EFFECT OF SULFUR ON SIDEROPHILE ELEMENT PARTITIONING BETWEEN OLIVINE AND MARTIAN PRIMARY MELT.

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Introduction: Since olivine is a common early crystallizing phase in basaltic magmas that have produced planetary and asteroidal crusts, a number of experimental studies have investigated elemental partitioning between olivine and silicate melt [e.g., 1, 2, 3]. In particular, olivine/melt partition coefficients of Ni and Co (D_{Ni} and D_{Co}) have been intensively studied because these elements are preferentially partitioned into olivine and thus provide a uniquely useful insight into the basalt petrogenesis [e.g., 4, 5]. However, none of these experimental studies are consistent with incompatible signatures of Co [e.g., 6, 7, 8] and Ni [7] in olivines from Martian meteorites. Chemical analyses of undegassed MORB samples suggest that S dissolved in silicate melts can reduce D_{Ni} up to 50 % compared to S-free experimental systems [9]. High S solubility (up to 4000 ppm) for primitive shergottite melts [10] implies that S might have significantly influenced the Ni and Co partitioning into shergottite olivines. This study conducts melting experiments on Martian magmatic conditions to investigate the effect of S on the partitioning of siderophile elements between olivine and Martian primary melt.

Methods: Melting experiments were conducted using a Quickpress non end-loaded piston-cylinder apparatus at Johnson Space Center (JSC) with a pressure assembly comprised of a $BaCO_3$ cell, MgO internal parts and a graphite sample capsule. The experiments employed a synthesized Y-980459 composition [11] for major element with an addition of ~200 ppm V, Co and Ni, because Y-980459 is interpreted as representing a Martian primary melt [7]. The starting composition was split into four aliquots; each of them was prepared to contain 0, 1000, 2000, and 3000 ppm S, respectively, by the addition of pyrite (FeS_2) powder. The starting compositions were heated at three different temperatures (1450, 1475 and 1500 °C) for ~3 hours at 7.5 kbar. To obtain large olivine crystals, the compositions were first heated above the liquidus temperature (1525 °C) for 0.5 hour before dropping to the target temperatures. Experimental charges were analyzed by ion microprobe (Cameca ims-4f) at University of New Mexico for trace elements (Ni in glass, V, Co) following the technique of [12] and by electron microprobe (Cameca SX-100) at JSC for other major and minor elements.

Results & Discussions: Experimental charges mainly consist of olivine (Fo_{81-84}) and glass. Melt fraction varies from 0.85 to 0.98 in weight. Spinel is present only in two 1450 °C charges. No sulfide phases are observed in the charges, suggesting sulfide undersaturation. Olivines (typically >100 μm) and glasses are homogeneous. The Fe-Mg exchange coefficient ($Kd_{Fe\text{-}Mg} = D_{Fe}/D_{Mg}$) values between olivine and glass (0.28-0.36, Fig. 1b) suggest that the experiments closely approached equilibrium.

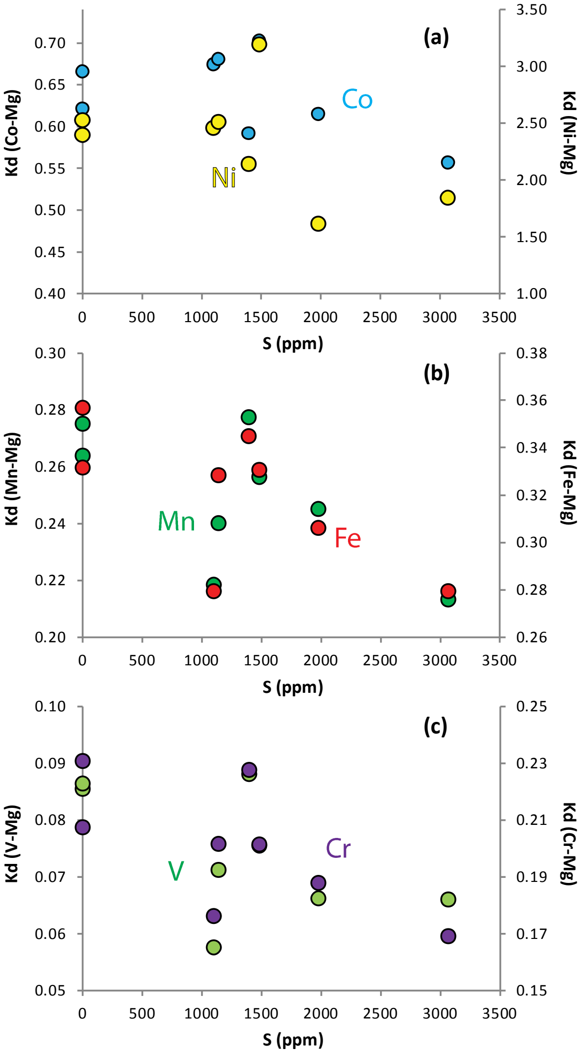

Figure 1: *$Kd_{M\text{-}Mg}$ versus S content of coexisting melt (M = V, Cr, Mn, Fe, Co and Ni). Considering analytical errors, uncertainties of the $Kd_{M\text{-}Mg}$ values would be <10 % except for $Kd_{Fe\text{-}Mg}$ (<3 %).*

We employed $Kd_{M\text{-}Mg}$ (M = V, Cr, Mn, Fe, Co and Ni) to examine the effect of S on partition coefficients of these elements to minimize effects of other variables such as temperature and olivine composition [e.g., 3]. The Kd values for V, Cr Mn and Fe decrease with increasing S contents, whereas those for Ni and Co slightly decrease but their correlations are barely discernible (Fig. 1).

The $Kd_{M\text{-}Mg}$ values are also correlated with melt compositions. Fig. 2 shows that $Kd_{V\text{-}Mg}$ increases with increasing the ratio of non-bridging oxygen to tetrahedrally coordinated cations (NBO/T) in the silicate melts. Such positive correlation between Kd and NBO/T is also recognized for Cr, Mn and Fe (though not shown here). These observations suggest that the Kd for V, Cr, Fe and Mn should be dependent on both S contents and major element compositions of the melts. In contrast, $Kd_{Co\text{-}Mg}$ is almost constant among the charges and the same is true for $Kd_{Ni\text{-}Mg}$.

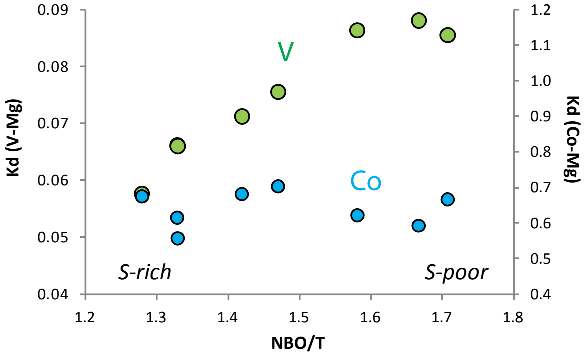

Figure 2: *Comparison of* $Kd_{V\text{-}Mg}$ *and* $Kd_{Co\text{-}Mg}$ *as a function of NBO/T. S-rich melt has a lower NBO/T value than S-poor melt. Considering analytical errors, uncertainties of the* $Kd_{V\text{-}Mg}$ *and* $Kd_{Co\text{-}Mg}$ *values would be <10 %.*

To assess the independent contribution of S on the siderophile element partitioning between olivine and melt, we calculated Kd using thermodynamic models based on S-free experiments [1, 3]. We did not calculate $Kd_{V\text{-}Mg}$ and $Kd_{Co\text{-}Mg}$ because no appropriate models exist for these two elements. This investigation suggests that S dissolved in the silicate melt slightly (up to 30 %) reduces the Kd values for all of the four elements (Fe, Mn, Co and Ni). Notice that the degrees of the Kd depletion are almost comparable among these four elements (Fig. 3) despite the more intense depletion of $Kd_{Fe\text{-}Mg}$ and $Kd_{Mn\text{-}Mg}$ against S than those of $Kd_{Ni\text{-}Mg}$ and $Kd_{Co\text{-}Mg}$ (compare Fig. 1a with 1b). This is probably because the depletion of $Kd_{Fe\text{-}Mg}$ and $Kd_{Mn\text{-}Mg}$ shown in Fig. 1 are partially attributable to the difference in melt compositions as seen for $Kd_{V\text{-}Mg}$ in Fig. 2.

Our study is basically consistent with a recent experimental study [13] that suggests that S in the silicate melt has a barely discernible effect on Fe, Co and Ni partition coefficients, although they did not recognize detectable effects on Cr, Mn and V. Although these experimental studies (our study and [13]) suggest that S could slightly reduce partition coefficients of siderophile elements, both D_{Ni} and D_{Co} are still distinctly greater than 1 even for high-S (>3000 ppm) melts. As considering S solubility for the Y-980459 starting composition is <4000 ppm within a range of reasonable shergottite magmatic conditions [10], we conclude that S cannot effectively reduce the siderophile element partitioning to explain the Ni and Co zoning features of shergottite olivines.

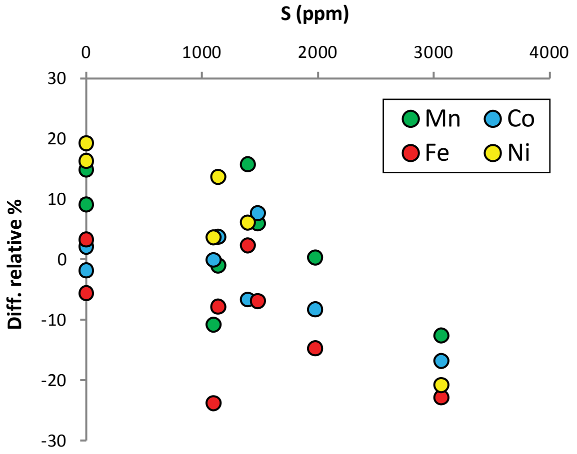

Figure 3: *Difference between measured and calculated* $Kd_{M\text{-}Mg}$ *as a function of S content of coexisting melt.* $Kd_{Mn\text{-}Mg}$ *,* $Kd_{Co\text{-}Mg}$ *and* $Kd_{Ni\text{-}Mg}$ *are calculated using Jones equations [3], whereas* $Kd_{Fe\text{-}Mg}$ *using a Toplis equation [1]. Diff. relative % = [Kd measured – Kd calculated]/[Kd calculated] × 100.*

References: [1] Toplis, M.J. (2005) *CMP*, *149*, 22-39. [2] Libourel, G. (1999) *CMP*, *136*, 63-80. [3] Jones, J.H. (1995) in *Rock physics & phase relations: a hand book of physical constants*, AGU: Washington, DC. p. 73-104. [4] Takahashi, E. (1978) *GCA*, *42*, 1829-1844. [5] Beattie, P., et al. (1991) *CMP*, *109*, 212-224. [6] Papike, J.J., et al. (2009) *GCA*, *73*, 7443-7485. [7] Usui, T., et al. (2008) *GCA*, *72*, 1711-1730. [8] Karner, J., et al. (2003) *Am. Mineral.*, *88*, 806-816. [9] Li, C., et al. (2003) *Chem. Geol.*, *201*, 295-306. [10] Righter, K., et al. (2009) *EPSL*, *288*, 235-243. [11] Shirai, N. and Ebihara, M. (2004) *Antarct. Meteorite Res.*, *17*, 55-67. [12] Shearer, C.K., et al. (2006) *Am. Mineral.*, *91*, 1657-1663. [13] Tuff, J. and O'Neill, H.St.C. (2010) *GCA*, *74*, 6180-6205.