

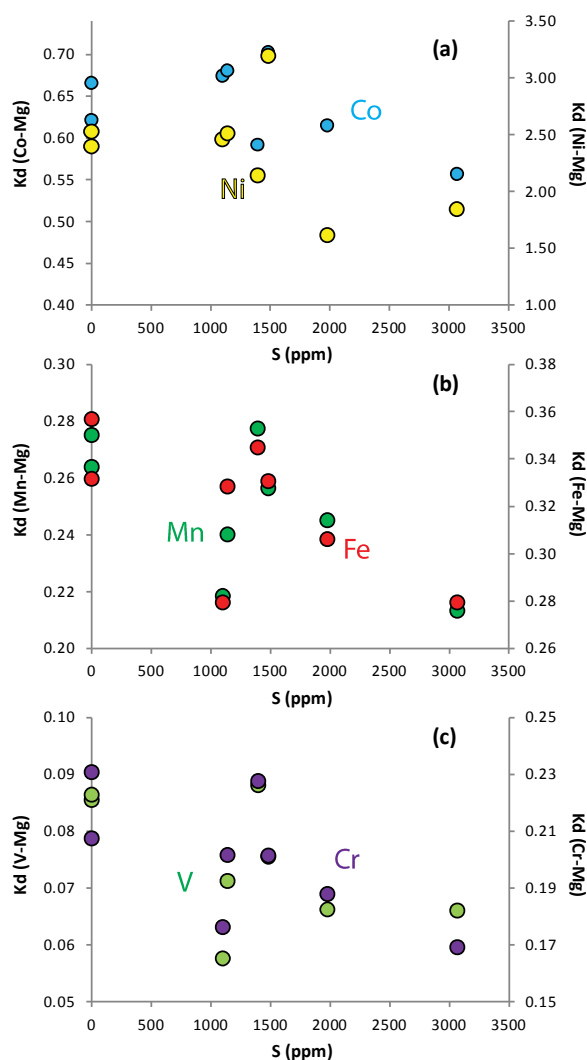
**EFFECT OF SULFUR ON SIDEROPHILE ELEMENT PARTITIONING BETWEEN OLIVINE AND MARTIAN PRIMARY MELT.** T. Usui<sup>1</sup>, C. K. Shearer<sup>2</sup>, K. Righter<sup>1</sup> and J. H. Jones<sup>1</sup>, <sup>1</sup>Johnson Space Center/NASA, Mail code KR, 2101 Nasa Pkwy, Houston, TX 77058 (tomohiro.usui@nasa.gov), <sup>2</sup>Institute of Meteoritics, University of New Mexico.

**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 ( $Fe_{81-84}$ ) and glass. Melt frac-

tion 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  $\mu m$ ) and glasses are homogeneous. The Fe-Mg exchange coefficient ( $Kd_{Fe-Mg} = D_{Fe}/D_{Mg}$ ) values between olivine and glass (0.28-0.36, Fig. 1b) suggest that the experiments closely approached equilibrium.

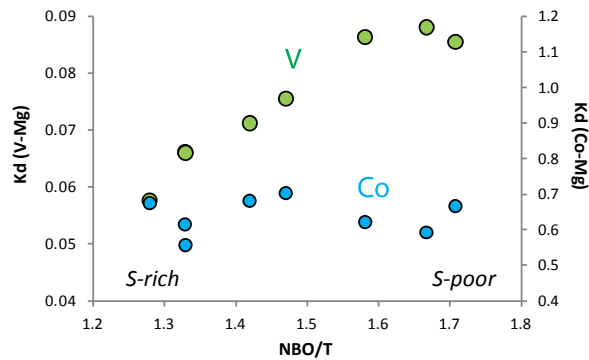


**Figure 1:**  $Kd_{M-Mg}$  versus  $S$  content of coexisting melt ( $M = V, Cr, Mn, Fe, Co$  and  $Ni$ ). Considering analytical errors, uncertainties of the  $Kd_{M-Mg}$  values would be <10 % except for  $Kd_{Fe-Mg}$  (<3 %).

We employed  $Kd_{M-Mg}$  ( $M = V, Cr, Mn, Fe, Co$  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  $K_d$  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).

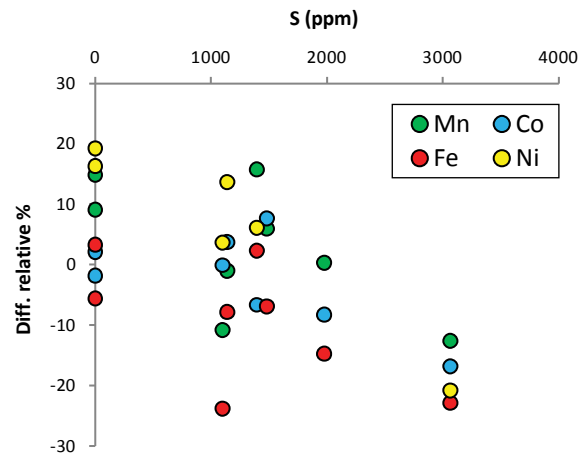
The  $K_{d_{M-Mg}}$  values are also correlated with melt compositions. Fig. 2 shows that  $K_{d_{V-Mg}}$  increases with increasing the ratio of non-bridging oxygen to tetrahedrally coordinated cations (NBO/T) in the silicate melts. Such positive correlation between  $K_d$  and NBO/T is also recognized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



**Figure 2:** Comparison of  $K_{d_{V-Mg}}$  and  $K_{d_{Co-Mg}}$  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  $K_{d_{V-Mg}}$  and  $K_{d_{Co-Mg}}$  values would be <10 %.

To assess the independent contribution of S on the siderophile element partitioning between olivine and melt, we calculated  $K_d$  using thermodynamic models based on S-free experiments [1, 3]. We did not calculate  $K_{d_{V-Mg}}$  and  $K_{d_{Co-Mg}}$  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  $K_d$  values for all of the four elements (Fe, Mn, Co and Ni). Notice that the degrees of the  $K_d$  depletion are almost comparable among these four elements (Fig. 3) despite the more intense depletion of  $K_{d_{Fe-Mg}}$  and  $K_{d_{Mn-Mg}}$  against S than those of  $K_{d_{Ni-Mg}}$  and  $K_{d_{Co-Mg}}$  (compare Fig. 1a with 1b). This is probably because the depletion of  $K_{d_{Fe-Mg}}$  and  $K_{d_{Mn-Mg}}$  shown in Fig. 1 are partially attributable to the difference in melt compositions as seen for  $K_{d_{V-Mg}}$  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  $K_{d_{M-Mg}}$  as a function of S content of coexisting melt.  $K_{d_{Mn-Mg}}$ ,  $K_{d_{Co-Mg}}$  and  $K_{d_{Ni-Mg}}$  are calculated using Jones equations [3], whereas  $K_{d_{Fe-Mg}}$  using a Toplis equation [1]. Diff. relative % =  $[K_d \text{ measured} - K_d \text{ calculated}] / [K_d \text{ calculated}] \times 100$ .

**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.