11	88						
11	89						
11	90						
11	91						
11	92						
11	93						
11	94						

Table 3 Summary of experimentally determined metal liquid - silicate melt partition coefficients (where available)

Table 4 Derived interaction parameters describing the effects of FeO and S in silicate1196melt and O in sulfide on sulfide liquid – silicate melt partition coefficients (D)

		Α	$m{\mathcal{E}}_{MS_{n/2}}^{FeO_{sulliq}}$	$arepsilon_{ m Fe0}^{ m S_{silmelt}}$	N	R ²	RMSE
	Pd ¹⁺	5.65(18)	9.74(583)	149(51)	10	0.71	0.316
	Ag ¹⁺	2.60(̀8) ́	n.s.s.	57(9̀)	12	0.80	0.177
	Re ¹⁺	5.20(33)	56.34(1398)	n.s.s.	8	0.73	0.419
	Re ⁴⁺	n.s.s.	_	_	8	-	_
	Re ⁶⁺	6.94(54)	-	119(58)	8	0.41	0.982
	lr ³⁺	6.21(21)	-39.41(497)	138(23)	9	0.93	0.220
	Pt ¹⁺	5.54(26)	n.s.s.	112(28)	8	0.73	0.381
	Pt ¹⁻	5.65(26)	47.49(740)	-163(49)	8	0.92	0.304
	Au	4.08(22)	n.s.s.	108(30)	12	0.56	0.542
1198 1199 1200 1201 1202 1203 1204 1205 1206 1207 1208 1209 1210 1211 1212 1213 1214 1215 1216 1217 1218 1219 1220 1221 1222 1223 1224 1225 1226	^a Not statistica subsequent mo	lly significant (ρ odeling (marked in	> 0.15). Paramet bold).	erizations for I	Pd ¹⁺ , Ag ¹⁺ , I	Re ¹⁺ , Ir ³⁺ , Pt ⁻¹ and	Au ¹⁺ were used in
1220 1227							
1227							
1229							
1230							
1231							

Supplementary information file for 'Partitioning of Ru, Pd, Ag, Re, Pt, Ir and Au between sulfide-, metal- and silicate liquid at highly reduced conditions: implications for terrestrial accretion and the aubrite parent body evolution".

A.1 Starting compositions

Sulfide starting compositions consisted of high-purity FeS powder doped with PGE powders. Seven different sulfide compositions were prepared: FeS + 5 wt.% Au (Fe-S A), FeS + 5 wt.% Au + 2 wt.% Ag (Fe-S B), FeS + 5 wt.% Pd (Fe-S C), FeS + 10% Re (Fe-S D), FeS + various low level doped trace elements (see Steenstra et al., 2020a) + 10 wt.% Ir (Fe-S E), FeS + various low level doped trace elements (see Steenstra et al., 2020a) + 10 wt.% Iv (Fe-S F) and FeS + 10 wt.% Ru + 2 wt.% Ag (Fe-S G).

A.2 EPMA and LA-ICP-MS analyses

EPMA analyses

Major and trace element compositions of the silicate melts, metals and sulfides were obtained using a JEOL JXA 8530F field emission electron microprobes at the Institute of Mineralogy, University of Münster, and the Geophysical Laboratory, Carnegie Institution for Science. Analyses were performed using a defocused beam (5-15 µm). Measurement points were set in random lines and/or raster grids, depending on the available surface area of the analysed phases. Beam currents were 15–20 nA and an accelerating voltage of 15 kV. Dwell times were 10-30 s on peak and 5-15 s on each background. The use of a large number of spot analyses per phase (>20-30 for silicate melts and sulfides) was used to ensure a representative average chemical composition was obtained. Standards used for analyses were diopside or anorthite for Ca, Fe metal, hematite or fayalite for Fe, Mn₂O, rhodonite or tephroite for Mn, anorthite, diopside or hypersthene for Si, PbS or pyrite for S, forsterite for Mg, sanidine or KTiPO₅ for K, kyanite or corundum for Al, jadeite for Na, MgCr₂O4 or Cr₂O₃ for Cr, TiO₂ or pure metal for TiO₂, periclase for O and only pure Astimex metal standards for Ru, Ag, Pd, Ir, Pt, Re and Au. Calibrations were considered successful when the primary standard compositions were reproduced within 1% relative deviation. Data reduction was performed using the $\Phi(\rho Z)$ approach or the ZAF correction, which corrects for the decrease in x-ray density due to the distance the x-rays have to travel through the specimen before they reach the detector.

Potential of nugget contamination

Fig. S.2 shows several examples of time-resolved spectra for LA-ICP-MS analyses of HSE-bearing silicate melts. The spectra confirm that nano-nuggets are not present in the silicate melt and that measured HSE concentrations are not affected by such issues.

Matrix effects for LA-ICP-MS

The use of non-matrix matched external reference materials for calibrating LA-ICP-MS analyses of the sulfide liquids may result in significant matrix effects (e.g., Steenstra et al., 2020b). To assess the potential matrix effects for Pt, Ir, Au, Ru, Pd and Ag, we compare EPMA-derived abundances with LA-ICP-MS measured concentrations from the same samples (Fig. S.1). The results show that the LA-ICP-MS derived concentrations of refractory HSE's Ru and Pt are underestimated relative to EPMA values (i.e. incomplete

ablation), whereas volatile element Ag is preferentially ablated (Fig. S.1). The LA-ICP-MS derived concentrations of Ag, Ru, and Pt were therefore corrected according to the fractionation indices listed in Fig. S.1. Fortunately, the vast majority of their concentrations in the sulfide liquids are measurable with EPMA, so that these corrections have very little effect on the overall results. Concentrations of the other trace elements that were above detection limits, such as Se and Te, were corrected using the fractionation indices from Steenstra et al. (2020b) derived for FeS liquids in conjunction with ⁵⁶Fe as the internal standard and NIST 610 as the external reference material.

A.3 Details of thermodynamic approach

Our study involves partitioning of trace elements between silicate melt, a FeS liquid and/or a Fe(-Si) liquid. The partitioning of these elements between the silicate melt and sulfide liquid depends on the ratio of the fO_2 to the fS_2 , but the latter cannot be explicitly determined for our experiments (e.g. Kiseeva and Wood, 2013; Wohlers and Wood, 2017). The partitioning was therefore redefined to an exchange reaction with Fe, which simplifies the theoretical treatment of the data (Kiseeva and Wood, 2013, 2015; Wohlers and Wood, 2017). For Ir³⁺, the exchange reaction would be:

$$Ir^{3+}O_{1.5 \text{ (sil melt)}} + 1.5FeS_{(\text{sulfide liq})} = 1.5FeO_{(\text{sil melt})} + Ir^{3+}S_{1.5 \text{ (sulfide liq)}}$$
(Eq. A.1)

The equilibrium constant for the later reaction is:

$$K \frac{a_{\text{FeO}}^{1.5} \cdot a_{\text{Ir}^{3+}\text{S}_{1.5}}}{a_{\text{FeS}}^{1.5} \cdot a_{\text{Ir}^{3+}\text{O}_{1.5}}}$$
(Eq. A.2)

where a_i refers to the activity of the various components. Assuming that that the ratio of the activity of $Ir^{3+}S_{1.5}$ to $Ir^{3+}O_{1.5}$ is approximately equal to the sulfide liquid - silicate melt partition coefficient of Ir3+, as proposed for many other chalcophile, siderophile and lithophile elements (Kiseeva and Wood, 2013, 2015; Wohlers and Wood, 2017), yields:

$$D_{Ir}^{\text{sul liq-sil melt}} = \frac{Ir_{\text{sulfide liquid}}}{Ir_{\text{silicate melt}}} \approx \frac{a_{Ir^3+S_{1.5}}}{a_{Ir^3+O_{1.5}}}$$
(Eq. A.3)

As developed by Kiseeva and Wood (2013), performing this substitution into Eq. (A.2) while assuming that the FeS liquid is close to pure FeS ($a_{\text{FeS}} = 1$) yields:

$$\log D_{\rm Ir}^{\rm sul \, liq-sil \, melt} \approx A - 1.5 \log({\rm FeO}_{\rm sil \, melt}) \tag{Eq. A.4}$$

In the latter equation constant A is related to the equilibrium constant and FeO refers to the FeO content of the silicate melt (Kiseeva and Wood, 2013, 2015; Wohlers and Wood, 2017). Besides FeO, O in sulfide and S in the silicate melt likely also affect the sulfide liquid – silicate melt distribution of the elements of interest. Kiseeva and Wood (2015) and Wohlers and Wood (2017) demonstrated that these effects can be successfully incorporated in the latter thermodynamic parameterizations by using the epsilon-model of non-ideal interaction that are typically applied to metallic liquids (Wagner, 1962; Ma, 2001). As described in Wohlers and Wood (2017), interactions between the component

of metal M (MS_{n/2}, where *n* is the valence of the element of interest), FeS and FeO within the sulfide are likely different for different elements. Thus, a term should be added that incorporates the differences in activity coefficients of $MS_{n/2}$ for FeO-rich and FeO-poor sulfide liquid. A interaction parameter is therefore included to account for these effects:

$$\log D_{\rm M}^{\rm sul \, liq-sil \, melt} \approx A - \frac{n}{2} \log({\rm FeO}_{\rm sil \, melt}) + \epsilon_{{\rm MS}_{n/2}}^{\rm FeO_{\rm sul \, liq}} \left(1 - x_{\rm FeO}^{\rm sul \, liq}\right)$$
(Eq. A.5)

which for example Ir³⁺ yields:

$$\log D_{Ir}^{\text{sul liq-sil melt}} \approx A - 1.5 \log(\text{FeO}_{\text{sil melt}}) + \varepsilon_{IrS_{1.5}}^{\text{FeO}_{\text{sul liq}}} \left(1 - x_{\text{FeO}}^{\text{sul liq}}\right)$$
(Eq. A.6)

Here, the $\varepsilon_{IrS_{1.5}}^{FeO_{sul liq}} (1 - x_{FeO}^{sul liq})$ term incorporates the interaction between Ir³⁺ and FeO in the sulfide liquid and $x_{FeO}^{sul liq}$ represents the mole fraction of FeO in the sulfide liquid (Wohlers and Wood, 2017). To include the effects of S-FeO interactions in the silicate melt on D, the model is extended to the following while assuming that the S-FeO term is only significant for D when FeO is present in low quantities:

$$\log D_{\rm M}^{\rm sul \, liq-sil \, melt} \approx A - \frac{n}{2} \log({\rm FeO}_{\rm sil \, melt}) + \varepsilon_{\rm MS_{n/2}}^{\rm FeO_{\rm sul \, liq}} \left(1 - x_{\rm FeO}^{\rm sul \, liq}\right) + \frac{n}{2} \varepsilon_{\rm FeO}^{\rm S_{\rm sil \, melt}} \left(1 - x_{\rm S}^{\rm sil \, melt}\right)$$
(Eq. A.7)

which for example Ir³⁺ yields:

$$\log D_{Ir^{3+}}^{\text{sul liq-sil melt}} \approx A - 1.5 \log(\text{FeO}_{\text{sil melt}}) + \varepsilon_{IrS_{1.5}}^{\text{FeO}_{\text{sul liq}}} \left(1 - x_{\text{FeO}}^{\text{sul liq}}\right) + 1.5\varepsilon_{\text{FeO}}^{\text{Ssil melt}} \left(1 - x_{\text{S}}^{\text{sil melt}}\right)$$
(Eq. A.8)

Here, the $\varepsilon_{\text{FeO}}^{\text{S}_{\text{silmelt}}}(1 - x_{\text{S}}^{\text{silmelt}})$ term incorporates the S-FeO interaction in the silicate melt and the variable S/(S+O) ratio of the melt (Wohlers and Wood, 2017).

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Fig. S.1 Comparison between measured concentrations (%, in mass) of Ru, Pd, Ag, Pt, Ir and Au using LA-ICP-MS and EPMA for Fe-S sulfide liquid. The solid lines are 1:1 identity line plotted for reference. The dashed lines are linear fits with a forced intercept at 0 and represent fractionation indices (F_i = concentration element *i* in sulfide liquid obtained using LA-ICP-MS / concentration element *i* in sulfide liquid obtained using EPMA. Horizontal and vertical error bars in left and right panels represent 2 standard errors.



Fig. S.2 Time-resolved spectra for LA-ICPMS analysis of silicate melts of runs ESS-93 (Re), ESS-95 (Pd), ESS-98 (Au), ESS-130 (Ir), ESS-141 (Ru an Ag).



Fig. S.3 Comparison between predicted log D values (calculated using Table 3) and measured log D values. Vertical error bars in left and right panels represent 2 standard errors. Dashed lines represent 1:1 identity lines. For comparison purposes, metal-absent experiments (i.e. *f*O₂ close to the CCO buffer) were included to excluded to the regression for comparison purposes.



standard. Elemer	it concentrations marked	I with an aste	risk are considered u	uncertain (no	error reported).	
NIST-610 int.	NIST-612		GSD-1G		GSE-1G	
standard	Measured (N = 58) ^a	Preferred ^b	Measured (N = 58)	Preferred	Measured (N = 58)	Preferred
Cu (ppm)	40(1)	38(2)	42(2)	42(2)	384(16)	380(40)
Pd	1.07(15)	1.05(10)	_	_	_	_
Ag	24(1)	22*	22(1)	23(3)	204(9)	200(20)
Re	7.0(3)	6.6(6)	4.8(5)	-	74(4)	79(8)
lr	_	_	-	_	_	_
Pt	2.65(10)	2.51(10)	6.9(11)	5.7*	20(6)	30*
Au	5.0(2)	4.8(3)	4.6(4)	4.4*	8(1)	7*
GSD-1G int.	NIST-610		NIST-612		GSE-1G	
standard	Measured (N = 58)	Preferred	Measured (N = 58)	Preferred	Measured (N = 58)	Preferred
Cu (ppm)	454(37)	441(15)	39(1)	38(2)	375(20)	380(40)
Pd	_	_	-	_	_	_
Ag	248(16)	251(9)	23(1)	22*	202(18)	200(20)
Re	_	_	-	_	_	_
lr	0.0107	_	0.005(1)	0.0045*	44(8)	120*
Pt	2.69(19)	3.12(8)	2.27(12)	2.51(10)	18(4)	30*
Au	22(2)	24(2)	4.5(3)	4.8(3)	8(1)	7*
CuS int.	NIST-610		NIST-612			
standard	Measured ($N = 5$)	Published	Measured ($N = 7$)	Published		
Ru (ppb)	3.3(17)	3	4.6(32)	10.5(5)		

Table S.1 Comparison between preferred/reported and measured (this study) elemental concentrations of Ru, Pd, Ag, Re, Ir, Pt, Au measured in silicate reference materials NIST SRM 612, GSD-1G and GSE1-G while using NIST 610, GSD-1G or CuS (Wohlgemuth-Ueberwasser et al., 2007) as internal reference material standard and ²⁹Si as internal element standard. Element concentrations marked with an asterisk are considered uncertain (no error reported).

^(a) N = indicates the number of analyses per sample ^(b) Preferred values taken from the GeoRem database (GeoRem database, Application Version 19 and references therein) or published values (if preferred are not available, in case of Ru).

Table S.2 Major and minor element composition of silicate melts determined by EPMA and LA-ICP-MS. Numbers in parentheses represent 2 standard errors in terms of least digits cited; *N* indicates the number of analyses per sample. The EPMA measurements are in wt.% and the LA-ICP-MS analyses in ppm unless otherwise stated.

Run #	ESS-90a	ESS-90b	ESS-91	ESS-93	ESS-94	ESS-95	ESS-96	ESS-97	ESS-98	ESS-99	ESS-100	ESS-102	ESS-103	ESS-104	ESS-107
EPMA	$N = 40^{a}$	N = 50	N = 50	N = 75	N = 40	N = 40	N = 33	N = 24	N = 31	N = 26	N = 15	N = 32	N = 38	N = 52	N = 46
SiO ₂ (wt.%)	65.17(31)	60.08(7)	45.37(8)	45.08(5)	45.62(10)	57.94(13)	51.07(8)	51.05(50)	59.01(15)	59.22(13)	56.93(17)	42.34(8)	62.76(16)	44.36(12)	64.38(12)
TiO ₂	0.130(4)	0.40(1)	0.447(5)	0.426(4)	0.50(1)	0.107(5)	0.41(1)	0.54(1)	0.413(4)	0.38(1)	0.41(1)	0.429(5)	0.44(1)	0.451(4)	0.394(4)
AI_2O_3	8.19(4)	7.63(2)	8.37(3)	8.34(1)	9.83(5)	5.92(2)	8.13(2)	9.37(14)	7.18(2)	6.91(7)	7.74(4)	8.03(2)	8.16(2)	8.00(2)	8.50(2)
Cr ₂ O ₃	0.010(3)	0.075(4)	0.26(1)	0.16(1)	0.12(1)	0.011(3)	0.102(4)	0.32(1)	0.098(6)	0.10(1)	0.14(1)	0.27(1)	0.087(5)	0.206(4)	0.020(4)
FeO	0.74(1)	5.69(5)	17.65(7)	17.65(8)	14.89(17)	0.41(1)	17.10(7)	8.66(6)	8.11(3)	7.40(5)	7.24(3)	20.37(7)	2.65(1)	19.64(6)	0.53(2)
MnO	0.009(2)	0.063(3)	0.041(3)	0.070(3)	0.082(4)	0.008(2)	0.12(1)	0.02(1)	0.066(4)	0.051(4)	0.05(1)	0.042(4)	0.030(3)	0.056(3)	0.017(3)
MgO	17.45(13)	16.83(5)	17.78(5)	17.82(4)	14.51(8)	19.89(12)	11.83(4)	16.00(23)	15.89(6)	15.92(13)	16.28(8)	17.73(5)	17.51(6)	16.97(5)	18.23(5)
CaO	7.57(4)	8.80(1)	8.80(1)	8.97(1)	11.97(4)	12.65(3)	8.95(2)	12.36(20)	8.43(3)	8.36(4)	9.01(3)	9.74(2)	9.18(2)	8.70(1)	8.41(1)
Na ₂ O	0.50(1)	0.057(2)	0.036(3)	0.119(3)	0.103(4)	0.232(5)	0.051(3)	0.067(4)	0.134(4)	0.038(2)	0.043(4)	0.032(3)	0.094(3)	0.06(1)	0.027(2)
K ₂ O	0.046(2)	0.023(2)	0.015(1)	0.030(1)	0.030(2)	0.035(2)	0.025(2)	0.012(3)	0.031(2)	0.015(2)	0.019(3)	0.013(2)	0.021(2)	0.021(2)	0.011(2)
S	0.88(1)	0.194(4)	0.49(3)	0.39(2)	0.26(1)	2.17(2)	0.257(4)	0.13(1)	0.164(3)	0.20(1)	0.20(1)	0.58(4)	0.262(4)	0.51(2)	1.00(1)
Total	100.68(21)	99.84(10)	99.26(13)	99.05(8)	97.91(7)	99.37(16)	98.05(7)	98.53(23)	99.52(16)	98.59(16)	98.07(25)	99.57(18)	101.19(17)	98.96(16)	101.53(17)
LA-ICP-MS	N = 10	N=8	N = 10	N = 6	N = 7	N = 12	N = 6	N=2	N = 18	N = 15	N=8	N = 18	N = 16	N = 22	N = 28
Ref material.	NIST 610	NIST 610	NIST 610	NIST 610	NIST 610	NIST 610	NIST 610	NIST-610	NIST-610	NIST 610	NIST 610	NIST-610	NIST-610	NIST-610	NIST-610
MgO (wt.%)	15.54(19)	14.61(19)	16.62(21)	14.99(22)	13.20(159)	17.12(24)	10.28(34)	14.79(87)	14.26(45)	13.32(41)	14.01(28)	14.69(16)	15.77(24)	14.92(42)	15.76(29)
CaO	7.57(19)	8.50(12)	8.65(12)	9.18(22)	11.77(56)	13.20(9)	8.46(28)	13.23(119)	8.92(33)	8.32(24)	8.68(15)	9.96(12)	9.80(23)	8.72(18)	8.61(12)
110_2	0.16(2)	0.41(1)	0.46(1)	0.42(1)	0.48(2)	0.106(2)	0.40(1)	0.51(5)	0.36(2)	0.35(1)	0.38(1)	0.39(1)	0.43(1)	0.40(1)	0.36(1)
v (ppm)	0.59(12)	6.1(3)	9.5(3)	13(1)	24(1)	0.85(6)	13(2)	25(5)	9.0(3)	9.7(20)	8.1(2)	20.2(3)	3.35(9)	11.5(3)	0.58(2)
Cr Ma	79(6)	521(17)	1721(39)	961(49)	783(10)	43(1)	768(100)	2189(52)	632(17)	667(37)	959(17)	1785(19)	558(12)	1324(35)	101(2)
	102(3)	561(15)	330(7)	561(22)	665(10) 0.55(0)	86(1)	809(107)	200(4)	553(16)	393(9)	399(5)	332(4)	300(6)	461(12)	169(3)
	<0.043(9)	0.13(2)	0.83(2)	0.71(3)	0.55(6)	D.O.I.	0.42(3)	0.11(2)	0.16(2)	0.13(1)	0.14(2)	0.96(2)	0.04(1)	0.96(3)	D.O.I.
	<0.13(3)	0.20(5)	0.93(20)	0.60(11)	0.46(13)	D.0.1.	<0.44	D.0.1.	0.24(6)	0.21(3)	0.25(1)	0.98(3)	0.11(2)	0.85(5)	D.U.I.
Zn	T.00(6)	2.02(3)	5.4(4) 45(1)	2.34(30)	2.20(37)	4.42(14) 51(1)	2.02(40)	2.47(4)	3.2(0)	Z.Z4(1Z)	3.20(34)	0.3(2)	2.37(13)	4.0(4)	0.41(4)
	0.9(4)	20(1)	40(1) 5 9(2)	44(<i>3</i>) 8 0(10)	16(3)	51(1)	02(3)	303(2)	221(17)	1 27(20)	01(1) 1 12(15)	00(Z) 9 2(2)	32(1)	02(9)	10.3(3)
Ge Ac	0.30(4)	1.07(20)	0.70(28)	0.9(10)	1 46(17)	0.1(2)	4.3(3)	3.3(10)	1.02(17)	1.37(20)	1.12(15)	0.2(3)	0.53(6) b.d.l	12.3(10) 1 12(10)	0.36(3)
AS Mo	<0.25(0)	0.23(4)	0.70(20)	5.1(1)	5.2(4)	0.72(7)	<0.25 0.96(11)	0.40(6)	0.20(2)	0.20(9)	<0.29 0.026(8)	11 9(2)	0.018(4)	7.12(10)	0.13(3)
Pd	D.u.i.	0.075(15)	4.7(1)	5.1(1)	0.16(6)	0.022(0)	0.00(11) 0.68(20)	0.10(3)	0.09(2)	0.031(0) 0.075(15)	0.030(8)	1 68(5)	0.018(4)	7.9(4)	0.014(4)
Cd	-	-	-0.09(3)	-	< 0.10(0)	0.30(3)	< 0.00(20)	0.22(4)	-	< 0.073(13)	-	0.02(1)	– hdl	-	- 0.018(5)
Sn	(0.00(2))	1.86(8)	4 3(1)	47(2)	4 0(3)	0.11(2)	<0.00(+) 4 3(1)	1 88(10)	2.00(0)	2 19(9)	1 28(6)	4 6(1)	0.66(2)	6 2(3)	0.010(3)
Sh	< 0.05(2)	h.dl	0.22(2)	0.28(3)	0.38(7)	b.d.l	< 0.10(2)	h.dl	b.d.	bdl	h.dl	0.23(2)	b.d.l	0.2(0)	b.d.l
W	< 0.012	0.11(2)	2.8(1)	6.4(3)	7.3(4)	0.003(1)	6.7(14)	4.7(7)	1.62(10)	3.1(20)	1.41(26)	5.9(2)	0.004(2)	3.73(18)	b.d.l.
Re (ppb)	_	_		697(152)	-	_	_	_	_	_	_	_	5.4(15)	888(104)	11(2)
Au	6.7(12)	2,4(7)	18(1)	_	_	_	_	_	3.41(29)	_	1.64(16)	_	_	_	_
Pb	0.05(1)	0.13(1)	0.35(6)	0.21(1)	0.46(14)	0.119(3)	0.43(14)	1.61(1)	1.16(6)	0.52(10)	0.50(2)	0.57(5)	0.13(1)	0.50(6)	0.052(8)
Run #	ESS-108	ESS-109	ESS-110	ESS-111	ESS-112	ESS-113	ESS-114	ESS-119	ESS-120	ESS-121	ESS-122	ESS-123	ESS-124	ESS-125#1	ESS-125#2
EPMA	N = 50	N = 32	N = 24	N = 45	N = 60	N = 43	N = 30	N = 47	N = 80	N = 53	N = 90	N = 32	N = 44	N = 25	N = 29
SiO ₂ (wt.%)	63.27(15)	64.02(24)	62.93(35)	41.82(7)	63.79(10)	42.92(8)	64.23(15)	61.40(21)	62.99(12)	57.67(16)	30.44(53)	34.61(17)	53.45(12)	63.23(13)	61.35(11)
TiO ₂	0.383(3)	0.448(5)	0.17(1)	0.441(4)	0.437(3)	0.455(5)	0.419(5)	0.376(4)	0.429(4)	0.28(1)	0.27(3)	0.33(1)	0.37(1)	0.23(1)	0.26(1)
AI_2O_3	7.01(2)	8.43(4)	7.62(7)	8.16(2)	7.81(2)	7.78(2)	8.33(2)	8.11(3)	8.24(2)	5.93(1)	6.26(78)	6.51(3)	7.70(2)	8.12(1)	8.48(2)
Cr_2O_3	0.046(4)	0.10(1)	0.009(5)	0.32(1)	0.116(4)	0.41(1)	0.063(5)	0.056(5)	0.097(3)	0.151(5)	0.22(1)	0.33(1)	0.268(4)	0.019(5)	0.034(4)
FeO	1.92(1)	1.25(1)	0.48(2)	21.68(6)	2.52(2)	21.81(4)	0.76(2)	1.08(2)	1.04(1)	13.41(16)	41.87(56)	35.38(9)	11.15(2)	0.42(1)	0.62(2)
MnO	0.035(4)	0.022(3)	0.007(3)	0.036(4)	0.026(2)	0.026(3)	0.017(3)	0.017(3)	0.020(2)	0.069(3)	0.054(4)	0.033(4)	0.045(3)	0.013(4)	0.012(3)

MgO	16.76(5)	17.81(8)	17.66(18)	17.07(5)	16.80(6)	16.54(7)	17.82(6)	17.80(7)	17.91(4)	12.90(5)	11.51(120)	13.26(9)	16.19(4)	16.52(4)	17.88(3)
CaO	10.14(5)	9.07(1)	10.30(7)	8.81(4)	8.61(2)	8.72(1)	9.11(1)	10.29(6)	9.38(1)	6.79(1)	7.18(63)	7.49(5)	8.58(2)	8.64(2)	9.08(2)
Na ₂ O	0.072(2)	0.068(2)	0.055(2)	0.064(2)	0.074(2)	0.068(3)	0.061(2)	0.082(2)	0.064(2)	0.115(4)	0.08(2)	0.05(1)	0.068(3)	0.069(4)	0.055(4)
K ₂ O	0.020(2)	0.030(2)	0.024(3)	0.031(2)	0.033(2)	0.038(2)	0.024(3)	0.032(2)	0.022(2)	0.016(2)	0.018(4)	0.012(3)	0.016(2)	0.016(3)	0.013(3)
S	0.275(4)	0.402(4)	2.77(3)	0.60(3)	0.229(3)	0.58(2)	0.71(1)	0.505(4)	0.38(1)	0.23(1)	1.37(32)	0.79(3)	0.198(3)	1.69(2)	0.81(2)
Total	99.92(11)	101.64(34)	102.03(38)	99.04(9)	100.44(11)	99.34(14)	101.53(23)	99.75(26)	100.58(10)	97.57(11)	99.30(31)	98.81(18)	98.05(11)	98.98(11)	98.61(11)
LA-ICP-MS	N = 14	N = 22	N = 7	N = 20	N = 9	N = 13	N = 7	N = 21	N = 17	N = 8	N = 8	N = 12	N = 11	N = 7	N = 7
Ref material.	NIST-610	NIST-610	NIST-610	NIST-610	NIST-610	NIST-610	NIST-610	NIST-610	NIST-610	NIST-610	NIST-610	NIST-610	NIST-610	NIST-610	NIST-610
		GSD-1G		GSD-1G			GSD-1G	GSD-1G							
MgO (wt.%)	14.74(42)	16.06(45)	15.06(39)	14.85(26)	14.38(30)	14.20(17)	15.17(74)	16.38(29)	15.50(13)	11.01(25)	10.91(60)	11.90(8)	13.95(8)	13.93(58)	15.66(10)
CaO	10.41(22)	9.32(23)	10.12(19)	8.46(22)	8.67(21)	8.58(11)	8.78(30)	11.46(27)	8.76(24)	6.56(15)	6.78(41)	6.91(13)	7.88(8)	7.46(28)	8.80(8)
	0.35(1)	0.42(1)	0.16(1)	0.39(1)	0.41(1)	0.41(1)	0.38(2)	0.37(1)	0.40(1)	0.29(1)	0.27(2)	0.31(1)	0.366(4)	0.24(1)	0.304(2)
V (ppm)	3.4(4)	38(1)	0.33(2)	479(15)	123(3)	273(3)	19(1)	32(1)	38(4)	10.9(3)	10.6(6)	10.0(1)	10.4(1)	0.42(2)	0.53(1)
Cr	297(7)	582(9)	59(1)	1988(52)	696(17)	2547(32)	370(9)	334(6)	695(32)	975(25)	1389(19)	2116(18)	1801(18)	139(12)	209(1)
Min	305(8)	187(4)	64(1)	306(5)	242(7)	225(3)	145(6)	164(2)	142(2)	504(14)	425(5)	270(3)	356(4)	105(2)	115(1)
Co	b.d.l.	0.46(3)	b.d.l.	42(1)	0.85(4)	40(1)	0.22(1)	0.42(2)	0.32(2)	0.31(3)	0.31(4)	0.26(1)	0.25(1)	b.d.l.	b.d.l.
	D.Q.I.	0.15(2)	<0.07(2)	3.7(1)	0.17(4)	3.5(2)	0.09(1)	0.12(1)	D.Q.I.	0.45(16)	0.75(14)	0.51(8)	0.39(14)	D.Q.I.	D.Q.I.
Cu Zn	1.06(7)	6.3(5)	2.29(8)	16(1)	2.11(12)	15.7(4)	1.69(18)	1.47(3)	1.53(19)	2.37(21)	18(2)	14.1(6)	3.0(2)	1.82(9)	2.08(9)
	20(1)	129(3)	14.6(3)	507(12)	175(5)	432(0)	92(4)	101(2)	139(7)	00(0)	139(0)	151(2)	123(1)	17.0(5)	10.4(Z)
Ge	2.27(17)	0.39(5)	1.15(9)	203(0)	1.24(23)	94(2)	0.35(7)	0.01(14)	0.34(5)	0.72(22)	0.52(15)	0.46(6)	0.50(4)	0.20(4) b.d.l	D.U.I. 0.09(1)
AS So	0.37(7)	2 9(2)	0.21(3)	0.77(3)	0.13(4)	0.27(2)	0.12(4)	<0.12	2.2(4)	<0.07	0.10(4)	0.09(1)	0.11(2)	D.u.I.	0.00(1)
Mo	-	5.0(5) b.d.l	– hdl	3.9(7)	2.02(2)	56(1)	4.7(4) b.d.l	4.9(Z)	3.2(4) 0.019(5)	-	- 0.52(5)	-	-	-	-
Dd	0.022(4)	b.u.i.	b.u.i.	20(1)	0.023(4)	50(1)	D.u.i.	D.u.i.	0.018(3)	1.00(3)	0.32(3)	0.10(2)	0.05(1)	0.009(4)	0.013(2)
Aa	0.12(2)	_	_	_	- 0.034(6)	-0.07(1)	_	_	-	1.00(40)	7.9(13)	- 268(6)	- 00(5)	- 85(7)	- 110(3)
C d	- 0.027(13)	10(1)	-	- 58(1)	11 4(3)	62(2)	- 8 7(1)	- 7 7(2)	11.2(5)	-	- 0.05(2)	200(0)	0.06(2)	b.d.l	0.03(2)
Sn	0.027(13)	10(1)	0.010(2)	187(3)	7 1(2)	$\frac{02(2)}{85(2)}$	2.7(4)	1.1(2)	2.16(10)	2.76(13)	2.49(20)	1.03(6)	1.30(3)	0.0.1.	0.03(2) 0.11(1)
Sh	b.d.l	4.0(3)	0.23(2) hdl	30(1)	0.06(1)	11 1(4)	2.3(1) h d l	4.1(1)	2.10(10)	2.70(13)	2.43(20) h d l	h.dl	h.d.l	0.14(2) b.d.l	bdl
Το		0.00(7)	_	4 1(1)	0.59(7)	37(2)	2 2(2)	1 13(5)	1.24(11)		- -	- -	_		- -
W	0.019(5)	0.030(7)	0.003(1)	599(12)	0.33(7)	524(10)	0.010(2)	0.016(2)	0.04(1)	0 79(5)	1 22(8)	0.58(3)	0 43(3)	bdl	bdl
Re (ppb)	-	-	-	_	-	-	-	-	-	-	-	-	-	_	_
lr (ppb)	_	2,5(9)	_	60(8)	_	_	4.9(16)	2.5(11)	_	_	_	_	_	_	_
Pt (ppb)	_	_	_	_	14(6)	1544(88)	_	_	27(6)	_	_	_	_	_	_
Au	_	_	35(1)	_	_	_	_	_	_	_	_	5.5(6)	2.50(8)	11.0(22)	3.27(41)
Pb	0.08(1)	13.7(3)	0.064(6)	82(2)	22(1)	99(2)	9.2(4)	8.8(1)	13(1)	0.60(1)	0.66(3)	1.39(2)	0.41(1)	0.052(4)	0.08(1)
Bi	_ ()	0.19(2)	_ ()	3.3(1)	0.13(1)	2.03(12)	0.18(2)	0.126(4)	0.17(1)	- ``	_ ()	- ``	_ ()	_ ()	_ ()
Run #	ESS-126	ESS-127	ESS-128	ESS-129	ESS-130	ESS-132	ESS-134	ESS-135	ESS-136	ESS-139	ESS-141	ESS-142	ESS-143	ESS-144	ESS-145
EPMA	N = 53	N = 25	N = 45	N = 65	N = 58	N = 50	N = 46	N = 40	N = 27	N = 58	N = 74	N = 53	N = 63	N = 30	N = 35
SiO ₂ (wt.%)	64.70(9)	61.58(21)	38.18(22)	65.53(12)	34.49(10)	64.31(10)	43.55(14)	60.94(10)	55.92(31)	59.99(18)	45.45(15)	43.85(9)	63.44(7)	34.80(10)	57.13(12)
TiO ₂	0.37(1)	0.12(1)	0.385(4)	0.279(5)	0.33(1)	0.400(5)	0.39(1)	0.07(1)	0.24(1)	0.091(3)	0.445(4)	0.42(1)	0.349(5)	0.34(1)	0.02(1)
Al ₂ O ₃	8.09(1)	7.50(5)	7.01(3)	7.79(3)	6.45(15)	7.88(2)	7.64(2)	7.89(1)	8.81(3)	8.53(2)	8.13(1)	8.03(1)	8.22(1)	6.38(5)	8.64(1)
Cr ₂ O ₃	0.046(3)	0.012(4)	0.35(1)	0.030(3)	0.34(1)	0.051(3)	0.35(1)	0.020(4)	0.023(4)	0.011(2)	0.327(4)	0.302(4)	0.038(3)	0.39(2)	0.005(2)
FeO	0.69(1)	0.84(9)	29.31(8)	0.61(1)	37.43(15)	1.08(1)	19.18(4)	0.51(2)	0.99(2)	0.43(1)	16.61(4)	18.77(3)	0.54(1)	35.44(10)	0.43(1)
MnO	0.019(3)	0.010(4)	0.035(3)	0.017(2)	0.028(3)	0.022(3)	0.030(3)	0.012(3)	0.041(4)	0.016(3)	0.085(3)	0.117(4)	0.017(2)	0.022(3)	0.012(4)
MgO	17.52(4)	17.28(8)	14.52(7)	16.97(6)	13.04(26)	17.53(5)	17.16(5)	17.78(3)	19.56(4)	17.90(14)	17.87(4)	16.97(4)	17.91(2)	13.73(10)	18.18(4)
CaO	8.69(2)	9.47(4)	7.97(3)	8.56(3)	7.13(13)	9.09(2)	9.44(3)	8.95(2)	10.67(3)	9.51(3)	9.54(3)	9.00(2)	9.36(2)	6.90(5)	9.23(2)
Na ₂ O	0.143(4)	0.08(1)	0.06(1)	0.308(5)	0.093(3)	0.070(3)	0.041(3)	0.089(3)	0.074(4)	0.053(3)	0.032(3)	0.062(3)	0.081(3)	0.070(4)	0.093(4)
K ₂ O	0.031(3)	0.041(6)	0.013(2)	0.058(4)	0.037(3)	0.019(2)	0.016(3)	0.025(2)	0.024(4)	0.020(3)	0.009(2)	0.013(2)	0.022(2)	0.017(4)	0.025(3)
S	0.60(1)	3.12(2)	0.63(1)	0.96(2)	1.00(6)	0.389(3)	0.47(1)	5.58(1)	0.71(2)	1.95(2)	0.40(1)	0.309(5)	0.97(1)	0.84(3)	4.08(1)
lotal	100.91(9)	100.05(20)	98.47(19)	101.12(8)	100.43(10)	100.83(8)	98.27(10)	101.86(9)	97.07(31)	98.50(9)	98.92(12)	97.86 (10)	100.95(8)	98.97(10)	97.85(11)

LA-ICP-MS	N = 14	N = 20	N = 16	N = 18	N = 30	N = 19	N = 10	N = 8	N = 19	N = 13	N = 31	N = 15	N = 15	N = 19	N = 4
Ref material.	NIST-610	NIST-610	NIST-610	NIST 610	NIST 610	NIST 610	NIST-610	NIST-610	NIST 610	NIST 610	NIST 610	NIST 610	NIST 610	NIST 610	NIST 610
				GSD-1G	GSD-1G	GSD-1G			Cu sulfide	Cu sulfide	Cu sulfide	Cu sulfide			Cu sulfide
MaQ (wt %)	14 68(26)	14 27(47)	13 23(8)	14 84(31)	11 77(7)	15 76(21)	14 41(28)	15 07(23)	17 02(19)	15 35(44)	15 79(16)	14 34(13)	15 10(39)	11 86(9)	14 41(59)
CaO	7 70(21)	8 15(39)	7 56(7)	8 73(19)	6 79(5)	9 42(8)	8 21(23)	7 97(16)	10.68(6)	9.37(14)	9 69(9)	8 48(13)	8 02(23)	6 59(11)	8 64(16)
TiO	0.34(1)	0.10(00)	0.361(4)	0.30(1)	0.341(2)	0.41(1)	0.35(1)	0.078(3)	0.28(1)	0.092(3)	0.00(0) 0.45(1)	0.40(1)	0.30(1)	0.33(1)	0.025(1)
V (nnm)	25(2)	0.10(1) 0.21(3)	11 1(1)	23(1)	322(2)	46(1)	14 3(1)	0.20(2)	1 23(15)	0.002(0)	16 5(2)	150(2)	11 1(6)	198(3)	0.020(1)
Cr	309(6)	70(8)	2429(26)	199(6)	2140(15)	378(8)	2357(19)	110(3)	156(9)	48(1)	2160(25)	1927(21)	244(9)	2403(42)	28(1)
Mn	142(3)	62(6)	274(2)	107(3)	195(1)	153(2)	206(3)	68(2)	341(15)	125(5)	625(7)	828(6)	110(4)	157(3)	89(2)
Co	0.20(4)	62(0) b.d.l	0.38(1)	0.24(2)	6 2(1)	0.37(2)	1.07(4)	bdl	0.18(2)	0.07(1)	5 4(1)	124(2)	0.20(13)	5 9(2)	0.10(2)
Ni	0.20(4) b.d.l	b.d.l.	0.50(1) 0.62(7)	0.24(2) b.d.l	1 78(8)	0.37(2)	1.07(4)	b.d.i.	0.10(2) 0.31(4)	0.07(1)	0.95(7)	1.24(2) 0.56(3)	-0.23(13)	1.3(2)	0.10(2) 0.12(2)
Cu	1 31(15)	3 5(3)	75(2)	3 5(2)	32(1)	1 59(17)	5 1(1)	12 2(5)	1 82(19)	2 08(12)	6.6(3)	4 9(2)	1 11(7)	32(2)	5.8(2)
Zn	86(3)	9.9(9)	107(2)	72(3)	354(3)	111(1)	95(2)	31(1)	17(1)	10.4(3)	91(2)	71(1)	63(2)	354(7)	5.0(2) 5.4(3)
Go	<0.17	0.32(5)	0.35(5)	0.31(5)	3 8(1)	0.46(6)	6.8(3)	0.20(8)	0.64(6)	0.15(2)	1 45(7)	0.24(4)	< 0.42	248(7)	0.35(2)
As	<0.17	0.32(3) b.d.l	0.03(0)	0.31(3)	0.07(1)	0.40(0)	0.0(3)	0.20(0) b.d.l	0.04(0)	0.13(2) b.d.l	1.43(7)	0.24(4)	<0.42 b.d.l	2.40(7)	0.33(2)
A3 Sa	(0.03)	b.u.i.	0.00(1)	0.21(3)	20 5(5)	4.7(2)	0.00(4)	b.u.i.	0.14(1)	b.u.i.	0.14(2)	0.07(1)	14(1)	4.0(2)	0.10(3)
Mo	hdl	– hdl	-0.07(1)	4.3(11) b.d.l	20.3(3)	4.7(2)	8 0(2)	-0.011(2)	0.09(1)	- 0.04(1)	0 62(4)	- 0.26(1)	0.04(1)	4.3(2)	– hdl
Ru (nnh)	b.u.i.	b.u.i.	0.07(1)	b.u.i.	0.97(2)	0.03(1)	0.3(2)	0.011(2)	7 5(20)	37(12)	52(10)	6.20(1)	0.04(1)	0.00(2)	22(3)
Pd	_	_	_	_	_	_	_	_	7.3(20)	57(12)	52(10)	0.7(27)	_	_	ZZ(3)
Aq	_	_			_	_	131(2)	313(15)	67(7)	84(3)	103(3)	113(3)	_	0 18(1)	165(2)
Cd	7 9(3)	0.02(1)	0.09(1)	7 5(3)	94(2)	7 3(2)	0.04(1)	0.04(1)	0.018(5)	0.022(5)	0.03(1)	0.03(1)	7 4(3)	106(2)	hdl
Sn	1 63(8)	0.02(1) 0.18(2)	2 28(2)	3 3(1)	58(1)	4.0(1)	4 5(1)	0.04(1)	5.2(4)	3.0(2)	88(1)	29.2(4)	1 66(10)	36 6(4)	A A(1)
Sh	0.02(1)	b.d.	b.d.l	b.d.l	0.55(1)	4.0(1) b.d.l	0.25(1)	b.d.l	5.2(4) bdl	b.d.l	0.29(1)	bdl	0.26(25)	0.37(2)	hdl
Το	1.00(22)	_	_	3 5(8)	163(4)	1 03(14)	0.20(1)	_	_	_	0.20(1)	_	3 1(8)	15.7(4)	- -
W	0.23(13)	bdl	0.27(1)	0.03(1)	124(1)	0.05(14)	2 08(3)	bdl	0.06(4)	bdl	6 3(1)	0 30(2)	0.03(1)	96(1)	hdl
Re (nnh)	-	3 4(13)	67(25)	-	-	-	2.00(0)	_	-	_	-	-	-	-	_
Ir (nnh)	_	- -	0.7(20)	8 0(15)	9 2(11)	5 6(10)	_	_	_	_	_	_	_	_	_
Pt (ppb)	51(11)	_	_	-	5.2(11) _	-	_	_	_	_	_	_	212(45)	74(7)	_
Διι	-	_	_	_	_	0.09(1)	16 5(2)	52(5)	_	_	_	_	_	0.05(1)	_
Ph	9 8(6)	0.06(1)	0 71(1)	10.6(3)	163(3)	10.9(2)	0.46(1)	0.13(1)	0.06(1)	0.04(1)	0.81(2)	0 46(2)	6.3(2)	102(2)	0.07(4)
Bi	0.0(0)	-	-	0.25(4)	24(1)	0.15(2)	-	_	0.09(2)	0.12(2)	0.86(2)	0.17(1)	0.24(11)	1.09(7)	0.019(2)
Run #	ESS-146	ESS-149	ESS-150	ESS-151	ESS-152	ESS-153			0.00(2)	0.12(2)	0.00(2)	0.17(1)	0.21(11)	1.00(1)	0.10(2)
FPMA	N = 20	N = 27	N = .31	N = 45	N = .38	N = 56									
SiO_{α} (wt %)	57 88(11)	59 61(21)	29 94(28)	60 40(14)	61.94(20)	57 00(19)	_								
	0.29(1)	0.18(1)	0.30(1)	0.40(14)	0.35(1)	0.24(1)									
	8.07(2)	8 18(3)	5 84(28)	7 59(2)	7 70(6)	8 62(4)									
$Cr_{0}O_{2}$	0.07(2)	0.10(0) 0.017(4)	0.04(20)	0.205(4)	0.058(5)	0.02(4)									
FeO	0.02(1) 0.40(2)	0.35(1)	41 16(53)	3.85(1)	1 99(3)	0.60(1)									
MnO	0.014(5)	0.008(3)	0.02(1)	0.034(3)	0.055(4)	0.036(3)									
MaQ	17 92(5)	18 17(5)	12 51(33)	16 76(4)	16.37(16)	18 58(11)									
CaO	9.84(3)	9.05(2)	7.06(29)	8 81(2)	9 33(3)	9 56(2)									
Na ₂ O	0.04(0)	0.00(2)	0.08(1)	0.01(2)	0.055(4)	0.00(2)									
K ₂ O	0.004(4) 0.018(3)	0.070(4)	0.00(1) 0.032(4)	0.000(0)	0.000(4)	0.044(0) 0.017(2)									
S	1.35(2)	2 59(1)	1.37(23)	0.017(2)	0.33(1)	0.95(1)									
Total	95 86(10)	98 28(29)	98 73(22)	98 29(12)	98 21(11)	95 66(9)									
I A-ICP-MS	N = .33	N = 13	N = 15	N = 11	N = 6	N = 29	_								
Ref material	NIST 610	NIST 610	NIST 610	NIST 610	NIST 610	NIST 610									
	GSD-1G				GSD-1G	Cu sulfide									
MaQ (wt %)	15 75(21)	14 62(20)	10.50(19)	14 24(30)	15 18(93)	14 63(33)	_								
CaO	9.40(10)	8.96(12)	6.80(11)	9.08(16)	9.80(32)	9.08(14)									
	- (/	· · · · · =/			()										

TiO ₂	0.25(1)	0.17(1)	0.30(1)	0.43(1)	0.40(4)	0.23(1)
V (ppm)	11.2(4)	3.9(1)	252(1)	6.6(1)	3.0(5)	0.36(2)
Cr	155(4)	119(3)	2075(39)	1396(19)	439(55)	116(3)
Mn	77(1)	61(1)	174(3)	265(6)	462(31)	267(5)
Co	0.18(1)	0.18(2)	7.5(5)	0.06(1)	0.18(4)	0.069(4)
Ni	0.15(3)	b.d.l.	3.7(13)	0.13(2)	0.26(9)	b.d.l.
Cu	3.6(5)	1.67(13)	52(7)	3.9(2)	3.9(11)	2.7(1)
Zn	61(1)	58(2)	458(11)	49(2)	21(1)	8.3(7)
Ge	0.97(5)	0.22(6)	4.1(1)	0.44(5)	0.97(78)	0.21(2)
As	0.27(2)	0.17(5)	0.17(2)	0.15(2)	0.36(12)	0.13(2)
Se	4.4(1)	3.8(1)	10.4(9)	_	_	_
Мо	b.d.l.	0.019(6)	1.16(4)	b.d.l.	b.d.l.	b.d.l.
Ru (ppb)	_	_	_	_	-	73(11)
Pd	_	_	_	0.039(13)	-	-
Ag	_	_	_	_	-	66(2)
Cd	6.3(2)	8.3(4)	100(5)	0.03(2)	b.d.l.	b.d.l.
Sn	1.32(3)	1.50(7)	42(1)	0.44(2)	18(2)	1.56(4)
Sb	b.d.l.	0.07(4)	1.8(8)	b.d.l.	b.d.l.	b.d.l.
Те	2.6(2)	4.9(5)	41(8)	_	-	-
W	0.10(1)	0.17(5)	158(4)	b.d.l.	0.02(1)	b.d.l.
Re (ppb)	_	_	_	_	-	-
lr (ppb)	19(4)	_	_	_	14(8)	_
Pt (ppb)	_	667(159)	381(198)	_	-	_
Au	_	_	_	_	_	_
Pb	5.4(4)	6.2(6)	112(9)	0.45(11)	0.23(3)	0.047(2)
Bi	0.10(1)	0.18(3)	15(7)	_	0.42(18)	0.063(4)

Table S.3 Major and minor element composition of sulfide liquids determined by EPMA and LA-ICP-MS. Numbers in parentheses represent 2 standard errors in terms of least digits cited; *N* indicates the number of analyses per sample. The EPMA measurements are in wt.% and the LA-ICP-MS analyses in ppm unless otherwise stated.

Run # EPMA	ESS-90 a N = 56 ^a	ESS-90b N = 39	ESS-91 N = 40	ESS-93 N = 29	ESS-94 N = 36	ESS-95 N = 44	ESS-96 N = 35	ESS-97 N = 70	ESS-98 N = 74	ESS-99 N = 26	ESS-100 N = 24	ESS-102 N = 94	ESS-103 N = 69	ESS-104 N = 43	ESS-107 N = 69
Fe (wt.%) S	64.56(35) 30.82(43)	65.70(38) 29.86(59)	63.78(45) 31.06(28)	64.49(21) 30.25(39)	63.17(29) 31.82(61)	67.34(48) 28.80(45)	63.94(12) 30.74(34)	65.93(50) 31.16(49)	63.73(32) 33.37(40)	65.82(36) 30.75(46)	67.25(47) 28.29(63)	60.57(38) 29.24(34)	67.86(47) 30.15(43)	64.14(23) 30.91(24)	68.27(42) 28.94(51)
Са	0.07(1)	0.009(5)	0.02(1)	0.023(5)	0.03(3)	0.20(4)	0.002(2)	0.03(1)	b.d.l.	n.d.	n.d.	n.d.	b.d.l.	0.015(6)	0.05(1)
Mg	n.d.	n.d.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	n.d.	n.d.	n.d.	b.d.l.	b.d.l.	n.d.
Ti	0.07(1)	0.012(6)	0.009(3)	0.004(2)	0.007(2)	0.16(2)	0.005(2)	0.003(1)	0.002(1)	0.005(2)	0.005(2)	0.004(1)	0.003(1)	0.006(3)	0.34(3)
Cr	0.19(3)	0.18(3)	0.29(6)	0.13(1)	0.12(1)	0.22(2)	0.08(1)	0.24(2)	0.16(1)	0.16(2)	0.18(1)	0.15(3)	0.35(2)	0.20(4)	0.36(2)
Mn	0.04(1)	0.021(5)	0.013(3)	0.019(6)	0.024(4)	0.048(5)	0.027(4)	0.007(2)	0.020(3)	0.008(4)	0.004(2)	0.009(2)	0.017(2)	0.015(3)	0.058(3)
Cu	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.093(4)	0.14(1)	0.05(1)	0.04(1)	0.072(4)	0.08(1)	0.07(1)	0.017(4)
Pd	-	_	-	-	1.15(43)	1.74(14)	2.60(30)	0.67(9)	-	0.74(7)	-	4.37(63)	-	-	-
Re	_	-	_	0.036(16)	_	_	_	_	-	-	_	_	0.049(34)	0.024(7)	0.074(25)
Au	3.66(52)	3.00(46)	1.50(81)	_	_	_	_	_	1.93(28)	-	3.71(43)	_	_	_	_
0	0.58(9)	0.65(9)	3.23(22)	3.68(30)	2.67(55)	0.28(5)	1.84(16)	0.57(10)	1.25(20)	0.73(7)	0.59(12)	3.44(26)	0.43(8)	3.65(19)	0.54(9)
Total	99.99(16)	99.47(16)	99.94(25)	98.76(18)	99.26(18)	98.82(10)	99.25(2)	98.72(8)	100.61(12)	98.26(27)	100.09(19)	97.87(39)	98.97(7)	99.07(29)	98.67(11)
LA-ICP-MS	N = 10	N = 16	N = 8	N = 8	N = 2	N = 8	N = 13	n.a.	N = 10	N = 4	N = 1	N = 2	N = 2	N = 9	N = 2
Ref material.	NIST 610	NIST 610	NIST 610	NIST 610	NIST 610	NIST 610	NIST 610	-	NIST 610	NIST 610	NIST 610	NIST 610	NIST 610	NIST 610	NIST-610
Si (ppm)	102(5)	145(78)	419(57)	var.	var.	786(639)	255(130)	_	311(124)	99(40)	389(47)	1490(785)	var.	461(276)	var.
Ca	1380(87)	98(39)	417(31)	var.	var.	3075(165)	83(27)	_	121(67)	b.d.l.	98(14)	588(224)	var.	423(169)	var.
Ti	595(39)	35(8)	65(5)	102(55)	70(29)	1677(108)	28(2)	_	23(7)	9.3(13)	6.6(6)	57(9)	224(102)	52(6)	2931(304)
V	10(1)	8.6(5)	4.2(2)	5.9(S)	7.9(5)	44(3) (6.1(Ź)	_	7.1(3)	6.5(5)	6.1(6)	5.6(6)	18.3(2)	3.7(4)	39(1) (
Cr	1545(97)	1405(75)	2511(76)	1372(72)	1109(39)	2251(157)	686(15)	_	1331(51)	1279(96)	1480(127)	1840(62)	3087(45)	162(114)	3612(796)
Mn	439(23)	247(9)	168(3)	277(18)	332(18)	634(33)	322(12)	_	219(7)	128(12)	42(3)	119(10)	232(28)	204(7)	644(75)
Fe	Int.	Int.	Int.	Int.	Int.	Int.	Int.	_	Int.	Int.	Int.	Int.	Int.	Int.	Int.
Co	19(1)	16(1)	21.6(2)	21(1)	21.4(1)	16.5(3)	18.8(3)	_	15.7(5)	17(1)	17(1)	21(1)	14.9(25)	21(1)	16.2(10)
Ni	222(10)	172(8)	235(6)	249(12)	239(4)	173(7)	171(5)	_	172(6)	184(8)	358(29)	251(9)	151(10)	226(8)	179(17)
Cu	487(18)	502(34)	894(29)	617(51)	911(7)	1445(57)	523(20)	_	1336(25)	594(16)	677(61)	695(8)	724(35)	662(29)	134(9)
Zn	48(3)	58(3)	47(2)	70(10)	145(6)	973(42)	56(2)	_	248(19)	59(4)	57(5)	78(9)	139(1)	107(13)	224(15)
Ge	8 3(5)	14(1)	40(5)	11(1)	7 0(2)	9 8(3)	9 9(4)	_	6 9(7)	10 0(7)	20(2)	64(11)	11 9(3)	14(4)	19(7)
Ge (corr)	6.0(4)	10(1)	2.8(4)	7 6(7)	5 1(2)	7 1(2)	7 1(3)	_	5.0(5)	7 2(5)	$\frac{20(2)}{14(1)}$	4 6(8)	8 5(2)	10(3)	14(5)
	71(4)	53(2)	2.0(4) 53(2)	66(5)	56(5)	33(2)	16(2)	_	59(4)	1.2(3)	52(4)	4.0(0) 63(2)	58(5)	60(13)	67(5)
Mo	100(4)	100(2)	125(2)	120(7)	125(1)	121(2)	121(4)		115(4)	404(4)	72(5)	121(5)	52(4)	142(15)	52(0)
Mo (corr)	140(5)	100(4)	123(3)	168(0)	123(1)	121(3)	121(4)	-	1/9(6)	124(4)	02(6)	160(6)	52(4) 68(6)	1942(13)	52(9) 67(12)
$Dd(wt \theta)$	140(5)	129(3)	101(4)	100(9)	102(1)	107(4)	274(12)	-	140(0)	0.71(5)	93(0)	2 21(22)	00(0)	104(19)	07(12)
Fu (wi. %)	- 0.20(6)	-	-	-	1.39(19)	1.90(13)	2.74(13)	-	-	0.71(3)	-	3.21(32)	-	-	-
	0.30(6)	0.20(4)	0.49(9)	0.32(7)	0.41(16)	0.73(10)	0.23(2)	_	0.31(5)	0.14(3)	1.07(11)	0.36(18)	0.39(10)	0.49(23)	1.52(44)
Ca (corr)	0.20(4)	0.13(3)	0.33(6)	0.21(5)	0.27(11)	0.48(6)	0.15(2)	_	0.21(3)	0.09(2)	0.71(7)	0.24(12)	0.26(7)	0.32(15)	1.00(29)
Sn On (norm)	12(2)	29(1)	7.6(14)	37(4)	27(2)	23(2)	21(1)	-	8.6(13)	25(2)	25(2)	27.6(2)	29(1)	44(11)	47(7)
Sn (corr)	8.5(7)	21(9)	5.5(10)	27(3)	20(1)	1/(1)	15(1)	_	6.3(10)	18(1)	18(2)	20.2(2)	21(1)	32(8)	34(5)
Sb	6.4(5)	8.2(3)	2.2(5)	8.1(6)	6.8(4)	4.7(4)	5.2(3)	-	4.7(3)	6.9(6)	9.2(8)	7.4(1)	7.7(5)	8.7(17)	11.6(12)
Sb (corr)	4.9(4)	6.4(2)	1.7(4)	6.2(5)	5.3(3)	3.6(3)	4.0(2)	-	3.6(3)	5.3(5)	7.1(6)	5.67(3)	5.9(3)	6.7(13)	8.9(9)
VV	1.42(12)	1.35(12)	0.22(5)	0.48(21)	0.22(7)	2.66(44)	0.47(4)	-	2.38(19)	2.26(19)	15(1)	0.13(1)	0.14(4)	0.25(8)	1.61(76)
W (corr)	1.87(15)	1.77(16)	0.26(3)	0.63(27)	0.29(10)	3.48(57)	0.61(6)	-	3.12(25)	2.96(25)	19(1)	0.17(2)	0.19(5)	0.33(11)	2.10(99)
Re	-	-	-	*Re nug.	14.1(4)	603(152)	128(4)	-	-	-	-	-	507(7)	*Re nug	387(121)
Au (wt.%)	2.89(29)	2.30(12)	1.48(33)	-	-	-	_	-	1.86(15)	-	3.19(31)	-	-	-	-

Pb Pb (corr)	3.3(5) 2.4(3)	3.4(3) 2.4(2)	4.0(3) 2.9(2)	4.9(8) 3.5(6)	6.2(7) 4.4(5)	45(6) 32(4)	2.46(34) 1.77(25)	_	22(2) 16(1)	3.4(5) 2.5(4)	13(1) 10(1)	7.5(1) 5.4(1)	6.3(4) 4.6(3)	6.6(13) 4.7(9)	15.7(27) 11(2)
Run # EPMA	ESS-108 N = 26	ESS-109 N = 89	ESS-110 N = 60	ESS-111 N = 80	ESS-112 N = 32	ESS-113 N = 96	ESS-114 N = 79	ESS-119 N = 82	ESS-120 N = 64	ESS-121 N = 49	ESS-122 N = 41	ESS-123 N = 28	ESS-124 N = 51	ESS-125 #1 N = 24	ESS-125 #2 N = 18
Fe (wt.%) S Ca Mg Ti Cr Cr Mn Cu Pd Ag Re Ir Pt Au O Total	69.59(41) 27.79(58) b.d.l. n.d. 0.004(2) 0.23(2) 0.027(4) 0.03(1) 3.10(24) - - - 0.25(5) 99.03(10)	67.59(30) 29.33(30) b.d.l. n.d. 0.032(2) 0.67(1) 0.019(2) 0.15(1) - - 0.060(10) - 0.25(2) 98.10(10)	59.05(31) 36.32(19) 1.04(22) n.d. 0.29(3) 0.60(3) 0.062(3) 0.08(1) - - - 0.99(25) 0.56(6) 98.77(30)	63.38(21) 30.02(22) 0.008(4) n.d. 0.35(6) 0.010(2) 0.22(1) - - - 0.80(31) - 3.90(16) 98.72(16)	67.13(63) 31.41(65) b.d.l. b.d.l. 0.42(3) 0.011(3) 0.06(1) - - 0.54(9) - 0.39(6) 99.88(16)	62.20(48) 31.97(38) b.d.l. n.d. 0.006(1) 0.26(3) 0.007(2) 0.25(1) - - 2.06(96) - 3.63(15) 100.43(23)	66.03(43) 30.65(39) 0.04(2) n.d. 0.14(1) 0.80(4) 0.028(2) 0.09(1) - - 0.096(19) - 0.35(4) 98.24(12)	66.22(44) 30.74(39) 0.010(5) n.d. 0.049(3) 0.53(2) 0.024(2) 0.057(4) - - 0.102(15) - 0.34(3) 98.09(13)	64.86(74) 30.23(81) 0.10(1) 0.007(1) 0.06(1) 0.83(7) 0.019(2) 0.11(1) - - 0.60(9) - 0.53(8) 97.25(22)	64.31(58) 28.99(95) b.d.l. b.d.l. 0.006(3) 0.12(3) 0.12(1) 2.58(39) - - - 1.69(12) 97.88(18)	65.26(34) 25.00(84) b.d.l. 0.02(1) 0.009(3) 0.08(4) 0.011(3) 0.16(2) 1.38(35) - - - 6.54(73) 98.51(40)	66.21(76) 29.48(77) b.d.l. b.d.l. 0.005(3) 0.03(1) 0.008(3) 0.11(1) - 1.28(42) - 0.31(7) 2.95(28) 100.41(22)	67.44(40) 27.61(50) b.d.l. b.d.l. 0.004(2) 0.17(2) 0.008(2) 0.08(1) - 0.58(13) - 3.41(34) 0.85(19) 100.18(21)	52.82(210) 35.22(76) 0.55(20) 0.35(10) 0.17(2) 0.88(5) 0.06(1) 0.20(2) - - 3.91(141) - 0.82(43) 0.67(15) 95.69(87)	66.72(71) 28.53(67) 0.01(1) 0.014(4) 0.13(2) 0.62(6) 0.05(1) 0.09(1) - 1.15(25) - 2.42(27) 0.45(21) 100.19(22)
LA-ICP-MS Ref material.	N = 5 NIST-610	<i>N</i> = 2 NIST610 GSD-1G	N = 4 NIST-610	N = 13 NIST-610 GSD-1G	N = 4 NIST-610	N = 4 NIST-610	N = 5 NIST-610 GSD-1G	<i>n.a.</i> NIST-610 GSD-1G	N = 9 NIST-610	N = 7 NIST-610	N = 7 NIST-610	N = 5 NIST-610	N = 11 NIST-610	N = 2 NIST-610	N = 3 NIST-610
Si (ppm) Ca Ti V Cr Mn Fe Co Ni Cu Zn Ge Ge (corr) As Se Se (corr) Mo Mo (corr) Pd (wt.%) Ag (wt.%) Ag (corr) Cd Cd (corr) Sn Sn (corr)	var. var. var. 15.6(7) 1886(77) 256(13) <i>Int.</i> 16.0(5) 197(7) 406(16) 109(12) 12.6(8) 9.1(6) 53(2) - - - 89(5) 115(6) 2.85(16) - - 0.33(4) 0.22(3) 26(2) 19(1)	var. var. 269(8) 449(36) 4886(155) 190(32) <i>Int.</i> 427(10) 554(7) 1211(158) 809(24) 271(33) 195(17) 35(2) 362(22) 486(21) 146(17) 188(16) - - 818(90) 540(42) 620(117) 452(60)	2914(976) 15214(1567 2374(156) 35(2) 5115(436) 700(73) <i>Int.</i> 3.81(13) 53(3) 822(55) 368(45) 5.0(2) 3.6(2) 20(4) - - 34(1) 44(1) - - 0.65(7) 0.43(5) 39(3) 29(2)	845(390) 7) 470(98) 83(9) 218(20) 2433(189) 138(9) <i>Int.</i> 1036(71) 1227(97) 2171(134) 634(44) 266(22) 191(16) 83(6) 323(37) 433(90) 354(19) 456(25) - - 1274(110) 841(73) 1299(136) 948(99)	463(328) 92(45) 33(14) 612(58) 3189(179) 113(14) <i>Int.</i> 375(53) 475(148) 605(160) 663(77) 66(5) 47(4) 33(5) 429(29) 575(39) 174(66) 225(86) - - - 835(150) 551(99) 394(23) 288(17)	293(130) 164(25) 36(4) 71(2) 2034(99) 71(5) <i>Int.</i> 842(26) 982(43) 2212(94) 374(18) 11.8(30) 8.5(21) 39(2) 488(10) 654(13) 892(38) 1151(49) - - 1059(26) 699(17) 200(18) 146(13)	88(23) 341(29) 1043(38) 578(31) 6001(185) 265(9) <i>Int.</i> 301(8) 374(12) 809(38) 855(44) 32(6) 23(4) 35(2) 300(13) 402(19) 62(3) 80(3) - - 1038(84) 685(56) 456(16) 333(12)		var. 458(194) 620(29) 789(24) 8320(388) 171(9) <i>Int.</i> 435(10) 667(32) 820(37) 1709(119) 45(5) 33(4) 24(1) 165(6) 221(11) 113(5) 145(7) - - 1489(165) 983(109) 423(26) 309(19)	271(121) b.d.l. 12(5) 6.3(10) 1276(131) 89(25) <i>Int.</i> 17(1) 203(8) 504(13) 107(13) 12(1) 8.6(9) 48(2) - - 137(2) 177(3) 2.12(15) - 1.15(11) 0.76(7) 22(2) 16(1)	892(168) 463(51) 56(14) 2.5(10) 615(281) 101(8) <i>Int.</i> 3.7(3) 104(13) 809(126) 114(13) 1.16(8) 0.84(6) 2.75(80) - 2.10(13) 2.71(17) 1.16(18) - 0.34(10) 0.22(7) 7.2(13) 5.3(10)	296(76) 94(38) 16(5) 1.01(23) 506(97) 32(1) <i>Int.</i> 3.2(3) 136(5) 1184(62) 87(4) 0.95(33) 0.68(24) 2.73(40) - - 0.65(12) 0.84(15) - 1.62(22) 1.02(14) 0.69(14) 0.46(9) 6.8(22) 5.0(16)	280(200) 83(7) 14(4) 6.3(20) 2304(596) 56(4) <i>Int.</i> 17.5(5) 229(7) 490(41) 78(9) 8.6(16) 6.2(11) 55(3) - 69(4) 89(5) - 1.12(19) 0.71(12) 0.38(7) 0.25(5) 6.3(14) 4.6(10)	var. var. 2202(566) 31(9) 8358(234) 891(639) <i>Int.</i> 1.7(1) 17(4) 2286(1249) 918(905) 4.5(1) 3.2(1) 14(6) - 6.0(18) 7.8(23) - 6.73(533) 4.24(336) 1.23(99) 0.81(65) 61(18) 45(13)	339(217) 791(88) 2243(78) 33(1) 6451(75) 462(4) <i>Int.</i> 11.8(7) 159(1) 750(15) 247(20) 6.4(6) 4.5(5) 44(2) - 48(3) 62(4) - 1.51(18) 0.95(10) 0.39(20) 0.26(13) 6.9(5) 5.1(4)

Sb Sb (corr) Te Te (corr) W W (corr) Re Ir (wt.%) Pt (wt.%) Pt (corr) Au (wt.%) Pb Pb (corr) Bi Bi (corr)	6.6(2) 5.1(2) - 2.46(32) 3.22(42) - - 4.9(3) 3.5(2) - - -	516(56) 397(30) 1062(56) 648(24) 159(110) 209(102) - <i>*lr nuggets</i> - - 1258(88) 906(45) 1158(22) 892(12)	6.7(9) 5.2(7) - 1.66(35) 2.17(45) - - 0.87(6) 17(4) 12(3) 0.80(17) 0.62(13)	1022(94) 787(73) 1773(180) 1082(110) 31(3) 41(4) - 0.49(20) - - 1999(297) 1439(214) 2134(306) 1643(236)	553(78) 426(60) 1302(369) 794(225) 54(2) 71(3) - 0.68(46) 1.17(79) - 1272(283) 916(204) 821(199) 632(153)	281(28) 216(22) 1836(130) 1120(79) 17(1) 22(1) - 0.86(16) 1.47(28) - 1525(37) 1098(27) 1114(45) 858(34)	592(27) 456(20) 1388(115) 847(70) 2.7(4) 3.5(5) - 0.132(21) - 1375(109) 990(79) 1116(76) 859(56)	- - - - - - - - - - - - - - - - - - -	979(68) 754(52) 2268(65) 1383(40) 16(3) - 0.53(9) 0.91(15) - 2285(129) 1645(93) 2671(244) 2057(188)	5.6(4) 3.3(3) - 2.11(24) 2.77(31) 47(7) - - - 9.8(9) 7.0(6) - - -	1.37(31) 1.06(24) - 0.11(4) 0.15(5) - - - 10.0(20) 7.2(14) - -	1.66(34) 1.28(27) - 0.10(5) 0.13(7) - - 0.32(8) 15(1) 11(1) - - -	6.7(7) 5.1(5) - 0.71(22) 0.94(29) - 2.52(22) 8.2(10) 5.9(7) - -	9.2(39) 7.1(30) b.d.l. 0.69(6) 32(17) 23(13) 	7.5(2) 5.8(2) - 0.08(1) 0.10(1) - - 1.90(4) 9.2(6) 6.6(4) - - -
Run # EPMA	ESS-126 N = 56	ESS-127 N = 49	ESS-128 N = 3	ESS-129 N = 52	ESS-130 N = 36	ESS-132 N = 36	ESS-134 N = 34	ESS-135 N = 27	ESS-136 N = 42	ESS-139 N = 104	ESS-141 N = 63	ESS-142 N = 54	ESS-143 <i>N</i> = 30	ESS-144 N = 28	ESS-145 N = 53
Fe (wt.%) S Ca Mg Ti Cr Mn Cu Ru Ag Re Ir Pt Au O Total	64.45(65) 31.32(72) 0.006(4) 0.017(2) 0.13(2) 0.70(6) 0.027(3) 0.07(1) - - - 0.44(10) - 0.52(9) 97.69(15)	60.12(37) 35.75(25) 0.15(7) 0.35(14) 0.43(7) 0.66(8) 0.07(1) 0.20(1) - - 0.023(8) - - 1.50(23) 99.32(24)	67.11(129) 29.48(151) b.d.l. b.d.l. 0.07(6) 0.005(2) 0.06(3) - - 0.01(2) - 2.65(37) 99.41(16)	64.29(73) 31.34(72) 0.03(2) 0.20(3) 0.20(3) 0.61(6) 0.041(3) 0.22(2) - - - 0.13(6) - - 0.45(5) 97.26(21)	64.09(87) 27.49(122) 0.01(1) 0.005(2) 0.037(4) 0.008(3) 0.31(2) - - 0.013(7) - 4.87(65) 96.92(48)	66.07(51) 30.86(50) b.d.l. 0.004(1) 0.049(5) 0.49(3) 0.024(4) 0.11(1) - - 0.10(3) - 0.30(5) 98.02(11)	61.69(46) 30.93(55) b.d.l. 0.01(1) 0.009(5) 0.32(13) 0.011(3) 0.09(1) - 1.00(36) - - 0.40(28) 3.88(44) 98.40(27)	61.00(146) 32.16(78) 0.27(22) 0.26(17) 0.43(16) 0.71(16) 0.06(1) 0.14(1) - 1.24(39) - 1.24(39) - 1.86(47) 0.74(26) 98.95(44)	59.34(66) 30.16(117) 0.05(3) 0.022(2) 0.03(1) 0.25(3) 0.08(1) 0.24(1) 4.68(208) 2.15(71) - - - 0.64(7) 97.69(42)	62.12(35) 32.19(79) 0.20(6) 0.095(4) 0.16(1) 0.29(2) 0.103(4) 0.09(1) 2.69(98) 1.08(22) - - - 0.51(7) 98.55(14)	55.93(111) 30.14(84) b.d.l. b.d.l. 0.28(4) 0.019(3) 0.17(1) 8.20(204) 1.54(29) - - - 2.83(29) 99.19(52)	65.63(91) 30.13(106) b.d.l. b.d.l. 0.14(2) 0.009(2) 0.13(1) 0.05(3) 1.12(27) - - 1.83(21) 99.08(28)	64.99(60) 30.62(56) 0.014(10) 0.022(4) 0.71(5) 0.031(4) 0.04(1) - - - 0.43(5) - 0.63(16) 97.68(19)	66.70(48) 28.32(58) b.d.l. b.d.l. 0.04(1) b.d.l. 0.27(1) - - 0.15(2) - 3.11(25) 98.61(23)	60.17(59) 33.15(53) 0.61(17) 0.35(8) 0.15(3) 0.23(2) 0.11(1) 0.11(1) 1.30(46) 1.73(54) - - - 0.40(7) 98.34(27)
LA-ICP-MS Ref material.	<i>N</i> = <i>10</i> NIST-610	<i>N</i> = <i>17</i> NIST-610	<i>N</i> = 4 NIST-610	N = 9 NIST-610 GSD-1G	N = 11 NIST-610 GSD-1G	n.a.	N = 9 NIST-610	<i>N</i> = 4 NIST-610	N = 27 NIST-610 Cu sulfide	N = 10 NIST-610 Cu sulfide	N = 26 NIST-610 Cu sulfide	N = 29 NIST-610 Cu sulfide	N = 4 NIST-610	N = 3 NIST-610	N = 12 NIST 610 Cu sulfide
Si (ppm) Ca Ti V Cr Mn Fe Co Ni Cu Zn Ge	314(205) 545(85) 1064(80) 692(132) 6257(369) 281(26) <i>Int.</i> 436(73) 736(69) 471(79) 1114(54) 31(8)	693(156) 4408(591) 3133(137) 24(1) 4957(160) 552(38) <i>Int.</i> 7.6(3) 137(6) 625(26) 150(9) 3.2(3)	152(36) 54(21) 14(4) 1.7(7) 829(365) 27(5) <i>Int.</i> 4(1) 182(22) 618(71) 48(7) b.d.l.	555(91) 1063(111) 2215(76) 1249(64) 6546(293) 417(17) <i>Int.</i> 367(6) 507(17) 1408(47) 1584(9) 54(8)	var. var. 26(8) 23(4) 236(60) 27(2) <i>Int.</i> 84(4) 322(17) 2020(195) 272(29) 12(6)	- - - - - - - - - - - -	677(216) 470(102) 67(7) 6.0(9) 3022(154) 100(2) <i>Int.</i> 26(1) 354(7) 849(17) 108(6) 3.6(10)	701(254) 9547(795) 7790(1166) 39(5) 8393(763) 841(66) <i>Int.</i> 6.6(4) 62(5) 1319(84) 519(50) 9.3(11)	193(43) 1183(82) 521(17) 20(1) 2667(78) 958(19) <i>Int.</i> 166(4) 382(10) 715(25) 125(4) 2.0(8)	var. 4255(611) 1786(113) 16(1) 3150(187) 1227(61) <i>Int.</i> 168(8) 385(38) 868(99) 143(9) b.d.l.	var. 1229(528) 67(21) 5.8(2) 2617(48) 238(6) <i>Int.</i> 196(2) 458(9) 1080(17) 106(2) 2.7(3)	330(94) b.d.l. 10.2(8) 4.9(3) 1557(98) 111(3) <i>Int.</i> 53(3) 263(9) 894(24) 67(3) b.d.l.	253(77) 684(66) 1815(75) 711(27) 7076(211) 285(6) <i>Int.</i> 349(10) 594(29) 341(6) 1018(52) 32(5)	var. 903(593) 48(23) 22(5) 765(159) 17(3) <i>Int.</i> 142(9) 566(56) 2794(221) 167(31) 3.7(9)	629(392) 8341(591) 1368(42) 24(1) 2090(62) 1060(67) <i>Int.</i> 142(4) 318(17) 983(45) 113(3) 1.34(21)
Ge (corr)	22(6)	2.3(2)	_	39(6)	9(4)	_	2.6(7)	6.7(8)	1.4(6)	_	1.9(2)	_	22(3)	2.6(7)	0.97(15)
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As	25(6)	39(2)	_	28(1)	b.d.l.	_	64(3)	33(2)	3.8(2)	3.3(5)	9.3(2)	1.08(14)	21(2)	5.3(7)	5.4(1)
Se	821(16)	_ ``	_	316(9)	242(31)	_	-	-	_	_	_	-	864(17)	164(15)	_
Se (corr)	1100(34)	_	_	423(19)	324(69)	_	_	_	_	_	_	_	1158(23)	220(18)	_
Mo`	95(37)	13(1)	1.14(18)	114(6)	7.3(16)	_	164(2)	43(1)	7.2(3)	5.5(6)	20(1)	0.70(7)	53(1) (14(1)	14.6(4)
Mo (corr)	123(48)	17(1)	1.47(23)	147(8)	9.4(21)	_	212(3)	56(2)	9.3(4)	7.1(8)	25(1)	0.90(9)	68(1)	18(1)	19(1)
Ru (wt.%)	_ ` `	_	_ ``	_	_	_	_	_	1.46(34)	1.41(69)	4.43(66)	0.0397(61)	_	_	1.58(18)
Ru (corr)	_	_	_	_	_	_	_	_	2.72(63)	2.63(128)	8.23(123)	0.0738(114)) —	_	2.89(33)
Pd (wt.%)	-	-	_	_	_	_	_	_	-	-	_	-	-	-	_
Ag (wt.%)	_	_	_	_	_	_	1.93(14)	2.05(20)	2.03(20)	2.47(30)	2.09(9)	2.02(12)	_	_	2.22(20)
Ag (corr)	-	-	_	_	_	_	1.22(9)	1.29(12)	1.28(13)	1.56(19)	1.32(5)	1.27(8)	-	-	1.40(12)
Cd	1235(145)	1.06(16)	0.56(12)	1797(156)	1443(469)	_	0.52(15)	1.79(42)	0.55(12)	0.72(21)	0.45(4)	0.63(8)	1175(54)	1238(255)	0.54(3)
Cd (corr)	815(95)	0.70(11)	0.37(8)	1186(103)	953(310)	_	0.34(10)	1.18(28)	0.36(8)	0.48(14)	0.30(3)	0.41(5)	775(36)	817(168)	0.35(2)
Sn	318(33)	32(2)	15(2)	536(40)	285(76)	_	6.9(18)	39(5)	667(67)	876(106)	768(31)	409(24)	417(21)	251(30)	1121(69)
Sn (corr)	232(24)	23(2)	11(2)	391(29)	208(55)	-	4.8(14)	28(4)	487(49)	639(77)	561(23)	299(18)	304(15)	183(22)	818(51)
Sb	541(74)	9(1)	3.5(3)	624(47)	200(37)	_	1.6(6)	8.2(7)	18(1)	26(3)	27(1)	15(1)	682(40)	321(18)	26(2)
Sb (corr)	417(57)	6.8(4)	2.7(2)	481(36)	154(28)	_	1.2(5)	6.3(5)	14(1)	20(2)	21(1)	11(1)	525(31)	247(14)	20(1)
Те	1699(167)	-	_	1596(190)	1393(505)	-	_	-	-	-	-	-	1511(45)	2028(385)	-
Te (corr)	1036(102)	-	_	973(116)	850(308)	-	_	-	-	-	-	-	922(28)	1237(235)	-
W	4.4(10)	0.05(1)	0.015(10)	4.9(11)	3.3(13)	_	0.11(1)	0.94(6)	0.19(6)	0.06(3)	0.26(7)	0.016(5)	4.6(10)	2.9(16)	1.26(25)
W (corr)	5.8(13)	0.06(1)	0.019(13)	6.4(14)	4.4(17)	_	0.14(2)	1.23(8)	0.25(8)	0.08(3)	0.34(10)	0.021(7)	6.0(13)	3.8(21)	1.66(32)
Re	-	78(38)	0.82(21)	-	-	_	-	-	-	-	-	-	-	-	-
lr	-	-	-	2350(486)	269(191)	_	-	-	-	-	-	-	-	-	-
Pt (wt.%)	0.25(7)	-	-	-	-	_	-	-	-	-	-	-	0.25(2)	0.0288(54)	-
Pt (corr)	0.43(12)	-	-	_	-	_	_	_	-	-	_	-	0.44(4)	0.0495(93)	-
Au (wt.%)	-	-	-	-	-	_	1.25(56)	1.87(13)	-	-	-	-	-	-	-
Pb	1424(178)	5.8(4)	7.7(14)	2257(222)	1728(612)	-	10(2)	24(3)	8.8(9)	6.5(11)	17(1)	10.5(6)	1271(47)	1284(232)	13(1)
Pb (corr)	1026(128)	4.1(3)	5.5(10)	1625(159)	1244(441)	-	7.2(14)	18(2)	6.3(6)	4.7(8)	12(1)	7.5(4)	915(34)	925(167)	9(1)
Bi	1113(128)	_	_	1603(154)	2022(577)	_	_	_	538(66)	849(104)	732(45)	685(41)	1041(40)	1526(161)	722(59)
Bi (corr)	857(99)	-	-	1235(118)	1557(444)	-	-	-	414(51)	654(80)	563(35)	527(32)	802(31)	1175(124)	556(45)
Run #	ESS-146	ESS-149	ESS-150	ESS-151	ESS-152	ESS-153									
EPMA	N = 32	N = 31	N=27	N = 43	N = 100	N = 90									
Fe (wt.%)	65.50(74)	62.51(48)	65.31(47)	66.91(17)	65.48(53)	64.80(46)									
S	30.98(64)	32.67(50)	28.46(63)	28.22(21)	31.08(63)	30.95(54)									
Ca	b.d.l.	0.14(7)	b.d.l.	b.d.l.	b.d.l.	0.02(1)									
Mg	0.038(3)	0.120(4)	0.008(5)	b.d.l.	b.d.l.	0.020(2)									
Ti	0.40(5)	0.71(7)	b.d.l.	b.d.l.	b.d.l.	0.13(1)									
Cr	0.79(6)	0.98(6)	0.03(1)	0.46(3)	0.34(3)	0.38(3)									
Mn	0.041(4)	0.055(4)	b.d.l.	0.46(3)	0.056(4)	0.092(4)									
Cu	0.08(1)	0.07(1)	0.21(2)	0.10(1)	0.09(1)	0.11(1)									
Ru	_ ``	_ ()	_ ``	_ ``	_ ``	0.78(18)									
Pd	_	_	_	3.31(16)	_	_ ``									
Ag	_	_	_	- `´´	_	1.66(31)									
lr -	0.09(3)	_	_	_	1.15(80)	_ ` `									
Pt	_ ``	0.37(7)	0.11(2)	_	-	_									
0	0.07(3)	0.13(4)	4.85(35)	0.10(3)	0.60(9)	0.48(4)									
Total	98.02(16)	97.79(13)	99.05(29)	99.58(14)	98.91(24)	99.46(12)	_								
I A-ICP-MS	N = .3	N = 4	N = 6	N = 4	N = 6	N = 11									
				r = r											

Si (ppm) var. var. var. 235(21) var. 1557(767) Ca 2400(1524) 3845(650) var. <297 var. 902(189) Ti 3971(95) 7436(394) 111(75) 23(3) 193(39) 1288(41) V 1361(34) 981(47) 41(17) 28(1) 21(1) 19(1) Cr 7281(170) 9922(425) 554(214) 5048(247) 3415(70) 3290(105) Mn 400(6) 549(21) 36(7) 71(2) 609(12) 898(16) Fe Int.		GSD-1G				GSD-1G	Cu sulfide
Ca2400(1524)3845(650)var.<297var.902(189)Ti3971(95)7436(394)111(75)23(3)193(39)1288(41)V1361(34)981(47)41(17)28(1)21(1)19(1)Cr7281(170)9922(425)554(214)5048(247)3415(70)3290(105)Mn400(6)549(21)36(7)71(2)609(12)898(16)FeInt.Int.Int.Int.Int.Int.Co584(9)510(22)126(16)15.6(2)124(3)111(1)Ni891(28)676(31)322(32)344(5)263(3)296(5)Cu946(31)444(17)1978(300)1469(55)783(15)966(15)Zn1697(152)1665(38)333(21)195(15)160(7)152(7)Ge87(5)71(9)23(20)4.2(6)2.21(45)0.74(13)Ge (corr)62(4)51(7)17(14)3.0(4)1.59(32)0.53(9)As49(2)35(2)4(1)40(2)6.1(2)2.7(2)Se219(3)114(2)165(16)Mo140(2)193(9)20(9)17(2)15(1)2.3(1)Mo140(2)193(9)20(9)17(2)15(1)2.3(1)Mo140(2)248(12)26(11)22(3)19.5(4)2.9(2)Ru (wt.%)1.44(8)Pd (wt.%) <td>Si (ppm)</td> <td>var.</td> <td>var.</td> <td>var.</td> <td>235(21)</td> <td>var.</td> <td>1557(767)</td>	Si (ppm)	var.	var.	var.	235(21)	var.	1557(767)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	Ca	2400(1524)	3845(650)	var.	<297	var.	902(189)
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	Ti	3971(95)	7436(394)	111(75)	23(3)	193(39)	1288(41)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	V	1361(34)	981(47)	41(17)	28(1)	21(1)	19(1)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	Cr	7281(170)	9922(425)	554(214)	5048(247)	3415(70)	3290(105)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Mn	400(6)	549(21) ´	36(7)	71(2) (609(12) [´]	898(16)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	Fe	Int.	Int.	Int.	Int.	Int.	Int. Ó
Ni $891(28)$ $676(31)$ $322(32)$ $344(5)$ $263(3)$ $296(5)$ Cu $946(31)$ $444(17)$ $1978(300)$ $1469(55)$ $783(15)$ $966(15)$ Zn $1697(152)$ $1665(38)$ $333(21)$ $195(15)$ $160(7)$ $152(7)$ Ge $87(5)$ $71(9)$ $23(20)$ $4.2(6)$ $2.21(45)$ $0.74(13)$ Ge (corr) $62(4)$ $51(7)$ $17(14)$ $3.0(4)$ $1.59(32)$ $0.53(9)$ As $49(2)$ $35(2)$ $4(1)$ $40(2)$ $6.1(2)$ $2.7(2)$ Se $219(3)$ $114(2)$ $165(16)$ $ -$ Mo $140(2)$ $193(9)$ $20(9)$ $17(2)$ $15(1)$ $2.3(1)$ Mo (corr) $180(2)$ $248(12)$ $26(11)$ $22(3)$ $19.5(4)$ $2.9(2)$ Ru (wt.%) $ -$ Pd (wt.%) $ -$ Ag (wt.%) $ -$ Ag (wt.%) $ -$ Ag (corr) $ -$ Ag (wt.%) $ -$ Ag (wt.%) $ -$ Ag (wt.%) $ -$ Ag (wt.%) $ -$ Cd $1467(168)$ <td>Со</td> <td>584(9)</td> <td>510(22)</td> <td>126(16)</td> <td>15.6(2)</td> <td>124(3)</td> <td>111(1)</td>	Со	584(9)	510(22)	126(16)	15.6(2)	124(3)	111(1)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Ni	891(28)	676(31)	322(32)	344(5)	263(3)	296(5)
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	Cu	946(31)	444(17)	1978(300)	1469(55)	783(15)	966(15)
Ge $87(5)$ $71(9)$ $23(20)$ $4.2(6)$ $2.21(45)$ $0.74(13)$ Ge (corr) $62(4)$ $51(7)$ $17(14)$ $3.0(4)$ $1.59(32)$ $0.53(9)$ As $49(2)$ $35(2)$ $4(1)$ $40(2)$ $6.1(2)$ $2.7(2)$ Se $219(3)$ $114(2)$ $165(16)$ $ -$ Mo $140(2)$ $193(9)$ $20(9)$ $17(2)$ $15(1)$ $2.3(1)$ Mo (corr) $180(2)$ $248(12)$ $26(11)$ $22(3)$ $19.5(4)$ $2.9(2)$ Ru (wt.%) $ -$ Pd (wt.%) $ -$ Ag (corr) $968(111)$ $924(88)$ $512(103)$ $0.94(19)$ $0.37(5)$ $0.20(3)$ Sn (corr) $501(45)$ $476(46)$ $110(10)$ $30(3)$ $764(38)$ $416(20)$ Sb (corr) $619(42)$ $943(61)$ $105(14)$ $8.1(4)$ $25(2)$ $15(1)$ Te (corr) $916(48)$ $975(83)$ $650(206)$ $ -$ <td>Zn</td> <td>1697(152)</td> <td>1665(38)</td> <td>333(21)</td> <td>195(15)</td> <td>160(7)</td> <td>152(7)</td>	Zn	1697(152)	1665(38)	333(21)	195(15)	160(7)	152(7)
Ge (corr) $62(4)$ $51(7)$ $17(14)$ $3.0(4)$ $1.59(32)$ $0.53(9)$ As $49(2)$ $35(2)$ $4(1)$ $40(2)$ $6.1(2)$ $2.7(2)$ Se $219(3)$ $114(2)$ $165(16)$ $ -$ Se (corr) $293(4)$ $153(3)$ $221(25)$ $ -$ Mo $140(2)$ $193(9)$ $20(9)$ $17(2)$ $15(1)$ $2.3(1)$ Mo (corr) $180(2)$ $248(12)$ $26(11)$ $22(3)$ $19.5(4)$ $2.9(2)$ Ru (wt.%) $ 0.61(4)$ Ru (corr) $ -$ Ag (wt.%) $ -$ Ag (wt.%) $ -$ Ag (corr) $968(111)$ $924(88)$ $512(103)$ $0.94(19)$ $0.37(5)$ $0.20(3)$ Sn (corr) $501(45)$ $476(46)$ $110(10)$ $30(3)$ $764(38)$ $416(20)$ Sb (corr) $619(42)$ $943(61)$ $105(14)$ $8.1(4)$ $25(2)$ $15(1)$ Te (corr) $916(48)$ $975(83)$ $650(206)$ $ -$ <	Ge	87(5)	71(9)	23(20)	4.2(6)	2.21(45)	0.74(13)
As $49(2)$ $35(2)$ $4(1)$ $40(2)$ $6.1(2)$ $2.7(2)$ Se $219(3)$ $114(2)$ $165(16)$ $ -$ Se (corr) $293(4)$ $153(3)$ $221(25)$ $ -$ Mo $140(2)$ $193(9)$ $20(9)$ $17(2)$ $15(1)$ $2.3(1)$ Mo (corr) $180(2)$ $248(12)$ $26(11)$ $22(3)$ $19.5(4)$ $2.9(2)$ Ru (wt.%) $ 0.61(4)$ Ru (wt.%) $ 0.61(4)$ Ru (wt.%) $ -$ Ag (wt.%) $ -$ Ag (corr) $ -$ Ag (corr) $ -$ Ag (corr) $ -$ Ag (corr) $968(111)$ $924(88)$ $512(103)$ $0.94(19)$ $0.37(5)$ $0.20(3)$ Sn (corr) $501(45)$ $476(46)$ $110(10)$ $30(3)$ $764(38)$ $416(20)$ Sb $804(55)$ $1224(80)$ $136(18)$ $11(1)$ $32(2)$ $19(1)$ Sb (corr) $619(42)$ $943(61)$ $105(14)$ $8.1(4)$ $25(2)$ $15(1)$ Te $1592(79)$ $1599(136)$ $1066(337)$ $ -$ W $7(1)$ $10(2)$ $24(14)$ $0.27(20)$ $0.39(12)$	Ge (corr)	62(4)	51(7)	17(14)	3.0(4)	1.59(32)	0.53(9)
Se219(3)114(2)165(16)Se (corr)293(4)153(3)221(25)Mo140(2)193(9)20(9)17(2)15(1)2.3(1)Mo (corr)180(2)248(12)26(11)22(3)19.5(4)2.9(2)Ru (wt.%)0.61(4)Ru (corr)1.14(8)Pd (wt.%)Ag (wt.%)Ag (corr)Ag (corr)1.46(8)Cd1467(168)1400(134)776(156)1.42(28)0.56(8)0.31(5)Cd (corr)968(111)924(88)512(103)0.94(19)0.37(5)0.20(3)Sn (corr)501(45)476(46)110(10)30(3)764(38)416(20)Sb804(55)1224(80)136(18)11(1)32(2)19(1)Sb (corr)619(42)943(61)105(14)8.1(4)25(2)15(1)Te1502(79)1599(136)1066(337)Te (corr)916(48)975(83)650(206)W7(1)10(2)24(14)0.27(20)0.39(12)0.08(2)W (corr)10(1)14(2)32(18)0.35(27)0.51(16)0.10(3)Ir (wt.%	As	49(2)	35(2)	4(1)	40(2)	6.1(2)	2.7(2)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Se	219(3)	114(2)	165(16)	_	_	_ ()
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Se (corr)	293(4)	153(3)	221(25)	_	_	_
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Mo	140(2)	193(9)	20(9)	17(2)	15(1)	2.3(1)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Mo (corr)	180(2)	248(12)	26(11)	22(3)	19.5(4)	2.9(2)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Ru (wt.%)	_	_	_		_	0.61(4)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Ru (corr)	_	_	_	_	_	1.14(8)
Ag (wt.%)2.31(12)Ag (corr)1.46(8)Cd1467(168)1400(134)776(156)1.42(28)0.56(8)0.31(5)Cd (corr)968(111)924(88)512(103)0.94(19)0.37(5)0.20(3)Sn686(62)652(63)151(27)40(4)1046(53)570(27)Sn (corr)501(45)476(46)110(10)30(3)764(38)416(20)Sb804(55)1224(80)136(18)11(1)32(2)19(1)Sb (corr)619(42)943(61)105(14)8.1(4)25(2)15(1)Te1502(79)1599(136)1066(337)Te (corr)916(48)975(83)650(206)W7(1)10(2)24(14)0.27(20)0.39(12)0.08(2)W (corr)10(1)14(2)32(18)0.35(27)0.51(16)0.10(3)Ir (wt.%)-0.294(39)0.198(150)Pt (corr)-0.505(67)0.340(257)Pb2182(79)2339(274)966(300)21(2)20(1)15(1)Pb (corr)1571(57)1684(197)695(216)15(1)14(1)11(1)Bi1395(81)1318(143)1232(407)-1007(50)720(37)	Pd (wt.%)	_	_	_	3.89(11)	_	_
Ag (corr)1.46(8)Cd1467(168)1400(134)776(156)1.42(28)0.56(8)0.31(5)Cd (corr)968(111)924(88)512(103)0.94(19)0.37(5)0.20(3)Sn686(62)652(63)151(27)40(4)1046(53)570(27)Sn (corr)501(45)476(46)110(10)30(3)764(38)416(20)Sb804(55)1224(80)136(18)11(1)32(2)19(1)Sb (corr)619(42)943(61)105(14)8.1(4)25(2)15(1)Te1502(79)1599(136)1066(337)Te (corr)916(48)975(83)650(206)W7(1)10(2)24(14)0.27(20)0.39(12)0.08(2)W (corr)10(1)14(2)32(18)0.35(27)0.51(16)0.10(3)Ir (wt.%)-0.294(39)0.198(150)Pt (corr)-0.505(67)0.340(257)Pb2182(79)2339(274)966(300)21(2)20(1)15(1)Pb (corr)1571(57)1684(197)695(216)15(1)14(1)11(1)Bi1395(81)1318(143)1232(407)-1007(50)720(37)Fi (ocur)1671(60)1018(143)1232(407)-1007(50)720(37)	Ag (wt.%)	_	_	_	_	_	2.31(12)
Cd1467(168)1400(134)776(156)1.42(28)0.56(8)0.31(5)Cd (corr)968(111)924(88)512(103)0.94(19)0.37(5)0.20(3)Sn686(62)652(63)151(27)40(4)1046(53)570(27)Sn (corr)501(45)476(46)110(10)30(3)764(38)416(20)Sb804(55)1224(80)136(18)11(1)32(2)19(1)Sb (corr)619(42)943(61)105(14)8.1(4)25(2)15(1)Te1502(79)1599(136)1066(337)Te (corr)916(48)975(83)650(206)W7(1)10(2)24(14)0.27(20)0.39(12)0.08(2)W (corr)10(1)14(2)32(18)0.35(27)0.51(16)0.10(3)Ir (wt.%)0.204(8)Pt (corr)-0.505(67)0.340(257)Pb2182(79)2339(274)966(300)21(2)20(1)15(1)Pb (corr)1571(57)1684(197)695(216)15(1)14(1)11(1)Bi1395(81)1318(143)1232(407)-1007(50)720(37)Fi (orr)1631(0)1438(143)1232(407)-1007(50)720(37)	Ag (corr)	_	_	_	_	_	1.46(8)
Cd (corr) $968(111)$ $924(88)$ $512(103)$ $0.94(19)$ $0.37(5)$ $0.20(3)$ Sn $686(62)$ $652(63)$ $151(27)$ $40(4)$ $1046(53)$ $570(27)$ Sn (corr) $501(45)$ $476(46)$ $110(10)$ $30(3)$ $764(38)$ $416(20)$ Sb $804(55)$ $1224(80)$ $136(18)$ $11(1)$ $32(2)$ $19(1)$ Sb (corr) $619(42)$ $943(61)$ $105(14)$ $8.1(4)$ $25(2)$ $15(1)$ Te $1502(79)$ $1599(136)$ $1066(337)$ $ -$ Te (corr) $916(48)$ $975(83)$ $650(206)$ $ -$ W $7(1)$ $10(2)$ $24(14)$ $0.27(20)$ $0.39(12)$ $0.08(2)$ W (corr) $10(1)$ $14(2)$ $32(18)$ $0.35(27)$ $0.51(16)$ $0.10(3)$ Ir (wt.%) $ -$ Pt (wt.%) $ 0.294(39)$ $0.198(150)$ $ -$ Pt (corr) $ 0.505(67)$ $0.340(257)$ $ -$ Pb $2182(79)$ $2339(274)$ $966(300)$ $21(2)$ $20(1)$ $15(1)$ Pb (corr) $1571(57)$ $1684(197)$ $695(216)$ $15(1)$ $14(1)$ $11(1)$ Bi $1395(81)$ $1318(143)$ $1232(407)$ $ 1007(50)$ $720(37)$	Cď	1467(168)	1400(134)	776(156)	1,42(28)	0.56(8)	0.31(5)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	Cd (corr)	968(111)	924(88)	512(103)	0.94(19)	0.37(5)	0.20(3)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	Sn ` ´	686(62)	652(63)	151(27)	40(4)	1046(53)	570(27)
Sb $804(55)$ $1224(80)$ $136(18)$ $11(1)$ $32(2)$ $19(1)$ Sb (corr) $619(42)$ $943(61)$ $105(14)$ $8.1(4)$ $25(2)$ $15(1)$ Te $1502(79)$ $1599(136)$ $1066(337)$ Te (corr) $916(48)$ $975(83)$ $650(206)$ W $7(1)$ $10(2)$ $24(14)$ $0.27(20)$ $0.39(12)$ $0.08(2)$ W (corr) $10(1)$ $14(2)$ $32(18)$ $0.35(27)$ $0.51(16)$ $0.10(3)$ Ir (wt.%) $0.204(8)$ Pt (wt.%)- $0.294(39)$ $0.198(150)$ Pt (corr)- $0.505(67)$ $0.340(257)$ Pb $2182(79)$ $2339(274)$ $966(300)$ $21(2)$ $20(1)$ $15(1)$ Pb (corr) $1571(57)$ $1684(197)$ $695(216)$ $15(1)$ $14(1)$ $11(1)$ Bi $1395(81)$ $1318(143)$ $1232(407)$ - $1007(50)$ $720(37)$	Sn (corr)	501(45)	476(46)	110(10)	30(3)	764(38)	416(20)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Sb	804(55)	1224(80)	136(18)	11(1)	32(2)	19(1)
Te $1502(79)$ $1599(136)$ $1066(337)$ $ -$ Te (corr) $916(48)$ $975(83)$ $650(206)$ $ -$ W $7(1)$ $10(2)$ $24(14)$ $0.27(20)$ $0.39(12)$ $0.08(2)$ W (corr) $10(1)$ $14(2)$ $32(18)$ $0.35(27)$ $0.51(16)$ $0.10(3)$ Ir (wt.%) $0.204(8)$ $ 1.29(46)$ $-$ Pt (wt.%) $ 0.505(67)$ $0.340(257)$ $ -$ Pb $2182(79)$ $2339(274)$ $966(300)$ $21(2)$ $20(1)$ $15(1)$ Pb (corr) $1571(57)$ $1684(197)$ $695(216)$ $15(1)$ $14(1)$ $11(1)$ Bi $1395(81)$ $1318(143)$ $1232(407)$ $ 1007(50)$ $720(37)$	Sb (corr)	619(42)	943(61)	105(14)	8.1(4)	25(2)	15(1)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Те	1502(79)	1599(136)	1066(337)	_ ``	- `´	_ ` ´
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Te (corr)	916(48)	975(83)	650(206)	_	_	_
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	W	7(1) (10(2)	24(14)	0.27(20)	0.39(12)	0.08(2)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	W (corr)	10(1)	14(2)	32(18)	0.35(27)	0.51(16)	0.10(3)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	Ir (wt.%)	0.204(8)	_ `´	- ` ´	- `´´	1.29(46)	_ ``
Pt (corr) - 0.505(67) 0.340(257) - </td <td>Pt (wt.%)</td> <td>_ ``</td> <td>0.294(39)</td> <td>0.198(150)</td> <td>_</td> <td>- ` ´</td> <td>_</td>	Pt (wt.%)	_ ``	0.294(39)	0.198(150)	_	- ` ´	_
Pb 2182(79) 2339(274) 966(300) 21(2) 20(1) 15(1) Pb (corr) 1571(57) 1684(197) 695(216) 15(1) 14(1) 11(1) Bi 1395(81) 1318(143) 1232(407) - 1007(50) 720(37) Di (corr) 1571(57) 1684(197) 695(216) 15(1) 14(1) 11(1)	Pt (corr)	_	0.505(67)	0.340(257)	_	_	_
Pb (corr) 1571(57) 1684(197) 695(216) 15(1) 14(1) 11(1) Bi 1395(81) 1318(143) 1232(407) – 1007(50) 720(37)	Pb	2182(79)	2339(274)	966(300) ⁽	21(2)	20(1)	15(1)
Bi 1395(81) 1318(143) 1232(407) – 1007(50) 720(37)	Pb (corr)	1571(57)	1684(197)	695(216)	15(Ì)	14(1)	11(1)
	Bi	1395(81)	1318(143)	1232(407)	_ ``	1007(50)	720(37)
BI (COTT) 1074(62) 1015(110) 949(313) – 775(39) 554(29)	Bi (corr)	1074(62)	1015(110)	949(3 [`] 13)	_	775(39)	554(29)́

Table S.4 Major and minor element composition of metal liquids determined by EPMA. Numbers in parentheses represent 2 standard errors in terms of least digits cited; *N* indicates the number of analyses per sample. The EPMA measurements are all in wt.%.

Run # EPMA	ESS-103 <i>N</i> = 4	ESS-109 N = 5	ESS-110 N = 5	ESS-112 <i>N</i> = 3	ESS-114 <i>N</i> = 7	ESS-119 <i>N</i> = 3	ESS-120 N = 12	ESS-122 N = 24	ESS-123 N = 19	ESS-125#2 <i>N</i> = <i>11</i>	ESS-126 N = 10	ESS-127 N = 2	ESS-128 N = 2	ESS-129 <i>N</i> = 12
Fe (wt.%) P	71.92(27) n.d.	85.68(79) n.d.	80.20(20) n.d.	71.04(53) n.d.	77.06(17) n.d.	72.02(13) n.d.	73.64(12) n.d.	88.75(13) n.d.	90.09(47) n.d.	92.35(14) n.d.	80.32(20) 0.13(1)	76.87(43) 0.026(3)	82.41(383) n.d.	66.97(16) 0.12(1)
S	0.41(7)	1.75(15)	0.21(1)	1.26(26)	0.89(3)	0.56(1)	1.39(9)	1.02(9)	0.89(3)	1.02(4)	1.27(7)	0.50(3)	0.66(2)	0.63(2)
Si	0.041(2)	0.012(2)	15.58(14)	b.d.l.	0.512(4)	0.035(3)	0.08(1)	b.d.l.	b.d.l.	0.68(1)	0.45(2)	7.27(6)	b.d.l.	1.10(1)
Cr	0.10(1)	0.10(2)	0.06(2)	0.04(1)	0.17(1)	0.09(1)	0.128(4)	0.006(2)	0.014(3)	0.18(1)	0.12(1)	0.02(2)	0.016(1)	0.09(1)
Cu	0.01(1)	0.08(1)	0.04(2)	D.d.I.	0.14(3)	0.16(2)	0.03(1)	0.02(1)	0.02(1)	0.02(1)	D.d.I.	D.d.I.	D.d.I.	0.01(1)
Pa	-	_	-	-	_	_	_	2.16(5)	- 0.011(5)	- 6 d l	-	_	-	-
Ag	-	_	_	-	_	_	_	_	0.011(5)	D.Q.I.	-	- 0 02(22)	- 9 16(205)	_
lr	23.30(41)	- 9 06(22)	_	_	_ 17 33(30)	- 24 68(17)	_	_	_	_	_	0.03(32)	0.10(393)	- 24 30(24)
Pt	_	-	_	24 02(87)	-	_	17 91(24)	_	_	_	10 37(19)	_	_	_
Au	_	_	3,85(9)	_	_	_	-	_	3.00(41)	1.24(3)	-	_	_	_
0	0.20(3)	0.15(5)	0.17(1)	0.11(1)	0.13(2)	0.06(2)	0.12(7)	0.09(2)	b.d.l.	0.04(4)	0.25(10)	b.d.l.	0.34(48)	0.10(4)
Total	96.14(38)	96.84(46)	100.15(15)	96.49(49)	97.22(15)	97.61(9)	93.41(25)	92.06(17)	94.04(12)	95.55(13)	92.91(20)	93.67(6)	91.60(55)	93.33(22)
C (calc) ^a	6.09 `´	6.11 `´	0.89 `´	6.12 `´	5.82 `́	6.10	6.07 `´	6.12 `́	6.12 `´	5.67 `´	5.82 `	2.59	6.12 `´	5.40 `´
γFe ^b														
Run # EPMA	ESS-130 N = 25	ESS-132 N = 15	ESS-136 N = 1	ESS-139 N = 15	ESS-142 N = 5	ESS-143 <i>N =</i> 6	ESS-144 N = 8	ESS-145 N = 15	ESS-146 N = 2	ESS-149 N = 5	ESS-150 N = 8	ESS-151 N = 18	ESS-153 N = 6	
Fe (wt.%)	83.81(15)	79.43(16)	87.12	71.09(15)	84.02(13)	69.25(32)	86.1(131)	66.43(18)	79.15(9)	71.41(24)	85.19(15)	90.48(8)	69.80(62)	
ΡÌ	b.d.l.	0.39(1)	n.d.	n.d. `´´	n.d. `´	0.06(1)	b.d.l.	0.009(3)	0.112(3)	0.039(3)	b.d.l.	b.d.l.	0.05(1)	
S	1.08(16)	1.04(3)	0.80	0.33(3)	0.68(3)	1.08(4)	1.05(16)	0.30(4)	1.17(2)	1.07(20)	1.20(9)	1.28(5)	1.00(5)	
Si	b.d.l.	0.02(1)	4.20	14.96(6)	b.d.l.	0.88(2)	b.d.l.	19.71(7)	1.17(9)	2.75(4)	b.d.l.	b.d.l.	0.44(2)	
Cr	0.016(3)	0.078(4)	0.032	0.020(5)	0.016(4)	0.09(1)	0.02(1)	0.015(3)	0.03(1)	0.01(1)	0.012(4)	0.11(1)	0.05(1)	
Cu	0.02(1)	0.01(1)	b.d.l.	0.03(1)	0.04(1)	b.d.l.	0.02(1)	0.02(1)	0.11(3)	0.02(2)	0.02(1)	0.1(1)	0.01(1)	
Ru	-	-	2.26	13.20(9)	11.95(7)	-	-	11.93(14)	_	-	_	-	22.64(86)	
Pd	-	-	-	.	.	-	-	-	_	-	-	1.98(5)		
Ag	-	-	-	b.d.l.	b.d.l.	_	_	0.016(5)	-	_	-	-	b.d.l.	
lr Dí	6.09(15)	11.77(10)	-	-	-	-	-	-	13.27(39)	-	-	-	-	
Pt	-	- 6 d l	-	-	-	22.15(23)	5.85(35)		- 6 d l	19.85(37)	6.40(12)	- b d l	- 6 d l	
Total	0.05(2)	0.0.1.	0.20 01.60	0.12(3)	0.03(2)	1.32(14)	D.U.I. 03 08(100)	D.U.I. 08 51(8)	05.01(16)	0.02(1) 95 17(11)	D.U.I. 02.83(18)	D.U.I. 03 80(12)	D.U.I. 04 02(48)	
C (calc)	6 1 2	52.14(14) 6 11	3 76	0.97	6 12	54.04(24) 554	6 12	0.50	5 35	4 46	6 12	6 12	5 82	
γFe	0.72	0.71	0.68	0.48	0.72	0.80	0.72	0.37	0.70	0.68	0.72	0.72	0.71	

^a C contents calculated using the carbon solubility model of Steenstra et al. (2020c). The latter model does not take the effects of dissolved HSE on C solubility into account, which probably results in an overestimation of C contents for very HSE-rich alloys ^b Activity coefficient calculated for Fe for Fe-Si-C alloys using the online metal activity calculator (Wade and Wood, 2005; MetalAct Website, <u>http://www.earth.ox.ac.uk/~expet/metalact/</u>, accessed on February 14, 2022); for calculations it was assumed that the interaction of HSE in the metal alloy is negligible, given the lack of such interaction coefficients for the alloys compositions/*P*-*T* conditions of interest