New geochemical models of core formation in the Moon from metal–silicate partitioning of 15 siderophile elements

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A B S T R A C T

We re-examine the conditions at which core formation in the Moon may have occurred by linking the observed lunar mantle depletions of 15 siderophile elements, including volatile siderophile elements (VSE) to predictive equations derived from a database compilation of metal–silicate partition coefficients obtained at lunar-relevant pressure–temperature–oxygen fugacity (P–T–fO$_2$) conditions.

Our results suggest that at mantle temperatures between the solidus and liquidus the depletions for all elements considered can be satisfied, but only if the Moon was essentially fully molten at the time of core formation while assuming a S-rich (>8 wt%) core comprising 2.5 wt% of the mass of the Moon. However, we observe that at temperatures exceeding the mantle liquidus, with increasing temperature the core S content required to satisfy the element depletions is reduced. As a S-poor core is likely from recent lunar mantle estimates of S abundance, this suggests much higher temperatures during lunar core formation than previously proposed.

We conclude that the VSE depletions in the lunar mantle can be solely explained by core formation depletion, suggesting that no significant devolatilization has occurred in later periods of lunar evolution. This is in agreement with the discovery of significant amounts of other volatiles in the lunar interior, but hard to reconcile with current lunar formation models.

1. Introduction

It is now well established that the Moon possesses a Fe-rich metallic core, based on re-analyses of Apollo era lunar seismograms (Weber et al., 2011), the lunar moment of inertia (Ferrari et al., 1980), the prolonged existence of a lunar core dynamo (Stegman et al., 2003; Laneuville et al., 2014) and the siderophile element depletions in the lunar mantle (e.g., Wänke et al., 1974; Newsom, 1984). However, the pressure (P) and temperature (T) that prevailed during lunar core–mantle differentiation remain debated. For example, Hauri et al. (2015) recently suggested that the temperature of an early lunar magma ocean could range anywhere between the liquidus of the lunar mantle and the midplane temperature of the disk of material from which the Moon is thought to have formed (3000–7000 K), whereas Rai and Van Westrenen (2014) consider temperatures between the lunar mantle solidus and liquidus. There is also considerable debate about the composition of the lunar core. Sulfur (S) may be present in

the lunar core, because of its high solubility in liquid Fe at lunar relevant pressures (Boujibar et al., 2014) and its ability to reduce core density, sound velocity and freezing temperature (Jing et al., 2014). Current S estimates for the lunar core range between 1 and 8 wt% S, based on Fe–S equation of state measurements (Jing et al., 2014), siderophile element depletions in the lunar mantle (Rai and van Westrenen, 2014) and lunar core dynamo modeling (Laneuville et al., 2014). However, a S-rich lunar core seems unlikely given the recently proposed S abundances of 74.5 ± 4.5 ppm in the bulk silicate Moon (Chen et al., 2015; Hauri et al., 2015), which would result in low S-core concentrations based on measured values of S partitioning between metal and silicate (Boujibar et al., 2014). This is substantiated with the homogeneous S isotope signature of lunar basalts, which suggests that only minor S degassed during the Moon forming event (Wing and Farquhar, in press).

Geochemical planetary differentiation models try to assess the pressure (P), temperature (T), silicate and metal composition (X) and oxygen fugacity (fO$_2$) that prevailed during core formation. Inferred present-day siderophile element mantle depletions are related to P–T–X–fO$_2$ differentiation conditions using experimentally determined metal–silicate partitioning behav-

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ior. This approach has been applied to core formation in the Earth (e.g., Righter and Drake, 1996; Wade and Wood, 2005; Cottrell et al., 2009; Siebert et al., 2011), Mars (e.g., Rai and van Westrenen, 2013; Righter et al., 2015), the Moon (e.g., Righter and Drake, 1996; Rai and van Westrenen, 2014) and asteroid Vesta (e.g., Righter and Drake, 1996; Holzheid and Palme, 2007; Steenstra et al., in press).

Our recent work showed that the estimated lunar mantle depletions of a subset of siderophile elements (P, V, Cr, Co, Ni, Mo and W) can be reconciled with core–mantle equilibration of a S-rich (6 wt% S) core in a hot ($\sim$2200 K), deep ($P = 4.5 \pm 0.5$ GPa) magma ocean (Rai and van Westrenen, 2014). However, it is unclear if the estimated lunar mantle abundances of volatile siderophile and chalcophile elements (Cu, Ga, Ge, Se, Cd, Sn, Te, Pb) can also be explained by segregation of a Fe-rich lunar core, and if so, at which P–T–X–fO_2 conditions. In light of recently published metal–silicate and sulfide–silicate partitioning data for a wide range of siderophile elements (Kiseeva and Wood, 2013; Mungall and Brenan, 2014; Wood et al., 2014) and recently reported new bulk silicate Moon estimates of these elements (Hauri et al., 2015), here we reassess the P–T–X–fO_2 conditions that prevailed during lunar core formation and provide constraints on the composition of the lunar core.

2. Methods

2.1. Parameterization approach

A common approach to quantify the variables affecting siderophile metal–silicate or sulfide–silicate partitioning is to fit compiled experimental data (Peach and Mathez, 1993; Thibault and Walter, 1995; Gaetani and Grove, 1997; Righter and Drake, 2000; Chabot and Agee, 2003; Kegler et al., 2008; Rose-Weston et al., 2009; Righter et al., 2010, 2011; Siebert et al., 2011; Wade et al., 2012; Ballhaus et al., 2013; Kiseeva and Wood, 2013; Mungall and Brenan, 2014; Wood et al., 2014; Supplementary Table 1) to equations of the following form by multivariate linear regression (Righter et al., 1997; Rai and van Westrenen, 2014; Steenstra et al., 2015, in press):

$$\log D = a + b(\Delta\text{IW}) + c(nbo/t) + d(1/T) + e(P/T)$$
$$+ f\ln(1 - X_S) + g\ln(1 - X_C) + h\ln(1 - X_{Ni})$$
$$+ i(S) \tag{1}$$

$$\log D = a + b(\Delta\text{IW}) + c_1(\text{MgO}) + c_2(\text{SiO}_2) + c_3(\text{Al}_2\text{O}_3)$$
$$+ c_4(\text{CaO}) + c_5(\text{FeO}) + d(1/T) + e(P/T) + f\ln(1 - X_S)$$
$$+ g\ln(1 - X_C) + h\ln(1 - X_{Ni}) + i(S) \tag{2}$$

in which coefficients a, d, and e are related to the expansion of the free energy term with T in K and P in GPa, and b relates to the valence n of the metal oxide. Oxygen fugacity (fO_2) relative to the Iron-Wüstite Buffer (IWB), denoted by ΔIW, can be approximated with Eq. (3):

$$\Delta\text{IW} = 2\log(X_{\text{FeO(melt)}}/X_{\text{Fe(metal)}}) \tag{3}$$

where $X_{\text{FeO(melt)}}$ is the mole fraction of FeO in the silicate and X_{Fe} the mole fraction of Fe in the metallic phase. The silicate composition is either represented in terms of k separate mole oxide fractions of the silicate melt (Eq. (2)) and $c_1, \ldots, c_k$ the corresponding coefficients or by nbo/t, that is defined as the number of non-bridging oxygen ions per tetrahedrally coordinated cation, with c the corresponding coefficient (Eq. (1)). The nbo/t term is a

single proxy for both melt composition and melt structure and is defined by the following equation (Mysen et al., 1982):

$$nbo/t = [2 \times O - 4 \times T]/T \tag{4}$$

where $[2O - 4T]$ refers to the number of non-bridging oxygen ions and T represents the number of tetrahedrally coordinated cations. Coefficient f in Eqs. (1) and (2) relates to the effect of dissolved S in the metallic liquid (where X_S is the molar fraction in the metallic phase), g to the effect of dissolved C in the metallic liquid (where X_C is the molar value of carbon in the metallic phase), h to the effect of dissolved Ni in the metallic liquid (where X_{Ni} is the molar fraction of Ni in the metallic phase) and i relates to the concentration of dissolved S (in ppm) in the silicate liquid. We exclude experiments which contain significant amounts of Si or O in the metallic liquid from the experimental dataset, because Si and O are not likely to be present in the lunar core in significant quantities and their effect on metal–silicate partitioning of siderophile elements can be significant (Tuff et al., 2011; Chabot et al., 2015).

Results from the multi-linear regressions on the compiled low-pressure ($\leq$5 GPa) partitioning data are shown in Table 1. This study shows that low valence elements Co, Ni, Cu, Sn are relatively insensitive to changes in melt composition and are most accurately predicted using the nbo/t approach, consistent with previous studies (Righter, 2003; Righter et al., 2010; Rai and van Westrenen, 2013, 2014; Table 1). For example, the 2+ valence state of Co and Ni in silicate melts seems to be better predicted if the nbo/t approach is used (Table 1). The low values of their nbo/t coefficients also suggest their metal–silicate partitioning remain largely unaffected by changes in silicate melt composition. For Cu and Sn, the oxide approach yields no statistically significant fO_2 term, which is not in agreement with their suggested valence state of 1+ and 2+ in silicate melts at low fO_2 (e.g., Capobianco et al., 1999; Corgne et al., 2008). Our regressions suggest that the metal–silicate partitioning behaviors of a number of siderophile elements (Cr, Ga, Ge, Cd, Pb) are more adequately quantified using separate mole oxide fractions rather than nbo/t as a proxy for silicate melt composition. This is clearly reflected by a better fit of their fO_2 term to their estimated valence states in silicate melts at lunar relevant conditions (Wood and Halliday, 2010; Kegler and Holzheid, 2011; Siebert et al., 2011; Kiseeva and Wood, 2013). The metal–silicate partitioning behavior of V and Te seems to be affected by changes in silicate melt composition, reflected by their high nbo/t term, and for these elements we therefore also applied the oxide approach. This is also the case for P, Mo and W, for which a strong dependency on silicate melt composition was previously observed (e.g., O'Neill and Eggins, 2002; Palme et al., 2011). For Se and Te, regressions yielded no significant fO_2 term in either approach, suggesting their metal–silicate partitioning is not directly affected by fO_2, which agrees with theoretical models (Rose-Weston et al., 2009).

Several recent partitioning studies (e.g., Siebert et al., 2011; Wade et al., 2012; Wood et al., 2014) have used the so-called Wagner ε formalism (Wagner, 1962) to parameterize metal–silicate and sulfide–silicate partitioning data, stating that the use of this formalism yields models that are thermodynamically more sound than the models based on Eqs. (1) and (2). This approach takes the interaction between the different solutes within the metallic alloy into account by using interaction coefficients and activity coefficients from the steelmaking industry (The Japan Society for the Promotion of Science and The Nineteenth Committee on Steelmaking, 1988; Wade and Wood, 2005; Siebert et al., 2011). We do not want to focus here on the respective merits and problems of these two approaches, but we stress that we have previously demonstrated quantitatively that the parameterizations derived from both approaches are very similar, and that the approach used in our