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Steenstra, E.S.; van Westrenen, W.

published in

Encyclopedia of Lunar Science
2017

DOI (link to publisher)

[10.1007/978-3-319-05546-6_76-1](https://doi.org/10.1007/978-3-319-05546-6_76-1)

document version

Publisher's PDF, also known as Version of record

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citation for published version (APA)

Steenstra, E. S., & van Westrenen, W. (2017). Siderophile elements in the lunar mantle. In B. Cudnik (Ed.), *Encyclopedia of Lunar Science* (Living ed., pp. 1-7). Springer. https://doi.org/10.1007/978-3-319-05546-6_76-1

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Siderophile Elements in the Lunar Mantle

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Introduction

From analyses of returned samples from the Apollo program, it became apparent that the refractory iron-loving (siderophile) elements were significantly depleted in the lunar mantle and crust relative to the composition of the inferred building blocks that formed the Moon (Ganapathy et al. 1970; Anders et al. 1971). Their depletion pattern is in agreement with their inferred siderophile nature based on metal-silicate partitioning experiments performed at conditions relevant for the lunar interior (e.g., Newsom and Beserra 1990). This implies they strongly partitioned in metallic phases during a single or multiple event(s) of metal-silicate segregation, most likely during core formation (Righter and Drake 1996; Righter 2002; Rai and van Westrenen 2014; Steenstra et al. 2016a). Siderophile element depletion patterns of lunar samples are therefore indicative of the metal-silicate fractionation before or during formation of the Moon and

provide a crucial test of models related to the origin of the Moon and its early evolution. They may also provide valuable constraints on the composition of the lunar core (*Lunar interior, Lunar Core Formation*).

Based upon their affinity for Fe-metal, three groups of siderophile elements can be distinguished. The slightly siderophile elements have metal-silicate partition coefficients (D 's) of $<10^1$, whereas the moderately siderophile and highly siderophile elements are characterized by D 's between 10^1 – 10^4 and $>10^4$ (Table 1). This is a general classification, as D 's can be strongly affected by a number of intrinsic variables. These variables include most notably oxygen fugacity (fO_2), pressure (P), temperature (T), and composition of the metal and silicate phase (X) upon differentiation.

Siderophile elements can also be subdivided based on their volatility, defined by their 50 % condensation temperatures at 10^{-4} atm (Table 1). Their diverse geochemical behavior allows for studying key processes in early lunar evolution, including core formation, subsequent magmatic processes, and the extent of devolatilization after the Moon-forming event. Here, we briefly discuss the methods used to estimate siderophile element abundances in the lunar mantle, and we provide an overview of these estimates and discuss their geochemical implications for early lunar evolution.

Siderophile Elements in the Lunar Mantle, Table 1 Classification of siderophile elements according to their affinity for Fe-metal and volatility

Volatility ^a	Slightly siderophile	Moderately siderophile	Highly siderophile
Refractory	V	Mo, W	Re, Os, Ir, Pt, Ru, Rh
Transitional	Cr	Co, Ni	Pd
Moderately volatile	Mn	P, Cu*, Ga*, Ge*, As*, Ag*, Sb*	Au
Highly volatile	Zn*	C, S*, Se*, Cd*, In*, Sn*, Te*, Hg*, Tl*, Pb*, Bi*	

*show affinity for sulfides (chalcophile)

^aBased on their 50 % condensation temperatures at 10^{-4} atm where refractory ≥ 1400 K, transitional = 1250–1400 K, moderately volatile = 800–1250 K, and highly volatile ≤ 800 K (McDonough and Sun 1995; Walter et al. 2000; Lodders 2003)

Estimating Siderophile Elements in the Bulk Silicate Moon

Unraveling the indigenous siderophile element abundances in the bulk silicate Moon (BSM) can be challenging, as the abundances of many siderophile elements are low in lunar rocks, and abundance measurements are therefore susceptible to analytical error and/or meteoritic contamination. This is especially the case for highly siderophile elements (HSE), which are often difficult to measure using radiochemical neutron activation analysis (RNAA) or instrumental neutron activation analysis (INAA) (except for Ir, Au). Another issue is sample heterogeneity, as siderophile elements are often concentrated in a few metal grains or specific mineral phases resulting in inconsistent replicate analyses. Another issue is that the reported abundances in lunar samples can be biased, especially for the more siderophile elements. Samples with the highest concentrations will be reported, whereas samples with concentrations below the detection limit cannot be taken into account.

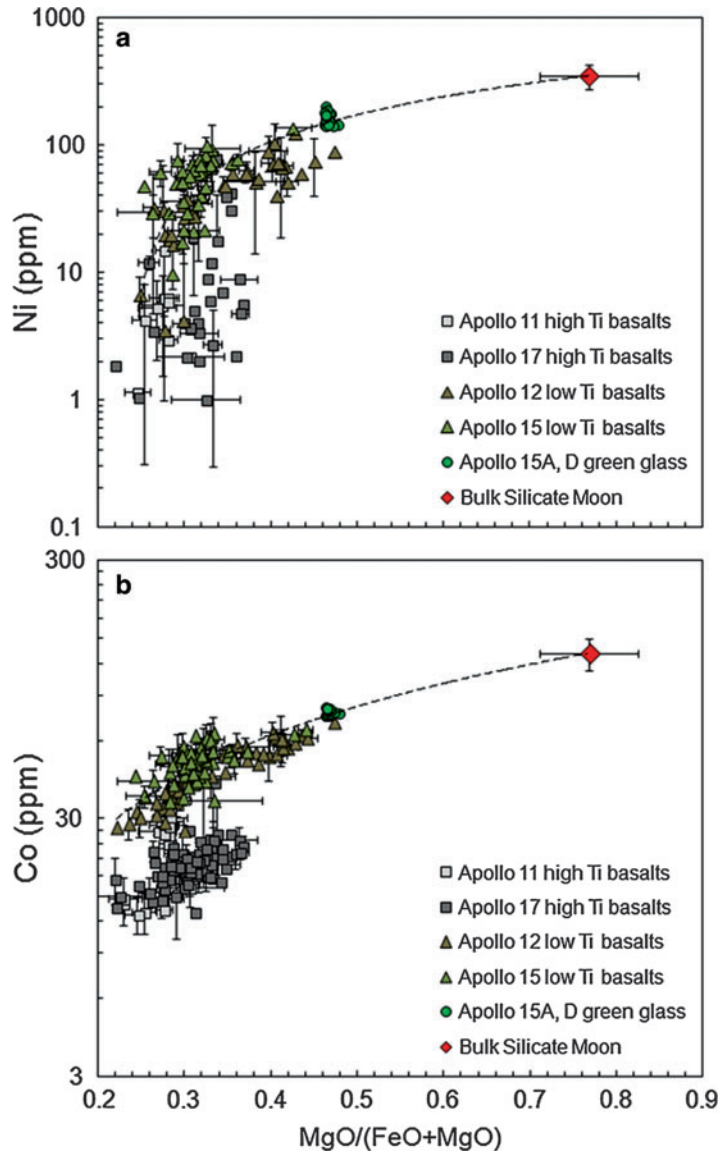
Estimates of indigenous siderophile element abundances are based on monomict (i.e., consisting of a single lithology) basalts or pyroclastic glasses, as polymict (i.e., consisting of two lithologies formed under different conditions and at different locations) samples are usually significantly affected by meteoritic contamination. Estimation for siderophile elements should be preferably based on the most primitive igneous samples returned from the lunar surface, which are most likely to reflect the more primitive

regions of the lunar mantle. These type of samples include the low Ti (<1 wt% TiO_2) pristine green volcanic glasses and the low Ti (<6 wt% TiO_2) mare basalts. The low Ti volcanic green glasses, and to a lesser extent the low Ti basalts, are characterized by the highest Mg# ($\text{MgO}/(\text{MgO} + \text{FeO})$) ratios, the least fractionated ratios (and lowest concentrations) among nonvolatile and incompatible elements, and have the highest concentrations of elements that behave compatibly in magmatic systems, such as Ni and Co (Ringwood and Kesson 1976; Delano 1986). Sample suites that have lower Mg# ratios, such as the high Ti volcanic glasses and high Ti basalts, have a more complex petrogenetic evolution and are therefore less likely to provide insights into the primitive lunar mantle composition.

The bulk silicate Moon siderophile element abundances can then be derived by using correlations between siderophile and refractory lithophile elements that both behave incompatible in magmatic systems (e.g., P/La; Newsom 1985; Steenstra et al. 2016b). Abundances of siderophile elements that behave compatibly in Fe- and Mg-rich minerals (e.g., Ni, Co) can be calculated by using their correlations with Mg# or MgO content (Delano 1986; Steenstra et al. 2016b) (Fig. 1). Extrapolation of this correlation to the estimated Mg# or MgO content of the bulk silicate Moon allows for estimation of indigenous siderophile element abundances in the lunar mantle. Previous workers have also used the positive covariation between the highly siderophile elements (HSE) and MgO in terrestrial MgO-poor and MgO-rich samples to estimate their

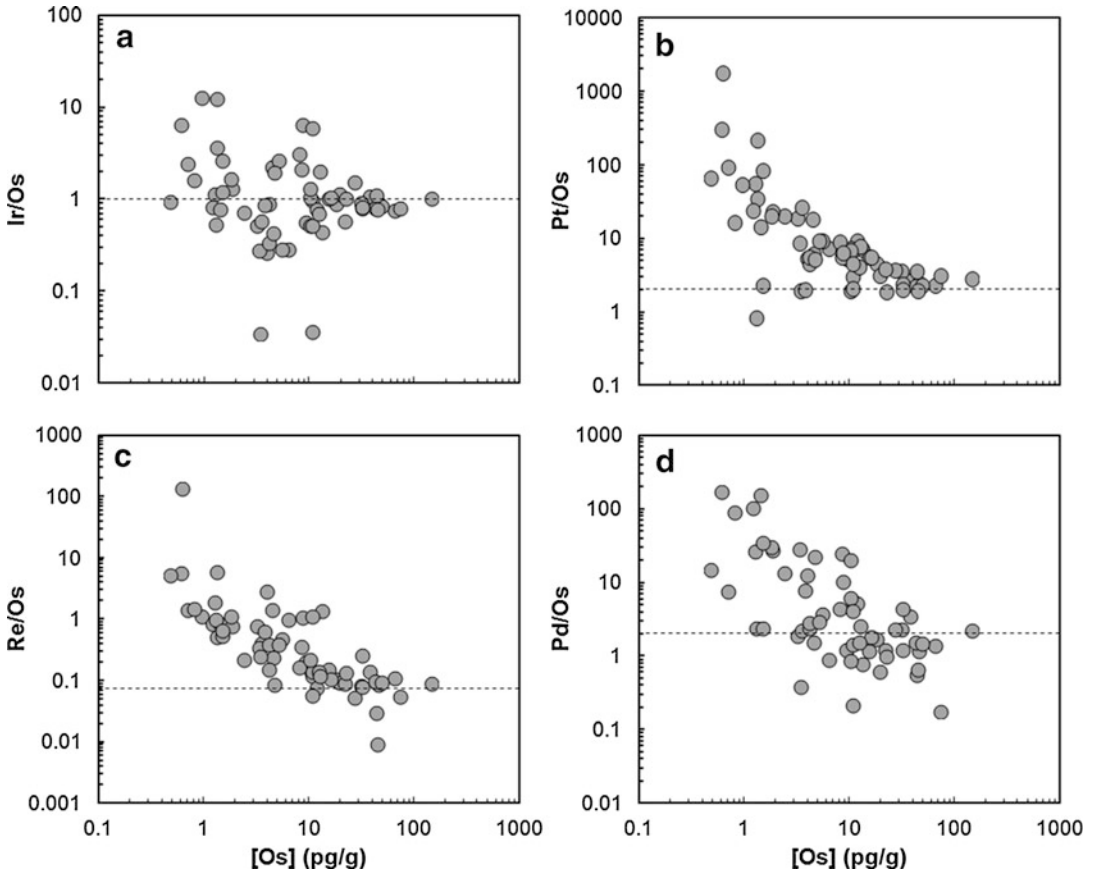
Siderophile Elements in the Lunar Mantle,

Fig. 1 Examples of elemental correlations between elements that behave compatibly in Fe- and Mg-rich minerals for low Ti (<6 wt% TiO₂) and high Ti (>6 wt% TiO₂) mare basalts for (a) Ni and (b) Co. Also indicated is the estimated concentration of Ni and Co in the primitive lunar mantle using the bulk silicate Moon Mg[#] estimates compiled by Rai and van Westrenen (2014). Compiled lunar data from the Lunar Sample Compendium (Meyer 2011) and references therein. Lunar green Apollo 15 A and D volcanic glass data were used from Steele et al. (1992)



abundances in the lunar mantle (Day et al. 2007). One major assumption is that the HSE behave similarly during melting of the lunar mantle and the Earth's mantle. However, conditions within the Earth's mantle (P, T, fO_2) are currently significantly different from the lunar mantle. An alternative approach is to compare the concentrations of two HSE that possess different compatibility in mineral structures (Dale et al. 2012) (Fig. 2). For example, Os is highly compatible in chromite and therefore preferentially retained in the residual

mantle or cumulate rocks (Shirey and Walker 1998). Elements such as Pt are moderately incompatible during mantle melting and therefore will preferentially partition into the melt. At low degrees of melting the Pt/Os ratios will be high, but with increasing degrees of melting this ratio will decrease until the ratio is approximately equal to the source. Extrapolation of the negative covariation between the ratio and the concentration of the less incompatible element in pristine



Siderophile Elements in the Lunar Mantle, Fig. 2 Estimation of HSE abundances in the lunar mantle or BSM using HSE ratios from Day et al. 2007, 2010; Day and Walker 2015. Dashed line is the CI ratio (Anders and Grevesse 1988)

lunar samples can then be used to estimate indigenous HSE BSM abundances.

Abundances of Siderophile Elements in the Lunar Mantle

Highly siderophile elements (HSE): The HSE (Table 1) are characterized by their extremely siderophile behavior during metal-silicate segregation, and their abundances in pristine lunar basalts are extremely low. Previous workers have noted the general lack of correlation between most of these elements and (non) siderophile elements, which is likely a result of the previously discussed challenges that are associated with measuring HSE abundances.

However, the use of HSE ratios does allow for approximating the upper boundary of HSE indigenous abundances in the lunar mantle (Fig. 1 and Table 2; Dale et al. 2012). The proposed abundances suggest homogeneous distribution of the HSE in the lunar mantle with approximately chondritic relative proportions and an overall depletion of $\sim 0.0002 \times$ CI-chondrite (Fig. 3a; Day and Walker 2015). This implies that the HSE were delivered after formation of the Moon, rather than inherited from the Earth, which is in agreement with the proposed ^{182}W excess in the BSM relative to bulk silicate Earth (BSE) (Kruijer et al. 2015; Touboul et al. 2015). This is also consistent with the relatively moderate HSE depletions in the BSM relative to the bulk Moon (BM), with their expected D's at lunar relevant conditions predicting far lower HSE abundances

Siderophile Elements in the Lunar Mantle, Table 2 Estimated indigenous siderophile element abundances in the bulk silicate Moon (BSM) based on previous studies (Sources: (1) Wetzel et al. 2015 (2) O'Neill 1991 (3) Righter and Drake 1996 (4) Righter 2002 (5) Newsom and Taylor 1989 (6) Drake 1987 (7) Hauri et al. 2015 (8) Chen et al. 2015 (9) Jones and Palme 2000 (10) Walter et al. 2000 (11) Delano 1986 (12) This study (13) Righter et al. 2011 (14) Dale et al. 2012)

	BSM	Refs.		BSM	Refs.		BSM	Refs.
C (ppm)	54 ± 10	1	As (ppb)	6.5 ± 5.5	2, 7	W	18 ± 6	2–6
P	19 ± 3	2–6	Se	24	7	Re	0.003 ± 0.002	14
S	74.45 ± 4.45	7, 8	Mo	1.55 ± 0.65	2–6	Os	0.085 ± 0.045	14
V	68 ± 9	2, 5, 6, 9, 10	Ru	0.10 ± 0.05	13	Ir	0.085 ± 0.045	14
Cr	2580 ± 335	2, 5, 6, 9, 10	Rh	0.026	7	Pt	0.09 ± 0.06	14
Mn	1046	7	Pd	0.025 ± 0.015	14	Au	0.024	7
Co	115 ± 30	2–4, 11, 12	Ag	0.18	7	Hg	0.093	7
Ni	415 ± 105	2–4, 11, 12	Cd	11.7	7	Tl	1.5	7
Cu	4.66 ± 2.56	2, 7	In	1.6	7	Pb	28	7
Zn	7.7	7	Sn	22.5 ± 16.5	2, 7	Bi	0.022	7
Ga	1.50 ± 0.84	2, 7	Sb	0.0089 ± 0.0011	2, 7			
Ge	0.0175 ± 0.0025	7, 13	Te	4.08	7			

in the BSM during core formation than observed (Dale et al. 2012; Fig. 3b).

Moderately siderophile elements (MSE):

The MSE constitute the majority of the siderophile element group and have a moderate affinity for Fe-metal and, in some cases, may also show chalcophile behavior (e.g., Se, Te) (Table 1). The abundances of many of these elements in the BSM can be derived using their ratios with incompatible, refractory elements (e.g., Mo, P, W, Ga) or with MgO or (MgO + FeO) for elements that behave compatibly in Fe- and Mg-rich minerals (e.g., Ni, Co) (Fig. 2). The abundances of siderophile elements with relatively high condensation temperatures (e.g., Ni, Co, Mo, W, P) are therefore relatively well constrained in the BSM (Table 2), and as a consequence most commonly used in geochemical models of lunar core formation (*Lunar interior, Lunar Core Formation*).

A number of MSE are also (highly) volatile, usually not extensively studied, and as a consequence their abundances in the BSM are less well constrained. Adding to the complexity, these volatile siderophile elements (VSE) are often highly enriched on the surfaces of the Apollo glass beads, which is thought to have resulted from quenching within a volatile-rich cloud upon eruption (Hauri et al. 2015). However, the abundance of the

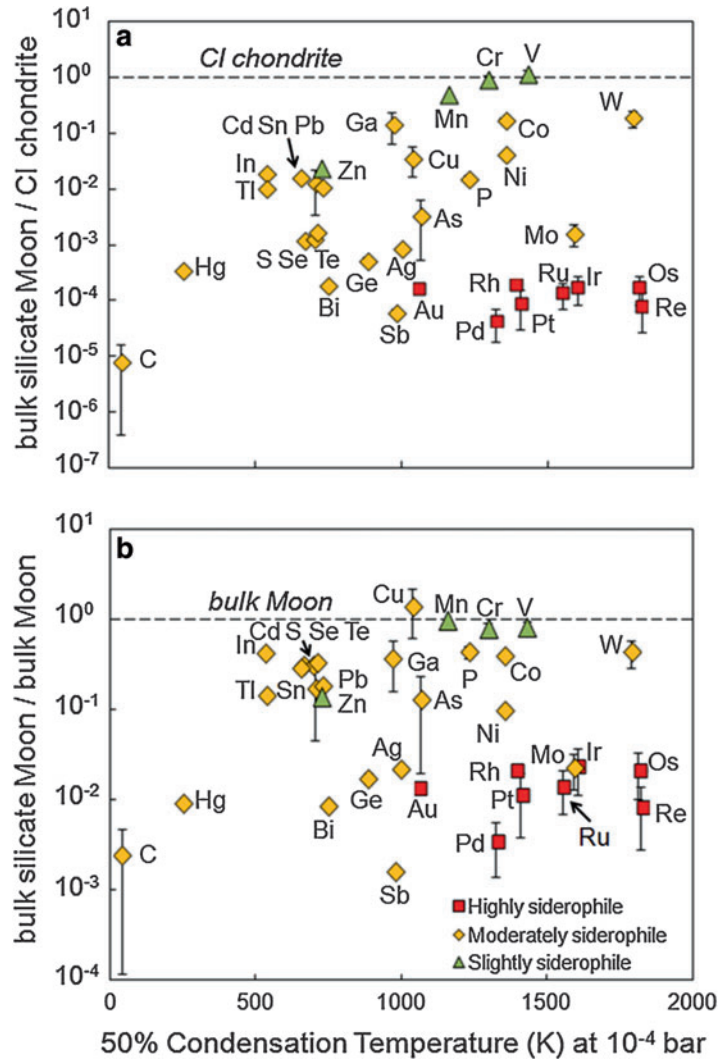
volatile siderophile elements may offer important clues on the extent of devolatilization of the Moon and therefore the early history of the Moon. This can be achieved by assessing their depletions through core formation and comparing these with their estimated mantle concentrations (Steenstra et al. 2016a, c). This suggests that the depletions of a significant number of (highly) volatile MSE (e.g., C, Cu, Ga, Ge, Se, Cd, Sn, Te) in the BSM can simply be explained by core formation depletion (*Lunar interior, Lunar Core Formation*), without the need to invoke significant devolatilization of these elements during the Moon-forming event.

Slightly siderophile elements (SSE):

The SSE (Table 1) show only minor siderophile behavior at certain pressure (P) – temperature (T) – compositional (X) – and redox (fO_2) conditions and often behave lithophile. As a result, the depletion of SSE provides important clues on the P - T - X - fO_2 conditions that prevailed during lunar core formation. For example, the lunar mantle depletion of V and Cr imply the existence of a S-rich lunar core and/or super-liquidus temperatures during core formation (Rai and van Westrenen 2014; Steenstra et al. 2016a). Relative to the bulk Moon, Mn is not depleted. Zinc does show a significant depletion, more than seems

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Fig. 3 Siderophile elements in the BSM as a function of 50 % condensation temperature at 10^{-4} bar (Lodders 2003) (a) relative to CI-chondrite (Anders and Grevesse 1988) and (b) relative to the bulk Moon (BM). Abundances of C, S, Mn, Zn, Ga, Ge, As, Se, Cd, In, Sn, Sb, Te, Hg, Tl, Pb, Bi, and HSE in the BM are assumed to be equal to BSE (McDonough and Sun 1995; Fischer-Gödde et al. 2011)



expected given its metal-silicate partitioning behavior (Fig. 3b). Additional depletion could be due to its high volatility, but this seems at odds with the overall minor devolatilization of other more volatile elements in the lunar mantle (e.g., Hauri et al. 2015; Wetzell et al. 2015; Steenstra et al. 2016a, c).

Outlook

Future studies should explore in particular the abundances of volatile siderophile elements in the Moon in more detail, as they may provide

valuable insights into the extent and mechanisms of volatile fluxes within the early Earth–Moon system. Advances in analytical techniques should aid to additionally constrain the range of HSE and VSE abundances in the Moon, as they may shed light on the material from which the Moon was formed as well as the extent and/or composition of the meteoritic flux during its early history. Samples returned from the lunar farside would provide insights into the distribution (homogeneous vs. heterogeneous) of siderophile elements in the Moon, which would be a decisive test for the interpretation of siderophile element depletion signatures in the lunar mantle.

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