



A synthesis of geochemical constraints on the inventory of light elements in the core of Mars



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ARTICLE INFO

Keywords:

Mars
Core
Siderophile
Chalcophile
Volatiles

ABSTRACT

Accurate constraints on the light element composition of the Martian core are required for models of the Martian core dynamo, the conditions under which the Martian core formed (i.e. the existence and extent of a magma ocean) and the overall volatile inventory of Mars. Here, we present a synthesis of geochemical constraints on the abundances of light elements S, C and O in the Martian core using mass balance calculations combined with published expressions that predict their high-pressure metal–silicate partitioning behaviour. We incorporate recently proposed bulk S Martian mantle abundances and find that the Martian core must be S-rich, virtually independent of the type of bulk composition considered and the *P-T* conditions during core-mantle differentiation of Mars. The core contains at least 7 wt % S and may be up to stoichiometric FeS in composition, depending on which *P-T* conditions (and bulk compositions) are assumed. If bulk Mars was formed from chondritic building blocks, the core S content is constrained to 13.5 ± 3.5 wt.%, in good agreement with geophysical models of the Martian interior and with measured siderophile element depletions in SNC meteorites. Our calculations yield O contents for the Martian core of < 4 wt.%, with the highest concentrations for the highest *P-T* conditions of Martian core formation. Carbon contents in the Martian core are expected to be low (< 1.4 wt.%) given the abundance of C in chondritic meteorite groups. The calculated solubility limit for C in Fe–Ni–S alloys is higher than calculated core C contents in virtually all cases, suggesting the Martian primitive mantle is not graphite saturated if the bulk Mars C budget is (close to) chondritic.

The estimated depletions of volatile elements Se and Te in the Martian interior can be reconciled easily with formation of a Martian S-rich core. This implies that these volatile elements may not have been lost from Mars by degassing in Mars early history.

The calculated Martian core S contents cannot be used to distinguish between the two different proposed modes of core crystallization, but do suggest the Martian core may still be fully liquid today.

1. Introduction

The composition of planetary cores is of interest due to the constraints it imparts on core formation models, core dynamo activity and the volatile element inventory of planetary bodies. Besides major elements Fe and Ni, light elements including O, C, Si, H and S may partition into planetary cores too, depending on the pressure (*P*), temperature (*T*), and oxygen fugacity (fO_2) during core formation, as well as the type of bulk planet composition considered (e.g., Rubie et al., 2004; Frost et al., 2010; Ricolleau et al., 2011; Tsuno et al., 2011; 2013; Boujibar et al., 2014; Chi et al., 2014; Fischer et al., 2015; Knibbe and Van Westrenen, 2016; Steenstra et al., 2017a,b; Clesi et al., 2018).

In this study, a synthesis is provided of constraints on light element abundances in Mars. We focus on S, C, and O as the pressure in the

centre of Mars is too low for H to be incorporated (Clesi et al., 2018), and the fO_2 in Mars is too high to incorporate Si in its core (Ricolleau et al., 2011). Many studies have previously suggested that the Martian core is S-rich (> 10 wt% S), based on considerations of siderophile element depletions in the Shergottite–Nahklite–Chassignite (SNC) Martian meteorite suite (e.g., Righter and Drake, 1996; Righter and Chabot, 2011; Rai and van Westrenen, 2013; Yang et al., 2015), bulk compositional considerations (e.g., Wänke and Dreibus, 1994; Lodders and Fegley, 1997; Sanloup et al., 1999; Taylor, 2013), the current physical state of the Martian core (e.g., Schubert and Spohn, 1990; Stewart et al., 2007) and from the Martian moment of inertia and other geophysical constraints (Khan and Connolly, 2008; Konopliv et al., 2011; Rivoldini et al., 2011; Khan et al., 2017). In contrast, Gaillard and Scaillet (2009) proposed a S-poor Martian core that

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contains only < 1.2 wt% S based on thermochemical calculations related to multi-component gas-melt equilibria at room pressure conditions, and assuming a bulk Mars S content of 0.35 wt%. Wang and Becker (2017) used qualitative consideration of the metal-silicate partitioning behaviour of S and Zn/S volatility systematics of SNC meteorites to propose that the Martian core contains 3 to 10 wt% S.

Oxygen partitions into Fe-rich alloys at relatively oxidizing conditions and/or at high P - T conditions (e.g., Rubie et al., 2004; Frost et al., 2010; Ricolleau et al., 2011; Tsuno et al., 2011; 2013; Fischer et al., 2015), and the O content of the Martian core has been estimated at 1 to 8 wt.% (Rubie et al., 2004; Asahara et al., 2007; Tsuno et al., 2011). Finally, C has been suggested to be a potentially important light element in the Martian core, given its siderophile behaviour at the P - T conditions relevant for Martian core formation (e.g., Chi et al., 2014; Li et al., 2017).

To date, the effects of simultaneous variations of the metal-silicate partition coefficients (D) of both S and O with P - T and composition (Ricolleau et al., 2011; Tsuno et al., 2013; Boujibar et al., 2014; Suer et al., 2017) have not been assessed quantitatively for Mars. Here, we synthesise constraints on the expected light element composition of the Martian core using these recently reported high-pressure models describing the metal-silicate partitioning of C, S and O for different P - T scenarios of Martian core formation and different bulk Mars compositions. A new model calibration is developed to predict the solubility of C in Fe-S bearing alloys. These results are used to calculate the maximum Martian core C content for the different P - T scenarios considered.

Implications of our synthesis are focused primarily on the metal-silicate partitioning systematics of volatile siderophile elements Se and Te, in conjunction with recently reported Martian mantle abundances of these elements. Se and Te are considered an important tracer for the addition of a late veneer and/or the chemical composition of such a late veneer (Wang and Becker, 2017). Wang and Becker (2017) recently proposed from new analyses on SNC meteorites that Se and Te systematics of the SNC meteorite suite most likely reflect a signature of core-mantle equilibrium in Mars. To test this hypothesis, we explore to what extent the absolute S, Se and Te abundances in the Martian mantle, as well as their ratios, may be explained by core formation processes given the light element inventory of the Martian core suggested by our synthesis. This exercise yields additional constraints on the volatile element inventory of Mars. Finally, an assessment is made of the geophysical and thermochemical implications of this synthesis.

2. Methods

2.1. Modelling of the geochemical behaviour of siderophile elements

Modelling of plausible Martian core compositions requires predictive expressions of the metal-silicate partitioning behaviour of C, O, and S. As shown below, a predictive model for the partitioning of Ni is also required because Ni affects the behaviour of these light elements. The metal-silicate partitioning of S as a function of P - T and composition is described using the work of Suer et al. (2017), who determined the metal-silicate partitioning behaviour of S across a wide P - T range:

$$\log D_S^{\text{met-sil}} = -3.30(\pm 0.47) + \frac{3000(\pm 1023)}{T(K)} + 33(\pm 11) \frac{P(\text{GPa})}{T(K)} + \log x_{\text{FeO}}^{\text{silicate}} - \log C_S + 14(\pm 2) \ln(1 - x_{\text{O}}^{\text{metal}}) \quad (1)$$

where $D_S^{\text{met-sil}}$ is the metal-silicate partition coefficient of S, T is temperature, P is pressure, $x_{\text{FeO}}^{\text{silicate}}$ is the molar fraction of FeO in the silicate melt and $x_{\text{O}}^{\text{metal}}$ is the molar fraction of oxygen in the metallic phase. Parameter C_S is the sulfide capacity and incorporates the effect of f_{O_2} on S partitioning. It is calculated using the silicate melt compositional parameters reported in Haughton et al. (1974). The model of Suer et al. (2017) is calibrated for P - T conditions ranging from 1–91 GPa and 1873–4100 K.

For O we use the predictive model for O partitioning from Ricolleau et al. (2011):

$$\log K_O^{\text{met-sil}} = 2.19(\pm 0.53) - \frac{10731(\pm 1329)}{T(K)} + 33(\pm 18) \frac{P(\text{GPa})}{T(K)} \quad (2)$$

This model is calibrated for P - T conditions ranging from 2–21 GPa and 2273–2873 K. The exchange coefficient $\log K_O^{\text{met-sil}}$ can be converted to the metal-silicate partition coefficient of O ($D_O^{\text{met-sil}}$) by considering the following expression:

$$\log D_O^{\text{met-sil}} = 2.19(\pm 0.53) - \frac{10731(\pm 1329)}{T(K)} + 33(\pm 18) \frac{P(\text{GPa})}{T(K)} + \log \left(\frac{x_{\text{FeO}}^{\text{silicate}}}{x_{\text{Fe}}^{\text{metal}}} \right) - \log \left(\frac{\gamma_{\text{O}}^{\text{metal}}}{\gamma_{\text{Fe}}^{\text{metal-1}}} \right) \quad (3)$$

This approach requires quantification of the activity coefficient (γ) of Fe and O in the metal alloy as a function of P - T and composition. These values were calculated for each modelled composition using the metal-activity calculator (Wade and Wood, 2005).

In order to constrain maximum C concentrations in the Martian core, a predictive model for describing the solubility of C in Fe-Ni-S alloys is required. To obtain a predictive model as a function of P - T and metal composition, we parameterized previously published solubility data of C in Fe(S) alloys (Wang et al., 1991; Wood, 1993; Tsymbulov and Tsemekhman, 2001; Dasgupta et al., 2013; Deng et al., 2013; Li et al., 2015; Tsuno and Dasgupta, 2015; $n = 137$) to the following equation (e.g., Wada and Pehlke, 1985):

$$CCGS_{\text{metal}}(\text{wt. \%}) = a + b(1/T) + c(P/T) + d \log(100 - Ni_{(\text{wt. \%})}) + e \log(100 - S_{(\text{wt. \%})}) \quad (4)$$

where $CCGS_{\text{metal}}$ is the carbon concentration at graphite saturation and terms d and e incorporate the possible effects of Ni and S on C solubility.

To quantify the effect of Ni on the outcome of the models, the predictive model from Fischer et al. (2015) was used to calculate the expected $D_{\text{Ni}}^{\text{met-sil}}$ values during Martian core formation as a function of P - T , using Eqs. (5)–(6):

$$\log K_{\text{Ni}}^{\text{met-sil}} = 0.46(\pm 0.16) + \frac{2700(\pm 300)}{T(K)} - 61(\pm 6) \frac{P(\text{GPa})}{T(K)} \quad (5)$$

where $\log D_{\text{Ni}}^{\text{met-sil}}$ is derived using Eq. (6):

$$\log D_{\text{Ni}}^{\text{met-sil}} = 0.46(\pm 0.16) + \frac{2700(\pm 300)}{T(K)} - 61(\pm 6) \frac{P(\text{GPa})}{T(K)} + \log \left(\frac{x_{\text{FeO}}^{\text{silicate}}}{x_{\text{Fe}}^{\text{metal}}} \right) - \log \left(\frac{\gamma_{\text{Ni}}^{\text{metal}}}{\gamma_{\text{Fe}}^{\text{metal}}} \right) \quad (6)$$

The model of Fischer et al. (2015) for Ni partitioning is based on metal-silicate partitioning data obtained from 1873–5700 K and 5–100 GPa. Activity coefficients γ for Ni and Fe in Eq. (6) were calculated for each modelled composition using the metal-activity calculator (Wade and Wood, 2005).

To compare the $CCGS_{\text{metal}}$ values with possible C contents of the Martian core, we model the C content of the Martian interior as a function of P - T using the predictive equation from Li et al. (2016):

$$\log D_C^{\text{met-sil}} = \frac{2920}{T(K)} + 115 \frac{P(\text{GPa})}{T(K)} - 0.66 \text{ nbo/t} - 0.15 \Delta \text{IW} - 0.17 x_{\text{H}_2\text{O}}^{\text{silicate}} - 2.9 x_{\text{Ni}}^{\text{metal}} + 2.26 \quad (7)$$

This model is based on metal-silicate partitioning data for C obtained at 1–8 GPa and 1673–2473 K. In these calculations we assume a nbo/t value of 2.5 for the Martian mantle based on estimates of the bulk composition of the Martian mantle (Elkins-Tanton, 2008; Righter and Chabot, 2011; Rai and van Westrenen, 2013), where nbo/t is the ratio of nonbridging oxygens and tetrahedrally coordinated cations (Mysen et al., 1982). The metal Ni content in Eq. (7) is derived from Eq. (6) describing Ni partitioning.

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