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Highlights

- Vestan mantle volatile element depletions do not only reflect degassing
- Many volatile elements partition into the Vestan core during core formation
- The Vestan core can be a major reservoir for volatile elements

Significant depletion of volatile elements in the mantle of asteroid Vesta due to core formation

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Abstract: Vesta, the second-largest body in the asteroid belt, is believed to be a prime example of a rocky protoplanet. Studies of the HED (Howardite - Eucrite - Diogenite) meteorite suite, considered to be sourced from the mantle of Vesta, provide insight into protoplanet differentiation processes. Eucrites and diogenites are depleted in many volatile elements, but the depletions of many volatile siderophile elements are not well constrained. Although previous work indicated that the Vestan core equilibrated with its mantle in a global melting event, the possible contribution of core formation to the volatile budget of HED meteorites has not been assessed to date. This prohibits an assessment of the overall volatile depletion systematics of Vesta.

Here, we use a compilation of published volatile siderophile element (VSE; C, S, Zn, As, Se, Cd, In, Sb, Te, Tl, Pb, Bi) abundances in diogenites and eucrites to constrain their depletions in the Vestan mantle. We assess to what extent these depletions may be volatility-related, caused by partitioning into sulfides in the mantle, and/or a result of their preferential partitioning into the Vestan core during coremantle equilibration. Our new estimates for VSE depletions in the Vestan mantle show no correlation with condensation temperature, suggesting the depletions are difficult to reconcile with partial condensation or degassing during accretionary processes only. Sulfide saturation of the diogenite and eucrite source region is also unlikely because of low indigenous S abundances in these samples compared to calculated S contents at sulfide saturation. Consideration of the metal-silicate partitioning behavior of the VSE shows that most of these elements are sufficiently siderophile to explain a significant part of their observed depletions in the Vestan mantle by their preferential partitioning into a S-rich core.

Moderately volatile elements As and Sb both appear more abundant in the Vestan mantle than expected from their highly siderophile behaviour in systems with basaltic melts. These apparent overabundances may be related to strong silicate melt compositional effects on their metal-silicate partitioning behavior. On the other hand, Zn, and to a lesser extent Te and TI are significantly more depleted than expected from metal-silicate partitioning alone. This could be evidence for volatile loss of these elements from Vesta through kinetic loss in a hard vacuum. Alternatively, the perceived loss of Zn may be the result of a Zn-poor Vestan bulk composition and/or partly by preferential partitioning of Zn into spinel. The additional depletion of TI and by extension other highly chalcophile elements such as Se and Te may be explained by segregation of sulfides in the eucritic melt source region(s), if significant amounts of S degassed from eucritic melts after sulfide segregation.

Our results underline the feasibility of planetary cores being a major reservoir for many volatile elements that are depleted in planetary mantles, and that are currently assumed to have suffered incomplete condensation during accretion or (partial) degassing after accretion.

Keywords: Asteroids, Core formation, Siderophile elements; Volatile elements; Accretion.

1. INTRODUCTION

The chemical compositions of the HED (Howardite - Eucrite - Diogenite) meteorite suite, thought to have been derived from asteroid Vesta, suggest an early differentiation of their parent body and widespread magmatic activity, possibly in a partial to global magma ocean type setting (Righter and Drake, 1996, 1997; Greenwood et al., 2005; Steenstra et al., 2016a; Zhang et al., 2018). Large-scale to complete melting of Vesta in a magma ocean type setting is consistent with the homogeneous Δ^{17} O and Δ^{33} S signatures of the HED meteorite suite (Greenwood et al., 2005, 2014; Wu et al., 2018), although Wiechert et al. (2004) reported heterogeneous O isotopic compositions in some of the HED's. Another line of evidence for large-scale melting of Vesta is provided from the peaks in Hf-W ages of zircons in eucrites (Roszjar et al., 2016). The ²⁶Al-²⁶Mg model ages and ¹⁸²Hf-¹⁸²W

chronology of the eucrite parent body suggest that Vesta differentiated <1 Ma after CAI formation, which implies that significant heat sources existed that are deemed to be required to largely or fully melt Vesta (Schiller et al., 2011; Formisano et al., 2013; Touboul et al., 2015; Hublet et al. 2017).

The use of experimentally determined metal-silicate partition coefficients of siderophile elements in conjunction with their depletions in planetary mantles are a useful tool to study the conditions that prevailed during early planetary differentiation (e.g., Righter and Drake, 1996, 1997; Wade and Wood, 2005; Wood et al., 2008; Siebert et al., 2011; Wood et al., 2014; Righter et al., 2015; Mahan et al., 2017; Steenstra et al., 2017c). In Vesta, rapid equilibration between metal and silicate during core-mantle differentiation may have occurred in a so-called "iron-rain" scenario, where small metal drops rapidly equilibrated with liquid silicate (Kiefer and Mittlefehldt, 2017). Previous studies that combined depletions of mostly refractory siderophile elements in eucrites and diogenites with expressions that predict their metal-silicate partitioning suggest that Vesta differentiated at mildly reducing conditions of ~ -2.2 log units below the iron-wüstite buffer (ΔIW) in a largely to fully molten state (Righter and Drake, 1996, 1997; Steenstra et al., 2016a). Steenstra et al. (2016a) showed that a bulk composition dominated by a H-chondrite component is consistent with siderophile element depletions in eucrites and diogenites, and that siderophile element depletions are consistent with an S-rich core. An S-rich core has also been suggested from bulk compositional considerations (Lodders, 2000; Toplis et al., 2013), the relatively high S contents of eucrites and diogenites (e.g., Kitts and Lodders, 1998) and the existence of a Vestan core dynamo in its earlier history (< \sim 3.7 Ga; Fu et al., 2012). The preservation of an advecting liquid metallic core for ~0.8 Ga suggests that light element(s) are present in the Vestan core. Most likely these are S and/or C (e.g., Boujibar et al., 2014; Chi et al., 2014; Li et al., 2016), as both elements are cosmochemically abundant, siderophile at the P-T conditions relevant for core formation in Vesta, and significantly decrease the liquidus temperatures of Fe-rich alloys (e.g., Boujibar et al., 2014; Li et al., 2016). Other light elements such as Si or O are unlikely to reside in the Vestan core because of the mildly reducing conditions inferred for Vestan core formation from refractory siderophile element depletions (e.g., Righter and Drake, 1997; Steenstra et al., 2016a) and the *P-T* conditions at the core-mantle boundary. Despite the inferred widespread magmatic activity on Vesta, analyses of water-bearing apatites in

eucrites suggest that the Vestan interior is not anhydrous (Sarafian et al., 2013; Barrett et al., 2016; Sarafian et al., 2017). This suggests that volatile degassing was not efficient.

The abundances of volatile siderophile elements (VSE, e.g., Zn, Pb, In, Cd, Sb, As, Se, Te, S) can be used to study the timing and extent of volatile loss in planetary bodies and the volatile fluxes in the early solar system (Righter et al., 2009; Wang et al., 2016; Righter et al., 2017, Steenstra et al., 2017a,b). Vesta is often considered to be the solar system's best representative example of a proto-planet (e.g., Russell et al., 2012), and knowledge of its volatile element distribution and evolution is a cornerstone for understanding the origin and distribution of volatile elements in the terrestrial planets. Currently, it is thought that volatile element depletions in HED meteorites are related to incomplete condensation and/or partial degassing in Vesta's building blocks, as inferred, for example, from the heavy Si isotopic signatures of HED meteorites (Pringle et al., 2013, 2014). Alternatively, these depletions could have arisen during magma ocean degassing events on Vesta itself (Sarafian et al., 2017; Pringle et al., 2017).

The stable isotopic compositions of the VSE Zn and Cd have been used to provide insight into the volatile systematics of early Vesta. Zinc isotopic compositions of individual fragments of brecciated HEDs exhibit only small scale isotopic heterogeneity, consistent with redistribution of Zn due to surface impacts (Paniello et al., 2012a). From Zn abundances in chondrites Paniello et al. (2012a) infer that 86–98% of the initial Vesta Zn budget may have been lost to space without resulting in Zn isotopic fractionation. Schönbächler et al. (2008) reported Cd isotopic compositions for eucrites Béréba, Bouvante and Juvinas that are within error of chondritic values. Cadmium isotopic compositions of monomict eucritic breccias also show no obvious sign of Cd isotopic fractionation despite the inferred depletion by a factor of 600 (Schönbächler et al., 2008; Wombacher et al., 2008). This suggests that processes other than degassing may have affected the abundances of these elements in the Vestan mantle.

Here, we aim to quantify VSE depletions in the Vestan mantle using an extensive database of published abundances in eucrites and diogenites. Results are used to study the processes that could have caused these depletions, including high temperature incomplete condensation or degassing, sulfide segregation and/or core formation. We specifically focus on assessing the possible effect of core formation

on VSE depletions, using a combination of previously reported high *P-T* experimental metal-silicate partition coefficients (Wood et al., 2008; Kiseeva and Wood, 2013; Wood et al., 2014; Mahan et al., 2017; Steenstra et al., 2017b) and new partition coefficients derived from additional high-precision measurements of some of our previous experiments (Steenstra et al. 2017b). These partition coefficients, in conjunction with Vestan core formation scenarios based on HED refractory siderophile element abundances (Righter and Drake, 1997; Steenstra et al., 2016a) enable a new assessment of the extent and timing of volatile loss in asteroid Vesta.

2. METHODS

2.1 Estimating indigenous VSE abundances in eucrites and diogenites

Measuring indigenous VSE abundances in basaltic achondrites is challenging, due to their low abundances, analytical issues, weathering effects and heterogeneous distribution due to meteoritic and/or troilite contamination (e.g., Gooley et al., 1976; Palme and Rammensee, 1981; Mukherjee and Viswanath, 1986; Palme et al., 1988; Mayne et al., 2009; Zhang et al., 2018; see section 3.2). To circumvent significant weathering effects, we excluded eucrites and diogenites found in Antarctica and other glacial environments from our compilation (Mittlefehldt and Lindstrom, 1991). Documented Ir and TI abundances (when available) were used to monitor the presence of meteoritic material and/or troilite in each of the sample. Measurements with significantly higher abundances of Ir (>1 ppb) and/or TI (>5 ppb) than average for a particular sample were excluded from the database (Appendix section A.1). In addition to the eucrite database of Kitts and Lodders (1998) and references therein, we incorporated the results of several more recent studies (Gibson et al., 1985; Barrat et al., 2003; 2007; Patzer et al., 2005). For diogenites, our estimates are mainly based on the abundances reported by Wolf et al. (1983), Gibson et al. (1985) and Mittlefehldt (1994).

To obtain estimates of siderophile element abundances in the Vestan mantle, one ideally uses correlations of these abundances with abundance ratios of incompatible, lithophile major and/or trace elements, such as P/La, Ga/La or Ni/MgO-FeO (e.g., Righter and Drake 1997; Dale et al., 2012; Steenstra et al., 2016a). Extrapolation of trends to the inferred bulk minor or major lithophile composition then yields an estimate of the abundance of the element(s) in question

in the mantle. Unfortunately, there are currently insufficient data to confidently apply this approach to the VSE in Vesta.

An alternative approach is to consider the abundances of the VSE measured in the most pristine non-cumulate eucrites as upper limits for the Vestan mantle, given the incompatible behavior of most of these elements in FeS-under-saturated magmatic systems (see section 3.2). The abundances of these elements in the most pristine diogenites are taken as lower limits for mantle abundances, given their cumulate nature. The range between lower and upper limit covers the maximum plausible range of VSE abundances in the Vestan mantle. The resulting estimated abundances in each of the non-cumulate eucrites, cumulate eucrites and diogenites are reported in Appendix section A.1 (Table S.1) and illustrated graphically in Fig. S.1.

2.2 Quantification of VSE abundances in metal alloys using LA-ICP-MS We extended our previous experimental metal-silicate partitioning dataset for the elements S, Se, Te and Sb (Steenstra et al. 2017b) by obtaining data on the abundances of As, Cd, In, and Pb in experimental metal phases using LA-ICP-MS, using analytical methods reported in Steenstra et al. (2017c). In some of the run products of Steenstra et al. (2017b), the abundances of Cd and Pb in metal were close to or below electron microprobe (EMPA) detection limits (<500–1000 ppm). In the sulfides, abundances of As previously measured by EMPA were close to limits of detection and heterogeneous (Table S.2). We used LA-ICP-MS to quantify their abundances in all metal phases (Cd, Pb) or sulfides (As) for the experiments described in Steenstra et al. (2017b). One potential problem with this approach is that volatile element abundances in metallic alloys may be systematically overestimated by LA-ICP-MS due to matrix-related preferential ablation (e.g., Loewen and Kent, 2012). We compiled EPMA- and LA-ICP-MS data from this study and other recent work (Crockett et al., 2017; Putter et al., 2017; Seegers et al., 2017) to quantify the extent of matrix effects on Cd, Pb, and As LA-ICP-MS measurements (Appendix section A.2). We find that the offsets between LA-ICP-MS and EPMA abundances are well quantified using linear fits and use these corrections (Table S.2) to obtain metal-silicate partition coefficients.

3. Results

3.1 Abundance of VSE in the Vestan mantle

Fig. 1a shows the new estimates of VSE depletions in the Vestan mantle, for the different bulk compositions considered for Vesta, as a function of their 50% condensation temperatures (Table 1). It is evident from Fig. 1a that the correlation between the observed depletions of the VSE and their 50% condensation temperatures is poor. This is further illustrated by comparing our newly derived VSE depletions with the inferred abundances of volatile *lithophile* elements in non-cumulate eucrites (Kitts and Lodders, 1998) and in the Vestan mantle (Sarafian, 2018) (Fig. 1b). This comparison also shows that the correlation between elemental depletions and their volatility is weak (Fig. 1b). Although C is the most volatile element considered here, it is also one of the most siderophile elements (e.g., Li et al., 2016). The VSE depletion systematics in the Vestan mantle are therefore likely affected by processes other than incomplete condensation or degassing.

3.2 Sulfide saturation of the Vestan mantle?

Sulfide saturation of the Vestan mantle would significantly affect the overall depletion systematics of the VSE, if it occurred during the formation of the HED rocks. We assess if eucritic source regions could have been sulfide saturated by comparing the measured S contents in non-cumulate eucrites with predicted sulfur solubility limits at sulfide saturation (SCSS) for their compositions. The SCSS values were calculated using the model of Smythe et al. (2017) in conjunction with the average major element bulk compositions of pristine non-cumulate eucrites reported by Warren et al. (2009).

Fig. 2 shows the S contents of non-cumulate eucrites reported in the literature as a function of their bulk FeO contents, together with predicted SCSS values for the *P*-T conditions inferred for non-cumulate eucrite genesis (0.0001 GPa; 1150 - 1250°C; e.g., Stolper et al., 1977). We find that all reported S contents in non-cumulate eucrites are at least 3000 ppm lower than the inferred S content at sulfide saturation. This suggests that the non-cumulate eucrite source region was not sulfide saturated, unless degassing of S during eucrite eruption exceeded 60 %.

Wu et al. (2018) reported the S isotopic composition of eight eucrites and showed that 6 of them are enriched in δ^{34} S relative to Canyon Diablo Troilite (CDT). This was interpreted as evidence for S loss, but it is unclear whether this loss occurred prior to

accretion and/or prior to or after core formation. Given the experimentally determined metal-silicate fractionation of S isotopes (Labidi et al., 2016) and the likely substantial amount of S in the Vestan core, core formation should have resulted in isotopically light δ^{34} S values in the residual mantle. The fact that eucrites cluster around a δ^{34} S value of 0.26±0.17‰ (2SD) could imply that the Vestan mantle was enriched in ³⁴S after core formation through kinetic volatile loss processes, such as evaporation into a hard vacuum (Wu et al., 2018).

Although native metal and troilite have been reported in several diogenites, it is thought these phases formed during later metamorphic episodes (Gooley et al., 1976; Mukherjee and Viswanath, 1986). Initial reduction of the siderophile elements in the pyroxenes and diffusion of metal to fractures resulted in annealing and/or recrystallization of pyroxene. Excess silica, which is also commonly associated with native metal, would form from the reduction of Fe in the pyroxene (Gooley and Moore, 1976). Similar post-magmatic thermal metamorphic or metasomatic processes have been suggested to lead to the formation of native metal and troilite in eucrites and diogenites (Palme et al., 1988; Mayne et al., 2009; Zhang et al., 2018). We therefore conclude it is unlikely that the eucrite source regions were sulfide-saturated during magma petrogenesis.

3.3. Modelling core formation in Vesta

The depletions of VSE in the Vestan mantle were calculated by consideration of a bulk composition dominated by H chondrites plus an additional 25% CM (Toplis et al., 2013) or 22% CV chondritic component (Lodders, 2000), as required from oxygen isotopic considerations. The metal-silicate partition coefficients (D's) that could yield the observed depletions in the Vestan mantle were then calculated using a simple mass balance approach:

$$D_{m}^{c}(i) = \left((C_{bV(i)} - xC_{bsV(i)}) / (C_{bsV(i)} (1 - x)) \right)$$
(1)

where $C_{bV(i)}$ is the concentration by weight of element *i* in the bulk of Vesta, assuming a H chondritic, H + 25% CM or H + 22% CV bulk composition (taken from Newsom, 1995). The $C_{bsV(i)}$ term represents the estimated abundance of element *i* in bulk silicate Vesta (Appendix section A.1; Table 1), and x is the assumed Vestan

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mantle mass fraction. In our calculations, we assume full chemical equilibrium between the mantle and core and a Vestan core mass of 25±2 %, which is an average based on bulk compositional calculations and refractory siderophile element modelling (Steenstra et al., 2016a).

This value is slightly higher than the estimates provided by geophysical constraints (18 mass %; Russell et al., 2012) and other bulk compositional calculations (15–20 mass %; Toplis et al., 2013; Righter and Drake, 1997). The value proposed by Russell et al. (2012) did not take the effect of S into account. With increasing S content of the Vestan core, its density is decreased and its mass fraction is increased (Russell et al., 2012; Toplis et al., 2013; Ermakov et al., 2014). We showed in Steenstra et al. (2016a) that the required metal-silicate partition coefficients are not strongly affected by uncertainties in core mass within the 15–25 mass% range.

We have previously shown that the expected Vestan core mass is a function of bulk composition, fO_2 and its assumed composition. The fO_2 value of $\Delta IW \sim -2.2\pm0.2$ reported by Righter and Drake (1997) and Steenstra et al. (2016a), based on predominantly refractory siderophile element depletions, corresponds with a core mass range of $25\pm2\%$. The Vestan mantle depletions of several refractory siderophile elements can be reconciled within this fO_2 range across a wide range of S core contents (up to $x_s^{metal} = 0.25$, equivalent to 16 wt.% S). All scenarios discussed below are fully consistent with our previous work (Steenstra et al., 2016a). We do not take the effects of C on VSE partitioning into account, as the effects of C on VSE partitioning are poorly quantified. In addition, C is unlikely to be a major element in the Vestan core, due to the expected high S contents of the Vestan core and the low solubility of C in S-rich metals (e.g., Li et al., 2016).

Parameter AIW is defined as the oxygen fugacity relative to the iron-wüstite buffer:

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

where $a_{\text{FeO}}^{\text{silicate}}$ and $a_{\text{Fe}}^{\text{metal}}$ are the activities of FeO in the silicate melt and Fe in the metallic phase, the product of their molar fractions (*x*) in each phase ($x_{\text{FeO}}^{\text{silicate}}$, $x_{\text{Fe}}^{\text{metal}}$) and their activity coefficients (γ) ($\gamma_{\text{FeO}}^{\text{silicate}}$, $\gamma_{\text{Fe}}^{\text{metal}}$). Assuming that the $\gamma_{\text{FeO}}^{\text{silicate}}$ value for Vesta's mantle is close to ~1.3 (O'Neill and Eggins, 2002), $\gamma_{\text{Fe}}^{\text{metal}}$ for Vesta's core is

close to 1 (Table A.3) and the core contains ~10 wt.% Ni (Toplis et al., 2013), differentiation of Vesta at $\Delta IW \sim -2.2\pm0.2$ corresponds with a Vestan mantle FeO content of ~8±2 wt.% or an average FeO molar fraction of ~0.06±0.02. The FeO content of the Vestan mantle assumed here is slightly lower than that reported by Toplis et al. (2013), because they based their work on the assumption of a 15 % Vestan core mass. Their estimate corresponds to a fO_2 of $\Delta IW \sim -1$, which has been shown to be incompatible with the Vestan mantle depletions of key siderophile elements Ni and Co. We note that a recent XANES study of V in chromite suggests a fO_2 value of $\Delta IW \sim -2$ to -1.5 for olivine diogenite GRA98108 (Righter et al., 2016).

The log D values of Tl¹⁺, Pb²⁺, Cd²⁺, Zn²⁺, In³⁺, Sb³⁺, and As⁵⁺ (Wood et al., 2008; Righter et al., 2009; Kiseeva and Wood, 2013; Wood et al., 2014; Mahan et al., 2017; Steenstra et al., 2017b) were corrected to $\Delta IW = -2.2$ (see e.g., Corgne et al., 2008; Siebert et al., 2011), where D is defined as the weight (%) ratio between the concentration of element *i* in metal or sulfide and the concentration of element *i* in the silicate melt. These corrections were made using the experimental ΔIW values calculated assuming non-ideal activities of Fe and FeO (Table S.3).

Parameter $\gamma_{\text{Fe0}}^{\text{silicate}}$ was modelled using the expression of Wood and Wade (2013), whereas $\gamma_{\rm Fe}^{\rm metal}$ for experiments with <10 wt.% S were calculated using the online metal activity calculator (Wade and Wood, 2005). The latter model likely overestimates $\gamma_{\rm Fe}^{\rm metal}$ in Fe-S alloys with >10. wt.% S. For experiments with metallic alloys containing >10 wt.% S, we therefore calculated the activity coefficients of Fe in metal using the model of Lee and Morita (2002) for the appropriate temperature (Table S.3). The log D values of S, Se, and Te were corrected to the FeO molar fraction value of ~0.06 appropriate for Vesta differentiation at $\Delta IW \sim -2.2$ using the relationships provided in Steenstra et al. (2017b). Although the dependency of S, Se, and Te partition coefficients on silicate FeO content (or fO_2) has a parabolic form (Rose-Weston et al., 2009; Seegers et al., 2017), a linear relation is valid for the fO₂ considered here (see Steenstra et al. 2017b). The metal-silicate partition coefficients that would be required to explain the observed depletions of VSE in the Vestan mantle are listed in Table 1. The consideration of different bulk compositions affects the required D's for the elements In, Cd, Pb, and Tl, which are more abundant in the volatile-rich CM and CV components (Table 1; Newsom, 1995).

The temperatures of most experiments considered here are directly relevant for differentiation of Vesta in a magma-ocean type of setting (Righter and Drake, 1997; Formisano et al., 2013; Steenstra et al., 2016a). The pressures of these experiments are higher than those relevant for the Vestan core-mantle boundary (0.1 GPa; Holzheid and Palme, 2007), but significant pressure effects on the metal-silicate partitioning of most of the elements considered here are excluded from the results of this study as well as previous studies (e.g., Siebert et al., 2011; Ballhaus et al. 2013; Bouhifd et al., 2013).

Bouhifd et al. (2013) used an extensive database of Pb metal-silicate partition coefficients to predict its metal-silicate partitioning behavior as a function of *P-T-* fO_2 and composition. They found that pressure has a negligible effect on Pb metal-silicate partitioning in the 0 to 25 GPa range, consistent with previous observations (Malavergne et al., 2007; Wood et al., 2008; Ballhaus et al., 2013). Corgne et al. (2008), Mann et al. (2009), Siebert et al. (2011) and Ballhaus et al. (2013) reported minor pressure effects on the metal-silicate partitioning of Zn, which was confirmed by recent diamond anvil cell experiments up to 81 GPa (Mahan et al., 2018). For TI, an insufficient number of high-pressure metal-silicate partition coefficients is currently available to fully assess the effects of pressure on its metal-silicate partitioning behavior. However, given its geochemically similar behavior to Pb, large pressure effects on its partitioning are unlikely (see Ballhaus et al., 2013), especially within the pressure range considered here (Wood et al., 2008).

Righter et al. (2009) reported a decrease of 1 log unit of D(Sb) within a pressure range of 1.5 to 13 GPa. Extrapolation of our 1 to 2.5 GPa metal-silicate partitioning data to the core/mantle boundary of Vesta is therefore expected to result in an offset of <0.2 log units for log D(Sb). For As, pressure effects are more significant (Siebert et al., 2011), but still inferior (<0.2 log units within the pressure range of 0.1 to 2.5 GPa considered here) compared to the much stronger effects of variable fO_2 and composition on D(As). Mann et al. (2009) and Wang et al. (2016) reported a decreasing effect of pressure on the metal-silicate partitioning behavior of In. Assuming the maximum effects of pressure from Mann et al. (2009), extrapolation of the 2.5 GPa log D(In) values to 0.1 GPa yields an offset of <0.14 log units. Finally, Ballhaus et al. (2013) proposed an overall lack of pressure effects on the metalsilicate partitioning behavior of Cd, whereas Wang et al. (2016) reported a decrease of 0.3 log units between 15 and 20 GPa, based on two data points. Assuming the latter pressure dependency, extrapolation of our results to the Vestan core mantle boundary results in a maximum offset of <0.15 log units for Cd.

Exceptions are S, Se, and Te, for which strong pressure effects have been reported (Rose-Weston et al., 2009; Boujibar et al., 2014; Steenstra et al., 2017b). Log D values of S, Se, and Te were therefore corrected to 0.1 GPa according to the pressure dependencies reported in Steenstra et al. (2017b). The primitive basaltic composition used in the majority of the partitioning experiments from Steenstra et al. (2017b) allows for direct application of most of our experimental partitioning results to Vesta, as the metal-silicate partitioning behavior of most VSE does not seem to be strongly dependent on silicate melt composition. However, it must be noted that there is evidence for significant silicate melt compositional effects on the metal-silicate partitioning of high valence elements Sb and As (Righter et al., 2009; Siebert et al., 2011), which will be discussed later in this study.

3.4 Depletions of VSE due to core formation in Vesta

Fig. 3 summarizes the D ranges required to explain the depletions of VSE in the Vestan mantle by core formation only. In the remainder of this study, a particular core formation model is considered to be successful for a particular element if the D value corresponding to the core formation model is within the error bars shown in Figure 3.

We first discuss the results for a Vestan H chondritic bulk composition. Our results suggest that the Vestan mantle depletions of S, Se, Cd, In, Te, Pb can be largely to completely reconciled with core formation depletion when a H chondritic bulk composition for Vesta is considered, as experimentally determined metal-silicate partition coefficients are within the required ranges (Fig. 4). The depletions of Cd and In due to core formation are consistent with the observed Vestan mantle depletions across the whole range of plausible S contents of the Vestan core (Righter and Drake, 1997; Lodders, 2000; Toplis et al., 2013; Steenstra et al., 2016a). The depletion of Pb can be achieved at low S contents, illustrating the significant potential for mantle depletion of Pb by formation of a S-bearing Vestan core . At higher S contents, the Pb mantle abundance remains higher than observed given its predicted metal-silicate partition behaviour. The experimentally determined metal-silicate partition coefficients for S, Se, Te are close to or within the range required for a S-rich core, when a bulk H chondritic bulk composition is considered.

However, their depletions cannot be reconciled with core formation only at low or intermediate S contents ($x_s^{\text{metal}} < .0.3$).

Next, we consider the effects of an addition of a 22% CV or 25% CM chondritic component to the bulk composition of Vesta. This addition is deemed to be required given the oxygen isotopic compositions of HED's (Lodders, 2000; Toplis et al., 2013). The depletions of S and In can still be achieved through core formation only, virtually independent of the added component(s). As for the pure H chondritic bulk composition, the depletion of Se can only be reconciled with formation of a Vestan core with $x_{\rm S}^{\rm metal}$ >0.3. For both bulk compositions, Pb is over-depleted across a wide range of Vestan core S contents. In the case of Cd and Te, their depletions cannot be solely explained with core formation depletion at low to intermediate S contents of the Vestan core. Their depletions could be explained by segregation of a FeS core, but the latter seems unlikely given the low S contents of non-cumulate eucrites (see section 3.2). Note that the modelled core formation conditions used here to assess VSE depletions are also compatible with the observed refractory siderophile element depletions in Vesta (Steenstra et al., 2016a),

We find that for all bulk compositions considered, the metal-silicate partition coefficients of moderately volatile elements As and Sb are several orders of magnitude too high to be compatible with their observed Vestan mantle depletions (Fig. 5). When considering the lowest measured abundance of As (Sioux County) and Sb (Bouvante), the abundances are still ~1 order of magnitude too high to be reconciled with the estimates S contents of the Vestan core. These discrepancies could be related to the use of more evolved silicate melt compositions, relative to the expected Vestan mantle composition. Previous experimental work showed that the metal-silicate partitioning of Sb and As is strongly dependent on the degree of melt polymerization (Righter et al., 2009; Siebert et al., 2011). Righter et al. (2009) demonstrated that log D values of Sb decrease by over 2 log units within a nbo/t range of 0.9 to 1.6, where nbo/t is the ratio of non-bridging oxygens relative to tetrahedrally coordinated cations and a proxy for melt polymerization (Mysen et al., 1982). Fig. 5 shows that the high nbo/t data for Sb from Righter et al. (2009) are close to or within the required range necessary to explain the Vestan mantle Sb depletion. The low nbo/t data from Righter et al. (2009) and intermediate nbo/t data (nbo/t = 1.3 - 1.7, similar to the average of ~1.8 observed for our experiments) from

Wood et al. (2014) plot much higher (Fig. 5). Siebert et al. (2011) found a similar, strong decrease of the siderophile behavior of As with increasing melt depolymerization, although these results were predominantly obtained for S-free, C-saturated metals. It is likely that As will show a similar trend to Sb, given their similar geochemical behavior (Fig. 5).

Deriving quantitative silicate melt compositional dependencies on the metalsilicate partitioning behavior of As and Sb from data compiled in this study is challenging given the range in metal compositions and the non-linear dependencies of As and Sb activities with S contents of the metal (Wood et al. 2014; this study). To further test this hypothesis, future work should be aimed at constraining the metalsilicate partitioning of Sb and As as a function of silicate melt composition for constant metal compositions.

Comparison of reported metal-silicate and sulfide-silicate partitioning data for TI shows it behaves slightly to moderately siderophile with coexisting FeS-rich metal at the conditions inferred for Vestan differentiation (Fig. 6). Partitioning data are only within the 'required' range when considering a S-rich Vestan core ($x_s^{metal} > 0.4$) and a H chondritic bulk composition. We note that at present it is not clear to what extent TI partitioning is affected by *T* and changes in silicate melt composition (e.g., Kiseeva and Wood, 2013). The Vestan mantle depletion of TI should therefore be further assessed when more experimental data is available.

Zinc is one of the few VSE for which Vestan mantle depletion does not seem to reflect a significant role for metal-silicate equilibration. All predicted metal-silicate partition coefficients of Zn are over one order of magnitude too low to explain its depletion in the Vestan mantle through core formation alone (Fig. 6). This could imply that Zn was largely lost before or during accretion and/or differentiation of Vesta, although this may be hard to reconcile with the lack of Zn isotopic fractionation observed in eucrites (Paniello et al., 2012a) and the fact that the elemental depletions of other, more volatile elements (e.g., C, In, S, Se and possibly Cd) do not necessarily require extensive devolatilization. Alternatively, Zn may be additionally depleted by its preferential partitioning into spinel (Chikami et al., 1999; Paniello et al., 2012b), which has been shown to form during partial melting and fractional crystallization of a Vesta-like bulk composition (Ashcroft et al., 2015). Experimental mineral-melt partitioning results suggest that Zn behaves as a

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compatible element, with spinel-melt partition coefficients of 3 to 5 at the P-T- fO_2 conditions relevant for Vesta (Chikami et al., 1999). However, given this only moderately compatible behavior of Zn in spinel, spinel modes would have to be unrealistically high to fully account for the observed Zn depletion.

Metal-silicate partitioning results for the volatile element Bi also point to siderophile behavior (log D = 0.5 - 1.5; Righter et al., 2017) that is likely sufficient to largely or possibly fully explain its observed depletion in the Vestan mantle (Fig. 3). In addition, Bi partitioning is likely increased with S (e.g., Li and Audetat, 2012).

Some volatile element degassing from Vesta has been suggested from the low carbon (C) contents in eucrites Juvinas, Pasamonte, Sioux County and diogenites Johnstown, Shalka, and Tatahouine (9–27 ppm; Grady et al., 1997). To assess to which extent C may have partitioned into the Vestan core, we use the predictive models of Li et al. (2016). Fig. 7 shows the results of our calculations and suggests the predicted siderophile nature of C is sufficient to explain the C depletion in eucrites and diogenites, independent of temperature or bulk composition considered.

Although the solubility limit of C in Fe-S alloys decreases with increasing S concentrations, C still behaves siderophile under these conditions. Steenstra and van Westrenen (2018) reported a predictive model describing the C solubility in Fe-S alloys as a function of pressure, temperature and metal composition (Appendix section A.3). We use this model to estimate the maximum possible C concentrations in the Vestan core as a function of its S content. Our results how that the C solubility limits are unlikely to be reached for a H and/or H + 22% CV bulk Vestan composition, unless its core is S-rich (> 22 wt. % S; Fig. 7b; Appendix section A.3). Consideration of the Li et al. (2016) model for metal-silicate partitioning of C predicts that for a bulk Vesta C concentration of 0.11 wt.% C, corresponding to a H chondritic bulk composition (Newsom, 1995), 0.44 ± 0.03 wt% C is expected to partition into the core. A Vestan core concentration of >25 wt.% S would therefore be required to generate graphite saturation of the Vestan mantle.

For a H + 22% CV and a H + 25% CM chondritic bulk composition, the abundance of C expected in the core increases to 0.84 ± 0.07 and 2.84 ± 0.23 wt. %, respectively. To obtain a graphite-saturated Vestan mantle, core S concentrations of >22 and 9 wt.% are required for a H + 22% CV and a H + 25% CM composition, respectively. It is evident that only for the H + 25% CM bulk composition a C-

saturated Vestan core is likely. These results are independent of the assumed parameterization of C metal-silicate partitioning due to its highly siderophile behavior.

Finally, we showed in our previous study (Steenstra et al., 2016a) that the abundance of moderately volatile elements P, Ga and Cu in the Vestan mantle can be reconciled with sequestration during core formation across a wide range of core formation conditions and (bulk) compositions.

Using the latter results, we calculated the magnitude of core formation depletion for the various elements for a Vestan core with 14.5 ± 1.5 wt.% S for each of the three bulk Vestan compositions (Table 2). Table 2 shows that the Vestan mantle depletions of S, Se, In and Pb are largely or fully explained by core formation depletion with depletion percentages of 27-130 %, 33-79 %, 36-208 % and 80-360 %, respectively, depending of the bulk Vestan composition considered). Vestan mantle depletions of Zn, Tl, Cd and Te are explained for less than 4 %, 55 %, 59%, 150 % by core formation depletion, the exact percentage depending of the type of bulk Vesta composition considered (Table 2).

Figure 8 shows these values as a function of the 50% condensation temperatures at 10^{-4} bar (Lodders, 2003). We find that there is no clear correlation between VSE volatility and their Vestan mantle depletions corrected for formation of a S-bearing Vestan core.

4. DISCUSSION

4.1 Sensitivity of model outcomes to uncertainties in bulk and core compositions The presence and size of a CV and/or a CM component in Vesta's bulk composition, which are still debated, could affect the models presented here. For example, the error bar on the 22% CV addition is ~5% (Lodders, 2000), whereas Boesenberg and Delaney (1997) estimate a ~30% CM component instead of the 25% proposed by Toplis et al. (2013). These uncertainties do not significantly affect the required metalsilicate partition coefficients for S, Se, As, and Sb because their abundances in the different components are similar. The abundances of Cd, In, Te and Pb in the components differ greatly, and therefore the interpretation of their depletions is more susceptible to uncertainties in the amount and nature of the mixed component(s) (Newsom, 1995; Table 2).

For example, H chondrites contain only 240 ppb Pb, whereas CM and CV contain 1700 and 1400 ppb Pb, respectively (Newsom, 1995). This could explain the inferred

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overabundance of Pb and/or the lower abundances of Te, relative to their predicted metal-silicate partition coefficients. It seems unlikely that Te would be preferentially devolatilized relative to elements that behave geochemically similarly such as S and Se, for which Vestan mantle depletions are largely compatible with segregation of a FeS-rich Vestan core. Variations in bulk compositions will also be reflected in variations of the Vestan core mass. Smaller core masses, relative to the modelled value of 25±2 mass %, will result in slightly higher required D values to explain the Vestan mantle depletions of the volatile elements considered here, whereas larger core masses result in lower required D values. Of course, it also remains possible that bulk Vesta is not represented by chondritic materials (e.g. Consolmagno et al., 2015), as may also be the case for the bulk Earth (e.g. Campbell and O'Neill, 2012).

Another potential uncertainty concerns the actual S content of Vesta's building blocks and its core. We showed in section 3.4 that the extent to which the various VSE depletions are reconciled with core formation can depend strongly on the assumed S content of the Vestan core. This is especially the case for the most chalcophile elements including Cd, Se, Te, Tl, and S itself. In our bulk Vesta calculations chondritic abundances of S are assumed, whereas S could have been partially degassed prior to or during Vestan accretion (Wu et al., 2018). Any degassing of S in this stage of Vesta's evolution would have resulted in lower Vestan S core concentrations than the preferred range considered here. In turn, this would result in larger discrepancies between modelled and required D values for Cd, Se and Te - i.e. more volatility-related losses would be required.

We also did not consider the potential effects of C on the metal-silicate partitioning of VSE in our models. Addition of C to the core is expected to decrease the siderophile and/or chalcophile behavior of S, Cd, Zn, As, Sb, Pb, Tl (Wood and Halliday, 2010; Crockett et al., 2017). Preliminary results for Se and Te show that addition of 6 wt.% C results in a decrease of their D values by 0.2 log units, whereas In remains largely unaffected by addition of C (Crockett et al., 2017). Given the S-rich nature of the Vestan core, the expected solubility of C in the Vestan core is likely significantly lower than 6 wt.% (see section 3.4). In addition, calculated core concentrations are in most cases even lower than the solubility limit (Fig. 7b). The effect of C on the models considered as successful here are therefore expected to be limited.

We conclude that despite a range of uncertainties, the main point of our work, namely that the Vestan core should be considered a significant reservoir for many volatile siderophile elements, is robust.

4.2 Effects of FeS crystallization on Vestan mantle VSE depletions

Although we have shown that the measured S concentrations in eucrites are far lower than modelled SCSS values, S isotopic data suggest S loss from eucrites did occur (Wu et al., 2018). This loss may isotopically "mask" and/or compensate for sulfide-silicate isotopic fractionation of S. It also suggests sulfide saturation may have occurred before later loss of S from the Vestan mantle. Here, we consider the potential effects of early sulfide saturation on the abundances of the VSE considered here. Segregation of sulfides during differentiation of the Vestan mantle would result in strong additional depletions of the more chalcophile elements S, Se, Te and TI (Kiseeva and Wood, 2013, 2015; Steenstra et al., 2018a; this study). Moderately chalcophile elements Pb, Cd and Zn would be considerably less depleted through extraction of sulfides from eucritic melts, whereas the abundances of chalcophobic elements such as As and Sb would remain largely unaffected (Kiseeva and Wood, 2013; 2015; Steenstra et al., 2018a this study). Figure 9 shows that the correlation between the inferred % of depletions through Vestan core formation and the predicted relative chalcophile behavior of the VSE is poor. This suggests that largescale sulfide segregation did not occur on Vesta.

4.3 Is volatile loss required to explain VSE depletions in the Vestan mantle? An important implication of this work is that a H-chondrite dominated bulk composition of Vesta and corresponding S-rich core has the potential to largely or fully explain the VSE depletions of the Vestan mantle (Fig. 8, Table 2.) This suggests that volatile loss to space may not have been efficient during Vestan differentiation, which agrees with the general lack of correlation between the depletions of the volatile elements and their volatility as shown in Fig. 1 (section 3.1). The lack of correlation between VSE volatility and the % of their depletion explained by core formation also excludes a sole and/or primary role of evaporative and/or kinetic volatile loss processes on VSE Vestan mantle abundances (Fig. 8).

We would like to stress that this does not mean that we claim that all volatile element depletions in Vesta can be explained by core-mantle equilibration only. Not all vapour loss processes would necessarily result in large isotopic fractionations of

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these elements. The similarity between stable isotopic compositions of VSE in HED's and chondrites, or lack of large internal stable isotopic variability within the HED suite, can therefore not be used to definitively argue for the absence of evaporative loss of the VSE during accretion and/or differentiation of Vesta. The VSE budget may also have been affected by evaporation processes at oxidizing conditions, which has recently been proposed for explaining Earth's volatile content (Norris and Wood, 2017). This could be reflected by the larger discrepancies between modelled core-mantle partition coefficients for Zn, Tl, Te, and Cd in the case of a bulk Vesta component that contains a CM and/or CV component (Fig. 8, Table 2). Significant degassing of VSE during differentiation of Vesta is neither excluded nor confirmed by minor isotopic fractionation of the volatile element Cd in eucrites (Wombacher et al., 2008; Schönbächler et al., 2008), whereas S isotopic compositions of eucrites may reflect kinetic loss of S in a hard vacuum (Wu et al., 2018). Vesta likely lost significant amounts of the highly volatile element CI (and other halogens and moderately volatile elements; e.g. Prettyman et al., 2015) during late magmatic degassing events, as evidenced by the Cl isotopic fractionations in eucritic apatite and merrillite phases and overall halogen abundances in eucrites (Sarafian et al., 2017). This latter process may not have significantly affected the abundance of the majority of other highly volatile elements considered here, which could be related to the distinctly different chemical behavior of the VSE, relative to halogens, during degassing events (e.g., Zelenski et al., 2013; Ustunisik et al., 2018).

In summary, the depletions of VSE in the Vestan mantle likely represent a mixture of both volatile loss and core formation depletion processes, especially for Zn and possibly Te, TI and Cd. Although unlikely from S concentrations in eucrites as well as trends between depletions and chalcophility, sulfide saturation would result in significant additional depletions of the most chalcophile elements Te and Tl, and to a lesser extent S, Se, Cd and Pb (see section 4.2). Our analysis shows that additional devolatilization is not *required* for S, In, Pb, As, Sb and possibly Cd and Se. Although Mn/Na ratios of eucrites indicate some volatility-related loss of Na (e.g., Prettyman et al., 2015), we recently showed that significant quantities of K and Na may also partition into a S-rich Vestan core (Murthy et al., 2003; Steenstra et al., 2018b), especially if Vesta differentiated at higher temperatures (> 2000 – 2200 K). This provides additional evidence for the significant storage capabilities of the Vestan core for volatile elements. If Vesta's building blocks were already initially

depleted in VSE to some extent compared to the chondrite types considered here, it also becomes more feasible to explain their final depletions by core formation.

Besides Vesta, it has been shown that the lunar core and terrestrial core can also be a significant reservoir for VSE and other volatile elements, including C, I, S, Se, Te, Sb and Pb (e.g., Righter et al., 2009; Wood and Halliday, 2010; Steenstra et al., 2016b; Steenstra et al., 2017a, b; Jackson et al., 2018). Different volatile depletion patterns may be related to distinctly different core formation conditions within these bodies, as the sulfide-silicate and metal-silicate partitioning behavior of VSE are uniquely dependent on variables such as *P*, *T*, and composition. Planetary cores may therefore be an important sink for many volatile elements, and volatile depletion patterns for the terrestrial planets are affected by core formation depletion processes.

5. CONCLUSIONS

We re-assessed the depletions of volatile siderophile elements (VSE) in the Vestan mantle using published compositional data for eucrites and diogenites. Depletions show no significant correlation with element volatility, suggesting other processes besides volatility-dependent depletion affected their abundances in the Vestan interior. Segregation of sulfides in the diogenite and eucrite source regions is deemed unlikely from the much lower S contents in these samples relative to calculated S contents at sulfide saturation, but cannot be excluded. Instead, we find that mantle depletion through segregation of a S-rich Vestan core at reducing conditions readily explains many VSE depletions in the Vestan mantle. A S-rich core agrees with Vesta's inferred bulk composition and with the existence of a core dynamo in its early history (Fu et al., 2012). Our results suggest that significant volatile loss from Vesta is not required for many VSE (C, S, As, Se, In, Sb, Pb and/or Cd, depending of the assumed bulk composition) if their siderophile behavior is taken into account. The suggested loss of other volatiles, such as the halogens, is therefore likely to have occurred after differentiation of Vesta. Other VSE, such as Zn, Te and TI, do require additional depletion through kinetic or evaporative loss and/or preferential partitioning into sulfides. The isotopic compositions of halogens in eucrites and the overall depletion of halogens in the Vestan mantle also require volatile loss for several elements from the Vestan magma ocean, perhaps in the form of metal halide degassing. Such loss is, however, not required for the majority of VSE considered here. Our results demonstrate the significant potential of planetary cores to be a major reservoir for the majority of volatile elements.

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Fig. 1 (a) The depletion of VSE in the Vestan mantle, relative to the bulk Vesta compositions inferred from isotopic compositions and major element considerations (100% H chondrite, 75% H + 25% CM chondrite or 78% H + 22 % CV chondrite; Lodders 2000; Toplis et al., 2013) as a function of their 50% condensation temperature at 10⁻⁴ bar in K (Lodders, 2003). Filled circles represent estimates for the Vestan VSE mantle concentrations derived from consideration of the average VSE abundances in cumulate lithologies (diogenites) and non-cumulate basalts (eucrites). Filled triangles and squares represent the different estimates of C depletions in eucrites and diogenites, relative to the various bulk compositional models considered. Errors are maximum errors based on the full range of VSE abundances in non-cumulate eucrites and diogenites (b) The depletion of volatile siderophile and lithophile elements in the Vestan mantle (Sarafian, 2018 and this study, based on the average of the range of VSE abundances between noncumulate eucrites and diogenites) and non-cumulate eucrites (Kitts and Lodders, 1998) relative to CI chondritic values as a function of their 50% condensation temperature at 10⁻⁴ bar in K (Lodders, 2003). Values for lithophile element abundances in non-cumulate eucrites are the average of the values proposed for each bulk non-cumulate eucrite reported in Kitts and Lodders (1998). Errors on these values are maximum errors based on 1 SE; errors on H and F abundances for nonequilibrated eucrites are based on estimates reported in Sarafian (2018).



Fig. 2 Sulfur in non-cumulate eucrites as a function of their FeO contents and the estimated sulfur content at sulfide saturation (SCSS) calculated using the model of Smythe et al. (2017) for the average major element composition of pristine non-cumulate eucrites (Warren et al., 2009). Errors are 1 SD.

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Fig. 3 The metal-silicate partition coefficients required to explain the depletions of VSE in the Vestan mantle for three different bulk compositions (100% H chondrite, 75% H chondrite + 25% CM chondrite, and 78% H chondrite + 22% CV chondrite), calculated using Eq. 1 and assuming a 25±2 mass% core. Also plotted are the depletions of As in Sioux County and Sb in the Bouvante non-cumulate eucrites. Errors are maximum errors based on the full range of VSE concentrations between eucrites and diogenites.



Fig. 4 Metal-silicate partition coefficients of VSE versus the molar fraction of S (x_S^{metal}) in the Vestan core. Different types of horizontal bars represent the different required metal-silicate partition coefficients for the different bulk Vesta compositions (solid = 100% H chondrite, dashed = H + 22% CV chondrite and finely dashed = H + 25% CM chondrite). Vertical bars represents the estimated S content of the Vestan core (14.5±1.5 wt.% S, or $x_S^{metal} = 0.23\pm0.02$;Toplis et al., 2013; Steenstra et al. 2016a). Letter in parentheses denote the type of silicate composition used in the experiment (B = basalt, G = granite) (Steenstra et al., 2017b). Variability in D values in low-S domains for some elements is due to the non-linear effects of S on their partitioning at low S concentrations.



Fig. 5 Metal-silicate partition coefficients of As and Sb versus the molar fraction of S (x_s^{metal}) in the Vestan core. Green dashed horizontal line represents lowest abundances in non-cumulate eucrites (Bouvante for Sb, Sioux County for As; Table 1). See Fig. 4 caption for explanation of vertical and horizontal bars. Letter in parentheses denote the type of silicate composition used in the experiment (B = basalt, G = granite) (Steenstra et al., 2017b). Also included are metal-silicate partitioning data for Sb from Righter et al. (2009) obtained at 1.5 GPa and 1773 – 2173 K, nbo/t = 0.9 – 2.9; and from Wood et al. (2014) obtained at 1.5 GPa and 1788–1838 K, nbo/t = 1.3 – 1.7. The results of Righter et al. (2009) show the strong effects of melt polymerization (here approximated using nbo/t, Mysen et al., 1982) on the metal-silicate partitioning behavior of Sb. The low nbo/t values denote values between 0.9–1.4 and high nbo/t values 1.8–2.9 (Righter et al., 2009).



Fig. 6 Compiled sulfide-silicate and metal-silicate partition coefficients of Zn and Tl versus the molar fraction of S (x_{s}^{metal}) in the Vestan core (W08 = Wood et al., 2008; KW13 = Kiseeva and Wood, 2013; W14 = Wood et al., 2014; M17 = Mahan et al., 2017). All experiments were conducted at C-free conditions, except for the experiments from Kiseeva and Wood (2013) that were conducted in graphite capsules. Experiments with significant amounts of dissolved oxygen (> 2 wt.%) were excluded from the latter dataset. See Fig. 4 caption for explanation of vertical and horizontal bars.



Fig. 7 (a) Predicted metal-silicate partitioning behavior of carbon as a function of temperature during Vestan differentiation. The figure shows two models for calculating log D(C) reported by Li et al. (2016). The first parameterization is appropriate for reducing conditions, such as Vestan differentiation ($\Delta IW < -1.5$). The other model is strictly speaking only valid for systems that are less reducing ($\Delta IW > -1.5$), but is plotted for reference purposes. The discontinuity at $\Delta IW = -1.5$ is the result of a change in C solubility due to speciation changes of C in the silicate melt (see Li et al., 2016 for additional details). See Fig. 4 caption for explanation of vertical and horizontal bars. **(b)** Calculated C concentrations of the Vestan core for the three different bulk Vesta models (horizontal shaded bars) and modelled carbon concentrations at graphite saturation (CCGS_{metal}; dashed and solid line; Steenstra and van Westrenen, 2018) as a function of S in the core, for a 0% Ni and 5% Ni bearing Vestan core (see Appendix section A.3).



Fig. 8 Summary of the effects of core formation on VSE element budgets in the Vestan mantle. There is no obvious correlation between volatility after correction for depletions of these elements through Vestan core formation. Errors are maximum errors based on the uncertainties on the estimated metal-silicate partition coefficients values, Vestan mantle abundances and Vestan core masses.



Fig. 9 The percent of calculated VSE depletions by Vestan core formation as a function of their relative chalcophile behavior. Relative chalcophile sequences are derived from Fig. 4 and 6. Errors are maximum errors based on the uncertainties on the estimated metal-silicate partition coefficients values, Vestan mantle abundances and Vestan core masses.



 Table 1 Abundances of volatile siderophile elements (VSE) in bulk (silicate) Vesta and the metal/silicate partition coefficients (D) required to fully explain these abundances by metal-silicate equilibration for each bulk composition.

	S (ppm)	Zn	As (ppb)	Se	Cd	In	Sb	Те	ТІ	Pb	Bi
Chondrites											
H chondrite ¹	20000	47	2050	7700	17	11	70	260	3.7	240	17
CV chondrite ¹	22000	116	1600	8300	373	33	85	1020	46	1400	48
CM chondrite ¹	33000	185	1800	12700	368	50	115	1910	92	1700	75
Bulk silicate Vesta ²	1308(449)	1.3(3)	52(16)	314(64)	8.0(32)	1.8(7)	6.6(27)	5.6(14)	0.8(3)	112(18)	0.7(4)
Bulk Vesta (H)	20000	47	2050	7700	17	11	70	260	3.7	240	17
Required D ³	39–98	100–202	110–248	73–131	3–12	13–44	25–75	135–266	10–31	4–8	57–235
_					Y						
Bulk Vesta (H + 25% CM)⁴	23250	82	1988	8950	105	21	81	673	26	605	32
Required D	46–114	176–353	106–240	85–152	32–92	28–85	30–87	353–693	88–235	15–25	108–438
Bulk Vesta (H + 22% CV)⁵	20440	62	1951	7832	95	16	73	427	13	495	24
Required D	40–100	134–269	104–236	74–133	29–83	21–64	26–78	223–439	43–117	11–20	81–331

¹Newsom (1995) ²Calculated assuming the abundances in non-cumulate eucrites as an upper limit and the abundances in diogenites as the lower limit of the Vestan mantle ³Calculated using Eq. (1), assuming a 25±2% Vestan core mass ⁴Toplis et al. (2013) ⁵Lodders (2000)

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Table 2 Summary of the percentage of each VSE depletion that can be explained by formation of a Vestan core with the preferred S contents (14.5±1.5 wt. % or $x_{s}^{metal} = 0.23\pm0.02$; Toplis et al., 2013; Steenstra et al., 2016a) for each of the three bulk Vestan compositions considered. Errors are maximum errors based on the uncertainties on the estimated metal-silicate partition coefficients, Vestan mantle abundances and Vestan core masses.