

**ELEMENT PARTITIONING BETWEEN OLIVINE AND MELT INCLUSIONS IN LUNAR SAMPLES.**

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**Introduction:** Current models of lunar magma ocean evolution suggest that olivine was the first mineral crystallized from the magma ocean. Olivine is also a major mineral in the lunar mantle and during lunar magma evolution. Element partitioning between olivine and melt has been used in geochemical models and as a geothermometer, geohygrometer, and geobarometer. Numerous partition coefficient data have been reported between terrestrial olivine and silicate melts, however, there are no systematic data documenting lunar conditions. The differences in chemical composition and oxygen fugacity between lunar and terrestrial basalts may lead to significantly different partition behaviors [1]. For example, lunar basalts show a much wider range of TiO<sub>2</sub> and often higher FeO than terrestrial basalts. The oxygen fugacity of lunar basalts is around IW-1 [2], whereas that of mid-ocean ridge basalts is about QFM, with a difference of ~5 log units. Oxygen fugacity is a key parameter affecting trace element partition coefficients, especially for those elements with multiple valences, such as V and Fe. In this study, we investigate trace element partition between olivine and coexisting melt inclusions from lunar mare basalts.

**Methods:** Olivine and melt inclusions crystals from four lunar samples, 15016, 15647, 12040, 74235, were investigated for major and trace element contents. These samples represent a wide range of compositions with TiO<sub>2</sub> ranging from 1.94% to 11.77% in associated melt inclusions. Olivine crystals containing melt inclusions were carefully picked from each sample and examined under a microscope to avoid cracked crystals. Melt inclusions measured were crystalline (i.e., not glassy) due to slow cooling. They were re-homogenized prior to analysis to achieve a homogeneous glass phase for analyses. Olivine crystals containing melt inclusions were heated to 1453-1503 K for 2-10 minutes to re-homogenize the inclusions. A graphite crucible was used in the heating process to maintain low oxygen fugacity comparable to the lunar conditions. After quenching, the crystals were polished to reveal the melt inclusions. Major and trace element concentrations in melt inclusions and the host olivine host were then analyzed. Major elements were measured by electron microprobe analysis (EMPA) at the University of Michigan. Only samples that were considered to be approximately in equilibrium based on Fe/Mg K<sub>D</sub> values between the host oli-

vine and the melt inclusion [1] were used in this study to investigate trace element partitioning. Trace elements in melt inclusions were measured by secondary ion mass spectrometry (SIMS) at the California Institute of Technology [3], while those in olivine were measured by laser ablation inductively coupled mass spectrometry (LA-ICP-MS) at the University of Windsor.

**Results:** In total, 20 trace elements, Li, Sc, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, Y, Zr, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu were precisely determined in olivine using a range of external calibration standards (NIST 610, 612, 614 and 616). Additional elements including Nb, Mo, Sn, Al, Ga, Ge, La, Ce, Pr, Nd, Sm, and Eu were also measured but either they are below detection limit or the errors are large due to low signal counts. For SIMS measurement on melt inclusions, precise concentrations were measured for Li, Na, K, V, Cr, Mn, Co, Ni, Cu, Sr, Y, Zr, Nb, Ba, and all REE. Using the concentrations in melt inclusions and their host olivines, we were able to obtain precise partition coefficient data for Li, Ti, V, Cr, Mn, Co, Ni, Cu, Y, Zr, and heavy REE, and order of magnitude estimations for Nb and LREE.

Figure 1 shows partition coefficients determined for lunar samples relative to the reported data for terrestrial basalts. Although a wide range in TiO<sub>2</sub> contents occurs in the melt inclusions investigated (11.77% in 74235-2 and 1.94-3.68% in other samples), no significant differences in partition coefficients were observed between high Ti and low Ti samples.

**Discussion:** Partition coefficients between olivine and melt in lunar basalts are similar to those in terrestrial basalts for most elements. For elements with such low concentrations in olivine, the difference could be explained by measurement error, however, some elements do show significant differences, especially V and Cr. Before any discussion, I should point out that partition coefficient data from literature was compared here only if oxygen fugacity is around QFM. The higher partition coefficient of V in lunar than in terrestrial basalts can be explained by difference in oxygen fugacity. V partitioning behavior depends mainly on its oxidation state. The more reduced environment on the Moon would increase the ratio of V<sup>2+</sup>/V<sup>3+</sup>. Because V<sup>2+</sup> substitutes for Mg<sup>2+</sup> more easily than V<sup>3+</sup>, the V partition coefficient between olivine and melt in lunar basalts is greater in lunar basalts by

approximately an order of magnitude than in terrestrial basalts. Using the V partition study of Mallmann and O'Neill [8], our V partition data indicate 2% to 7% of V as  $V^{2+}$ , and the remainder is  $V^{3+}$ . Such partitioning behavior of V could potentially be used to estimate the redox state of lunar basalt [4, 5].

Al partitioning has been reported to increase with pressure [6]. Therefore, the lower partition coefficient of Al in lunar samples could be a reflection of melting depth.

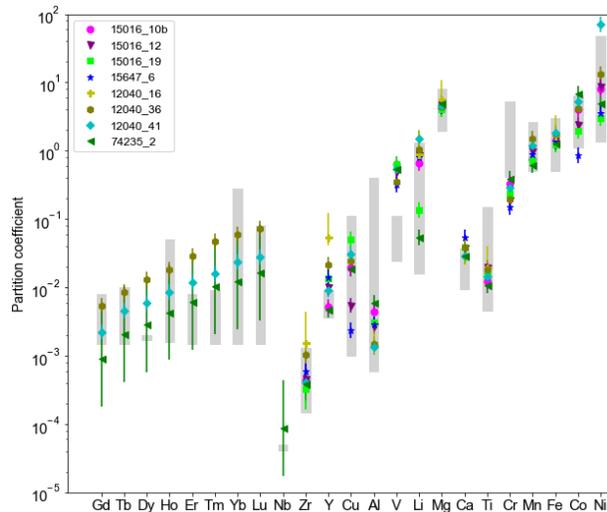


Fig 1: Equilibrium partition coefficients of 23 elements (Na, Mg, Al, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Y, Zr, Nb, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) between olivine and lunar basalt. Colored symbols are for lunar samples (this study) and grey areas show literature data ranges of partition coefficients for terrestrial samples (e.g. [6, 10, 11, 12, 13], most of which are from GERM Partition Coefficient Database).

Cr is usually compatible or slightly incompatible in terrestrial olivine, with partition coefficients ranging from 0.63 to 5.2. Lunar samples show lower partition coefficients (0.15 to 0.43) for the eight pairs of coexisting olivine and melt inclusions investigated. Reduced lunar samples are expected to have a larger proportion of  $Cr^{2+}$  in the melt, which should facilitate the substitution, however, partition data show otherwise. Previous experimental study show insensitivity of Cr partition coefficient to  $fO_2$  [7, 8], but may change with composition and temperature. The smaller Cr partition coefficient between olivine and melt in lunar basalts than in terrestrial basalts could be a compositional effect or combined effect with other factors.

Lattice strain model [9] has been proposed to explain how radius and charge of an ion affects ionic substitution. The model is useful in predicting parti-

tion coefficients based on valence and ionic radius. In this study, we present a parameterized lattice strain model for both  $M^{2+}$  and  $M^{3+}$  element partitioning between olivine and lunar basalt. It might be used to predict the partition coefficients of elements that were not measured or could not be measured precisely, such as light REE (excepting Eu), and volatile elements, such as Zn and Sc.

**Summary and Implications:** Partition coefficients between olivine and basaltic melt for lunar samples are provided for 23 elements. Most of the data are in agreement with those in terrestrial basalts despite the large differences in basalt composition and oxygen fugacity, except for partition coefficients of V and Cr. The insensitivity of the partitioning behavior of most elements to basalt composition and redox conditions indicates that our approach provides reasonable data. Higher V partition coefficients in lunar basalts can be readily explained by the lower oxidation state of lunar compared to terrestrial basalts, however, the lower partition coefficients of Cr cannot be readily explained.

The partition coefficients determined during this study can be applied to model lunar magma evolution, to infer melt composition from olivine composition, and to model partial melting of the lunar mantle. For volatile elements, such as Zn and Cu, the concentration and partition coefficient data may be used to infer the volatile composition in the lunar mantle, which is essential to our understanding of the formation and evolution of the Earth-Moon system. Partition coefficients for elements with multiple valences, such as V, can be employed to estimate  $fO_2$ .

**References:** [1] Xirouchakis, Hirschmann, and Simpson, (2001) *GCA*, 65, 2201-2217. [2] Wadhwa, M. (2008) *Rev. Mineral. Geochem.*, 68, 493-510. [3] Ni et al. (2019) *Geochim. Cosmochim. Acta*, in press. [4] Papike et al., (2013) *Am. Mineral.* 98, 2193-2196. [5] Papike, J.J et al., (2016) *Am. Mineral.* 101, 907-918. [6] Bedard JH (2005), *Lithos*, 83, 394-419. [7] Hanson and Jones (1998) *Am. Mineral.*, 83, 669-684. [8] Mallmann and O'Neill, (2009) *J. Petrol.*, 50, 1765-1794. [9] Blundy and Wood (1994) *Nature*, 372, 452-454. [10] Taura et al. (1998) *Phys. Chem. Minerals*, 25, 469-484. [11] Grant and Wood (2010) *GCA*, 74, 2412-2428. [12] Beattie, Ford, and Russell (1991) *Contrib. Mineral. Petrol.* 109, 212-224. [13] Beattie P (1994) *Chem Geol*, 117, 57-71.