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Stimulated by new experimental results [1, 2] we have revisited the question of core formation in Mars. Earlier studies suggested metal/silicate equilibrium in Mars, but led to the paradox that Mars accreted homogeneously while the Earth accreted heterogeneously. Using the new elevated pressure and temperature metal/silicate partition coefficients, we conclude that there are no temperatures and pressures except near the surface of Mars [3] where metal/silicate partition coefficients for Ni, Co, and W can be consistent with core/mantle equilibrium.

Treiman *et al.* [3] used one atmosphere metal/silicate partition coefficients determined by Jones and Drake [4] to investigate the accretion of and core formation in Mars. They concluded that Mars probably accreted homogeneously, and that the core of Mars constituted about 30% of the mass of the planet, was S-rich, and had probably formed in chemical equilibrium with its mantle. A similar conclusion was drawn by [5]. However, Treiman *et al.* [3] noted that the best fits are for moderately siderophile elements less sensitive to core formation, such as Ni, Co, and W. Some of the more siderophile elements such as Mo and Au did not fit the homogeneous accretion/core-mantle equilibrium model very well. However, there is only one determination of Mo in a Martian meteorite, and Au is somewhat volatile, so it is unclear if these poor fits are significant.

Major advances in high pressure technology in the 1990s have permitted the determination of metal/silicate partition coefficients at high pressures and temperatures [1, 2]. In addition, the effect on metal/silicate partition coefficients of S dissolved in metallic liquid has been quantified [6], and the effects of T, P, oxygen fugacity, and S-content of the metallic liquid on metal/silicate partition coefficients have been parameterized [7]. Using these new data, we revisited the question of core formation in Mars.

We base our model on Ni, Co and W, which are sufficiently siderophile to be useful probes of core formation, for which we have well-determined liquid-metal/liquid-silicate partition coefficients and defensible estimates of Martian mantle abundances. See Table 1 [3,8]. Also listed are S-free liquid metal/liquid silicate partition coefficients determined by [2] at 100 kbars, 2000°C and 1.6 log units below the iron-wüstite buffer (IW-1.6). To model core formation at such high temperatures, we have calculated the values of liquid-metal/liquid-silicate partition coefficients necessary for a metallic liquid core of Mars to have formed in equilibrium with a molten silicate mantle. Because the mass of the Martian core is unknown, we have performed the calculation for a plausible range of mass fractions (0.15 - 0.3).

It can be seen from Table 1 that measured partition coefficients at 100 kbars and 2000°C are much lower for Ni, consistent for Co at a core mass of 30%, and higher

for W than those required by core/mantle equilibrium. If the temperature dependence of partition coefficients of [2] can be extrapolated, there are no temperatures and pressures except near the surface of Mars [3] where metal/silicate partition coefficients for Ni, Co, and W can be consistent with core/mantle equilibrium.

Above we have assumed that both metal and silicate in Mars were completely molten. If the mantle of Mars was partly solid during core formation, calculated metal/silicate partition coefficients for W would be higher, bringing them closer to measured values because W is highly incompatible in solid silicates. Calculated metal/silicate partition coefficients for Ni and Co will remain essentially unchanged because mineral/melt partition coefficients for the most abundant solid phase, olivine, are close to unity at elevated temperatures [9, 10].

If Mars is more oxidizing than IW-1.6, measured liquid metal/liquid silicate partition coefficients in Table 1 will be too large, which may lead to a poorer match with required Ni and Co partition coefficients, but will yield a better match for W.

Hillgren *et al.* [2] determined liquid metal/liquid silicate partition coefficients in a S-free system. Because Mars is volatile-rich, it is reasonable to infer that metallic liquids on Mars may also contain S. At one atmosphere it is well known that solid metal/liquid metal partition coefficients are strongly sensitive to the S-content of the metallic liquid. The effect of S at high temperatures and pressures may be less important because partition coefficients for Fe and Ni in a S-bearing system [1] are virtually identical to those determined in a S-free system [2], when considering comparable redox states and slight differences in temperature and pressure.

In spite of the uncertainty in the importance of S dissolved in metallic liquids at elevated temperatures and pressures, we use the work of Jones and Malvin (1990) to calculate the general effect of S on metal/silicate partition coefficients. The effect of different S-contents in the metallic liquid on liquid metal/liquid silicate partition coefficients for Ni, Co, and W is shown in Table 2. Increasing S decreases S-bearing metallic liquid/silicate liquid partition coefficients. Again, if the temperature dependence of partition coefficients of [2] can be extrapolated, there are no temperatures and pressures except near the surface of Mars [3] where

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metal/silicate partition coefficients for Ni, Co, and W can be consistent with core/mantle equilibrium.

Whether one atmosphere and low temperature or elevated pressure and temperature metal/silicate partition coefficients are appropriate to modeling core formation in Mars depends on how metal segregated from silicate as Mars and its core grew. During accretion, planets will likely experience non-disruptive collisions with objects up to 1/3 to 1/10 their mass [11], suggesting that very high temperatures were possible. If metal segregated in small (cm-scale) masses during such an impact and accreted to the growing core, the metal would probably reequilibrate continuously with the mantle, because of short diffusional length scales and long transit times to the core. In this case, partition coefficients for elevated pressures and temperatures would control compositions of the mantle and core. If metal quickly agglomerated into large (km-scale) masses after a large impact before accretion to the core, the metal composition might reflect low-pressure equilibria, because of large diffusional length scales and short transit times to the core. And if metal was delivered to the planet in large (km-scale) masses, equilibrium might not be obtained at all if the transit time to the core were short enough.

There is no unequivocal way to distinguish between these possibilities. However, we note that low-temperature, -pressure metal/silicate partition coefficients are consistent with core/mantle equilibrium for the best determined moderately siderophile elements in Mars, while elevated pressure and temperature

metal/silicate partition coefficients are not. A similar conclusion may be drawn from the parameterizations of [7], where a Ni, Co, and W are consistent with core/mantle equilibrium with a best fit at 25 kbars, 1370°C, a 30% by mass metal core which is 40% liquid with a molar S-content of 15%, and IW-1.25.

Mars contrasts with the Earth, where simple core/mantle equilibrium appears unlikely at low or high pressures and temperatures. This contrast raises a paradox, namely that Earth may have accreted heterogeneously and did not efficiently mix late-accreting material down to the core, while Mars, which is only one half of an astronomical unit in semi-major axis from Earth, either accreted homogeneously [5] or efficiently mixed late-accreting material down to the core. Reliable data on the abundances of other refractory siderophile elements such as Mo may help resolve this dilemma.

References: [1] Walker *et al.* (1993) *Science* **262**, 1858; [2] Hillgren *et al.* (1994) *Science* **264**, 1442; [3] Treiman *et al.* (1987) *Proc. Lunar Planet. Sci. Conf. 17th*, E627; [4] Jones and Drake (1986) *Nature* **322**, 221; [5] Wänke and Dreibus (1988) *Phil. Trans. R. Soc. Lond.* **325**, 545; [6] Jones and Malvin, 1990) *Metall. Trans.* **21B**, 697; [7] Righter *et al.* (1995) This volume; [8] Treiman *et al.* (1986) *Geochim. Cosmochim. Acta* **50**, 1071; [9] Drake (1989) *Z. Naturforsch.* **44a**, 833; [10] McFarlane and Drake (1990) *In Origin of the Earth*, 135; [11] Wetherill (1990) *Annu. Rev. Earth Planet. Sci.* **18**, 205.

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Table 1. Martian mantle concentrations (conc.) and uncertainties (range), measured liquid metal/liquid silicate partition coefficients ($D_{[meas.]}$) with uncertainties (D_{\pm}), and metal/silicate partition coefficients (D) required for core mantle equilibrium for different core mass fractions (0.15* etc.).

	conc. (xCD)	range	D [meas.]	D 0.15*	D 0.20*	D 0.25*	D 0.30*
Ni	0.004	$\pm x2$	135 \pm 15	1661	1246	997	831
Co	0.05	$\pm x2$	60 \pm 3	128	96	77	64
W	0.3	$\pm x2$	320 \pm 38	17	13	10	9

Table 2. Changes in liquid metal/liquid silicate (lm/ls) partition coefficients (D) for various mole fractions of sulfur in the metallic liquid ($X(S)=0.05$ etc.).

D(lm/ls)	X(S)=0.05	X(S)=0.10	X(S)=0.15	X(S)=0.20	X(S)=0.25	X(S)=0.30
Ni	144	137	131	123	114	104
Co	57	52	47	42	36	30
W	245	175	119	76	44	22