GEOCHEMICAL CONSTRAINTS ON THE COMPOSITION OF THE MARTIAN CORE. W. van
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Introduction: Accurate constraints on the abundances of elements lighter than Fe in the Martian core feed into models of the Martian core dynamo, the conditions under which the Martian core formed (which is linked to the existence and depth of a magma ocean) and the overall volatile element inventory of Mars. Current estimates for the sulfur (S) content of the Martian core range anywhere between 1 and 25 wt% S, based on geochemical and geophysical constraints [1-8]. Other possible light elements in the Martian core include O and C [9-11].

Here, we provide quantitative constraints on the distribution of S and other (light) elements (Ni, O, C) in the Martian interior using mass balance calculations, combined with published models that predict their high-pressure metal-silicate partitioning behavior [12-15]. We explore a wide range of plausible Martian bulk compositions, core masses and pressure (*P*) - temperature (*T*) scenarios [1,2,5-7]. We also assess the bulk volatile element inventory of Mars by consideration of the metal-silicate partitioning behavior of Se and Te. Ref. [3] suggested that the S/Se and Se/Te values of the Martian mantle most likely represent core-mantle equilibrium, instead of reflecting a late veneer. We quantitatively explore to which extent Martian mantle Se and Te abundances may represent a signature of core formation, using revised models for their metal-silicate partitioning based on recent experimental data from our lab [16] combined with previous work [17].

Methods: We adopt a simple mass balance approach with which the amount of element *i* in the Martian core can be calculated [18]:

$$C_{core}^i = C_{bulk\ Mars}^i / [x_{core} + (1 - x_{core})/D(i)] \quad (1)$$

$$C_{mantle}^i = C_{bulk\ Mars}^i / [x_{mantle} + (1 - x_{mantle}) * D(i)] \quad (2)$$

where C_{mantle}^i, C_{core}^i, and $C_{bulk\ Mars}^i$ are defined as concentrations by weight of element *i* in the Martian core, mantle and bulk Mars. Parameter *x* is the Martian core or mantle mass fraction and D is the metal-silicate partition coefficient (wt% *i* in metal/wt% *i* in silicate). To predict $D_{O,S,C,Ni}$ values as a function of *P-T*, we used the models of refs. [12-15]. We explore a Martian core mass range of 21-28 % [1,2,5-7] and *P* between 0-25 GPa and corresponding liquidus *T*. Liquidus *T* were calculated between 0-25 GPa using T_{liq} (K) = 1835 + 35*P (GPa) [1]. Models for $D_{Se,Te}$ were obtained by parameterizing exisiting data [16,17] to:

$$\log D_{Se,Te} = a + b\frac{1}{T} + c\frac{P}{T} + d\log X_{FeO}^{silicate} - \log C_S + e\log(1 - X_S^{metal}) \quad (3)$$

where *T* is in K, *P* is in GPa, $X_{FeO}^{silicate}$ is the molar fraction of FeO in the silicate melt, C_S is the sulfide capacity which incorporates the effect of fO_2 on Se and Te partitioning [12] and X_S is the molar fraction of S in the metal phase. Constants a-e were derived using multilinear regressions. It was found that FeO, *P*, X_S^{metal} are the most important parameters affecting $D_{Se,Te}$, in agreement with previous work [16,17]. Activities of the light elements for each modeled core composition were calculated using the metal activity calculator [19]. The C_S and $X_{FeO}^{silicate}$ values, as well as fO_2, were recalculated for each scenario considered.

Results: Quantitative assessment of the expected partitioning behavior of O suggests the Martian core is O-poor (<0.2 wt%), virtually independent of *P-T* and bulk composition (Fig. 1) Only at unrealistic high *P* (>20 GPa) or extremely oxidizing conditions (>20 wt% FeO in the Martian mantle) do O concentrations in the Martian core become significant. The minor role of O in the Martian core agrees with previous findings where only O was considered [9,10]. In case of C and Ni, their siderophile nature results in their near-complete (>99%) partitioning into the core, independent of *P-T* conditions, core mass or composition. The Ni and C contents in the Martian core for the various core masses and bulk Mars compositions range between 7.3±0.5 wt.% and 1.2±0.2 wt.%, respectively (Fig. 1). Fig. 2 shows the computed S concentrations in the Martian interior for a shallow (10 GPa) and deep (20 GPa) Martian Magma Ocean (MMO) scenario for the previously discussed core compositions. The S content of the Martian core is predominantly a function of the assumed bulk Mars S content and to a lesser extent core mass (Figs. 1,2). Variables *P, T* and core composition do not significantly change estimated Mars core S contents.

Consideration of the four proposed bulk compositions, which significantly vary in bulk S content (2.2-4.8 wt%) and core mass (21-28%), constrain the permissible S content of the Martian core to 13.7±3.4 wt%. If we constrain the Martian mantle S abundance to 360±120 ppm [3] and loosen bulk Mars S constraints, a 21 mass% Martian core should contain at least 22 wt% S and could even consist of stoichiometric FeS if it formed in a deep MMO. This is reduced to 22.5±7.5 wt% S for a 28 mass% Martian core. A 21 and 28 mass% Martian core formed in a shallow MMO yields even higher S contents (>26.2 wt% up to

stoichiometric FeS). We note that the bulk Mars abundance of >4.3 wt% S calculated using the Martian mantle S estimate of ref. [3] is significantly higher than the S abundances found in any major chondrite group [20] (Fig. 2). Altogether, our results demonstrate that the S-rich nature of the Martian core is robust given current geochemical estimates of S in the Martian mantle and the partitioning behaviour of S.
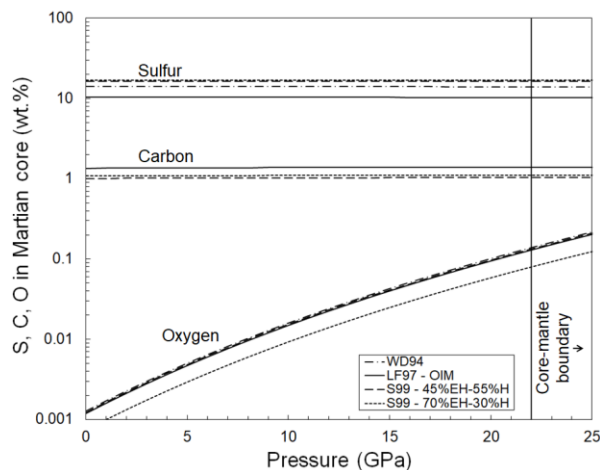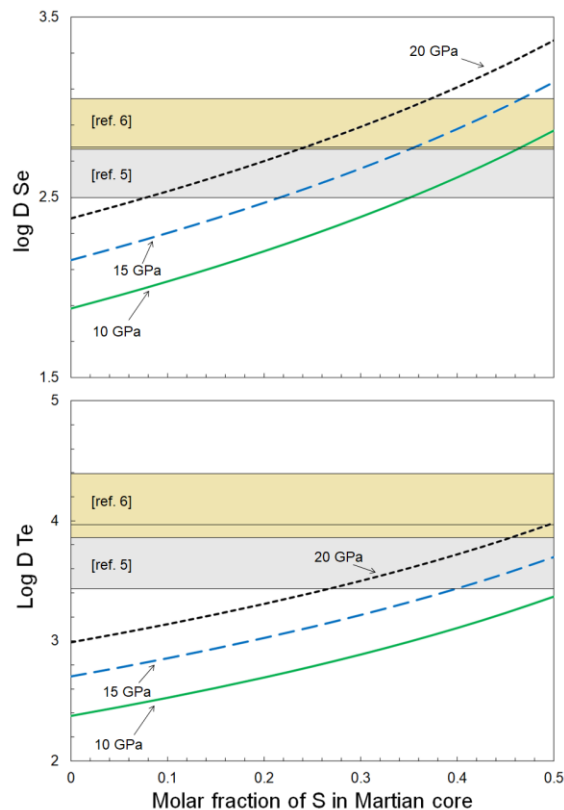

Fig. 1 S, O and C concentrations in the Martian core calculated using the model from [12-15] for the four bulk compositions considered (WD94 = [7], LF97 = [5], S99 = [6]).
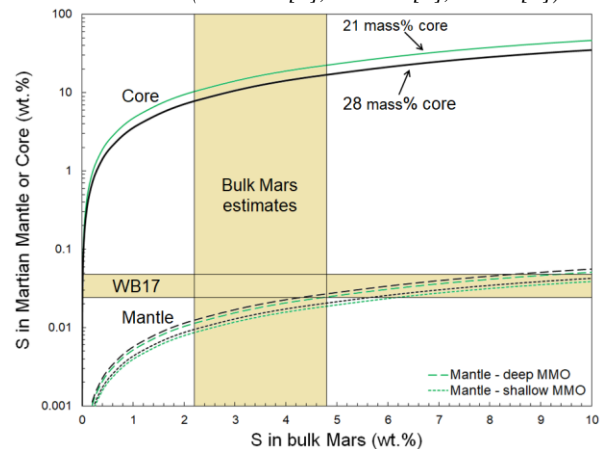
Fig. 2 S concentrations in the Martian interior calculated using the model from [12]. Horizontal shaded bar represents estimated S mantle abundance from WB17 [3].

We assessed to which extent Se and Te are expected to partition into the Martian core during core formation. Fig.3 illustrates that the estimated Martian mantle depletions of Se and Te [3] can be reconciled with their preferential partitioning into the Martian core under a wide range of *P-T* conditions if S is the dominant light element in the Martian core. This agrees with [3] who proposed that the Se and Te abundances in the Martian interior reflect Martian core-mantle equilibrium. We conclude that the mantle depletions of Se, Te indeed appear to be mostly set by core for-

mation processes. This suggests a minor role of a late meteoritic veneer and/or partial volatilization and/or incomplete condensation in Mars' early history, at least in terms of Se, Te.

Fig. 3 Calculated $D_{Se,Te}$ values as a function of the molar fraction of S in the Martian core. Horizontal shaded bars represent required log D value ranges for different bulk Mars Se or Te concentrations [5,6]. Different lines represent different core-mantle equilibration depths.

References: [1] Righter & Chabot (2011) *MAPS 46,* 157 [2] Rai & van Westrenen (2013) *JGR 118,* 1195 [3] Wang & Becker (2017) *EPSL 463,* 51 [4] Rivoldini et al (2011) *Icarus 213*, 451 [5] Lodders & Fegley (1997) *Icarus 126,* 373 [6] Sanloup et al (1999) *PEPI 112,* 43 [7] Wanke & Dreibus (1994) *PTRS A349*, 285 [8] Gaillard & Scaillet (2009) *EPSL 279,* 34 [9] Rubie et al (2004) *Nature 429,* 61 [10] Asahara et al (2007) *EPSL 257,* 435 [11] Chi et al (2014) *GCA 139,* 447 [12] Suer et al (2017) *EPSL 469,* 84 [13] Ricolleau et al (2011) *EPSL 310,* 409 [14] Fischer et al (2015) *GCA 167,* 177 [15] Li et al (2016) *Nat Geosci 9,* 781 [16] Steenstra et al (2017) *Sci Rep* 7, 14552 [17] Rose-Weston et al (2009) *GCA 73,* 4598 [18] Steenstra et al (2017) *AM* 102, 92 [19] Wade & Wood (2005) *EPSL 236,* 78 [20] Newsom (1995) *Global Earth Physics: A handbook of physical constants*