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Core-mantle differentiation in Mars

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[1] The physical and chemical conditions under which Martian core formation took place are not well constrained. We modeled the pressure, temperature, and oxygen fugacity conditions under which it would be possible to match the inferred depletions of moderately siderophile elements Ni, Co, W, Mo, Ga, P, and Ge in the Martian mantle, using new constraints on their metal-silicate partitioning behavior. Using literature metal-silicate partitioning data, we characterize the dependence of the metal-silicate partition coefficients (D) on the temperature, pressure, oxygen fugacity, and composition of the silicate melt and the metal using a uniform parameterization approach for each element. Our results show that it is impossible to simultaneously account for the Martian mantle depletions of moderately siderophile elements if the Martian core sulfur content exceeds 10.5 wt% at reducing conditions (1 log unit below the iron-wüstite (IW) buffer). At 10.5 wt% core S, the conditions that best satisfy Martian mantle abundances of the seven siderophile elements are a mean pressure of 13(\pm 1) GPa at 2330 K, corresponding to the presence of a magma ocean at least 1000 km deep during Martian core formation. More oxidizing conditions than the iron-wüstite buffer as suggested by iron meteorites are inconsistent with mantle siderophile element abundances. Extension of our approach to the highly siderophile elements Ru, Pd, Re, Ir, and Pt shows that their Martian mantle abundances are orders of magnitude too high to be accounted for by metal-silicate equilibration at high pressure and high temperature in a magma ocean, requiring a “late veneer” stage after core formation.

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1. Introduction

[3] In the absence of mantle samples, Martian mantle geochemistry has been largely reconstructed based on the elemental and isotopic composition of SNC (Shergotty-Nakhla-Chassigny) meteorites that reflect the chemical composition of their source regions in the Martian interior [e.g., *McSween*, 1994; *Folco et al.*, 2000; *Taylor et al.*, 2002; *Treiman et al.*, 2000; *Jones*, 2003; *Kleine et al.*, 2004; *Anand et al.*, 2008]. These meteorites exhibit quite diverse and highly fractionated compositions and ages. Most have ages of 1.3 Ga and younger [*Nyquist et al.*, 2001, 2009; *Borg et al.*, 2003; *Misawa et al.*, 2006; *Shafer et al.*, 2010]. They have distinctive FeO/MnO ratios and differ in oxygen isotopic composition from the Earth and Moon. Similarities between the isotopic compositions of nitrogen and the noble gases xenon and argon trapped within impact-produced glasses present in some shergottites and the Martian atmosphere as determined by the Viking Landers [*Nier and McElroy*, 1977; *Owen et al.*, 1977] strongly suggest that these are Martian samples [*McSween and Treiman*, 1998; *Bogard et al.*, 2001; *Nyquist et al.*, 2001; *McSween*, 2002].

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[4] The Martian mantle composition proposed by *Wänke and Dreibus* [1988] is based on elemental abundance correlations in the SNC meteorites. Compared to the terrestrial mantle, many moderately siderophile elements including manganese, chromium, tungsten, and phosphorus are estimated to be present in relatively higher abundances in Martian meteorites [*Dreibus and Wänke*, 1985; *Wänke and Dreibus*, 1988; *Halliday et al.*, 2001]. This could indicate more oxidizing, volatile- and sulfur-rich conditions were present during core-mantle differentiation in Mars [*Halliday et al.*, 2001]. *Wänke and Dreibus* [1988] proposed mixing together oxidized components containing volatiles in CI chondrite proportions with reduced components during accretion to explain this composition. The oxygen isotope signature in SNC meteorites being markedly distinct from that of terrestrial and lunar samples, two other geochemical models for Mars were proposed based on matching the oxygen isotopic composition of SNC meteorites by mixing various classes of chondrites. *Lodders and Fegley* [1997] proposed a combination of H, CV, and CI chondrites while *Sanloup et al.* [1999] proposed a combination of H and EH chondrites, in proportions appropriate to match the oxygen isotope signature of the Martian meteorites. They used a mass balance approach to derive the bulk elemental compositions from the mean compositions of these chondrite groups. These Martian mantle compositional models differ in their high-pressure normative mineralogy despite having some chemical characteristics in common. These models [*Wänke and Dreibus*, 1988; *Lodders and Fegley*, 1997;

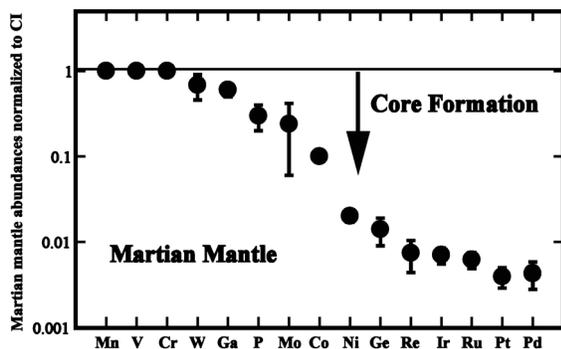


Figure 1. Depletion factors of siderophile elements estimated relative to CI chondrites and a refractory lithophile element for the Martian mantle. Estimates are based on *Richter and Chabot* [2011] and *Brandon et al.* [2012].

Sanloup et al., 1999] suggest that the Martian core comprises 20.6–23% of the mass of Mars with the sulfur content of the core ranging between ~10 and 16 wt%. In contrast, a far lower value of 0.4 wt% S has been suggested for the Martian core on the basis of element partitioning between olivine, molten sulfide, and silicate melt phases [*Gaetani and Grove*, 1997].

[5] It was previously established that after accretion, Mars underwent very fast and large-scale differentiation into a metallic core and a silicate mantle [*Kleine et al.*, 2002, 2004; *Foley et al.*, 2005; *Nimmo and Kleine*, 2007; *Dauphas and Pourmand*, 2011]. As a result of the segregation of an iron-rich core from the silicate mantle, the majority of siderophile elements are strongly partitioned into the core, leaving the silicate mantle and crust relatively depleted in those elements (Figure 1). Since the partitioning of these elements into metallic phases is governed by their metal/silicate partition coefficients (D) and the pressure-temperature-composition conditions during core formation, the measured or estimated abundances of these elements in Martian silicate reservoirs can, in principle, be used to constrain core formation conditions.

[6] There is considerable disagreement between the different Martian core formation models proposed so far, as regards the mean pressure and temperature conditions under which core-mantle differentiation occurred in Mars. Previous attempts [*Treiman et al.*, 1987; *Kong et al.*, 1999; *Richter and Drake*, 1996; *Richter et al.*, 1998; *Richter and Chabot*, 2011] suggest a very wide range of T (1900–2500 K) and P conditions (1 bar to 14 GPa) at which core-forming metallic melts equilibrated with the silicate phase to establish the measured siderophile element abundances in Martian meteorites.

[7] *Treiman et al.* [1987] suggested that metal-silicate equilibration at low pressure was adequate to explain the abundance of most siderophile elements in the shergottite parent body mantle. *Kong et al.* [1999] on the basis of elemental analysis of over 24 elements in six SNC meteorites and experimentally derived metal-silicate partition coefficients of the moderately siderophile elements Fe, Ni, Co, W, Mo, and Ga concluded that equilibrium between core-forming metal and silicates in Mars was established at low-pressure conditions (<1 GPa) and at high temperatures (>2473 K). In contrast, *Richter and Drake* [1996] and *Richter et al.* [1998] modeled the P - T - fO_2 conditions during

Martian core formation and suggested metal-silicate equilibration at ~1900 K and conditions of 6 GPa and 7.5 GPa, respectively. Recently, *Richter and Chabot* [2011] presented a new model for core formation in Mars that proposed equilibration of molten metal with a largely molten Martian mantle at 14 ± 3 GPa in a magma ocean scenario. This model is based on new estimates of Martian mantle siderophile element depletions and uses parameterizations for the metal-silicate partitioning behavior of Ni, Co, W, Mo, P, Ga, V, and Cr from several experimental metal-silicate partitioning studies.

[8] The observed discrepancy between the different Martian core formation models [*Treiman et al.*, 1987; *Richter and Drake*, 1996; *Kong et al.*, 1999; *Richter and Chabot*, 2011] could be due to several reasons. Model outcomes for core formation conditions depend upon multiple factors including (a) estimates for siderophile element depletions in the Martian mantle and of core/mantle mass ratios, (b) the range of the S content for the core of Mars, (c) the experimental metal-silicate partitioning data set used and the range of P - T - fO_2 - X conditions covered by that experimental data set, (d) the type of predictive expression used to parameterize the metal-silicate partition coefficients, and (e) uncertainties related to the regression coefficients associated with the resulting partition coefficient parameterizations. For example, *Kong et al.* [1999] used only low-pressure (<1 GPa) metal-silicate partition coefficients combined with elemental abundance data measured from only six Martian samples. *Richter and Drake* [1996] and *Richter et al.* [1998] used predictive expressions for the metal-silicate partition coefficients derived from a limited data set including several 1 bar partitioning data that was available at the time.

[9] The most recent study by *Richter and Chabot* [2011] used revised estimates of Martian mantle siderophile element abundances based on new meteorite and surface (Mars Exploration Rovers) analyses, but the predictive expressions used to parameterize metal-silicate partition coefficients were not derived using a uniform approach. *Richter and Chabot* [2011] used the empirical approach of *Richter et al.* [2010] to parameterize the metal-silicate partitioning behavior of Ga and P, but they used the parameterizations for V and Cr reported by *Wood et al.* [2008] that were based on a thermodynamic approach. For Ni and Co, the parameterizations were based on only high-pressure (>5 GPa) data from *Kegler et al.* [2008], while for Ga, P, V, and Cr, the same criterion of using only > 5 GPa data was not used. In addition, the *Richter and Chabot* [2011] study assumes a Martian core S content of ~10 wt%.

[10] Here we reexamine whether a consistent set of core formation (P - T - X - fO_2) conditions can be obtained to match the observed siderophile element depletions in silicate Mars, based on recent advances in our understanding of siderophile element metal-silicate partitioning and the latest estimates for siderophile elements depletions in the Martian mantle [*Richter and Chabot*, 2011, and references therein]. We also quantify the effect of varying the assumed core sulfur content and oxygen fugacity on such core formation models.

[11] Constraining the depth of a Martian magma ocean during core-mantle differentiation is important for several other key aspects of early Mars research. Accurate prediction of the mineral phases that are involved in differentiation processes during the magma ocean stage is required to model the

Table 1. Martian Mantle Concentrations of Siderophile Elements and Implied $D(\text{Core/Mantle})$ Values for Mars^a

	Mantle Concentrations	$D(\text{Core/Mantle})$	References ^b
Ni	350–450	155–200	1
Co	65–75	42–50	1
W	0.04–0.2	2.7–18	1
P	300–600	3.1–9.8	1
Mo	0.08–0.6	12–100	1
Ga	8–11	0.35–0.85	1
Ge	0.25–0.85	77–270	2
Pd	1–3	1300–3900	3
Re	0.05–0.35	910–6360	3
Ir	2–4	900–1570	3
Ru	3–5	1000–1660	3
Pt	1.8–3.5	1820–3530	3

^aFrom Ni to Ge, mantle concentrations are given in parts per million, and Pd to Pt are given in parts per billion.

^bReferences: 1, *Richter and Chabot* [2011]; 2, *Richter et al.* [2011]; 3, *Brandon et al.* [2012].

interior constitution and evolution of Mars [*Brandon et al.*, 2000; *Borg and Draper*, 2003; *Richter and Chabot*, 2011] and depends on magma ocean depth. Fractionation between the refractory lithophile-siderophile element pair Hf-W during metal-silicate equilibration in a magma ocean influences the ¹⁸²W in Martian meteorites and is relevant in age dating [*Richter and Shearer*, 2003; *Foley et al.*, 2005; *Kleine et al.*, 2009]. Magma ocean depth is also one of the most important parameters in theoretical and geophysical models for the Martian interior [*Elkins-Tanton et al.*, 2005a, 2005b; *Reese and Solomotov*, 2006; *Debaille et al.*, 2007]. Finally, constraining Martian magma ocean depth influences the interpretation of the observed Martian mantle abundances of the highly siderophile elements (HSEs, i.e., Pd, Re, Os, Ir, Ru, Pt, and Au). Analyses of HSEs in shergottites suggest that their Martian mantle sources have similar HSE abundances to the Earth’s mantle [*Jones*, 2003; *Walker*, 2009; *Brandon et al.*, 2012]. Relatively high HSE abundances in the silicate portion of terrestrial planets have been explained either by high-pressure high-temperature metal-silicate partitioning at the base of a magma ocean (e.g., *Richter et al.* [2008] for Pd) or by invoking the hypothesis that these elements were added in a late veneer which must have occurred after the crystallization of the last Martian magma ocean [*Brandon et al.*, 2012; *Dale et al.*, 2012]. Using the high-pressure high-temperature partitioning behavior of these elements between molten metal and silicate melt, we test whether the estimated Martian depletions of these elements [*Brandon et al.*, 2012] can be explained by core-mantle equilibration in a magma ocean.

2. Approach

[12] Table 1 gives the estimated values of the metal-silicate partition coefficients that would be required to satisfy the Martian mantle depletions for a range of moderately and highly siderophile elements. We combined recently published metal-silicate partitioning data for Ni, Co, W, Mo, P, Ga, and Ge with literature data [*Walker et al.*, 1993; *Thibault and Walter*, 1995; *Li and Agee*, 1996; *Jana and Walker*, 1997; *Chabot and Agee*, 2003; *Wade and Wood*, 2005; *Kegler et al.*, 2008; *Wood et al.*, 2008; *Corgne et al.*, 2008; *Cottrell et al.*, 2009; *Mann et al.*, 2009; *Siebert et al.*,

2011] and characterized the dependence of metal-silicate partition coefficients (D) on temperature, pressure, oxygen fugacity, silicate melt structure and composition, and composition of the metallic phase. We used a uniform approach to derive equations of the following form [*Richter et al.*, 2008]:

$$\log D = a + b(\Delta IW) + c(\text{nbo}/t) + d(1/T) + e(P/T) + f \ln(1 - X_s) + g \ln(1 - X_c) \quad (1)$$

[13] In equation (1), T is the temperature in kelvin and P is the pressure in gigapascal. X_s is the molar fraction of sulfur in the metallic phase, and X_c is the molar value of carbon in the metallic phase. ΔIW is the oxygen fugacity calculated relative to the iron-wüstite (IW) buffer defined by the following equation:

$$\Delta IW = 2 \times \log(a_{\text{FeO}}/a_{\text{Fe}}) \quad (2)$$

where a_{FeO} is the measured mole fraction of FeO in the silicate phase and a_{Fe} is the activity of the Fe in the metallic liquid. The melt structural parameter nbo/t [*Mysen et al.*, 1982] is used as a proxy for silicate melt composition and structure. It is a measure of the degree of polymerization and was calculated as the ratio

$$\text{nbo}/t = [2 \times \text{O} - 4 \times \text{T}]/\text{T} \quad (3)$$

where $[2\text{O} - 4\text{T}]$ represents the number of nonbridging oxygen ions, i.e., oxygen ions that are directly bonded to tetrahedrally coordinated cations, and T represents the number of tetrahedrally coordinated cations in the silicate melt. This parameter ranges from 0 (fully polymerized) to 4 (fully depolymerized) with terrestrial basalt having a value of ~ 1 , komatiite 1.7, and garnet peridotite 2.8. Although nbo/t is too simple a term to define all properties of silicate melt [*O’Neill and Eggins*, 2002], it remains the best [*Richter and Drake*, 1999; *Wood et al.*, 2008; *Cottrell et al.*, 2009; *Mann et al.*, 2009; *Siebert et al.*, 2011] and serves the practical purpose of describing complex silicate melt compositions under a single term. *Richter and Drake* [1999] demonstrated that regressing the effect of melt composition against a proxy for activity such as melt oxide mole fractions rather than nbo/t does not lead to significant improvement in parameterization.

[14] All partitioning data were parameterized using a uniform approach [*Richter et al.*, 2008] to derive predictive expressions for the metal-silicate partitioning behavior of Ni, Co, W, Ga, P, Mo, and Ge. *Kegler et al.* [2008] showed that the P dependencies for the metal/silicate partitioning behavior of the elements Ni and Co were different between the lower pressure regime (≤ 5 GPa) and the higher-pressure regime (≥ 5 GPa) regressions. We recently came to the same conclusion for W, Mo, P, V, and Cr (N. Rai and W. van Westrenen, Lunar core formation: New constraints from metal-silicate partitioning of siderophile elements, submitted to *Earth and Planetary Science Letters*, 2013). Using low-pressure regressions (< 6 GPa), we did not find any solutions for Ni, Co, W, Ga, and Ge in the pressure range 0–5 GPa that could simultaneously satisfy the Martian mantle abundances of these elements. Hence, our parameterizations are based on partitioning data obtained at pressures between 6 GPa and 25 GPa, covering the range of pressures in silicate Mars. Table 2 lists the resulting parameterizations used in this study, including uncertainties.

Table 2. Results of Multivariate Linear Regressions to the Compiled Partitioning Data for Ni, Co, W, P, Mo, Ga, Ge, Ru, Pd, Re, Ir, and Pt^a

	a	b	c	d	e	f	g
Ni	1.3 (0.29)	-0.48 (0.05)	-	2011 (614)	-84 (12)	-	-
Co	0.84 (0.2)	-0.43 (0.03)	-	1766 (429)	-49 (9)	-	-
W	2.00 (0.9)	-0.98 (0.16)	-0.96 (0.14)	1866 (1631)	-96 (23)	3.08 (1.41)	-2.80 (0.58)
P	-0.003 (0.56)	-0.99 (0.19)	-0.21 (0.08)	45 (18)	130 (88)	-	3.81 (0.49)
Mo	0.78 (0.27)	-0.83 (0.12)	-0.42 (0.05)	4837 (608)	-77 (10)	-0.61 (0.42)	-
Ga	-3.68 (0.87)	-0.76 (0.15)	-	7181 (1699)	-64 (38)	-11.20 (5.04)	-
Ge	-1.47 (0.07)	-0.29 (0.04)	-0.18 (0.02)	8830 (234)	-20 (05)	1.95 (0.09)	-
Ru ^b	0.64 (0.27)	-0.5	-	12,760 (32)	63 (47)	-	-
Pd ^b	0.10 (0.14)	-0.25	-	10,235 (126)	-103 (25)	-	-
Re ^b	-0.04 (0.15)	-0.5	-	12,760	-26 (28)	-	-
Ir ^b	-0.97 (0.64)	-0.5	-	17,526 (55)	-19 (117)	-	-
Pt ^b	-4.08 (0.15)	-0.25	-	23,824 (211)	-17 (29)	-	-

^aUncertainty on regression coefficients is one standard error (given in parentheses).

^bValues based on the regressions of the 6–18 GPa metal-silicate partitioning data from *Mann et al.* [2012], assuming fixed valence states of +1 for Pt and Pd and +2 for Re, Ir, and Ru.

[15] Using the parameterizations derived from fitting the metal-silicate partition coefficient data sets for each element to equation (1) (Table 2), we model the core formation conditions in Mars assuming the proposed bulk Mars chemical composition of *Lodders and Fegley* [1997]. We use a Monte Carlo approach (N. Rai and W. van Westrenen, Lunar core formation: New constraints from metal-silicate partitioning of siderophile elements, submitted to *Earth and Planetary Science Letters*, 2013) to sample the parameter space in terms of pressure and oxygen fugacity for a specified mantle composition ($nbo/t \sim 2.55$) and Martian mantle liquidus [*Elkins-Tanton*, 2008; *Righter and Chabot*, 2011]. During core-mantle differentiation in a magma ocean, metal would settle at the base of the magma ocean, which must be saturated in crystals and should therefore lie at or below the silicate liquidus [*Wade and Wood*, 2005]. Hence, we forced the temperature to lie on the Martian mantle liquidus in our models [*Elkins-Tanton*, 2008; *Righter and Chabot*, 2011]. We calculate the number of acceptable solutions, taking into account the uncertainty in the regression coefficients of our D parameterizations (Table 2) and in the permissible range of core/mantle abundance ratios ($D(\text{core/mantle})$; Table 1) valid for Mars. The numbers of valid solutions are calculated by allowing 10,000 iterations of the Monte Carlo runs for each 2 GPa interval in pressure. The domain for possible inputs in pressure was defined to lie between 6 and 20 GPa.

[16] Oxybarometry of SNC group of meteorites that are thought to represent Martian crustal rocks records a wide range of oxygen fugacities [*McSween*, 1994; *Halliday et al.*, 2001; *Hirschmann and Withers*, 2008; *Wadhwa*, 2008]. The basaltic shergottites show a range of fO_2 values from ~ 2 log units above the IW buffer to slightly below the IW buffer, whereas the cumulate nakhlites (and chassignites) are relatively oxidized at ~ 3 –4 log units above the IW buffer [*Wadhwa*, 2008]. Following early core-mantle and crust-mantle differentiation on Mars, it is likely that the oxygen fugacity of the depleted Martian mantle is close to that of the IW buffer [*Hirschmann and Withers*, 2008; *Wadhwa*, 2008]. Oxygen fugacity estimates for the Martian mantle can also be made based on consideration of the simple redox reaction $FeO = Fe + 0.5 O_2$, which represents the reduction of iron as it transfers from its normal oxidation state two in the silicate melt to oxidation state zero in the metal. Using estimates of FeO in the Martian mantle (18 ± 2 wt%) and of Fe in the core (76–80 wt%) [*Wänke and Dreibus*, 1988;

Lodders and Fegley, 1997; *Sanloup et al.*, 1999; *Taylor*, 2012] and the simple relationship defined by equation (2) as a proxy for fO_2 , we obtain a value of $\Delta IW = 1.3(\pm 0.2)$. A range in oxidation conditions from 1 log unit above the IW buffer to relatively more reduced conditions of $\Delta IW = 1.5$ was considered realistic here, based on these estimates.

[17] Geochemical models for Mars differ in the amount of S in the Martian mantle and core [*Wänke and Dreibus*, 1988; *Lodders and Fegley*, 1997; *Sanloup et al.*, 1999] but generally agree that the Martian core has high (between ~ 10 and 16 wt%) S concentrations consistent with the limited depletion in volatile elements in Mars [*Longhi et al.*, 1992]. In contrast, recent experimental partitioning studies reporting the effects of variations in the fugacities of oxygen and sulfur on the partitioning of first series transition metals (V, Cr, Mn, Fe, Co, Ni, and Cu) and W among coexisting sulfide melt, silicate melt, and olivine yielded a far lower concentration of ~ 0.4 wt% S in the Martian core [*Gaetani and Grove*, 1997]. We explore the effect of varying the S content of the Martian core between 0 and 16 wt% on the model outcome. In the model, we do not consider carbon to be present in the Martian core. Finally, with regard to the highly siderophile elements, we use the predictive expressions for $D(\text{metal/silicate})$ for Ru, Pd, Re, Ir, and Pt at pressure conditions between 6 and 18 GPa, derived from the recent experimental study by *Mann et al.* [2012] to probe whether metal-silicate partitioning during core-mantle differentiation in a magma ocean scenario can account for the estimated abundances of these elements in the Martian mantle.

3. Effect of Oxygen Fugacity During Core-Mantle Equilibration in Mars

[18] Our calculations show that for a Martian core with $X_S = 0.25$ (corresponding to 16 wt% S in the core), with oxygen fugacities in the range $\Delta IW = -1$ to $\Delta IW = +1$, there is no overlap in the P - T solution space which could simultaneously satisfy the Martian mantle abundances of all seven moderately siderophile elements (Ni, Co, W, Mo, Ga, P, and Ge) considered here. The same conclusion is drawn for any core S content higher than $X_S = 0.17$ (10.5 wt% S). Figures 2a through 2c show how the solution space for Ni, Co, W, P, Mo, Ge, and Ga varies between 6 and 20 GPa along the Martian mantle liquidus, at $nbo/t = 2.55$ for a Martian core with $X_S = 0.17$, for oxygen fugacities of

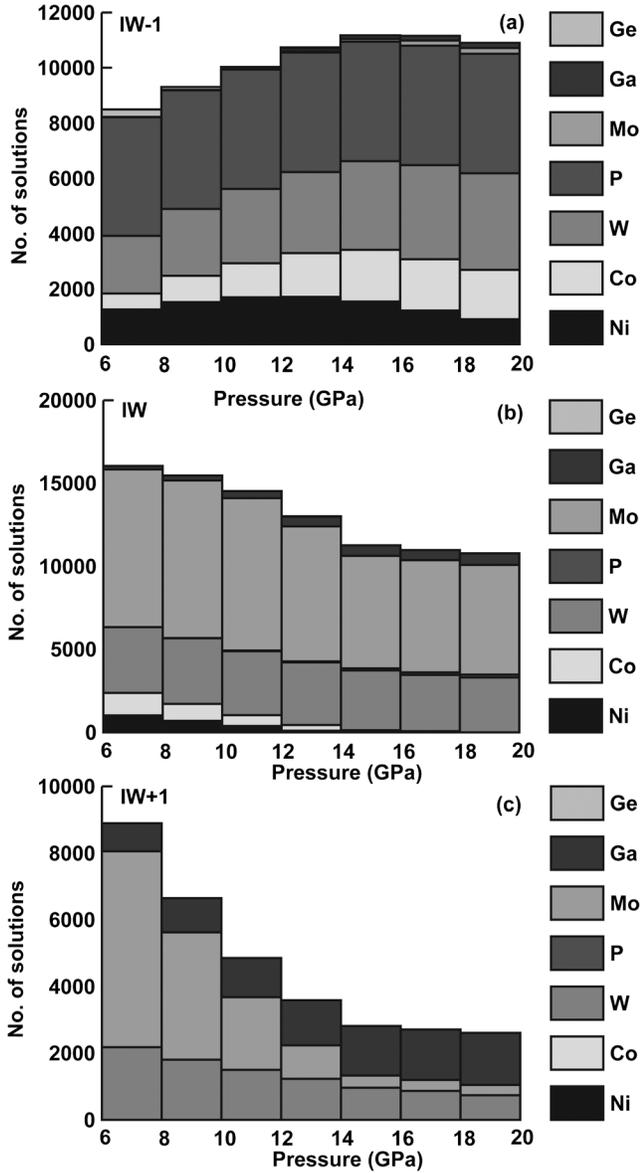


Figure 2. The solution space for Ni, Co, W, Mo, P, Ga, and Ge in the pressure range of 6–20 GPa along the Martian magma ocean liquidus in a single-stage core formation scenario for a Martian core containing 10.5 wt% S (a) for oxygen content of the Martian mantle corresponding to $\Delta IW - 1$, (b) for oxygen content of the Martian mantle corresponding to ΔIW , and (c) for oxygen content of the Martian mantle corresponding to $\Delta IW + 1$.

$\Delta IW - 1$, ΔIW , and $\Delta IW + 1$, respectively. In Figure 2a ($fO_2 = \Delta IW - 1$), we find the seven-element solution space to be restricted to the 12–14 GPa pressure range, as there are no solutions for Mo at pressures below 12 GPa and none for Ge above 14 GPa. Our calculations show that at $X_s = 0.17$, with oxygen fugacities in the range $\Delta IW - 1.5$ to $\Delta IW - 0.5$, there is an overlap in the P - T solution space at 13 ± 1 GPa and 2330 K which could simultaneously satisfy the Martian mantle abundances of all seven siderophile elements considered here. For a similar sulfur content of the Martian core but under conditions more reducing than $\Delta IW - 1.5$, we do not find any further overlap in the seven-element solution space

as there are no valid solutions that can satisfy the Martian mantle depletion of Mo under such conditions.

[19] This minimum oxygen fugacity value ($\Delta IW - 1.5$) constrains the lower bound for the Martian mantle FeO content at ~ 16 wt%. For conditions more oxidizing than $\Delta IW - 1$, the FeO content of the Martian mantle would have to be more than 20 wt% which exceeds the estimated range (14–20 wt%) based on SNC meteorites and their proposed parent magmas [Agee and Draper, 2004]. Our results based on moderately siderophile element behavior in the Martian interior are therefore in excellent agreement with the current range of estimates of FeO in the Martian mantle and of Fe in the Martian core.

[20] Figure 3 shows the model-predicted $\log D(\text{metal/silicate})$ values for Ni, Co, W, Mo, P, Ga, and Ge for specific core-mantle equilibration conditions at 13 GPa, corresponding to a Martian mantle liquidus temperature of 2330 K at $\Delta IW - 1$, $X_s = 0.17$ (10.5 wt% S in the core), and $nbo/t = 2.55$ based on the bulk Martian mantle composition assumed in this work [Lodders and Fegley, 1997], along with the $\log D(\text{metal/silicate})$ values calculated on the basis of the observed Martian mantle depletion of these elements for a 22 wt% Martian core. We find good agreement between the model-predicted values and the required values for Ni, Co, W, Mo, P, Ga, and Ge. This indicates that the Martian mantle depletions of these seven elements can be satisfied simultaneously if a molten iron-rich metal containing 10.5 wt% S segregated at a depth equivalent to 13 ± 1 GPa in a completely molten Martian magma ocean. This estimate for the depth of the Martian magma ocean is slightly lower than the value of 14 ± 3 GPa reported by Righter and Chabot [2011] for identical core sulfur content, oxygen fugacity, and nbo/t conditions using six elements and a combination of different parameterization approaches.

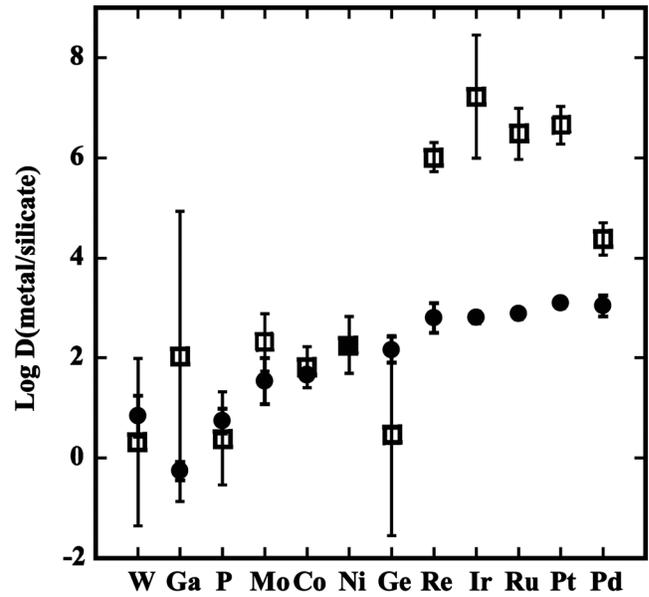


Figure 3. The $\log D(\text{metal/silicate})$ for Ni, Co, W, Mo, P, Ga, Ge, Ru, Pd, Pt, Ir, and Re. Shown by solid circle symbols are values based on the estimated Martian mantle depletions for a 22 wt% Martian core. The predicted values based on regressions given in Table 2 for conditions of 13 GPa, 2330 K at $\Delta IW - 1$, and $nbo/t = 2.55$ are shown by open square symbols.

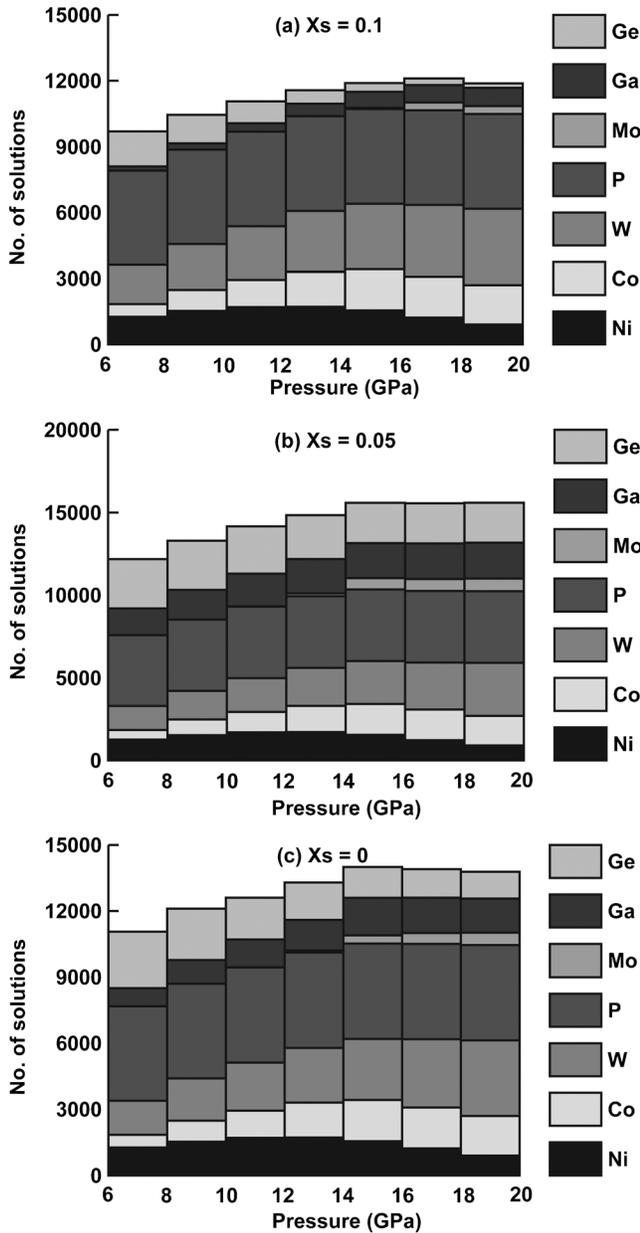


Figure 4. The solution space for Ni, Co, W, Mo, P, Ga, and Ge in the pressure range of 6–20 GPa along the Martian magma ocean liquidus in a single-stage core formation scenario for oxygen content of the Martian mantle corresponding to $\Delta IW - 1$ for a Martian core containing between 0 and 16 wt % S. (a) For a Martian core with S mole fraction (X_s)=0.1. (b) For a Martian core with S mole fraction (X_s)=0.05. (c) For a pure iron Martian core.

[21] In Figure 2b for an oxygen fugacity at the IW buffer, we do not find any acceptable solution, as there are no solutions for Ge. Problems mount further at higher oxygen fugacity. As shown in Figure 2c, for fO_2 conditions of $\Delta IW + 1$, we find that there are no solutions for Ge, Ni, Co, and P in the entire pressure range of 6–20 GPa. We conclude that oxidizing conditions such as measured for the N and C meteorites [Wadhwa, 2008] are inconsistent with an equilibrium core formation scenario at high X_s .

4. Effect of Variable Amounts of S in the Martian Core

[22] Figures 4 and 5 illustrate how the solution space for Ni, Co, W, P, Mo, Ge, and Ga changes in response to a change in the assumed S content of the Martian core. Figure 4 shows how the solution space for each of the seven elements varies between 6 and 20 GPa along the Martian mantle liquidus at $nbo/t=2.55$ for values of mole fraction of S in the Martian core corresponding to $X_s=0.1$, $X_s=0.05$, and $X_s=0$, all at an oxygen fugacity of 1 log unit below the IW buffer.

[23] In Figure 4a ($X_s=0.1$, corresponding to 6 wt % S in the core), we find the seven-element solution space to be restricted to pressures above 12 GPa, as there are no solutions for Mo at pressures below 12 GPa. At the high-pressure end, the seven-element solution space is no longer limited to a maximum of 14 GPa as the solution space for Ge is expanded to higher pressures. Lowering the S content of the core further at constant oxygen fugacity of 1 log unit below the IW buffer, in Figure 4b ($X_s=0.05$, corresponding to 3 wt % S in the core), we start to find solutions for Mo at pressures below 12 GPa and find an overlap for all seven elements at a wide range of pressures (10–20 GPa). In Figure 4c for a pure iron Martian core without any S, still at an oxygen fugacity of 1 log unit below the IW buffer, we again find an overlap in the solution space for all seven elements between 10 and 20 GPa. Overall, we find that while there is a decrease in the number of solutions for W with decreasing S content of the Martian core, the solution space for Ge, Ga, and Mo expands with decreasing S content.

[24] We assessed how the extent of the solution space was affected by increasing the oxygen fugacity. We found that at $\Delta IW + 1$, no P - T conditions can be found that can simultaneously satisfy the abundances of Ni, Co, W, P, Mo, Ge, and Ga, even if the S content of the Martian core is decreased to zero. However, for oxygen fugacities at the IW buffer, we do find an overlap in the solution spaces of all seven elements between 8 and 10 GPa if the S content of the Martian core is decreased to 6 wt % ($X_s=0.1$) (Figure 5a). Phosphorous defines the lower bound for the pressure conditions with no solutions below 8 GPa, and Ge defines the upper bound with no solutions above 10 GPa in pressure. With a further decrease in the S content of the Martian core to 3 wt % ($X_s=0.05$) and 0 wt % ($X_s=0$) at the IW buffer, the overlap in the seven-element solution space expands to lie between 8 and 12 GPa with P and Ge still bracketing the lower and upper limits of the overlap in the solution space in pressure (Figures 5b and 5c). Our results thus suggest a clear trade-off between the effects of decreasing the S content of the Martian core and increasing the oxygen fugacity of the Martian interior. If the Martian mantle fO_2 during core formation lies at ΔIW , the S content in the Martian core cannot be more than 6 wt %; if the Martian mantle fO_2 during core formation lies at $\Delta IW - 1$, the S content in the Martian core cannot be more than 10.5 wt %. These results are in good agreement with the findings of Tsuno *et al.* [2011], who suggested that the oxygen content of Fe-rich metallic cores would decrease with declining sulfur content. Their study suggests that with a decrease in the S content of the Martian core from 10.5 wt % to 6 wt %, there would also be a decrease in the oxygen content of the core. This would, in turn, imply a more oxidized Martian mantle.

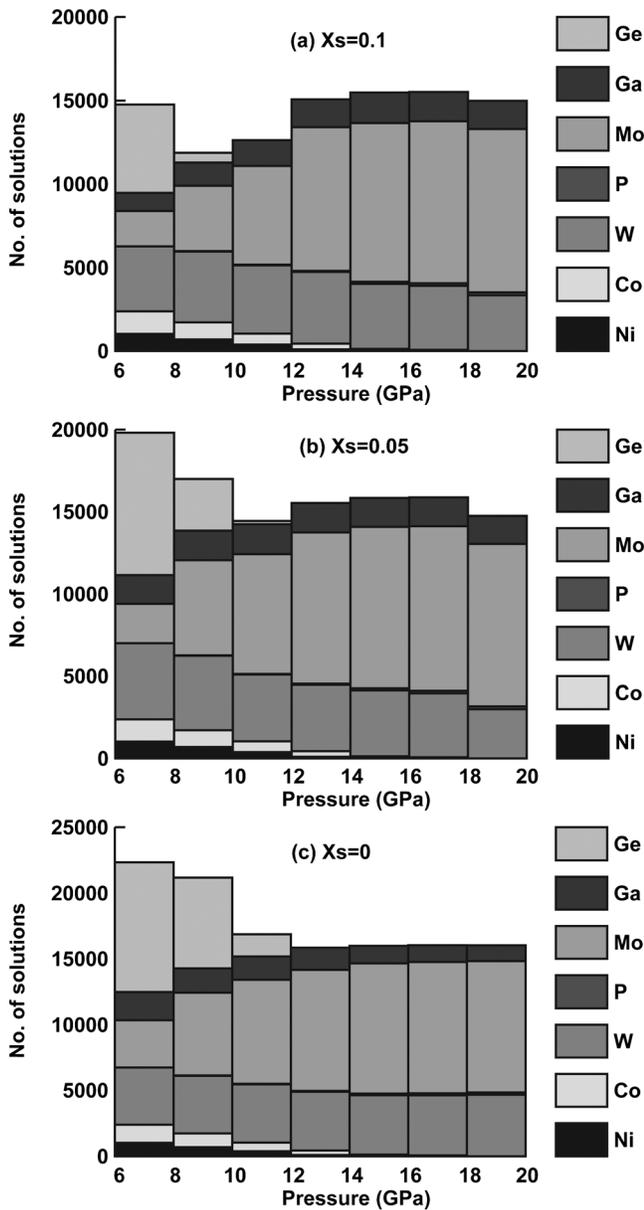


Figure 5. The solution space for Ni, Co, W, Mo, P, Ga, and Ge in the pressure range of 6–20 GPa along the Martian magma ocean liquidus in a single-stage core formation scenario for oxygen content of the Martian mantle corresponding to the IW buffer for a Martian core containing between 0 and 6 wt% S. (a) For a Martian core with S mole fraction (X_S)=0.1. (b) For a Martian core with S mole fraction (X_S)=0.05. (c) For a pure iron Martian core.

5. More Complex Core Formation Models

[25] Although the discussion above shows that the physical conditions of core-mantle differentiation in Mars can be successfully modeled using a range of single-stage equilibrium scenarios, the actual scenario may not have been so simple. In view of current accretion models [Chambers and Wetherill, 1998; Agnor et al., 1999; O’Brien et al., 2006; Rubie et al., 2011], terrestrial planets must have undergone multiple stages of large-scale melting due to impacts during accretion, and magma oceans of varying depths probably

occurred multiple times during this process. Magma ocean depths derived from single-stage core-mantle differentiation models more likely represent average pressure conditions [Wade and Wood, 2005; Frost et al., 2008; Wood et al., 2008; Rubie et al., 2011] of multiple magma ocean stages during accretion.

[26] Additionally, in the case of the Earth, dynamic accretion models, in which pressure increased as the Earth grew at fixed oxygen fugacity based on the present estimates for the Fe content of the terrestrial core and upper mantle, do not improve the match for many siderophile element abundances in the terrestrial mantle. This prompted development of more complex multistage models that propose continuous core segregation during accretion under progressively oxidizing conditions for the Earth [Wade and Wood, 2005; Wood et al., 2008]. At present, weakly siderophile element depletions in the Martian mantle are either not significant (for, e.g., V and Cr) or not known with sufficient accuracy [Richter and Chabot, 2011; Lodders and Fegley, 1997] to assess if such multistage models are required for Mars, too.

6. Overabundance of Highly Siderophile Elements in the Martian Mantle

[27] Our knowledge of HSE abundances in the Martian mantle [Dale et al., 2012] remains limited, and the best estimates can be made by projecting meteorite abundances [Brandon et al., 2012] to mantle abundances (see Table 1). Using the high-pressure high-temperature metal-silicate partitioning behavior of the highly siderophile elements Re, Ru, Pd, Ir, and Pt [Mann et al., 2012], we tested whether high-pressure equilibration at the base of a magma ocean as suggested by the moderately siderophile elements could account for their abundances in the Martian mantle. Figure 3 shows a plot of the predicted $\log D(\text{metal/silicate})$ for these elements compared to the $\log D(\text{metal/silicate})$ values that are required to satisfy the estimated depletions of these elements in the Martian mantle at 10.5 wt% core S content. For conditions of 13 GPa, 2330 K, $\Delta IW = -1$, and $\text{nbo}/t = 2.55$ that can satisfy simultaneously the Martian mantle depletions of Ni, Co, W, P, Mo, Ga, and Ge, we find that the HSEs (Re, Ru, Pd, Ir, and Pt) are clearly overabundant in the Martian mantle. Our calculations show that unless our mantle estimates for Re, Ir, Ru, and Pt are too high by a factor of at least 3 orders of magnitude and for Pd by a factor of at least 1 order of magnitude, it is impossible to account for the Martian mantle depletions of these elements by core-mantle equilibration in a magma ocean.

[28] Since all these elements are present as low valence cations in silicate melt [Mann et al., 2012; Ertel et al., 1999], raising the oxygen fugacity to very oxidizing conditions of $\Delta IW + 3$ [Wadhwa, 2008], inconsistent with the abundances of the moderately siderophile elements, did not change this model outcome. We infer that metal-silicate equilibration at the base of a deep molten silicate layer is not able to account for the HSE abundances in the Martian mantle. Our results support the hypothesis of late accretion of primitive chondritic material to Mars after core formation had ceased, which can explain both the absolute and relative abundances of the HSEs in the Martian mantle [Dale et al., 2012; Brandon et al., 2012].

7. Summary

[29] We model the conditions of Martian core formation based on the estimated depletions of moderately siderophile elements in the Martian mantle and the metal-silicate partitioning behavior of these elements at Martian pressure conditions of >6 GPa. We find that if the Martian core contains 16 wt% S as suggested by some models [Sanloup *et al.*, 1999], then it is not possible to simultaneously account for the Martian mantle depletions of these elements by metal-silicate equilibration in a magma ocean within the pressure range relevant to the Martian interior. Model results for a Martian core containing 10.5 wt% S suggest that core-mantle differentiation in a Martian magma ocean at mean conditions between 13 ± 1 GPa and $\Delta IW - 1$ can simultaneously account for the Martian mantle depletions of Ni, Co, W, Mo, P, Ga, and Ge. The solution space expands significantly at lower S core contents at this oxygen fugacity. We show that the range of possible core S contents is very sensitive to the oxygen fugacity conditions during core formation. At slightly more oxidizing conditions (equivalent to the IW buffer), valid solutions are found in the 8–12 GPa pressure range at 0–6 wt% core S contents. These values provide independent evidence for the presence of a deep magma ocean in Mars. Irrespective of the precise conditions of equilibrium core formation, we find that the highly siderophile elements abundances in the Martian mantle cannot be satisfied by metal-silicate equilibration at the base of a molten magma ocean and require a late veneer component.

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