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Highly reduced accretion of the Earth by large impactors? Evidence from elemental partitioning between sulfide liquids and silicate melts at highly reduced conditions

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Abstract: The Earth may have formed at very reducing conditions through the accretion of (a) large reduced and differentiated impactor(s). Segregation of Fe-S liquids within these bodies would have left a geochemical mark on the mantles of reduced impactors and on the proto-Earth's mantle. Here, we study the geochemical consequences of highly reduced accretion of the Earth by large impactors. New insights into the partitioning of trace elements between Fe-S liquid and silicate melt at (highly) reduced conditions (Δ IW = -5 to +1) were obtained by performing 21 high pressure experiments at 1 GPa and 1683–2283 K. The observed Fe-S liquid-silicate melt partitioning behavior is in agreement with thermodynamic models that predict a significant role for O in Fe-S liquid and S in the silicate melt.

The experimental results were combined with literature data to obtain new and/or revised thermodynamic parameterizations that quantify the effects of composition and redox state on the elemental distribution between Fe-S liquids and highly reduced silicate melts. The results were used to assess which elements would most likely retain the geochemical signature of accretion of reduced impactors. Under the assumption of

instantaneous core merging, impact delivery to the proto-Earth's mantle was found to be significant (>10% of present-day BSE concentrations) only for S, Zn, Se, Te and TI, whereas the abundances of the other elements remain largely unaffected.

The results also show that present-day BSE S/Se, Se/Te, TI/S and potentially In/Zn as well as their absolute abundances are inconsistent with their delivery by (a) large, highly reduced chondritic differentiated impactor(s) during terrestrial accretion. Continued core-mantle equilibration in the proto-Earth, volatility-related loss and/or post-accretion sulfide liquid segregation in the terrestrial magma ocean would further increase or not affect these discrepancies. We conclude that a significant contribution of (a) large (>10% of Earth's mass) reduced and differentiated chondritic impactor(s) during accretion of the Earth is not reflected in the present-day S, Zn, Se, Te and TI systematics of the terrestrial mantle. This suggests that significant overprinting of the primordial BSE S/Se, Se/Te and S/TI signature could have occurred and/or (2) that the S/Se and Se/Te ratios were set by accretion of more oxidised CI-like materials.

Keywords: Chalcophile, Siderophile, Core formation, Earth, Accretion

1. INTRODUCTION

Geochemical analyses and dynamic models suggest that the redox state (fO_2) in the early solar system ranged considerably, from as low as –6 log units below to around the iron-wüstite buffer (Δ IW; Wadwha, 2008, Namur et al., 2016). It has been hypothesized from the geochemistry of primitive terrestrial mantle samples that the Earth may also have accreted at reduced to highly reduced conditions (e.g., Javoy, 1995; Wade and Wood, 2005, 2016; Javoy et al., 2010; Wohlers and Wood, 2015, 2017; Dauphas, 2017; Münker et al., 2017). A significant contribution of a highly reduced component to the accreting

Earth would be consistent with isotopic similarities between bulk Earth and enstatite chondritic materials (e.g., Ca, Dauphas et al., 2014; Mo, Burkhardt et al., 2011; O, Clayton et al., 1984; Cr, Trinquier et al., 2007, Mougel et al., 2017). Such a contribution could have been achieved via accretion of a Mercury-like highly reduced precursor body of about 10–20 % of the Earth's present mass during the Moon-forming impact (e.g., Wohlers and Wood, 2015; Wade and Wood, 2016).

Incorporation of a significant mass of highly reduced materials may be reflected by present-day terrestrial mantle trace element ratios depending on their geochemical behavior in highly reduced Fe-S liquid-saturated magmatic systems. The latter would be important particularly in cases of low degrees of impactor core-terrestrial mantle equilibration or efficient core-merging, as predicted from numerical and geochemical studies (e.g., Dahl and Stevenson, 2010; Rubie et al., 2011; Fischer and Nimmo, 2018 and references therein) or in case of late accretion of highly reduced materials, as proposed by Wade and Wood (2016). Ratios of chalcophile and/or siderophile elements in the present-day terrestrial mantle have been used to study processes during the accretion of the Earth. The Se/Te of the terrestrial mantle has, for example, been used to argue for a chondritic late veneer to the bulk silicate Earth (BSE; Wang and Becker, 2013) or could reflect mantle metasomatism (König et al., 2014). On the other hand, the Ni/Co of the BSE has been interpreted to reflect core-mantle equilibrium in the Earth at high pressures (e.g., Siebert et al., 2011; Fischer et al., 2015). The Mo/W of the BSE (e.g., Liang et al., 2017) was explained by the addition of S-enriched impactors in late stages of terrestrial differentiation (Wade et al. 2012), but the In/Zn and In/Cd of the BSE have been used to argue for a non-chondritic volatile composition of the bulk Earth (Wang et

al., 2016). The sub-chondritic Nb/Ta of the BSE may be explained by incorporation of differentiated reduced impactors and efficient core-merging (Münker et al., 2017).

In most of these models, the potentially large effects of the addition of (a) differentiated, highly reduced impactor(s) on specific chalcophile and siderophile element ratios in the BSE has not been quantitatively assessed. It is well established that Fe-S sulfide liquids are important sinks for many (trace) elements. Previous studies have shown that the magnitude of (trace) element partitioning into Fe-S liquid is highly dependent of the prevailing fO_2 and to a lesser extent pressure (*P*) - temperature (*T*) and silicate melt composition (Kiseeva and Wood, 2013, 2015; Wohlers and Wood, 2017; Steenstra et al., 2018, 2019a, 2020a–c).

The elemental partitioning between Fe-S liquids and highly reduced silicate melts has been quantified for several elements, including the actinides, nominally siderophile and chalcophile elements, as well as the REE (e.g., Wohlers and Wood, 2015, 2017, Wood and Kiseeva, 2015; Steenstra et al., 2019a, 2020a,b). Wohlers and Wood (2017) proposed a new thermodynamic model for Fe-S liquids that predicts the observed increase of the chalcophile behavior of nominally lithophile elements (e.g., Ti, U and Th) and decrease of the chalcophile behavior of a subset of nominally chalcophile elements (Cu) with increasing S contents of the silicate melt. Steenstra et al. (2020a) extended this work to a larger group of elements, but for many elements no statistically significant fits to this thermodynamic model could be obtained due to the limited availability of Fe-S liquid - silicate melt partitioning data at either highly reduced or highly oxidized conditions. This group includes elements Se and Te, which are key for unravelling the chalcophile cycle and the potential extent and nature of terrestrial late accretion. The solubility of O in Fe-

S liquids under highly reduced conditions is also not fully constrained, although such knowledge is important for estimating the Fe-S liquid-silicate melt distribution coefficients at such conditions using the Wohlers and Wood (2017) model.

To improve our understanding of the distribution behavior of trace elements between sulfide liquids and highly reduced silicate melts, we performed 21 experiments with which Fe-S liquid - silicate melt partition coefficients ($D_M^{Fe-S \, liq-sil \, melt}$) were determined for a large number of elements (Li, O, Mg, Si, P, S, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Rb, Nb, Mo, Cd, In, Sn, Sb, Te, Cs, Ta, W, Tl, Pb, Bi). The results were combined with previously reported experimentally determined values (Steenstra et al., 2020a), collected at (near)-identical conditions, to obtain new and/or revised thermodynamic parameterizations that predict the elemental partitioning between Fe-S liquids and silicate melts as a function of composition and fO_2 .

The resulting set of thermodynamic models was used to study the potential effects of highly reduced accretion on chalcophile and siderophile element abundances and ratios in the terrestrial mantle. Using the thermodynamic parameterizations, elemental ratios of putative reduced impactor mantles were calculated and compared with proposed presentday bulk silicate Earth (BSE) values (Wang and Becker, 2013; Wang et al., 2016; Wang et al., 2018). It was then assessed if highly reduced terrestrial accretion can be reconciled with present-day BSE chalcophile and siderophile element systematics – and quantitative limits of the fraction of these elements that could have been delivered to the BSE by addition of such (a) reduced impactor(s) were provided.

2. METHODS

2.1 EXPERIMENTAL

High pressure-temperature experiments were conducted in Bristol-type piston cylinder presses (Boyd and England, 1960) in the high-pressure laboratories of the Vrije Universiteit Amsterdam and the University of Münster, Germany (Table 1; Appendix section A.1). All experiments were conducted at 1 GPa at temperatures between 1683-2283 K. Lower temperature (<1883 K) experiments were performed using the regular $\frac{1}{2}$ inch talc pyrex assembly (see Van Kan Parker et al., 2011). Three higher temperature experiments were conducted using a customized talc-pyrex assembly with a 3.1 mm I.D. graphite heater. Pressures for both assemblies were estimated using the pressure calibration based on the fayalite + quartz = ferrosillite and albite = jadeite + quartz equilibria, the quartz-coesite transition and the reaction MgCr₂O₄ + SiO₂ = MgSiO₃ + Cr₂O₃ reaction (Bose and Ganguly, 1995; Klemme and O'Neill, 1997; Van Kan Parker et al., 2011). The calibrations have an estimated pressure uncertainty of ~0.1 GPa. Experiments were performed using a combination of synthetic sulfide and silicate powders (Appendix section A.1). For the silicate starting material we used a primitive basaltic composition to facilitate comparison of the new results with those of previous studies. Sulfide powders were prepared by adding various amounts of major- and trace elements in the form of metal powders (Appendix section A.1). Variable amounts of Fe-Si powder were added to generate variable redox states in the different experiments (Table 1).

Most experiments were conducted in graphite capsules only (3.5–5 mm long and 1.2– 1.5 mm I.D.) that were machined from high-purity graphite rods. The synthetic starting compositions were added to the capsules using multiple layers of each phase. Several experiments were performed using graphite-lined Pt capsules that were welded shut after insertion of the graphite inner capsule (Appendix section A.1). Temperatures were

monitored and controlled using a type D (97%W/3%Re-75%W/25%Re) thermocouple in conjunction with a Eurotherm 2404 programmable controller. Samples were initially pressurized to 0.5 GPa. During heating, the samples were gradually pressurized to the target pressure of 1 GPa. Samples were sintered at 1083 K for 30 to 60 min to reduce the capsule porosity, followed by further heating to target temperatures. Run durations at peak temperatures were 3–130 min, depending of peak temperature, and based chemical equilibration times that were determined and discussed extensively in our previous work (Steenstra et al., 2018, 2020a). After the intended run durations, the experimental charges were rapidly quenched, embedded in epoxy and dry-polished using various grades of SiC sandpaper in conjunction with graphite powder. Samples were then carbon coated and analysed using EPMA and LA-ICP-MS for major and trace elements, respectively.

2.2 ANALYTICAL

The major element concentrations in the experimental run products were quantified with JEOL JXA 8530F field emission electron microprobe analysers (EPMA) at the University of Münster, Germany and the Earth and Planets Laboratory, Carnegie Institution for Science (Tables S.2, S.3). Oxygen abundances in the sulfide liquids were measured using the LDE1L crystal at the Earth and Planets Laboratory, Carnegie Institution for Science. Estimated uncertainties on measured O concentrations are approximately 0.1–0.2 wt.% given known blank oxygen signals on nominally O-free samples. This uncertainty is only significant for the O content measured in the sulfide liquid of run EK-05 (~0.3 wt.%), but nevertheless within range of the overall reported uncertainty on O

content (~0.1 wt.%). All phases were analysed using a defocused beam (5–15 µm). Analyses were performed using a beam current of 20 nA and an accelerating voltage of 15 kV. Dwell times were 10-30 s on peak and 5-15 s on each background. Electron microprobe spots were set in lines and/or raster grids, depending on the available surface area of the analysed phases. Analyses for sulfide- and silicate phases were calibrated on well-characterized natural and synthetic reference materials. Standards used for samples analyses were diopside, hypersthene and/or anorthite for Ca and/or Si, forsterite for Mq, anorthite or corundum for AI, KTiPO5 or orthoclase for K, Fe metal, FeS₂ or fayalite for Fe, jadeite for Na, Mn₂O, tephroite or rhodonite for Mn, pure metal reference material or MgCr2O4 for Cr, Zn-metal or willemite for Zn, PbS or Pb-Zn glass for Pb, InAs or GaAs for As, PbS or (chalco)pyrite for S, MgCr₂O₄ or Cr₂O₃ for Cr, NiSe, Ni or NiO for Ni, NiSe or pure metal for Se, CdTe or pure metals for Cd and Te, InAs or pure metal for In, KTiPO5 or GaP for P, TiO₂ or pure metal for Ti, ThO₂ for Th, UO₂ for U, Cs₂O for Cs and only pure metal standards for V, Co, Cu, Ge, Sn, Sb, Mo, W and Bi. The calibrations were considered successful when the primary reference material compositions were reproduced within 1% relative deviation. All EPMA data reduction was performed using the $\Phi(\rho Z)$ correction (Armstrong, 1995).

Trace element concentrations were quantified using LA-ICP-MS at the University of Münster (Tables S.2, S.3). All analyses were performed using a 193 nm ArF excimer laser (Analyte G2, Photon Machines) with a repetition rate of 10 Hz and energy of ~3–4 J/cm² throughout the entire session while using beam sizes ranging between 25–50 μm. The following isotopes were measured: ⁷Li, ²⁴Mg, ²⁹Si, ³¹P, ⁴³Ca, ⁴⁷Ti, ⁴⁹Ti, ⁵¹V, ⁵³Cr, ⁵⁵Mn, ⁵⁶Fe, ⁵⁹Co, ⁶⁰Ni, ⁶¹Ni, ⁶³Cu, ⁶⁶Zn, ⁶⁹Ga, ⁷³Ge, ⁷⁵As, ⁸²Se, ⁸⁵Rb, ⁹³Nb, ⁹⁵Mo, ¹¹¹Cd, ¹¹⁵In,

¹¹⁸Sn, ¹²¹Sb, ¹²⁵Te, ¹³³Cs, ¹⁸¹Ta, ¹⁸²W, ¹⁹⁵Pt, ²⁰⁵Tl, ²⁰⁸Pb, ²⁰⁹Bi, ²³²Th and ²³⁸U. The LA-ICP-MS data reduction was performed using GLITTER software (van Achterbergh et al., 2001, Griffin et al., 2008) and included monitoring and/or identification of heterogeneities, such as sulfide inclusions in the silicate melt and vice-versa or vertical/horizontal compositional variation across the sample.

The USGS NIST 612 silicate glass was used as an external reference material for analyses of all phases (Jochum et al., 2005). The Si and Fe contents measured by electron microprobe were used as internal standards for the silicate- and sulfide liquids, respectively. The USGS reference materials BIR-1G and BCR-2G were analysed every ~20–25 spots to monitor accuracy and precision of measured trace element concentrations. Trace element contents of volatile and refractory elements in sulfides and metals were corrected for matrix effects using the analytical approaches outlined in Steenstra et al. (2019b, 2020d).

Both ⁶³Cu and ⁶⁹Ga have a potential interference on ²³Na⁴⁰Ar and ¹³⁸Ba²⁺, respectively. Figure S.2 shows that measured concentrations of both Cu and Ga in the BIR-1G glass agree well with literature values, suggesting that their measured concentrations are not strongly affected by the latter interferences (see Steenstra et al., 2020c). In case of the BCR-2G glass, the measured concentrations of Cu (17.9 is slightly lower but within error of preferred values (Norman et al., 2004; Jochum et al., 2005). The higher Ga concentrations measured in the BCR-2G glass, relative to preferred values, is explained by the substantially greater Ba/Ga of the latter glass, resulting in an overestimation of Ga contents due to the interference of ¹³⁸Ba²⁺ on ⁶⁹Ga⁺. However, given that the experimental charges are nominally Ba-free, with significantly higher Cu contents,

it is unlikely that the Cu measurements of experimental samples are significantly affected by this interference.

3. RESULTS

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

Highly reduced run products show well-segregated quenched sulfide- and metal liquids in a homogeneous silicate glass (Fig. 1). Due to the increase of Si concentrations as a result of addition of Fe-Si metal, the most reduced experiments (EK-06, EK-08) contained quartz, consistent with previous observations for highly reduced systems (Steenstra et al., 2020a, Table 1). All silicate melts were sulfide liquid-saturated, reflected by the presence of small (<1 μ m) FeS quench specks in the silicate melt (Fig. 1). These specks constitute stoichiometric FeS (Boujibar et al., 2014), which agrees with the homogeneous distribution of elemental concentrations in the silicate melts measured by each LA-ICP-MS spot analysis (Table 2).

In the most reduced experiments immiscible (Fe,Mg,Ca)-S liquids were present in the quenched Fe-S liquid (Malavergne et al., 2014; Steenstra et al., 2020a, Fig. 1). Malavergne et al. (2014) concluded that this phase was an immiscible melt at high *P-T* and that its composition remains unaffected by quenching, consistent with their homogeneous compositions (Table 3).

For experiments to which metal powders were added in addition to sulfide powers, the oxygen fugacity ($f0_2$) of each run was defined relative to the iron-wüstite buffer or ΔIW :

$$\Delta IW = 2\log\left(\frac{a_{Fe0}^{\text{cil} \text{ melt}}}{a_{Fe}^{\mu_{e}-\text{Si} \text{ liq}}}\right) = 2\log\left(\frac{x_{Fe}^{\text{cil} \text{ melt}}}{x_{Fe}^{\mu_{e}-\text{Si} \text{ liq}}}\right) + \log\left(\frac{\gamma_{Fe0}^{\text{cil} \text{ melt}}}{\gamma_{Fe}^{\mu_{e}-\text{Si} \text{ liq}}}\right)$$
(1)

where $a_{\text{Fe0}}^{\text{cil melt}}$ and $\chi_{\text{Fe0}}^{\text{cil melt}}$ are the activity and molar fraction of FeO in the silicate melt, $a_{\text{Fe}}^{\text{Fe}-\text{Si liq}}$ and $\chi_{\text{Fe}}^{\text{Fe}-\text{Si liq}}$ the activity and molar fraction of Fe in the Fe-Si liquid and $\gamma_{\text{Fe0}}^{\text{cil melt}}$ and $\gamma_{\text{Fe}}^{\text{Fe}-\text{Si liq}}$ the activity coefficients of FeO and Fe in the silicate melt and Fe-Si liquid, respectively. For the most reduced experiments, the f_{0_2} can also be defined relative to the Si-SiO₂ buffer (Δ Si-SiO₂) (Rose-Weston et al., 2009; Steenstra et al., 2020a,b):

$$\log fO_2 \left(\Delta \text{Si} - \text{Si}O_2\right) = 2\log\left(\frac{a_{\text{Si}O_2}^{\text{sil}\text{ melt}}}{a_{\text{Si}}^{\text{re}-\text{Si}\text{ liq}}}\right) = 2\log\left(\frac{x_{\text{Si}O_2}^{\text{sil}\text{ melt}}}{x_{\text{Si}}^{\text{re}-\text{Si}\text{ liq}}}\right) + 2\log\left(\frac{y_{\text{Si}O_2}^{\text{sil}\text{ melt}}}{y_{\text{Si}}^{\text{re}-\text{Si}\text{ liq}}}\right)$$
(2)

where $a_{SiO_2}^{\text{eil melt}}$ and $\chi_{SiO_2}^{\text{eil melt}}$ are the activity and molar fraction of SiO₂ in the silicate melt and $a_{Si}^{\text{Ee}-\text{Si}\log^2} = a_{SiO_2}^{\text{Ee}-\text{Si}\log^2} =$

As discussed in Steenstra et al. (2020a,b), there are no predictive models for $\gamma_{\text{Fe0}}^{\text{sil melt}}$ or $\gamma_{\text{SiO}_2}^{\text{sil melt}}$ at highly reducing conditions, although it is well established that $\gamma_{\text{Fe0}}^{\text{sil melt}}$ dramatically decreases from moderately to highly reduced conditions (Wohlers and Wood, 2017; Steenstra et al., 2020a,b). We therefore re-calculated the Δ IW values for

these experiments using the offset between the ΔIW and $\Delta Si-SiO_2$ values as a proxy for changes in $\gamma_{Fe0}^{sil \,melt}$ (see Steenstra et al., 2020a,b and references therein) (Table 1).

Some experiments (EK-07 and all ESS-marked runs) were run without Fe(-Si) metal powder in addition to Fe-S powder, yielding relative more oxidized conditions in the experimental run products compared to the metal-saturated experiments. Previous studies have shown that the fO_2 in experiments performed in graphite capsules is approximately 1 unit below the CCO buffer (Kiseeva and Wood, 2013; Ni et al., 2017 and references therein) i.e. 1 log unit above the IW buffer. The Fe metal-absent experiments yield higher O contents of the sulfide liquid at a given FeO content, consistent with the previously proposed increase of O solubility with more oxidized conditions (Fonseca et al., 2008) (see section 3.3).

No dedicated time series was performed to prove that equilibrium was obtained in the experiments. However, the strong correlations between sulfide-silicate partition coefficients and values of the silicate melt sulfur concentrations at sulfide liquid saturation (SCSS) with FeO contents of the silicate melt (sections 3.2, 3.4) are consistent with a steady-state between Fe-S liquids, Fe-Si liquids and silicate melts upon quenching. It was previously shown that a steady-state between sulfide liquid and silicate melt in similar experimental charges is attained within <30 min at 1673 K and 1783 K, respectively, and probably much faster (Kiseeva and Wood, 2013; Steenstra et al., 2018). Steenstra et al. (2018) reported a steady-state of Fe-S liquid and silicate melt for all elements that were considered, while each having a significantly different silicate melt diffusion coefficient (Zhang et al., 2010). Similar behavior was observed for these same elements between Fe-Si liquids and silicate melts (Steenstra et al., 2020b). Given that the experiments from

this study were kept at peak conditions for much longer, it is concluded that equilibrium must have been attained in all experiments.

3.2 Sulfur concentration at sulfide liquid saturation (SCSS) and activity of FeO in the silicate melt

The sulfur concentration at sulfide liquid saturation (SCSS) of the silicate melts varies between ~0.3 and 5.5 wt.% and drastically increases with decreasing FeO contents and fO_2 , consistent with previous findings (e.g., Wood and Kiseeva, 2015; Wykes et al., 2015; Namur et al., 2016; Wohlers and Wood, 2017; Steenstra et al., 2020a). Figure 2 shows the SCSS values as a function of FeO concentration of the silicate melt from this study and our previous studies. The SCSS decreases from ~0.65 to 0.3–0.4 wt.% between ~20 wt.% to ~14 wt.% FeO, whereas it increases again from ~0.65 to up to 5.5 wt.% with FeO contents decreasing from ~0.5 to 0.4 wt.%. The SCSS values obtained in graphite and Pt-lined graphite capsules both agree well with previously reported values (Fig. 2). The results are also consistent with the previously observed dependencies of the SCSS on the FeO contents of the silicate melt (Wallace et al., 1992; Mavrogenes et al., 1999; Holzheid and Grove, 2002, O'Neill and Mavrogenes, 2002; Wykes et al., 2015; Steenstra et al., 2020a).

However, there are strong differences with the SCSS values derived at low pressure by Namur et al. (2016) for a given FeO content compared to the results from the other studies. Despite the extremely reducing conditions of the experiments from the previous studies, FeO contents always exceed 0.4 wt.%, due to the additional decrease of $\gamma_{\text{FeO}}^{\text{sil melt}}$ as the S contents of the silicate melt increase (Steenstra et al., 2020a). Namur et al.

(2016) reported FeO contents as low as 0.025 wt.%, but only at the lowest pressures. A substantial decrease of $\gamma_{\text{FeO}}^{\text{sil}\,\text{melt}}$ at highly reduced conditions with pressure, suggested by these observations, may also (partly) explain the previously derived negative pressure effects on interaction parameters in Fe-Si alloys (Steenstra et al., 2020b), as a decrease in $\gamma_{\text{FeO}}^{\text{sil}\,\text{melt}}$ would also result in overall lower metal-silicate exchange coefficients (K^D_M values). Altogether, the results provide compelling evidence that $\gamma_{\text{FeO}}^{\text{sil}\,\text{melt}}$ decreases with increasing pressure.

3.3 Oxygen solubility in sulfide liquids at low fO2

Given the effect of O in sulfide liquid on trace element activities (Kiseeva and Wood, 2013, 2015), the variation of O contents in sulfide liquids as a function of intrinsic variables such as FeO and fO_2 should be constrained. Fig. 3 shows the O contents of the Fe-S liquids versus the FeO content of the co-existing silicate melt. Although the results are consistent with previous observations that O contents of Fe-S liquid decrease with decreasing FeO content of the silicate melt (e.g., Kiseeva and Wood, 2013, 2015), it is observed here that at the lowest fO_2 (i.e., highest S content of the silicate melt) O contents increase. The model of Kiseeva and Wood (2015) predicts O contents of 0.1–0.2 wt.%, for the most reduced sulfide liquids, whereas the results here show that up to 0.5–3 wt.% O is dissolved at the most reduced conditions. This observation is most readily explained by the aforementioned decrease of $\gamma_{\rm Fe0}^{\rm sil\,melt}$ at very low FeO (and high S) contents of the silicate melt (Fig. 3), as an increase of FeO results in an increase of O in the sulfide liquid. The low number of data points at such conditions does not allow for the development of obtaining a thermodynamic model to model the sulfide liquid O contents at the highly

reduced conditions, but it is evident that O solubility in Fe-S liquid is likely non-ideal at highly reduced conditions.

3.4 Elemental fractionation of trace elements by Fe-S liquid - silicate melt

partitioning

To re-assess the sulfide liquid-silicate melt partitioning behavior of the various elements, the Fe-S liquid-silicate melt partition coefficients ($D_M^{Fe-S \, liq-sil \, melt}$) were defined as:

$$D_{M}^{\text{Fe}-\text{Sliq}-\text{silmelt}} = \frac{C_{M}^{\text{Fe}-\text{Sliq}}}{C_{M}^{\text{silmelt}}}$$
(3)

where $C_{M}^{sul \, liq}$ and $C_{M}^{sil \, melt}$ are the weight concentrations of element M in the sulfide liquid and silicate melt, respectively. Table 2 lists the $D_{M}^{Fe-S \, liq-sil \, melt}$ values derived in this study, as graphically depicted in Figs. 4–6.

To assess the possibility of elemental depletion and fractionation due to sulfide liquid segregation in reduced, differentiated impactors, the S content of the co-existing silicate melt needs to be considered, as previous studies have demonstrated that the S content of the silicate melt is the dominant variable affecting $D_M^{Fe-S \, liq-sil \, melt}$ at highly reduced conditions (Wood and Kiseeva, 2015, Wohlers and Wood, 2017, Steenstra et al., 2020a).

The experimental results generally confirm previous predictions related to the geochemical behavior of trace elements in highly reduced Fe-S saturated systems, although with important differences. Some examples of the dependency of $D_M^{Fe-S \, liq-sil \, melt}$ on FeO contents of the silicate melt are shown in Figs. S.3 and discussed in more detail in Steenstra et al. (2020a) and references therein. Lithophile elements Li, Rb and Cs behave lithophile across the full fO_2 and compositional range considered,

although they behave significantly more chalcophilic at high O contents of the Fe-S liquid (i.e., high FeO contents of the silicate melts), whereas high S contents (and lower $\gamma_{\text{FeO}}^{\text{sil}\,\text{melt}}$) do not affect their partitioning into Fe-S liquids (Fig. 4). The results for lithophile elements U and Th show that their chalcophilic behavior is increased, relative to ideal behavior, with increasing O of the sulfide liquid, but that is more dramatically increased with increasing S contents (and lower $\gamma_{\text{FeO}}^{\text{sil}\,\text{melt}}$) of the silicate melt, consistent with previous observations (e.g., Wohlers and Wood, 2015, 2017). Nominally chalcophile elements such as Bi, Se, Te, Cd, Pb as well as nominally siderophile elements (e.g., Mo, W) behave less strongly chalcophilic with increasing S (i.e., lower $\gamma_{\text{FeO}}^{\text{sil}\,\text{melt}}$ due to S-FeO interaction) of the silicate melt (Wood and Kiseeva, 2015; Steenstra et al., 2020a and references therein).

Some elements that behave similarly to one other at moderately reduced or oxidized conditions significantly fractionate from each other at highly reduced conditions, as previously proposed for Nb and Ta (e.g., Münker et al., 2017). Despite the similar geochemical properties of Ni and Co in moderately reduced metal- and sulfide liquid - silicate melt systems (e.g., Kegler et al., 2008; Siebert et al., 2011; Kiseeva and Wood, 2015; Steenstra et al., 2019a), the $D_M^{Fe-S \, liq-sil \, melt}$ values of Ni and Co converge or may even invert at highly reduced conditions (Fig. 7). This is a result of the very different effect of S-FeO interaction on $D_{Ni}^{Fe-S \, liq-sil \, melt}$ (negative S-FeO interaction parameter) and $D_{Co}^{Fe-S \, liq-sil \, melt}$ (positive S-FeO interaction parameter; see section 3.5), which in turn is explained by the nominally more chalcophile behavior of Ni relative to Co, resulting in a stronger avoidance of Ni in S-rich silicate melts (Wood and Kiseeva, 2015; Wohlers and Wood, 2017; Steenstra et al., 2020a). Significant fractionation also occurs for Mo and W

at highly reduced conditions (Fig. 7). Molybdenum, a typical chalcophile element, behaves increasingly less chalcophilic with increasing S contents of the silicate melt (i.e., lower $\gamma_{\text{Fe0}}^{\text{sil}\text{ melt}}$ due to S-FeO interaction) whereas W, a typical non-chalcophile element, behaves in the opposite way (Fig. 6). This is consistent with the prediction of Wohlers and Wood (2017) that S-FeO interaction parameter $\varepsilon_{\text{Fe0}}^{\text{S_{sil}\text{ melt}}}$ (see section 3.5) becomes larger with decreasing nominally lithophile and increasing nominally chalcophile behavior. Highly reduced sulfide liquid segregation from silicate melt would therefore be accompanied by a dramatic increase of the Mo/W of the silicate melt (Fig. 7).

Finally, significant fractionation due to Fe-S liquid- and Fe-Si liquid - silicate melt partitioning is also observed for many other element pairs (U/Pb, S/Se, In/Cd), whereas for others it is largely neglible (Se/Te, In/Zn, Th/U) (Fig. 7). These results overall confirm the importance of both Fe-S- and Fe-Si liquid - silicate melt fractionation on the geochemistry of highly reduced planetary mantles (e.g., Cartier et al., 2014; Malavergne et al., 2014; Wohlers and Wood, 2015; Vogel et al., 2018; Righter et al., 2018; Steenstra et al., 2020a,b).

3.5 Revised parameterizations describing the distribution of trace elements

between highly reduced silicate melts and Fe-S liquids

Using the new experimental data in conjunction with previously reported data, we fit Eq. (4) to the Fe-S liquid - silicate melt partitioning data for the various elements, following the approach of Wohlers and Wood (2017), as described in more detail in Steenstra et al. (2020a):

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

$$(4)$$

In Eq. 4, A is a constant and *n* is defined as the valence of element M. Parameter $x_{Fe0}^{Fe0-S liq}$ is the mole fraction of FeO in the Fe-S liquid and *x* is the mole fraction of S in the silicate melt. Terms $\varepsilon_{MS_{n/2}}^{Fe0_{Fe-S liq}}$ and $\varepsilon_{Fe0}^{S_{sil melt}}$ are interaction parameters that 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). Compiled and new $D_M^{Fe-S liq-sil melt}$ values (Steenstra et al., 2020a, this study), mostly obtained at 1883 K, were parameterized to Eq. 4 while assuming the valence states reported in Steenstra et al. (2020a) and references therein.

Table 3 lists the regression results. The regression results generally agree well with the results of Steenstra et al. (2020a), where available. We do observe that the new regressions are often more accurate at less reduced conditions, relative to the expressions of Steenstra et al. (2020a) and Wohlers and Wood (2017). This is a result of the larger range of sulfide liquid O contents considered in this study (Fig. S.3–S.6).

4. DISCUSSION

4.1 Modeling the accretion of highly reduced, differentiated impactors to the proto-Earth

The new experimental results and parameterizations are first used to constrain the delivery potential of predominantly siderophile and chalcophile elements to the mantle of the growing Earth. This requires constraints on the concentrations of the elements of interest in the highly reduced impactor mantle. The elemental abundances in the silicate mantle of the highly reduced impactor ($C_{impactor mantle}^{M}$) were calculated using Eq. (5):

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

where $C_{\text{bulk impactor}}^{\text{M}}$ is the bulk abundance of element M in the reduced impactor, x is the silicate mantle mass fraction of the reduced impactor and bulk $D_{M}^{core - mantle}$ represents the estimated bulk core-mantle partition coefficient of trace element M. To calculate the latter value, we considered various scenarios. The bulk compositions of the impactor were considered to be EH- or EL chondritic (Newsom, 1995; Palk et al., 2018; Alexander, 2019, Creech and Moynier, 2019; and references therein; Table S.4). The large range of volatile element abundances in the volatile-poor EL suite relative to the volatile-rich EH chondrites allows for an optimal assessment of the extent of volatile element delivery to the growing Earth. For each bulk composition, mantle abundances were calculated assuming (1) a 15 mass% pure FeS liquid core, (2) a 15 mass % FeS liquid outer and 15 mass% Fe-Si inner core or (3) a 15 mass% FeS outer core and a 50% Fe-Si inner core. The impactor mass was assumed to be 20% of the mass of the Earth (Wohlers and Wood, 2015, 2017). For the same models, mantle S contents of 3 and 7 wt.% were assumed, as appropriate for a Mercury- or aubrite parent body-type of impactor (Fogel et al., 2005; Namur et al., 2016, Wohlers and Wood, 2015, 2017), and the corresponding silicate melt FeO contents illustrated in Fig. 3. For a 20 mass% impactor (e.g., Wade and Wood, 2016), these impactor S contents correspond with a terrestrial core S content of 3.8 wt.% S (Wohlers and Wood, 2017).

The corresponding $D_M^{Fe-S \, liq-sil \, melt}$ values were calculated using Eq. (4) in conjunction with the fit parameters listed in Table 3. Due to a lack of predictive models that incorporate the effects of S in silicate melt on $D_M^{Fe-Si \, liq-sil \, melt}$, the $D_M^{Fe-S \, liq-sil \, melt}$ values were

calculated using the well-established correlations between $D_M^{Fe-S \, liq-sil \, melt}$ and $D_M^{Fe-Si \, liq-sil \, melt}$ for the same set of experiments that were considered in the fitting (see Steenstra et al., 2020a). As in previous studies, the impactor contribution to the proto-Earth was approximated by a single stage of instantaneous core-merging (e.g., Wade and Wood, 2016; Wohlers and Wood, 2015, 2017). The fit parameters listed in Table 3 are largely based on experimental data obtained at 1 GPa and ~1883 K, whereas core/mantle differentiation in larger, highly reduced impactors could have occurred at higher *P-T*. Due to lack of higher *P-T* partitioning data for highly reduced systems, it was assumed that *P-T* effects on $D_M^{Fe-Si \, liq-sil \, melt}$ and $D_M^{Fe-S \, liq-sil \, melt}$ are negligible relative to the very strong effects of variable FeO and corresponding variations of S in the silicate melt. This assumption is justified by the only limited deviation of $D_M^{Fe-S \, liq-sil \, melt}$ and $D_M^{Fe-S \, liq-sil \, melt}$ values that were obtained at different *P-T* at a given S and/or FeO content of the silicate melt (see section 3.4 and Steenstra et al., 2018, 2020a).

4.2 Geochemical consequences of accretion of highly reduced, differentiated impactors to the proto-Earth

To assess whether the present-day BSE contains evidence for the accretion of a large highly reduced differentiated impactor, we first quantified the potential trace element contribution from merging of the impactor mantle and the proto-BSE. Fig. 8 shows the calculated contribution (in %) of trace element budgets by reduced accretion, relative to abundances in the present-day BSE (Wang et al., 2018). The results show that coremantle differentiation within a 20% Earth mass reduced EH impactor would strongly deplete the majority of the trace elements considered (In, Sn, Bi, Ge, Sb, Ni, Co, V, Nb, Mo, W) in the impactor mantle, with a maximum contribution to their present-day BSE

abundance of only <1 %. The highly depleted nature of the latter elements is largely independent of the assumption of impactor redox state within the highly-reduced domain (i.e., $\Delta IW = -7$ to -4; Fig. 8). For Cd, Zn, Pb, Ga, Cu, As, P, Ta, U and Th accretion of a 3 wt.% S-bearing reduced impactor mantle could explain 1 to 10% of the present-day BSE concentrations. In this scenario, only the S, Zn, Se, Te and TI budgets of the presentday BSE could predominantly or completely reflect a reduced accretion stage. Assuming more reduced conditions of the impactor (i.e., higher mantle S contents) yields similar results, except that larger amounts of As and P than found in the BSE today would be delivered. Consideration of a putatitive, more volatile-depleted EL impactor yields a similar pattern but lower absolute abundances that could have been delivered to the BSE, again largely independent of the amount of S in the impactor mantle. It is therefore concluded that accretion of a large reduced impactor would be most strongly reflected by the geochemical systematics of S, P, Zn, As, Se, Te and Tl, under the assumption of highly efficient core merging (Deguen et al., 2014). This in turn implies that the presentday BSE Mo/W, Ni/Co, Th/U, Nb/Ta, In/Cd are unlikely to have been established by accretion of large, highly reduced differentiated impactors.

Another important observation is that highly reduced impactor mantles would have been highly depleted in all of the other volatile elements considered here (In, Cd, Sn, Pb, Bi, Ge, Ga, Sb, Cu), further decreasing the potential role of enstatite chondritic materials in delivery of volatile elements to the terrestrial planets by large impactors (e.g., Rubie et al., 2015; Hirschmann, 2016).

4.3 Does the Earth's mantle record accretion of large highly reduced impactors?

In the previous section we identified the potential elementals (i.e., S, Zn, As, Se, Te, TI) that could trace the accretion of (a) large(r) highly reduced, differentiated impactor(s). Using the results from section 4.2, the elemental ratios of the putative EH- or EL impactor mantle were calculated and compared with the values of the present-day BSE (Wang and Becker, 2015; Wang et al., 2018).

4.3.1 S, Se, Te and TI

As shown in section 4.1, the calculated delivery of S, Se and Te by a 20 mass% EH or EL chondritic impactor would yield significantly higher S, Se and Te contents (up to a factor 10) of the terrestrial mantle, relative to the proposed present-day BSE (80±17 ppb Se and 11±1.7 ppb Te; Wang and Becker, 2013). More importantly, the calculations show that the reduced impactor mantles would have had significantly higher S/Se and Se/Te (S/Se = 4625±700 and 4300±650 and Se/Te = 47±6 and 32±4 for an EL and EH chondritic impactor, respectively) values relative to those inferred for the present-day terrestrial mantle (S/Se = 2600 ± 700 and Se/Te = 7.9 ± 1.6 ; Wang and Becker, 2013) (Fig. 9). However, the latter concentrations and ratios were calculated using lithospheric Iherzolites, i.e., assuming that the subcontinental lithospheric mantle is representative of the BSE. This may not be appropriate, as it has been suggested that lithospheric Iherzolites preserve only little of the primary melt depletion signature and represent refertilized, previously-depleted harzburgites (Le Roux et al., 2007; König et al., 2014; Yierpan et al., 2019). If estimates for S, Se, Te for primitive MORB mantle are considered $(S = 185\pm15 \text{ ppm}; Se = 49\pm11 \text{ ppb}, Te = 3.5\pm1.3 \text{ ppb}; S/Se = 4050\pm1215; Se/Te =$ 17.6±9.7; Lorand and Luguet, 2016; Yierpan et al., 2019), it is clear that modeled

abundances and relative ratios of Se and Te in impactor mantles are still (significantly) higher. However, the S/Se ratios more closely approximate the modeled values in case of primitive MORB mantle.

Depending on the timing of reduced accretion, core-mantle differentiation in the growing Earth could have affected the S, Se and Te systematics of the proto-Earth's mantle (Rose-Weston et al., 2009; Boujibar et al., 2014; Steenstra et al., 2017). Current experimental data obtained at pressures up to 20 GPa show that Te always behaves more siderophilic and chalcophilic than Se, and Se more siderophilic and chalcophilic than S, independent of fO_2 (Rose-Weston et al., 2009; Steenstra et al., 2019c, 2020a,b). Thallium behaves less siderophilic and chalcophilic than S (e.g., Steenstra et al., 2020a). Potential core formation equilibration in the Earth itself during the accretion of (a) reduced impactor body/bodies would therefore further increase the S/Se, Se/Te and S/TI of the terrestrial mantle.

Significant volatile loss on the reduced impactors (before colliding with Earth) or, less likely, during terrestrial magma ocean degassing in the aftermath of a collision could have affected S/Se, Se/Te and S/TI as well. Significant degassing at the accretion stage seems to be required to reconcile the large modeled overabundances of S, Se, Te and TI in the bulk silicate Earth with the accretion of (a) reduced impactor(s), largely independent of the exact impactor redox state or extent of differentiation (Fig. 5, 8). This would be consistent with the findings of Hin et al. (2017), who demonstrated that the isotope ratios of Mg requires volatility-driven fractionation during energetic collisions between planetesimals prior to their accretion to the Earth. Similarly, Norris and Wood (2017) also proposed that the Earth's concentrations of several chalcophile elements (e.g., Cu, In, TI)

are most readily explained by melting and subsequent evaporative loss on Earth-forming impactors.

In terms of condensation from a solar gas, TI is the most volatile of the four elements, whereas Te is more volatile than S and S more than Se (Wood et al., 2019). Under the assumption that the *relative* volatility sequence holds for melt - vapor reactions in the absence of nebular gas, initial volatile loss during melting on the impactor bodies would have increased S/TI and Se/Te and decreased S/Se.

It is therefore concluded that the S, Se, Te systematics of the present-day BSE are unlikely to reflect the addition of highly reduced, differentiated impactors to the growing Earth. This is also in agreement with interpretations of the observed Se (Varas-Reus et al., 2019) and S (Labidi et al., 2013) isotopic composition of the terrestrial mantle. Instead, the S/Se and Se/Te could reflect a late veneer contribution of non-differentiated, oxidized CI chondritic impactors (Wang and Becker, 2013; Ballhaus et al., 2013) following terrestrial accretion, although this is difficult to reconcile with results for Zn, Cd and In (Wang et al., 2016). In addition, Labidi and Cartigny (2016) concluded that the sub-chondritic ³⁴S/³²S ratio of the terrestrial mantle (e.g., Labidi et al., 2013) cannot be easily reconciled with S predominantly being delivered by any form of chondritic late accretion.

It is also inconsistent with the S/TI of CI chondrites (S/TI = 440140; Newsom, 1995 and references therein) compared to be much higher S/TI of the present-day BSE (S/TI = 86500±30200; Wang et al., 2018). The latter discrepancy may simply be a reflection of the great difficulty in obtaining reliable TI concentrations for primitive terrestrial rocks (Nielsen et al., 2017 and references therein). Finally, it must be noted that the present-day BSE S/Se, Se/Te and S/TI ratios could have been severely overprinted and not reflect

the primordial signature of terrestrial accretion, for example through mixing of residual Fe-Ni monosulfide solid solutions or platinum group minerals or metasomatic processes (König et al., 2014, 2015).

4.3.2 Nb, Ta, In and Zn

The subchondritic Nb/Ta of the present-day BSE has been used to argue for addition of highly reduced asteroidal impactor mantles to the proto-BSE during terrestrial differentiation (Münker et al., 2017). Our results confirm previous experimental data suggesting that highly reduced core formation dramatically decreases the Nb/Ta of the impactor mantle, with an overall modeled value of Nb/Ta = 0.26±0.08 for an EH chondritic impactor (Cartier et al., 2014; Münker et al., 2017). This value is significantly lower than the Nb/Ta value of 10–15 calculated by Münker et al. (2017) for various reduced impactor mantles. This discrepancy is most likely due to the fact that Münker et al. (2017) did not take into account the fractionation of Nb from Ta due to Fe-Si liquid in the reduced impactors, as segregation of Fe-Si liquid would additionally fractionate Nb/Ta. However, given the low abundances of Nb and Ta in the impactor mantle(s) (Fig. 8), relative to the present-day BSE, it seems unlikely that accretion of a highly reduced, large (i.e., >10 mass%) impactor mantle would result in a meaningful change in Nb/Ta. For example, accretion of a 20% mass differentiated EH impactor could only have delivered approximately <0.01 and 2 % of the present-day BSE Nb and Ta budget, under the assumption of highly efficient core-merging (see section 4.3). It should be noted that fractionation of Nb and Ta would not occur during liquid sulfide segregation in the terrestrial magma ocean, given their overall incompatibility in sulfide liquids under

moderately reduced conditions (e.g., Münker et al., 2017; Steenstra et al., 2020). This suggests that the Nb/Ta of the present-day BSE may instead be the result of reduced core formation and accretion of non-differentiated impactors (Cartier et al., 2014) or possibly due to the addition of many lower mass reduced differentiated impactors to the proto-Earth (Münker et al., 2017) (Fig. 9).

In the event of terrestrial accretion by differentiated reduced impactors only part of the present-day In and Zn budget could have been delivered to the growing Earth (Fig. 8). Nevertheless it is illustrative to assess the potential effects of the latter process on the Zn/In of the present-day BSE, given its importance for considerations of the source of terrestrial volatiles (Wang et al., 2016; Norris and Wood, 2017). The impactor mantle has a low In/Zn ratio (Fig. 9) and accretion of reduced (differentiated) impactors would be accompanied by a much larger delivery of Zn relative to In.

Accretion of reduced and differentiated impactors would therefore result in an overall decrease of In/Zn as well in a dramatic increase of overall TI concentrations (Fig 8). Although unlikely from S/Se, Se/Te and S/TI systematics, accretion of reduced and differentiated impactors could therefore be a potential mechanism for (partly) explaining the discrepancy between the apparent overabundant In, relative to Zn and TI, in addition to volatile loss through melting and evaporation (Wang et al., 2016; Norris and Wood, 2017).

4.4 Effects of impactor mass and degree of impactor core equilibration

In the above calculations perfect core-merging was assumed (i.e., no chemical reequilibration between impactor core and the terrestrial mantle). Current estimates of the

degree of impactor core re-equilibration vary significantly. Studies focused on terrestrial siderophile element modeling (e.g., Rubie et al., 2011), fluid-dynamics (e.g., Dahl and Stevenson, 2010) and the Hf-W chronometer (e.g., Fischer and Nimmo, 2018 and references therein) require a significant percentage of dis-equilibrium between larger impactor cores and the terrestrial mantle (up to 40–80%), whereas others argue for only <3 % of impactor core equilibration, based on modeling of Hf/W and Nb/Ta (Wade and Wood (2016). Other numerical models also suggested that large impactor (>10 mass% relative to proto-Earth) cores would have likely have limited interaction (<17% impactor core re-equilibration) with the proto-BSE (Deguen et al., 2014; Canup et al., 2008). The extent of interaction also depends on the angle of impact, as oblique impacts could yield scenarios in which the impactor cores could have been largely sheared past the planet, before re-impacting the proto-Earth (e.g., Canup et al., 2004). Although the modeling results are not directly dependent on the assumption of a single or multiple highly reduced impactors given the limited effects of P-T on $D_M^{\text{Fe}-\text{Si liq}-\text{sil melt}}$ compared to redox state and S in the silicate melt, decreasing impactor size will increase the potential of impactor core equilibration with the proto-BSE (Deguen et al., 2014).

In terms of S, Se and Te, any degree of inefficient core-merging would further increase the already significant offset between modeled absolute and measured BSE abundances of Se and Te. It would yield lower S/Se and Se/Te of the terrestrial mantle, but Se/Te and S/TI would still be significantly higher than the present-day BSE (Fig. 9).

Inefficient core-merging would significantly increase the amounts of Nb and Ta delivered to the proto-BSE and would simultaneously reduce the relative fractionation of Nb and Ta (see Fig. 9). In the case of large degrees of impactor core equilibration with

the proto-BSE (i.e., lower mass impactors), the Nb/Ta of the present-day could therefore represent accretion of smaller highly reduced differentiated planetesimals. as proposed by Münker et al. (2017).

5. CONCLUSIONS

It has been hypothesized that the Earth may have accreted from a single or several larger (i.e., differentiated) highly reduced impactors (e.g., Wohlers and Wood, 2015, 2017). To further test this hypothesis, we experimentally determined the elemental distribution between Fe-S liquid and highly at highly reduced conditions. Using this data, revised and/or new thermodynamic parameterizations were obtained. The parameterizations allow for the prediction of $D_M^{Fe-S \, liq-sil \, melt}$ for 34 elements as a function of redox state and S content (i.e., degree of S-FeO interaction) of the silicate melt. The parameterizations were used to model the geochemical consequences of the accretion of highly reduced, differentiated impactor(s) to the proto-Earth.

The results show that differentiated EH- and EL chondritic impactor mantles would be highly depleted in many of the siderophile and chalcophile elements considered, relative to the present-day BSE. Under the assumption of highly efficient core-merging as appropiate for larger (>10% of Earth's present mass) impactors, significant quantities of S, Zn, Se, Te, Tl could have been delivered to the terrestrial proto-mantle during their accretion, whereas the absolute abundances and ratios of the other elements considered in the proto-BSE would remain largely unaffected.. The absolute and relative abundances of these elements in the present-day bulk silicate Earth (BSE) are however, inconsistent with accretion of (a) large highly reduced chondritic impactor(s). Accretion by such

impactors would result in much higher absolute abundances of S, Se, Te in the proto-BSE as well as significantly higher S/Se, Se/Te and S/TI, relative to the present-day bulk BSE. Subsequent core formation, volatility depletion processes and/or sulfide liquid segregation in the Earth would only further increase the latter discrepancies. It is therefore concluded that accretion of the Earth by highly reduced chondritic impactors cannot be reconciled with the absolute and relative abundances of S, Se, Te and TI, suggesting the present-day Se/Te and S/TI of the BSE were severely overprinted during secondary processes and/or were (partly) set by delivery of CI-like chondritic materials.

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RESEARCH DATA

Research Data associated with this article can be accessed at xxxxxxxxxxxx.

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Figure captions

Fig. 1: Backscattered electron images of a typical run product (EK-11).

Fig. 2: The sulfur content at sulfide liquid saturation (SCSS) at highly reduced conditions. Data from this study, Malavergne et al. (2014), Wood and Kiseeva (2015), Namur et al. (2016), Wohlers and Wood (2017) and Steenstra et al. (2020a). The data was obtained at comparable *P*-*T* conditions (*P* = 1–1.5 GPa; *T* = 1683–1910 K), except for the data of Namur et al. (2016) (*P* = 1 atm – 4 GPa; *T* = 1473–2023 K). Horizontal displacement of low-pressure SCSS data of Namur et al. (2016) is due to the effects of pressure on $\gamma_{\text{Fe0}}^{\text{sil melt}}$. Both horizontal and vertical errors represent error bars based on 2 standard errors (2SE). Vertical variation of the SCSS at a given FeO content is due to variations in *P*, *T* and composition.

Fig. 3: The solubility of O in Fe-S liquids as a function of FeO or S content of the silicate melt. Data from this study, Kiseeva and Wood (2013, 2015), Wood and Kiseeva (2015) and Steenstra et al. (2020a,c). Experiments conducted in graphite capsules in the

absence of Fe metal, with a corresponding fO_2 of approximately 1 log unit below the CCO buffer (Kiseeva and Wood, 2013; Ni et al., 2017), are indicated in different shades of green. Experiments conducted in graphite capsules with co-existing Fe(-Si) metal are indicated in different shades of blue and were thus equilibrated at far more reduced conditions (i.e., up to several log units below the IW buffer; e.g., Steenstra et al., 2020a). Dashed line represents calculated O solubility in Fe-S liquids using the model of Kiseeva and Wood (2015).

Fig. 4: Experimentally determined $D_M^{Fe-S \, liq-sil \, melt}$ values for several nominally lithophile elements (Li, Rb, Cs, U, Th) from this study and previous work obtained at comparable *P-T* conditions (Steenstra et al., 2019a) as a function of S content of the silicate melt (i.e., the effect of S-FeO interaction on their activities). Dashed lines represent the modeled dependencies (see section 3.4; Table 2). Horizontal shaded bars encompass the S range inferred for Mercury and enstatite achondrites and was plotted for comparison purposes. Both horizontal and vertical errors represent error bars based on 2 standard errors (2SE). Vertical error bars were calculated using simple error propagation.

Fig. 5: Experimentally determined $D_M^{Fe-S liq-sil melt}$ values for the various trace elements of interest. Data from this study and previous work obtained at comparable *P-T* conditions (Steenstra et al., 2019a, 2020a,c) as a function of S content of the silicate melt. See Fig. 4 caption for additional details.

Fig. 6: Experimentally determined $D_M^{\text{Fe}-S \, \text{liq}-sil \, \text{melt}}$ values for the various trace elements of interest as a function of S content of the silicate melt. Data from this study and previous work obtained at comparable *P-T* conditions (Steenstra et al., 2019a, 2020a,c). See Fig. 4 caption for additional details.

Fig. 7: Ratios of $D_M^{Fe-S \, liq-sil \, melt}$ for several commonly used element trace element pairs (Ni/Co, In/Cd, In/Zn, Th/U, U/Pb, Mo/W, S/Se, Se/Te) as a function of S in the silicate melt. Data from Steenstra et al. (2019a, 2020a,c). Dashed lines represent the modeled dependencies (see section 3.4; Table 2). Both horizontal and vertical errors represent error bars based on 2 standard errors (2SE). Vertical error bars were calculated using simple error propagation.

Fig. 8: Modeled delivery of trace elements to the growing Earth by accretion of a highly reduced differentiated impactor, expressed in % relative to the present-day BSE (Wang et al., 2018). Impactor size mass was assumed to be 20% relative to the present-day Earth and considered to be having a EL- or EH chondritic composition (Table S.4). Three different type of impactors were considered: one having a 65% core mass consisting of a 50% Fe-Si inner core and 15% Fe-S outer core; one possessing a 30 mass % core consisting of a 15% Fe-Si inner core and 15% Fe-S outer core and one having a 15% Fe-S core only.

Figure 9: Calculated elemental ratios of reduced impactor mantles, compared to values of the bulk impactor (see Table S.4) and of the present-day BSE (Wang et al., 2018).

Error bar range of calculated elemental ratios for impactor mantles encompass the modeling results for S contents of impactor mantles between 3–7 wt.% and core masses of 15–65 %, respectively. Illustrated are the relative effects of impactor core - proto-BSE equilibration on elemental ratios.

Figure 1







Figure 3



Figure 4



Figure 5



Figure 6



Figure 7



Figure 8







Run	<i>Т</i> (К)	t (min)	Capsule + Comp. ^a	Phases ^b	Fe/S	ΔIW °	γ ^{Fe – Si liq}	∆IW ^d	∆Si-SiO ₂ º	γ ^{Fe – Si liq} YSi	∆Si-SiO ₂ ^f	∆IW corr ^g	log FeO (wt.%)	SCSS
EK-01	1883	120	C + GG + A + 15% Si	GI, Fe-S, Fe	2.43	-1.70	0.72	-1.41	-	-		-	1.212(4)	0.28(2)
EK-02	1783	120	C + GG + A + 15% Si	GI, Fe-S, Fe	2.11	-1.46	-	-1.84	-	-	-	_	1.075(2)	0.18(1)
EK-03	1883	120	C + GG + A + 30% Si	Gl, Fe-S, (Fe,Mg,Ca)-S, Fe-Si	1.75	-4.81	0.63	-4.40	1.12	0.055	3.64	-5.03	-0.36(3)	5.11(4)
EK-04	1783	120	C + GG + A + 30% Si	GI, Fe-S, Fe-Si	2.22	-4.46	0.72	-4.17	3.40	0.028	6.50	-2.97	-0.15(9)	0.67(3)
EK-05	1883	120	C + GG + A + 45% Si	GI, Fe-S, Fe-Si	1.94	-4.88	0.68	-4.54	1.86	0.042	4.61	-4.33	-0.37(3)	2.34(2)
EK-06	1783	120	C + GG + A + 45% Si	Gl, qtz, Fe-S, (Fe,Mg,Ca)-S, Fe-Si	1.85	-4.76	0.68	-4.42	1.70	0.037	4.58	-4.35	-0.31(3)	5.32(5)
EK-07	1883	30	C + GG + A + 0% Si	GI, FeS	1.82	-	-	-	-	_	-	_	1.312(5)	0.66(11)
EK-08	1783	120	C + GG + A + 60% Si	GI, qtz, Fe-S, Fe-Si	1.70	-4.91	0.69	-4.59	1.99	0.034	4.92	-4.10	-0.38(6)	3.74(7)
EK-09	1883	120	C + GG + A + 60% Si	GI, Fe-S, Fe-Si	1.60	-4.73	0.65	-4.36	1.43	0.049	4.05	-4.73	-0.32(5)	3.23(4)
EK-10	1783	45	C-Pt + GG + A + 0% Si	GI, Fe-S	1.80	-	-	-	_	_	-	-	1.11(1)	0.34(3)
EK-11	1783	45	C-Pt + GG + A + 0% Si	GI, Fe-S	1.87	-	-	_		_	-	_	1.14(1)	0.40(2)
EK-12	1733	60	C-Pt + GG + A + 0% Si	GI, Fe-S	1.91	-	-	-	-	-	-	-	1.23(1)	0.39(3)
EK-13	1733	60	C-Pt + GG + A + 0% Si	GI, Fe-S	1.89	-	-	-	-	-	-	_	1.21(2)	0.38(7)
EK-14	1733	60	C-Pt + GG + A + 0% Si	GI, Fe-S	1.84	-	-	-	_	-	-	-	1.15(1)	0.34(5)
ESS-13	1683	120	C + GG + A + 0% Si	GI, Fe-S	1.78	-	-	-	_	-	-	_	1.259(1)	0.42(1)
ESS-14	1883	45	C + GG + A + 0% Si	GI, Fe-S	1.76	-	-	-	-	-	-	-	1.216(3)	0.48(6)
ESS-16	1783	120	C + GG + A + 0% Si	GI, Fe-S	1.80	-	-		-	-	-	_	1.236(4)	0.43(2)
ESS-20	1733	130	C + GG + A + 0% Si	GI, Fe-S	1.95	-	-	_	-	-	-	-	1.302(2)	0.44(3)
ESS-58	2023	15	C + GG + A + 0% Si	GI, Fe-S	1.81	-	-	-	-	-	-	_	1.378(5)	0.82(5)
ESS-60	2188	8	C + GG + A + 0% Si	GI, Fe-S	1.84	-	-	-	-	-	-	-	1.268(5)	0.61(9)
ESS-63	2283	3	C + GG + A + 0% Si	GI, Fe-S	2.02	-		-	-	-	-	-	1.280(3)	0.58(8)

Table 1 Summary of experiments. All experiments were performed at 1 GPa.

^a GG = Apollo 15 green glass doped with 1500 ppm of Li, Rb, Cs and 2000 ppm of Th and U. A defines sulfide composition: FeS + 0.1 wt.% of P, V, Co, Ni, Cu, Zn, Ga, Ge, Se, Nb, Mo, Cd, Sn, Sb, Te, Ta, W, Pb, Bi. The Si contents of the metal starting compositions (50% by volume of total sample powder) were varied using 100 wt.% FeS, 50% FeS - 50% Fe doped with 15 wt.% Si, 50% FeS - 50% Fe doped with 45 wt.% Si, 50% FeS - 50% Fe doped with 60 wt.% Si ^b Phases present in experimental run products: GI = glass, qtz = quartz ^c Calculated assuming ideal mixing behavior of Fe and FeO, while using Fe(-Si) metal or FeS if Fe(-Si) metal was not present in the run product ^d Calculated assuming ideal behavior of FeO and non-ideal mixing behavior of Fe, where $\gamma_{\text{Fe}}^{\text{Fe}-\text{Siliq}}$ was calculated using the online metal activity calculator (Wade and Wood, 2005) for the given temperature ^e Calculated assuming ideal mixing behavior of Si and SiO₂ ^fCalculated assuming ideal mixing behavior of Si, where $\gamma_{\text{Fe}}^{\text{Fe}-\text{Siliq}}$ was calculated using the online metal activity calculator (Wade and Wood, 2005) for C-saturated systems previously reported in Steenstra et al. (2020b). The experiments performed without added Fe(-Si) metal (EK-07, EK10–EK14, and all ESS-marked runs) were equilibrated at approximately 1 log unit below the CCO buffer (Kiseeva and Wood, 2013; Ni et al., 2017).

Table 2 Summary of Fe-S sulfide liquid – silicate melt partition coefficients ($D_M^{Fe-S \, liq-sil\, melt}$) that were derived in this study. Numbers in parentheses denote errors on $D_M^{Fe-S \, liq-sil\, melt}$ in terms of least digits cited that were calculated using simple error propagation while assuming 2 standard errors on sulfide liquid and silicate melt abundances of element M. The $D_M^{Fe-S \, liq-sil\, melt}$ values of Ti, Zn, Ga, Ge, Se, Rb, Mo, Cd, In, Sn, Sb, Te, Cs, W, Tl, Pb, Bi, U and Th for Fe-S liquids are based on matrix effect-corrected Fe-S liquid abundances (see Appendix section A.2; Steenstra et al., 2020d).

	EK-01	EK-02	EK-03	EK-04	EK-05	EK-06	EK-07	EK-08	EK-09	EK-10	EK-11	EK-12
Li	0.004(1)	0.004(3)	0.099(7)	0.024(1)	0.062(3)	0.098(2)	0.046(3)	0.070(6)	0.091(2)	0.086(8)	0.052(3)	0.107(7)
Са	0.003(1)	0.002(1)	0.084(24)	0.010(1)	0.038(5)	0.113(42)	0.011(1)	0.038(13)	0.055(12)	0.009(1)	0.011(1)	0.008(1)
Si	0.0014(4)	0.0011(2)	0.002Ò(1)	0.0013(3)	0.0030(15)	0.0041(18)	0.0037(7)	0.0042(17)	0.0019(4)	0.0014(1)	0.0017(2)	0.0022(2)
Mg	0.0006(2)	0.00006(4)	0.036(10)	0.002(1)	0.011(1)	0.028(11)	0.006(1)	0.019(3)	0.018(2)	0.0016(2)	0.0022(4)	0.0021(3)
Ti	0.006(1)	0.005(2)	21(5) ^a	0.890(11) ^a	4.2(5) ^a	21(8) ^a	0.047(8)	14.5(6)	12.9(17) ^a	0.025(2)	0.030(2)	0.029(2)
Ρ	0.88(31)	n.d.	1.55(52)	1.80(4̀5)	1.45(56)	4.20(136)	0.014(2)	10.6(35)	1.14(44)	0.032(2)	0.011(4)	0.030(22)
V	0.335(49)	0.412(62)	199(21)	60(3)	125(19)	225(55)	0.434(96)	258(18)	162(15)	0.354(38)	0.403(33)	0.293(33)
Cr	0.674(75)	0.706(126)	68(5)	23(1)	53(3)	84(10)	1.31(25)	76(10)	59(5)	1.62(12)	1.65(9)	1.17(12)
Mn	0.066(5)	0.071(6)	9.2(12)	2.69(8)	6.1(2)	9.7(17)	0.515(19)	10.4(7)	7.8(3)	0.692(60)	0.663(28)	0.559(27)
Со	76(7)	97(7)	599(327)	423(83)	389(25)	680(111)	21(1)	1210(297)	1114(231)	37(3)	34(4)	27(1)
Ni	879(276)	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	244(24)	b.d.l.	b.d.l.	385(144)	427(97)	303(152)
Cu	103(16)	172(19)	91(13)	500(44)	290(29)	105(12)	110(11)	170(36)0	144(98)	388(71)	269(40)	364(49)
a 7n	0.557(46)	0 846(124)	13 4(14)	13 0(7)	19 0(20)	12 7(13)	1 08(6)	22(3)	17 2(7)	1 67(13)	1 54(13)	1 23(9)
Ga	0.333(50)	0.320(51)	29(2)	22(2)	25(4)	38(3)	0.135(32)	39(8)	22(2)	0.070(8)	0.099(9)	0.051(8)
Ge	15.4(30)	26(6)	52(21)	b.d.l.	b.d.l.	128(33)	0.792(70)	249(105)	18.6(36)	0.389(32)	0.495(44)	0.220(19)
As	b.d.l.	b.d.l.	30(15)	b.d.l.	b.d.l.	b.d.l.	93(18)	b.d.l.	b.d.l.	25(5)	30(5)	13.3(34)
Se	177(32)	197(62)	21(1)	117(21)	39(2)	22(1)	83(14)	32(6)	32(1)	143(26)	143(35)	151(26)
Rb	0.0014(2)	0.0011(1)	0.0081(8)	0.0027(3)	0.0059(11)	0.0139(19)	0.049(3)	0.0129(7)	0.0058(13)	0.023(4)	0.057(10)	0.0061(11)
Nb	0.003(1)	0.008(1)	1380(284)	84(7)	634(75)	1848(322)	0.031(5)	1806(156)	1242(95)	0.013(1)	0.018(2)	0.018(2)
Мо	524(1Ò4́)	938(349)	479(116)	563(243)	b.d.Ì.	938(422)	18.7(6)	2330(1294)	1317(581)	28(2)	16.6(ÌÓ)	9.7(7) (
Cd	9.7(12)	15.1(19)	55(8)	119(19)	93(14)	53(8)	12.2(8)	114(38)	91(12)	21(4)	21(4)	18.3(38)
In	13.4(26)	16.6(34)	103(45)	110(49)	101(42)	195(60)	4.6(3)	271(178)	213(55)	6.1(13)	7.4(13)	5.2(10)
Sn	10.4(11)	14.0(12)	194(29)	275(33)	247(22)	214(46)	3.93(24)	312(59)	225(24)	5.1(6)	6.2(8)	4.32(39)
Sb	2961(1690)	3972(1415)	1907(1657)	1119(260)	b.d.l.	3014(598)	19.1(13)	3971(2651)	2564(1472)	14.9(36)	15.0(26)	7.1(6)
Cs	0.0014(1)	0.0010(1)	0.0062(5)	0.0018(3)	0.0043(11)	0.012(2)	0.082(5)	0.011(2)	0.004(1)	0.055(11)	0.106(10)	0.015(3)
Те	383(54)	762(207)	98(10)	375(111)	107(27)	83(19)	173(27)	104(59)	154(32)	373(100)	460(120)	354(97)
Та	0.00004(1)	0.00008(3)	20(2)	0.412(18)	4.9(10)	26(4)	0.009(2)	12.0(10)	11.1(6)	0.0028(4)	0.0045(5)	0.0052(7)
W	0.335(52)	1.27(23)	89(31)	32(22)	215(147)	1575(1226)	0.096(11)	481(395)	314(209)	0.036(4)	0.045(3)	0.034(4)
ТΙ	0.68(11)	0.67(13)	3.75(34)	2.08(16)	3.36(57)	5.1(8)	4.29(41)	4.80(186)	3.66(57)	3.94(93)	5.9(13)	4.46(94)
Pb	9.8(10)	15.1(10)	145(9)	157(10)	143(18)	193(19)	10.9(6)	262(58)	219(32)	20(2)	21(2)	16.6(10)
Bi	1972(282)	3790(592)	2270(268)	6540(1884)	2110(1019)	1660(564)	239(32)	3358(1221)	3343(630)	301(59)	427(48)	385(51)
Th	0.00002(1)	0.00008(4)	0.100(9)	0.0017(2)	0.022(3)	0.194(23)	0.0039(8)	0.043(8)	0.072(14)	0.0015(1)	0.0023(2)	0.0023(1)
U	0.00015(5)	0.00010(1)	2.11(21)	0.053(4)	0.440(42)	4.36(52)	0.039(4)	1.46(26)	1.15(15)	0.022(3)	0.030(4)	0.031(3)

	EK-13	EK-14	ESS-13	ESS-14	ESS-16	ESS-20	ESS-58 ^a	ESS-60 ª	ESS-63 ^a
Li	0.157(21)	0.065(8)	0.045(2)	0.060(4)	0.056(2)	0.047(2)	n.d.	n.d.	n.d.
Са	0.011(1)	0.007(1)	0.008(1)	0.012(1)	0.009(1)	0.007(1)	0.018(15)	0.010(1)	0.023(1)
Si	0.0020(2)	0.0018(2)	0.0029(1)	0.0022(1)	0.0032(2)	0.0018(1)	n.d.	n.d.	n.d.
Mg	0.0022(3)	0.0017(6)	0.0018(2)	0.0024(5)	0.0031(5)	0.0011(2)	n.d.	n.d.	n.d.
Ti	0.029(2)	0.024(5)	0.033(1)	0.032(3)	0.039(3)	0.029(2)	n.d.	n.d.	n.d.
Р	0.014(3)	0.032(7)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
V	0.293(19)	0.295(31)	0.384(25)	0.470(51)	0.470(52)	0.325(34)	n.d.	n.d.	n.d.
Cr	1.18(9)	1.29(8)	1.37(7)	1.57(14)	1.68(15)	1.08(11)	0.12(3)	0.49(2)	0.67(3)
Mn	0.574(23)	0.561(16)	0.531(17)	0.675(43)	0.629(35)	0.514(15)	0.430(325)	0.421(226)	0.484(291)
Со	29(1)	37(1)	33(3)	32(2)	34(1)	29(1)	n.d.	23(4)	n.d.
Ni	430(84)	526(65)	705(138)	422(60)	514(81)	354(69)	72(52)	88(53)	110(50)
Cu	277(40)	401(58)	317(47)	219(20)	219(9)	192(16)	37(6)	50(9)	88(18)
a 		. =							
Zn	1.40(8)	1.50(8)	1.27(7)	1.60(12)	1.34(7)	1.01(4)	0.86(29)	0.94(31)	0.78(57)
Ga	0.064(4)	0.061(8)	0.081(6)	0.148(23)	0.111(13)	0.070(8)	n.d.	n.d.	n.d.
Ge	0.332(23)	0.327(25)	0.544(32)	1.10(11)	0.749(37)	0.511(20)	n.a.	n.a.	n.d.
AS	14.0(9)	13.2(21)	43(6)	97(14)	53(14)	95(10)	n.a.	n.a.	n.d.
50	131(18)	131(15)	142(21)	99(8)	115(22)	124(20)	n.a.	54(12)	n.a.
	0.0084(21)	0.0036(9)	0.032(5)	0.054(6)	0.039(4)	0.030(2)	n.a.	n.a.	n.a.
Mo	0.017(1)	0.015(1)	0.021(1)	0.019(2)	0.025(3)	0.010(1)	n.u. n.d	11.U. 40(12)	n.d.
	12.0(7)	10.7(5)	17.0(0)	31(1)	20(1)	19.1(0)	hdl	40(13)	n.u.
Ln Un	23(2)	29(3)	21(2)	ZZ(Z) Z 0(6)	6 5(6)	5.6(6)	D.U.I. n d	19(3) nd	n.d.
Sn	5.6(6)	5.7(6)	5.3(3)	67(6)	5 3(3)	4.71(41)	n.u.	n.u.	n.d.
Sh	10 9(10)	10 2(8)	12 9(8)	27(2)	20(1)	20(2)	n d	n.d.	n.d.
Cs	0.029(11)	0.017(3)	0.084(8)	0.125(10)	0.091(6)	0.084(9)	n d	n d	n d
Te	281(42)	531(115)	383(61)	321(37)	438(61)	292(57)	n d	53(17)	n d
Ta	0.0047(3)	0.0036(4)	0.0055(5)	0.0031(5)	0.0061(8)	0.0040(4)	n.d.	n.d.	n.d.
W	0.035(5)	0.035(2)	0.049(5)	0.066(7)	0.076(7)	0.050(4)	n.d.	n.d.	n.d.
TI	5.7(12)	4.93(73)	6.2(9)	7.9(10)	5.7(8)	5.8(8)	n.d.	n.d.	n.d.
Pb	21(1)	23(2)	17.5(10)	18.4(14)	16.2(9)	15.3(14)	n.d.	25(4)	n.d.
Bi	371(51)	528(49)	312(61)	390(58)	457(99́)	434(54)	91(16)	122(73)	n.d.
Th	0.0024(2)	0.0016(1)	0.0020(2)	0.0023(1)	0.0025(3)	0.0018(2)	n.d.	n.d.	n.d.
U	0.028(3)	0.024(2)	0.030(3)	0.035(4)	0.032(3)	0.033(À)	n.d.	n.d.	n.d.

^a Based on sulfide liquid abundances measured by EPMA

Table 3 Fit parameters obtained using Eq. (4) while incorporating the data presented in this study and compiled sulfide liquid-silicate melt partition coefficients from Steenstra et al. (2020a), obtained at the same experimental pressures (1 GPa), similar temperatures (1733–1883 K) while using the same silicate and sulfide starting composition

This study			_			Steenstra et al. (2020a)						
	Α	$arepsilon_{\mathrm{MS}_{n/2}}^{\mathrm{FeO}_{\mathrm{sulliq}}}$	$\varepsilon_{\rm Fe0}^{\rm S_{silmelt}}$	N	R²	Α	$arepsilon_{{ m MS}_{n/2}}^{ m FeO_{sul liq}}$	$\varepsilon_{\rm Fe0}^{\rm S_{\rm silmelt}}$	N	R ²		
Cu ¹⁺	2.52(7)	-10.42(181)	29.99(371)	26	0.90	2.48(5)	-8.13(257)	24.83(232)	10	0.96		
Cs1+	-2.43(18)	-37.00(470)	n.s.s.	16	0.82	_	_	-	-	_		
Li ¹⁺	-1.33(10)	-15.53(268)	n.s.s.	16	0.71	-	-	-	_	_		
Rb1+	-2.33(17)	-26.94(451)	n.s.s.	16	0.72	-	-	- ()	-	_		
TI ¹⁺	0.31(5)	-21.92(158)	n.s.s.	24	0.90	0.22(6)	-30.17(331)	n.s.s.	8	0.93		
Ca ²⁺	-1.99(9)	-24.70(229)	-6.70(169)	25	0.84	-2.13(7)	-37.23(377)	-7.10(112)	9	0.95		
Mg ²⁺	-2.70(11)	-25.72(291)	-10.87(194)	28	0.76	-2.81(15)	-39.65(807)	-11.63(221)	12	0.82		
Cr ²⁺	-1.23(4)	-2.30(102)	-6.00(68)	28	0.77	1.26(5)	n.s.s.	-5.56(90)	12	0.79		
Mn ²⁺	0.36(5)	-12.80(144)	-2.93(96)	28	0.76	0.32(8)	-12.94(447)	-3.18(123)	12	0.56		
Co ²⁺	2.72(5)	n.s.s.	5.09(236)	24	0.17	_	n.s.s.	n.s.s.	10	_		
Ni ²⁺	2.86(19)	-22.88(419)	24.07(654)	18	0.88	_	-	_	_	_		
Zn ²⁺	0.99(3)	-7.80(87)	5.25(89)	26	0.90	0.97(5)	-9.07(239)	4.66(108)	10	0.88		
Cd ²⁺	1.99(7)	–12.24(165)	15.77(169)	26	0.93	1.92(11)	-19.19(532)	14.49(240)	10	0.92		
Sn ²⁺	1.98(2)	n.s.s.	n.s.s.	24	_	-	n.s.s.	n.s.s.	8	_		
Pb ²⁺	2.07(5)	-8.82(123)	6.35(124)	25	0.92	2.04(6)	-13.05(290)	5.86(128)	9	0.92		
Ga ³⁺	-0.54(29)	-21.59(670)	-24.21(695)	24	0.40	-	n.s.s.	n.s.s.	8	_		
ln ³⁺	1.66(7)	-21.05(220)	n.s.s.	23	0.81	_	-	_	_	_		
Sb ³⁺	3.15(10)	n.s.s.	n.s.s.	23	_	-	n.s.s.	n.s.s.	7	_		
V ³⁺	1.22(6)	-2.76(126)	-10.65(133)	24	0.79	1.27(7)	n.s.s.	-9.37(122)	8	0.78		
Ge ⁴⁺	2.28(13)	n.s.s.	12.98(314)	19	0.50	-	n.s.s.	n.s.s.	5	_		
Bi ³⁺	3.46(12)	-22.13(304)	9.25(208)	26	0.86	3.45(17)	-36.50(861)	7.38(223)	10	0.85		
Si ⁴⁺	-3.56(17)	-71.56(559)	n.s.s.	28	0.86	-4.33(27)	-114(15)	-6.23(203)	12	0.87		
Ti ⁴⁺	-0.35(8)	–26.84(215)	-9.79(72)	28	0.90	-0.39(12)	-38.88(646)	-9.84(89)	12	0.94		
Mo ⁴⁺	3.16(27)	-15.00(617)	9.84(469)	22	0.59	_	n.s.s.	n.s.s.	7	_		
W ⁴⁺	2.00(19)	17.30(589)	n.s.s.	24	0.28	_	n.s.s.	n.s.s.	8	_		
U ⁴⁺	-1.42(28)	-47.11(567)	-11.95(473)	16	0.88	_	_	_	_	_		
Th ⁴⁺	-2.89(33)	–51.84(657)	–11.91(548)	16	0.88	_	_	_	_	_		
As ⁵⁺	2.29(54)	-54.17(1120)	18.94(597)	14	0.90	_	_	_	_	_		
P ⁵⁺	-0.24(19)	–36.18(730)	n.s.s.	19	0.59	_	n.s.s.	n.s.s.	7	_		
Nb ⁵⁺	1.17(7)	n.s.s.	-12.80(139)	24	0.79	1.10(16)	n.s.s.	-13.09(299)	8	0.76		
Ta⁵⁺	–1.07(12)	-35.93(280)	–14.13(177)	24	0.89	–1.32(16)	-54.17(688)	–17.06(253)	8	0.94		
S ²⁻	1.72(6)	22.17(150)	-11.55(100)	28	0.91	_	_	_	_	_		
Se ²⁻	2.19(9)	27.51(233)	-14.05(239)	26	0.86	_	_	_	_	_		
Te ²⁻	2.78(11)	30.67(286)	-16.08(293)	28	0.83	-	-	-	-	-		

^a Not statistically significant (p > 0.05) ^b Elements for which poor fits were obtained (e.g., Co, Sn, Sb, W) are accurately predicted using A + n/2 (log FeO (in wt.%)), as their sulfide liquid-silicate melt partitioning behavior as a function of fO_2 (and corresponding variations in S) was found to be (close to) ideal

Declaration of interests

 \boxtimes The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

□The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: