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

Revision 1.1

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Abstract - Ni and Co variations in primary martian magmas exhibit anomalous incompatible behavior, which has remained an unexplained conundrum. Because martian magmas are S-rich, and some trace metals have reported enhanced solubility in S-bearing magmas, we have carried out a series of experiments to evaluate the effect of high-S melts on the olivine/melt partitioning of Ni, Co, Mn, V, and Cr. Near-liquidus experiments on a synthetic primary martian mantle melt (Yamato-980459 [Y98]) were completed in a piston cylinder apparatus at 0.75 GPa. Previous studies in S-free systems illustrate that the partition coefficients for these elements are dependent chiefly on $D(Mg)_{ol/melt}$ (the partition coefficient defined as wt% Mg in olivine / wt% Mg in melt), a proxy for temperature, and were used to calibrate a predictive expression that includes the effects of temperature [i.e., $D(Mg)_{ol/melt}$], melt composition, and oxygen fugacity. These predictive expressions are then used to isolate any effect in D(M) olivine/melt due to dissolved sulfur. The results show that S might have a small effect for Co, but not enough to change Co partitioning from compatible to incompatible in our experiments. Addition of a sulfur term to the D(Co) predictive expressions shows that nearly 8000 ppm of sulfur would be required in the melt (at liquidus temperature of Y98) for D(Co) to become <1. These S contents are 2 times higher than those of a sulfide saturated melt at the (P,T) conditions of a martian mantle source region. Therefore, the anomalous incompatible behavior observed in these primary magma suites must be due to another mechanism. High temperature, oxygen fugacity, and diffusion are not viable mechanisms, but magma mixing, assimilation, or kinetic crystallization effects remain possibilities.

Keywords: shergottite; olivine; transition metals; sulfur; basaltic magma

Introduction

First-row transition elements (FRTE, including Mn, Ni, Co, Fe, V, and Cr) are useful indicators of primary planetary mantle melts (Sato, 1976; Wänke and Dreibus, 1986) and the source mineralogy of mantle melts (Sobolev et al., 2007), and their ratios can be used to infer source heterogeneities in mantle-derived melts (e.g. Fe/Mn; Humayun et al., 2004; LeRoux et al., 2011). 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., Toplis, 2005; Libourel, 1999; Jones, 1995). In particular, olivine/melt partition coefficients of Ni and Co (D(Ni) and $D(Co)_{ol/melt}$) 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., Takahashi, 1978; Beattie et al., 1991; Longhi et al., 2010). Ni and Cr have both been used as indicators of primary melts of planetary mantles (e.g., Sato, 1977; Wänke and Dreibus, 1986; Sobolev et al., 2007). Vanadium partitioning between olivine and melt is sensitive to changes of oxygen fugacity and has been used as an oxybarometer (Shearer et al., 2006; Mallmann and O'Neill, 2013; Lee et al., 2003; Canil and Fedortchouk, 2001; Nakada et al. 2020). Chromium partitioning between olivine and melt is also dependent upon oxygen fugacity since Cr^{2+} is stable in melts at low fO_2 (e.g., Hanson and Jones, 1998). Finally, Mn partitioning differences between peridotite and pyroxenite can be used to place constraints on sources of mantle melts (LeRoux et al., 2011; Sobolev et al., 2007). Fe/Mn ratios in meteorites are used to trace the origins of various meteorite groups due to the variable volatility of Mn in the solar system (e.g., Papike, 1998; Goodrich and Delaney, 2000; Karner et al., 2003), but a comprehensive interpretation of this ratio must include an understanding of differences in olivine melt

partitioning for Fe and Mn. Overall, the FRTE are very useful in delineating source characteristics and origin of planetary basalts.

Extensive studies of olivine/melt partitioning of FRTE have demonstrated the role of pressure, temperature, oxygen fugacity, and melt composition in controlling the magnitude of D (olivine/melt) (e.g., Takahashi, 1978; Beattie et al., 1991; Matzen et al., 2013; Longhi et al., 2010; Elardo et al., 2011; Hanson and Jones, 1998; Mallmann and O'Neill, 2013; LeRoux et al., 2011; Filiberto et al., 2009). Despite the many studies carried out on the partitioning behavior of Ni and Co, basic chemical trends in terrestrial and planetary samples remain unexplained. For example, Co exhibits incompatible behavior in olivines from Martian meteorites and lunar basalts, while Ni exhibits compatible behavior **(Figure 1;** Papike et al. 2009; Usui et al., 2008; Karner et al., 2003). High temperatures (~ 2000 °C) might be the cause of the opposite behavior of Ni and Co as shown by Longhi et al. (2010) and Elardo et al. (2011) for lunar magma ocean conditions, but these temperatures are much higher than liquidus temperatures of the olivine-phyric shergottites, near 1500 °C at 0.5 GPa (e.g., Rapp et al., 2013) and therefore cannot be the cause of the incompatible behavior. Similarly, Ni and Co exhibit de-coupled behavior in terrestrial peridotite and pyroxenite, compared to their expected compatible behavior (Sobolev et al., 2007; Herzberg et al., 2016).

A distinctive aspect of martian magmas and shergottites that might provide an explanation for compatible Ni and incompatible Co is the high S contents of primitive shergottite liquids (up to 2700 ppm; Franz et al., 2014). Sulfur is known to enhance the solubility of some trace metals in terrestrial magmas. For example, chemical analyses of S-rich Mid-Ocean Ridge Basalt (MORB) samples (i.e. un-degassed with respect to sulfur) suggest that S dissolved in silicate melts can reduce $D(Ni)_{ol/melt}$ up to 50 % compared to S-free experimental systems (Li et

al., 2003). MORB glasses typically contain ~ 1000 ppm S at 8% MgO (e.g. Le Voyer, et al., 2019), and even at those concentration levels, S has a discernable effect on D(Ni) olivine/melt. Martian basaltic melts are known to contain even higher S contents (up to 2700 ppm; Dreibus et al., 1982, 2000; Zipfel et al., 2000; Shirai and Ebihara, 2004; Franz et al., 2014). The high S contents of shergottites in general as well as the high solubility of S in primitive shergottite melts (up to 4000 ppm; Righter et al., 2009) implies that S might be responsible for significantly influencing the Ni, Co, and other FRTE partitioning in shergottite olivines. Although Mn, V, and Cr all exhibit incompatibility in olivine for martian magmatic conditions (e.g., Karner et al., 2007; Righter et al., 2006; Hanson and Jones, 1998), the extent of their incompatibility (e.g. Mn in Herd et al., 2009) must be explored in S-bearing systems. Existing experimental data are not ideal for evaluating these effects for martian melt compositions at martian mantle and magmatic conditions. There are some studies that utilized S-bearing melts, but do not include martian compositions (e.g. Tuff et al., 2010), or have been carried out at low PT conditions that are not directly relevant to martian melt generation (e.g., Gaetani and Grove, 1997). Thus, the relevant set of P-T-fO_2 conditions and melt compositions have not yet been explored together in one study, and utilizing literature data would require extrapolation of one or more variables.

To explore the possible effects of S on the olivine/melt partitioning behavior of Ni, Co, Mn, V, and Cr, we have conducted experiments to examine partitioning between olivine and Martian primary mantle melt at Martian magmatic conditions (give P, T, fO_2) and variable and high S contents (up to 3000 ppm). Conditions of Martian magma genesis have been explored by several studies, and multiple saturation is thought to occur from 0.8 to 2 GPa and 1450 to 1575 °C (e.g., Rapp et al., 2013; Collinet et al., 2015; Filiberto et al., 2010; Gross et al., 2011). Given the known negative pressure dependence of sulfide saturation and S solubility in melts (Righter

et al. 2009; Holzheid and Grove, 2002), we chose the low pressure end of this range to allow the maximum values of S solubility - up to ~3000 ppm. In addition, oxygen fugacity was defined below the FMQ (fayalite-magnetite-quartz) buffer which is an appropriate value for the Martian mantle. The most primitive, unfractionated mantle melts are thought to be the olivine-phyric shergottites high MgO (15-20 wt%) and relatively low Al_2O_3 (<7 wt%). Therefore we chose the Yamato-980459 olivine-phyric shergottite as a starting composition for the experiments; this sample has also been featured in studies of Ni, Co, and V in olivines (Usui et al., 2008; Nakada et al., 2020) and thus is directly relevant to the results. The new results on this S-bearing martian melt composition, obtained at conditions of martian magma genesis, are then used to interpret trace metal contents in martian magmatic suites. The FRTE are very useful elements utilized in determining source characteristics and origin of planetary basalts, and evaluation of the role of S will make their prediction more accurate and applicable to natural systems such as martian magmas.

Experimental and analytical methods

Y-980459 is an olivine-phyric shergottite (martian meteorite) interpreted as representing a Martian primary mantle melt based on its bulk and olivine Mg#, Ni and Cr contents (Usui et al., 2008; Greshake et al. 2004), is ideal for this study, and experiments employed a synthesized Y-980459 composition (Shirai and Ebihara, 2004) for major and minor elements. Synthetic glass of the Y-980459 composition was prepared from reagent grade oxide powders in an agate mortar. This mixture was then fused into glass at fO_2 of ~FMQ buffer, and then reground into a powder followed by addition of ~200 ppm V, Co and Ni. This starting composition was then 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 addition of minor amount of FeS_2 (up to 3000 ppm) did not alter the phase relations of the run products.

Melting experiments were conducted using a Quickpress non-end-loaded piston-cylinder apparatus at Johnson Space Center (JSC). Pressure was generated within $BaCO_3$ cells, and calibrated on the location of the diopside-melting curve; pressures were corrected by –0.3 kbar and only corrected pressures are reported [see Filiberto et al. (2008) for calibration results]. Experimental details of pressure, temperature and the assemblies were also presented in Righter et al. (2009) and Filiberto et al. (2008). Samples were heated with graphite furnaces. A type C thermocouple (W–Re) wire, with an accuracy of ±2 °C, was used to measure the temperature. Samples were pressurized to the desired pressure (0.75 GPa), and then heated above the liquidus temperature (1525 °C) for 0.5 hour before dropping to the target temperatures of 1450, 1475, and 1500 °C. The initial superheating followed by cooling to sub-liquidus temperatures is to promote growth of large olivine crystals, as superheating should destroy more olivine nucleation sites in the melt. Experiments were terminated by power quenching the samples, usually resulting in glassy run products.

All major elements in olivines and glasses were analyzed with a Cameca SX100 electron microprobe at NASA-JSC, using an accelerating voltage of 20 kV and sample current of 20 nA. Standards included both natural (kaersutite, andradite, wollastonite, chromite, rutile, olivine, rhodonite, potassium feldspar, albite) and synthetic (V metal, NiO) standard materials. Count times for major elements were typically 10 s, and as long as 120 s for low concentrations of V or Cr in olivines and glasses. Under the latter conditions, detection limits were approximately 100 ppm for V. Interference of Ti*K*α on V*K*α peaks (Snetsinger et al. 1968) were avoided by counting Ti on PET using integral mode, and V on LiF in differential mode. PAP φ-ρ-Z

corrections were used in data reduction (Pouchou and Pichoir, 1991). All analyses are reported in **Tables 1 and 2**.

Ion microprobe analyses of experimental charges were conducted using a Cameca IMS 4f instrument at the University of New Mexico following the approach of Shearer et al. (1990, 2005, 2006) The olivine analyses involved repeated cycles of peak counting on $^{51}V^+$, $^{59}Co^+$, $^{60}Ni^+$, and $^{30}Si^+$. Ten cycles were used per analysis. The $^{30}Si^+$ was used as a reference species. The analytical procedure included counting on a background position to monitor detection noise. Background was collected on each standard and unknown at mass 18.7. Measurements at this mass produced a background of 1-3 counts. Absolute concentrations of each element were calculated using empirical relationships of measured peak $^{51,59,60}X^+/^{30}Si^+$ ratios normalized to known SiO_2 content (calibration curves are (($^{51,59,60}X^+/^{30}Si^+$) x SiO_2) plotted against trace elements for each standard) to element concentrations as derived from daily calibration measurements of the following olivine and glass standards: KAUG, K1OPX, D1OL, PM150, SC, MARJ, 610, 614, WUSTL1, and WUSTL2. Calibration curves for these elements have previously been determined by Papike et al.(1999) and Shearer et al. (1996, 2006). Analyses were made by bombardment of the sample with primary O^- ions accelerated through a nominal potential of 10 kV. A primary ion current of 15-20 nA was focused on the sample over a spot diameter of 15 µm. Sputtered secondary ions were energy filtered using a sample offset voltage of -105 V, and an energy window of ±25 V, to eliminate effectively most isobaric interferences (Shimizu et al., 1978). Secondary ions are detected by an electron multiplier in pulse counting mode. Peak counting times were varied to optimize precision. For olivine and glass analyses, precisions of better than 3% and 5%, respectively, were achieved. All ion microprobe analyses were conducted at locations analyzed previously with the electron microprobe, and the SiO_2

concentrations determined by EMP were used in reducing the SIMS data. Inclusion of contaminating phases in the SIMS analyses was avoided by selecting optically clean olivine grains and by mass imaging of major elements before and after each spot SIMS analysis.

Results

Phase equilibrium

Experimental charges mainly consist of olivine (Fo_{81-84}) and glass (**Figure 2**). Melt fractions were determined by using Ca mass balance between the bulk composition, glass and olivine, and varied from 0.85 to 0.98 in weight. Spinel is present only in two 1450 °C charges, the lowest temperature of our experimental suite. No sulfide phases are observed in the charges, suggesting sulfide under-saturation. Run products were sliced vertically to ensure that sulfide liquids had not settled to the bottom of the experimental charge. Neither olivines (typically >100 μm) nor glasses are zoned and are compositionally homogeneous in each experiment. The Fe-Mg exchange coefficient [K_d(Fe-Mg) = D(Fe)/D(Mg)] values between olivine and glass (0.28-0.36) suggest that the experiments closely approached equilibrium (e.g., Filiberto and Dasgupta, 2011).

Oxygen fugacity

Our graphite capsule does not buffer fO_2 in systems that contain melt – instead fO_2 is ultimately established in each experimental run by an interplay between Fe^{3+}/Fe^{2+}, CO_2 solubility and graphite-CO-CO_2 gas equilibria (Pawley et al., 1992; Holloway et al., 1992). Because every bulk composition has a slightly different CO_2 solubility, and different FeO and Fe_2O_3 content, these equilibria can define fO_2 across a window from FMQ-3 to FMQ, and thus it has to be measured for each specific bulk composition. Righter et al. (2009) and Righter et al (2013) used Co-(CoO,MgO) sliding sensor (after Taylor et al., 1992) for shergottite melt compositions to

calculate fO_2 for experiments in graphite capsules and they are FMQ-1.5. This relative fO_2 is slightly higher than measured in Y98 (FMQ-2.5 to FMQ-3.5; Shearer et al., 2006; Nakada et al., 2020), but the difference is not significant enough to influence partitioning and this will be discussed in more detail below.

Partition and exchange coefficients

Partition coefficients, D(M) olivine/melt, are the ratio of wt% element M in the olivine / wt% element M in silicate melt, and are known to vary with temperature, pressure, melt composition, and fO_2. Because D(M)'s can be dependent upon subtle melt compositional parameters, and temperature and oxygen fugacity, it is useful to also examine exchange coefficients based on the equilibria such as

$$\underset{\text{melt}}{MO} + \underset{\text{olivine}}{Mg_2SiO_4} = \underset{\text{melt}}{MgO} + \underset{\text{olivine}}{MgMSiO_4}$$

where M = V, Cr, Mn, Fe, Co or Ni, and the $K_d(M\text{-}Mg) = (X_{M2SiO4})(X_{MgO}) / (X_{MO})(X_{MgMSiO4})$ which simplifies to D(M)/D(Mg). We examine Ni, Co, Mn, V and Cr partitioning between olivine and melt using both the partition coefficient and exchange coefficients (**Table 3**), to examine the effect of S on partitioning of these elements.

The D(M) values for Ni, Co, show a slight decrease and those for V, Cr, and Mn exhibit no variation with increasing S contents (up to 3066 ppm). On the other hand, the ln K_d(M-Mg) values for all five elements decrease with increasing melt S contents (**Fig. 3a,b; Figure 4a,b**). Because partitioning is sometimes dependent upon melt composition or structure, we use the ratio of non-bridging oxygen to tetrahedrally coordinated cations (NBO/T), which is a gauge of melt structure using composition (Mysen, 1991). NBO/T is a simple concept of melt

polymerization that can be used to assess variation in melt composition from a polymerized melt like a rhyolite (NBO/T < 1) to more depolymerized like peridotitic melt (NBO/T=2.7). The D(M) values for Ni decrease slightly with increasing NBO/T, whereas those for Co, V, Cr, and Mn all show little to no correlations (**Fig. 3c,d**). On the other hand, $\ln K_d$(M-Mg) values for Ni, Mn, V, and Cr all increase with increasing NBO/T and those for Co remain nearly constant (**Fig. 4c,d)**. Examination of D(M) and $\ln K_d$(M-Mg) variation with NBO/T and Sulfur shows more correlations with NBO/T, and may indicate the importance of melt compositional effects for olivine/melt partitioning of Ni, Co, Mn, V, and Cr. Trends with melt S content and melt composition and/or structure (NBO/T) might be inter-related or co-dependent and so below we look at previous studies for guidance on how to interpret our results.

Discussion

Comparison to previous studies

There have been many systematic studies of trace metal partitioning that can be compared to our new results. When making comparisons, differences in temperature, fO_2, and melt composition are important to understand. For example, Mallmann and O'Neill (2013) studied V, Mn, and Cr between 1200 and 1530 °C, FMQ-2.85 to +3, with melts including a wide range of FeO contents, but higher Al_2O_3 contents than martian melts, and no sulfur. LeRoux et al. (2011) studied Ni, Co, and Mn at 1310-1500 °C, FMQ-1.5, and for terrestrial basaltic melts with low FeO, high Al_2O_3, and no S. Gaetani and Grove (1997) carried out experiments at 1350 °C, FMQ-1 to -4, on terrestrial basaltic melt compositions with high Al_2O_3, and low FeO. Their study had variable melt S contents up to ~ 1500 ppm, and also a specified f_{S2}. Filiberto et al.

(2009) examined Ni partitioning at 1300-1420 °C, FMQ-2, for an S-free Gusev (Martian) basalt melt composition. Herd et al. (2009) studied Ni and Co between 1150 and 1290 °C, FMQ-0.5 to -3.0, for three S-free melt compositions (martian, lunar, eucritic). Matzen et al. (2013) studied Ni between 1350 and 1500 °C, 1 bar to 3 GPa, FMQ-1.7, for melts of mid-ocean ridge basalt composition. Hanson and Jones (1998) examined Cr partitioning between olivine and melt for various melt compositions, 1160-1230 °C, and at FMQ and FMQ-4. With a goal of evaluating Ni and Co behavior at high temperatures relevant to a lunar magma ocean, Longhi et al. (2010) studied olivine/melt partitioning to over 2000 °C and FMQ-4. Shearer et al. (2006) studied V at 1300-1380 °C, FMQ to FMQ-4.5, and for S-free Yamato 980459 melt compositions. Elardo et al. (2011) measured Ni and Co partitioning in two lunar mantle bulk compositions and at near liquidus conditions between 1 and 3 GPa, and up to 1800 C. Tuff et al. (2010) studied Ni, Co, V, Cr, Mn at 1370-1400 °C, with melts that were medium in FeO and Al_2O_3, FMQ-2 to -3, and variable S. Given the overlap in elements, S-contents and fO_2, their study will be of interest to compare directly to our results. These experiments will be very useful for making comparison of V, Cr, and Mn results at the same T, fO_2, and melt FeO.

Effect of temperature with D(Mg) as a proxy

Previous work has shown that D(Mg) olivine/melt is a good proxy for temperature dependence of partitioning (Jones, 2003, 1995, 1984; Matzen et al., 2013). This is demonstrated with numerous studies for all five elements (**Figure 5**). Positive correlations of D(M) and D(Mg) are observed for Ni, Co, Mn and Cr. Correlations with D(V) are not as clear, but this is due to the strong dependence of D(V) on fO_2 (see next section).

Effect of oxygen fugacity

There is no clear dependence of D(Ni), D(Co), or D(Mn) on oxygen fugacity as might be expected for these three elements that exhibit 2+ valence in fO_2 range of natural magmas. Chromium exhibits two oxidation states in natural magma – 2+ and 3+, yet D(Cr) does not exhibit strong dependence upon fO_2, as the Cr^{2+}/Cr (tot) varies only slightly across the fO_2 range of natural magmas (Hanson and Jones, 1998; Bell et al., 2017). However, D(V) varies strongly with fO_2 (**Figure 5**), and strong fO_2 dependence has led some previous studies to utilize D(V) olivine/melt as an oxybarometer (Hanson and Jones, 1997; Canil and Fedortchouk, 2001; Mallmann and O'Neill, 2013). When our study is combined with several literature datasets, D(V) clearly varies between 0.001 and 0.4 between FMQ+3 and FMQ-3 (**Figure 5**). The decrease in D(V) at higher fO_2 is caused by a shift from lower valence of V (3+ and 2+) at lower fO_2 to higher valence of V (4 and 3+) at higher fO_2 (e.g., Sutton et al., 2005; Righter et al., 2006).

Effect of melt composition

Melt composition is considered an important variable for Ni, Co, and V partitioning between olivine and melt (Herd et al., 2009; Filiberto et al., 2009; Mallmann and O'Neill, 2013; Tuff and O'Neill, 2010; Matzen et al., 2013). Because of the potential for melt compositional effects, we use the NBO/T melt compositional/structural parameter to assess the effects for each element. D(M) exhibits clear dependence on NBO/T for all five elements (**Figure 5**). For our experiments, K_d(M-Mg) values are also correlated with melt compositions (**Figure 3c, d and 4c, d**). For example, K_d(Ni-Mg), K_d(V-Mg), K_d(Cr-Mg), and K_d(Mn-Mg) all increase with increasing NBO/T in the silicate melts (**Fig. 4c, 4d, 6)**. In contrast, K_d(Co-Mg) is nearly constant among the samples in our experimental series, (**Fig. 4c, 6**). Thus, predictive expressions for all

of these elements will have to include terms for D(Mg), fO_2, and melt composition, and are developed in more detail below with specific studies forming the foundation for comparison.

Effect of S on olivine/melt partition coefficients

To assess the independent contribution of S on the siderophile element partitioning between olivine and melt, we calculate D(M) utilizing predictive expressions whose specific form is based on our assessment in the previous section.

Because we are searching for variations in D(Ni) or D(Co) well outside of the experimental error associated with these predictive expressions (typically 10-15%), we will use a simple form to predict D(Ni) and D(Co) in S-free systems to compare to our S-bearing experiments, using D(Mg) and NBO/T as the independent variables. Because Mn does not exhibit valence change across the fO_2 range considered relevant to terrestrial, martian or lunar samples utilized in these studies, and thus it should exhibit similar behavior to Ni and Co, we use these correlations with D(Mg) for Mn as well. Thus, for Ni, Co, and Mn we use D(Ni) = a D(Mg) + b (NBO/T) + d, calibrated with S-free experiments that were carried out at otherwise similar conditions (Ni and Co: Longhi et al., 2010; LeRoux et al., 2011; Tuff and O'Neill, 2010; Herd et al., 2009; Filiberto et al., 2009; Elardo et al., 2011; Mn: Tuff and O'Neill, 2010; Mallmann and O'Neill, 2013; LeRoux et al., 2011; and Longhi et al.,2010). Previous studies have adequately modelled D(Ni) and D(Co) as a function of D(Mg) (Jones, 1995; Matzen et al., 2014; Herd et al., 2009).

V and Cr both show dependence upon D(Mg) and NBO/T like Ni, Co, and Mn. In addition, studies have shown that D(V) is dependent upon melt composition (Mallmann and O'Neill, 2013). Since these two elements exhibit valence changes over the oxygen fugacities of

relevance to terrestrial, martian or lunar samples utilized in these studies, D(V) and D(Cr) will vary with fO_2. Thus, for V and Cr, we use the expression D(V) = a D(Mg) + b (NBO/T) + c (ΔFMQ) + d, calibrated with data from Mallmann and O'Neill (2013), Tuff and O'Neill (2010), and Elardo et al. (201) (For V) and data from experiments of Tuff and O'Neill (2010), Mallmann and O'Neill (2013), Longhi et al. (2010), and Hanson and Jones (1998) (for Cr), across a wide T, fO_2 and melt composition range.

Multiple linear regression of D(M) against the two or three variables was done using Sigma Plot 12. Regression results are summarized in **Table 4**, and **Figure 7**. The data used to derive the regression coefficients cover a wide range of temperature, melt composition and fO_2. The standard error associated with each equation is small, and this error will be critical to evaluating and isolating the effect of sulfur on the olivine/melt partitioning of each element. The difference between the predicted values to the measured values for each of our experiments (**Figure 8**) shows that for most or all of the range of sulfur content, the measured values is within error the same as the predicted value, thus indicating that sulfur does not have a strong effect on partitioning for most elements. However, Co exhibits statistically different values at the highest S contents, indicating that D(Co) can be lower in S-bearing systems compared to S-free. Thus, at the highest S melt values explored here, D(Co) will be slightly lowered, but all other elements – Ni, Mn, Cr, and V – show no variation outside the predicted values in S-free systems.

Although our experimental studies suggest that S could slightly reduce partition coefficients of siderophile elements, both D(Ni) and D(Co) are still distinctly greater than one even in our highest S (~3000 ppm) melts. Whether Co can become incompatible depends on how much sulfur is dissolved into the melt, at what temperature, and whether the melts are sulfide saturated. There is evidence from both bulk S and highly siderophile elements that

martian melts are sulfide under-saturated (Jones et al., 2003; Righter et al., 2009). However, putting this data aside for a moment, we calculate S content at sulfide saturation to illustrate the potential effect on D(Co) olivine/melt of the highest possible melt S contents. For example, if shergottitic liquids are sulfide saturated in their mantle source, contain >4000 ppm S, and liquidus olivines crystallize at a temperature of ~1450-1500 C, these conditions could push D(Co) to values near or below 1. To test under what conditions D(Co) becomes <1, we have added our S-bearing dataset, as well as S-bearing experiments from Gaetani and Grove (1997) and Tuff and O'Neill (2010), to the regression analysis, and a sulfur term to quantify the effect of dissolved S on D(Co). The equation has the form: D(Co) = a D(Mg) + b(NBO/T) + d (ppm S) + e, and results in a = 0.495 , b = -0.311, d = -0.0000824, e = 0.843, with standard error = 0.22 (**Table 4**). Application of this equation to martian primary liquids (NBO/T = 1.5, D(Mg) = 2.5) results in D(Co) < 1 if S contents are >8000 ppm. These values are a factor of ~4 higher than measured in primitive martian basalts (1600-2700 ppm S; Ding et al., 2015; Righter et al., 2009 and references within), and are 2 times higher than S contents expected if such melts were sulfide saturated in their source (~ 4000 ppm). Therefore, dissolved sulfur is not a realistic way to lower D(Co), even under high S, sulfide saturated conditions.

Conclusions and implications

This investigation demonstrates that dissolved S in melts has minimal to no effect on the olivine/melt partitioning of Ni, Co, Mn, V and Cr. Only at high S contents of ~3000 ppm or higher is there a discernable difference in partitioning for Co. These results are essentially consistent with Tuff and O'Neill (2010) whose results suggest that S in the silicate melt has a barely discernible effect on Fe, Co and Ni partition coefficients. Furthermore, they did not

recognize detectable effects on Cr, Mn and V. Considering S solubility for primitive martian melts (such as Y-980459) can be as high as ~4000 ppm within a range of reasonable shergottite magmatic conditions (Righter et al., 2009), the olivine/melt partition coefficients for these five elements will only be affected at near sulfide saturation conditions; S contents in sulfide-under-saturated martian liquids are typically not high enough (~1500-2000 ppm) to affect the partitioning.

If a change in olivine/melt compatibility is not responsible for the Ni and Co systematics in shergottite olivine, another mechanism or process is causing the apparent incompatibility of Co in shergottite olivines. The de-coupling of Ni and Co is also observed in lunar and terrestrial igneous suites (Sobolev et al., 2007; Karner et al., 2003; Papike et al., 1999), suggesting that finding a solution to the martian sample suite might have wider implications for planetary basalts. Lower oxygen fugacity cannot be an explanation because studies have shown that neither D(Ni) nor D(Co) olivine/melt are dependent upon fO_2 (e.g., **Figure 5**). High temperatures can cause lowering of D(Ni) and D(Co), but even as Longhi et al. (2010) show, the temperatures required are ~ 2000 °C, which are superliquidus for the shergottite or primary martian mantle melts. Changes during fractionation might be called upon to affect the behavior of Co relative to Ni, but the partitioning of these elements would be controlled by clinopyroxene and spinel as other magmatic phases, both of which are hosts for Ni and Co and thus exhibit compatible behavior as well (Righter et al., 2006; Dygert et al., 2014). An additional possible mechanism is a difference in diffusion behavior between Co and Ni in olivine at these conditions. There is diffusion data for both elements that indicates they have very similar diffusion coefficients (Morioka, 1980; 1981), so a diffusion-controlled mechanism is unrealistic

as well. Thus, changes in Ni or Co behavior due to fO_2, temperature, fractionation, or diffusion are not viable explanations.

One possibility, suggested by Herd et al. (2009), is that magma mixing may have altered the concentrations of Ni and Co, leading to the apparent incompatible behavior. Shearer et al. (2013) and Usui et al. (2008) suggested the possibility that Y98 olivine cores are xenocrystic. This idea is supported by the presence of xenocrysts in many of the olivine-phyric shergottites (e.g., Castle et al., 2020). Another possibility would require assimilation of a Co-rich material into the shergottite primary liquids after the initial crystallization of olivine, thus causing an apparent incompatibility of Co. Such Co-rich material on Mars is apparently not common, but has been identified in exploration of the Gale Crater region of Mars (Lanza et al., 2016; Berger et al., 2017). Co-rich (~300 ppm Co) and Mn-rich (~3.5 wt.%) deposits have been documented there, associated with hydrothermal activity and oxidation, and the possible presence of oxides. The positive correlation of Co and Mn in olivines and bulk shergottites (and negative correlation with Ni) might support such an idea. A third possibility is that the Ni and Co trends documented in the shergottite olivines are due to possible kinetic crystallization effects (e.g., Kennedy et al., 1993; Papike et al., 1999; Hagerty et al., 2006; Albarede and Bottinga, 1972). All three of these possibilities could be fruitful avenues for future investigations.

Implications

Our partitioning results, in combination with previously published data, show that dissolved sulfur does not affect olivine/melt partitioning of Ni, Mn, Cr, or V, but might have a small effect on Co. However, nearly 8000 ppm of sulfur would be required in martian primary melts for Co to become incompatible (D(Co) <1), 2 times higher than those of a sulfide saturated melt at the (P,T) conditions of a martian mantle source region. Therefore, the anomalous

incompatible behavior observed in these primary magma suites must be due to another mechanism. High temperature, oxygen fugacity, and diffusion are not viable mechanisms, but magma mixing, assimilation, or kinetic crystallization effects remain possibilities.

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Figure Captions

Figure 1: Ni and Co concentrations in shergottite olivines showing compatible behavior of Ni with fractionation (or increasing XFe), and incompatible behavior of Co (from Papike et al., 2009; Shearer et al., 2008; Usui et al., 2008). These trends suggest that in shergottite systems Co exhibits incompatibility in olivine, counter to evidence from many partitioning studies that show it is compatible. Usui et al. (2008) also demonstrate Ni and Co incompatibility in high Fo olivines from Y-980459. Error on Ni and Co measurements are smaller than the symbols; arrows also show the direction of differentiation.

Figure 2: Back scattered electron image of run product from experiment #16, at 0.75 GPa, 1475 °C, with sample composition of synthetic Y-980459 melt with 1000 ppm S added. Duration was 3 hours, with a 30 minute dwell at 1500 °C before lowering to 1475 °C for olivine growth.

Figure 3: (a,b): D(M) versus S content [S] of coexisting melt for the experiments in this study. (a) Ni and Co, and (b) Mn, Cr, and V. Hatched line indicates a 1-sigma deviation of each regression line.

$D(Ni) = -0.0003 * [S] + 7.2739$ ($R^2 = 0.0365$);

$D(Co) = -(7x10^{-6}) * [S] + 1.4543$ ($R^2 = 0.0012$);

$D(Mn) = -(4x10^{-6}) * [S] + 0.7313$ ($R^2 = 0.0084$);

$D(Cr) = -(5x10^{-6}) * [S] + 0.5975$ ($R^2 = 0.0483$);

$D(V) = -(4x10^{-6}) * [S] + 0.2243$ ($R^2 = 0.0855$).

(c,d): D(M) versus NBO/T of coexisting melt for the experiments in this study; (c) Ni and Co, and (d) Mn, Cr, and V. Hatched line indicates a 1-sigma deviation of each regression line.

$D(Ni) = -1.6595 * (NBO/T) + 9.3734$ ($R^2 = 0.036$);

$D(Co) = -0.7374 * (NBO/T) + 2.532$ ($R^2 = 0.4018$);

$D(Mn) = -0.0857 * (NBO/T) + 0.8623$ ($R^2 = 0.1128$);

$D(Cr) = -0.0394 * (NBO/T) + 0.6497$ ($R^2 = 0.0917$);

$D(V) = + 0.0587 * (NBO/T) + 0.133$ ($R^2 = 0.548$).

Figure 4: (a,b): $\ln K_d(M\text{-}Mg)$ versus S content [S] of coexisting melt for the experiments in this study, where M = (a) Ni and Co, and (b) Cr and V. Hatched line indicates a 1-sigma deviation of each regression line.

$\ln K_d(Ni\text{-}Mg) = -(1.11\text{x}10^{-4}) * [S] + 0.970$ ($R^2 = 0.28$);

$\ln K_d(Co\text{-}Mg) = -(4.22\text{x}10^{-5}) * [S] – 0.398$ ($R^2 = 0.282$);

$\ln K_d(Mn\text{-}Mg) = -(6.0\text{x}10^{-5}) * [S] – 1.3162$ ($R^2 = 0.4057$);

$\ln K_d(Cr\text{-}Mg) = -(7.58\text{x}10^{-5}) * [S] - 1.52$ ($R^2 = 0.468$);

$\ln K_d(V\text{-}Mg)$: $y = -(8.35\text{x}10^{-5}) * [S] - 2.50$ ($R^2 = 0.299$).

(c, d): $\ln K_d(M\text{-}Mg)$ versus NBO/T of coexisting melt for the experiments in this study, where M = (c) Ni and Co, and (d) Mn, Cr, and V. Note that the S-rich melts have a lower NBO/T value than S-poor melts. Hatched line indicates a 1-sigma deviation of each regression line.

$\ln K_d(Ni\text{-}Mg) = 0.4133 * NBO/T + 0.2211$ ($R^2 = 0.1027$);

$\ln K_d(Co\text{-}Mg) = 0.016 * NBO/T - 0.4749$ ($R^2 = 0.0011$);

$\ln K_d(Mn\text{-}Mg) = 0.5213 * NBO/T – 2.1634$ ($R^2 = 0.7408$);

$\ln K_d$(Cr-Mg) = 0.5706 * NBO/T - 2.4537 (R^2 = 0.7006);

$\ln K_d$(V-Mg): y = 0.8983 * NBO/T - 3.9291 (R^2 = 0.9112).

Figure 5: Comparison of D(Ni), D(Co), D(Mn), D(V), and D(Cr) to those from previous studies, examining variations with D(Mg), NBO/T, and relative fO_2 (ΔFMQ).

Figure 6: Comparison of K_d(Ni-Mg), K_d(Co-Mg), K_d(Mn-Mg), K_d(Cr-Mg), and K_d(V-Mg) from previous studies, examining variations with NBO/T.

Figure 7: Comparison of measured vs. predicted D(Ni), D(Co), D(Mn), D(V), and D(Cr) olivine/melt. Predicted values were calculated using equations and constants tabulated in Table 4.

Data sources are listed in the legends, and also summarized in Table 4.

Figure 8: Difference between measured and calculated D(M) as a function of S content of coexisting melt. D(M) olivine/melt predicted are calculated using equations summarized in Table 4. Shaded areas shows 2σ error on the predicted values.

Figure 1

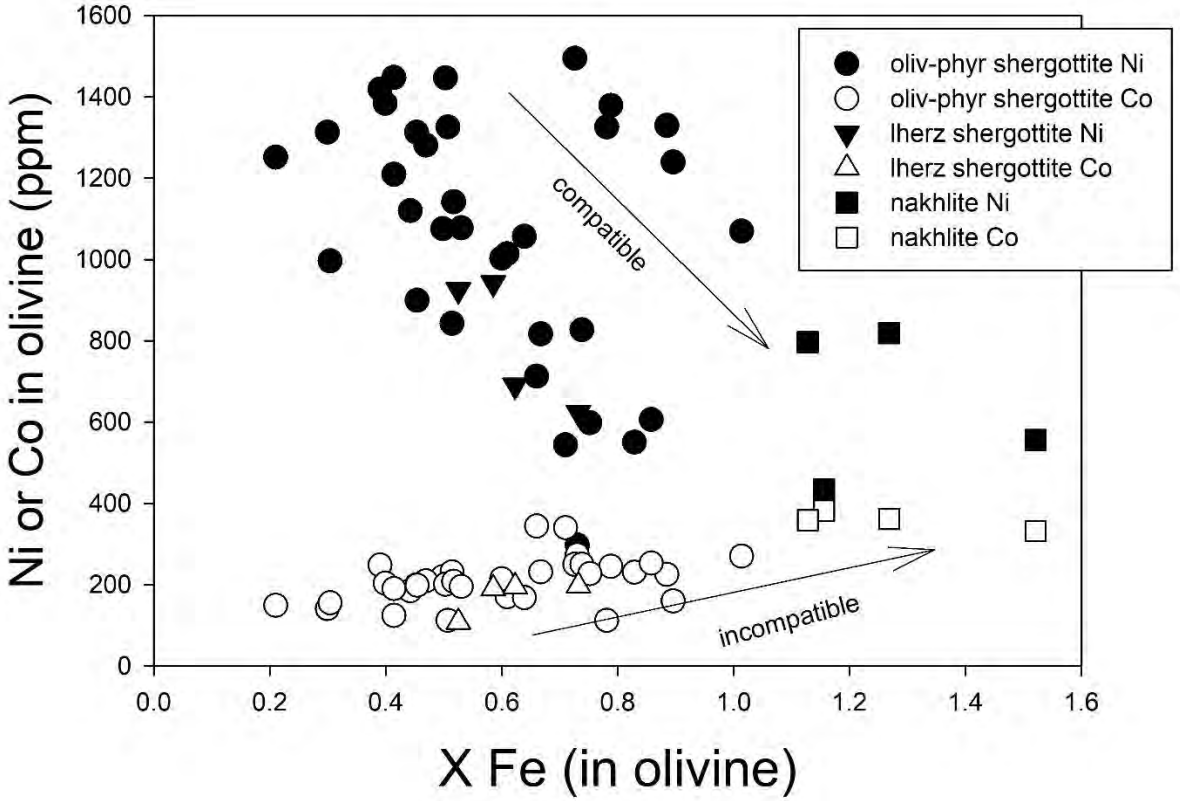

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Figure 2

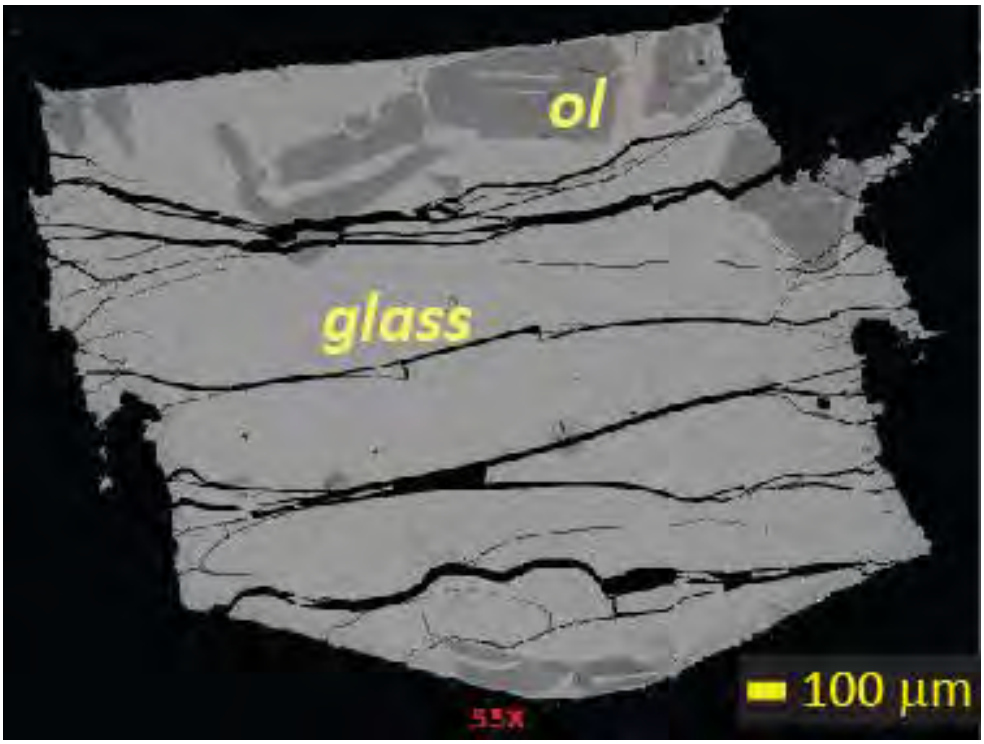

Figure 3:

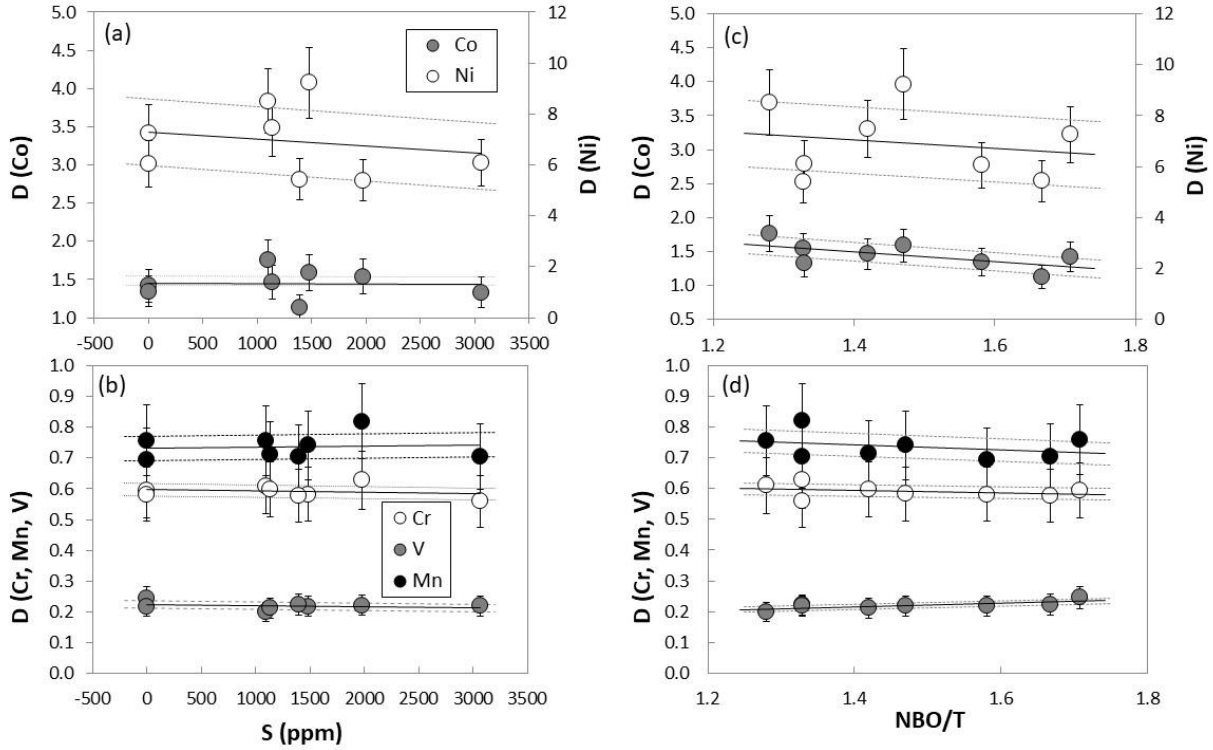

Figure 4:

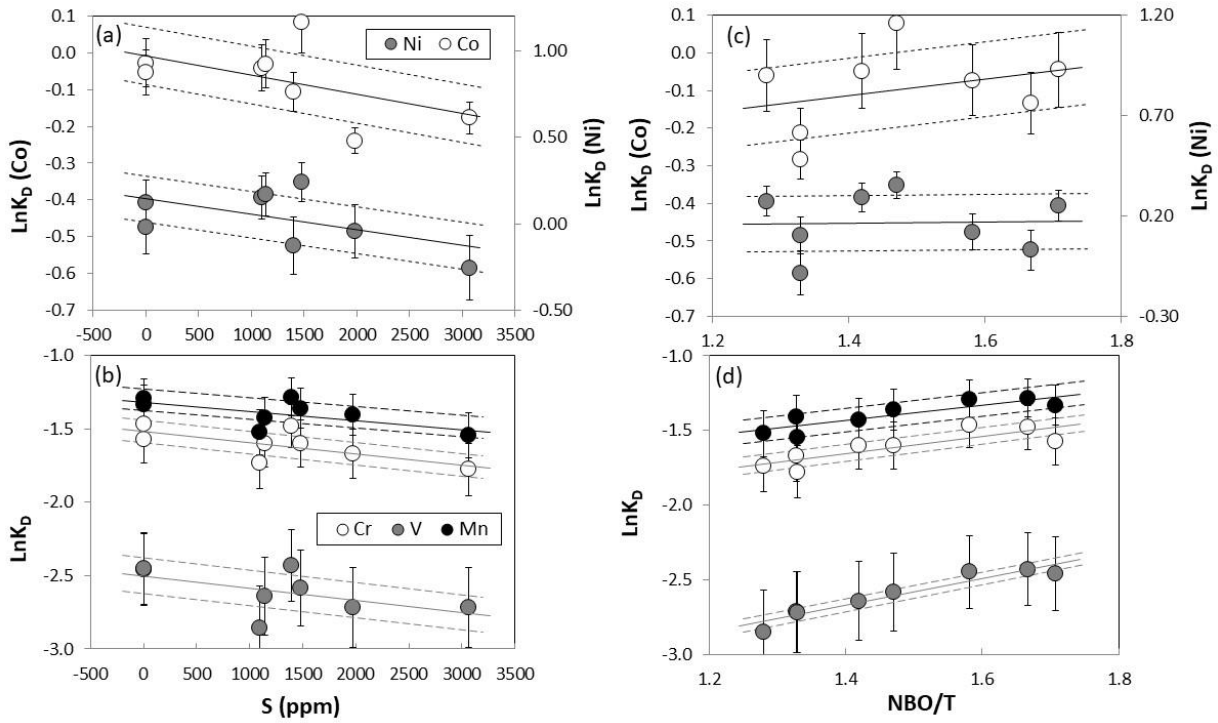

Figure 5:

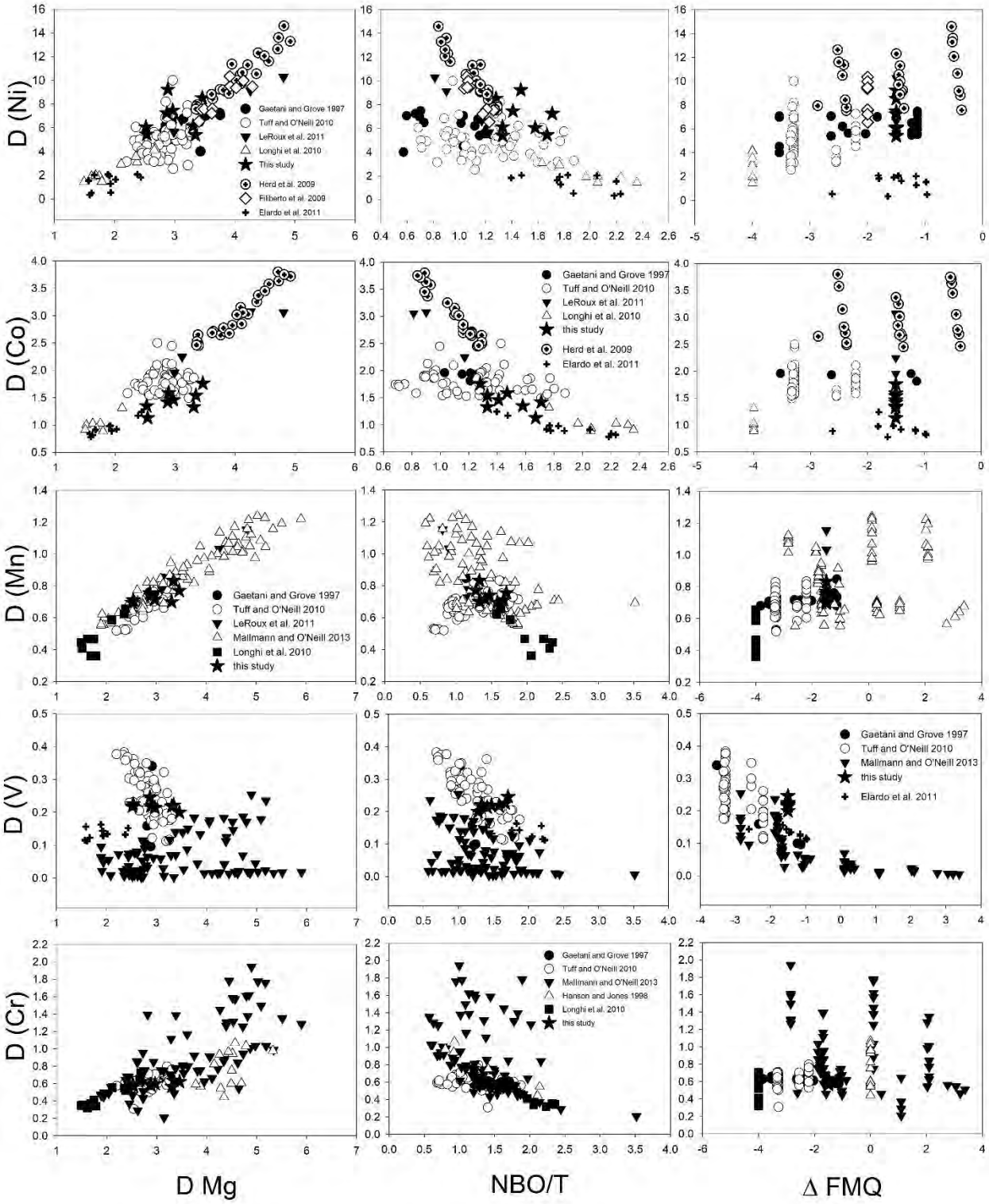

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Figure 6:

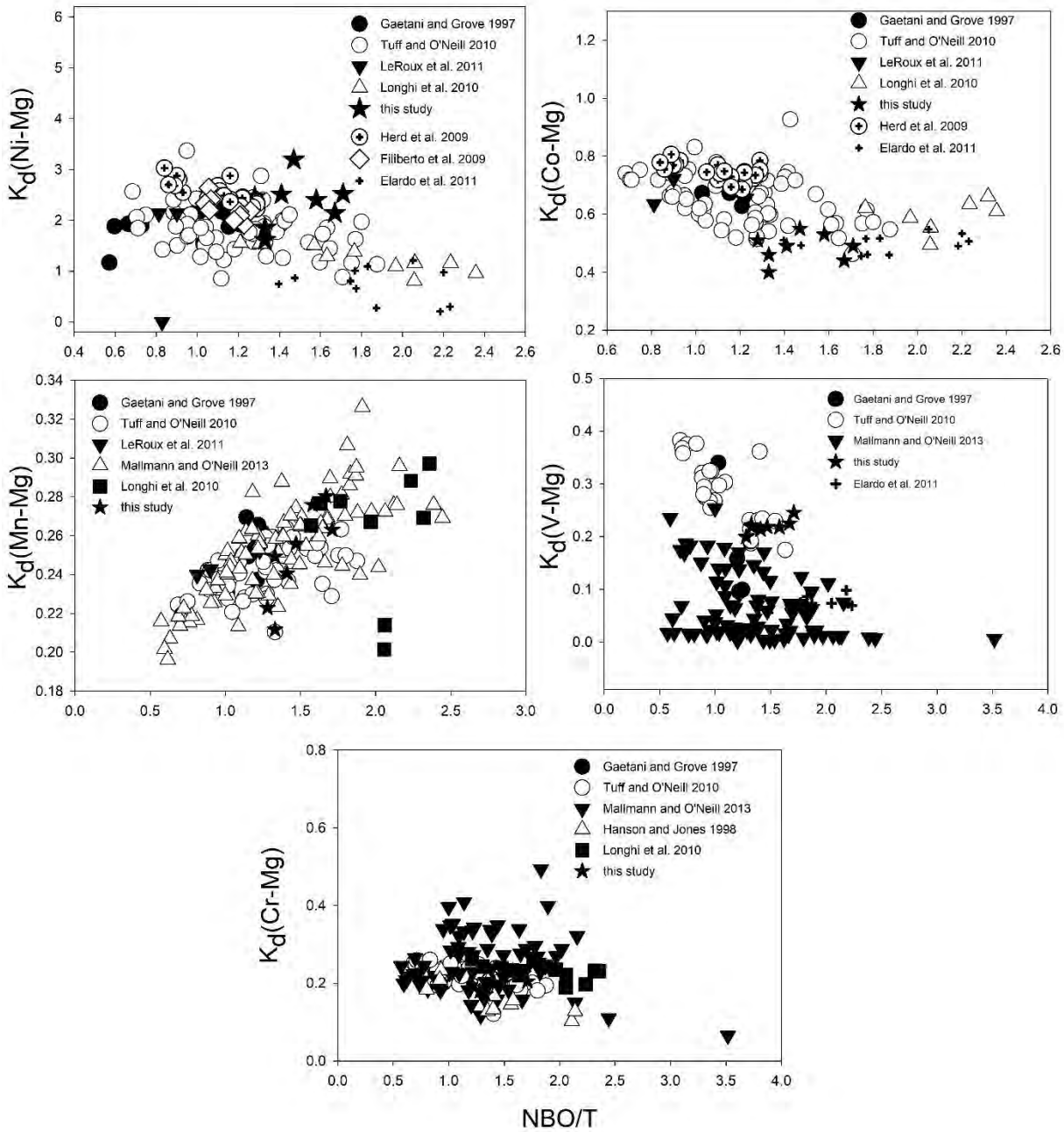

Figure 7:

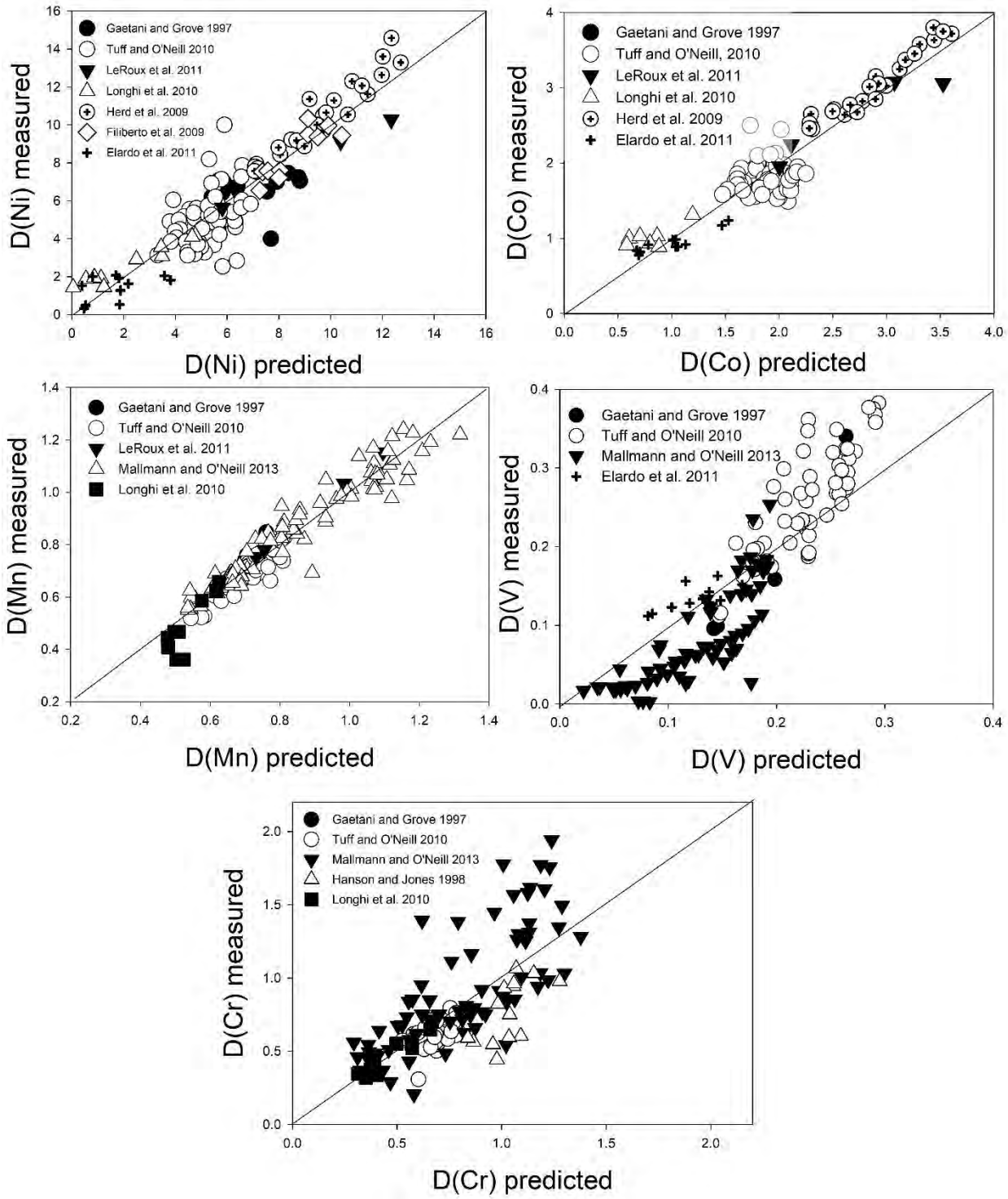

Figure 8:

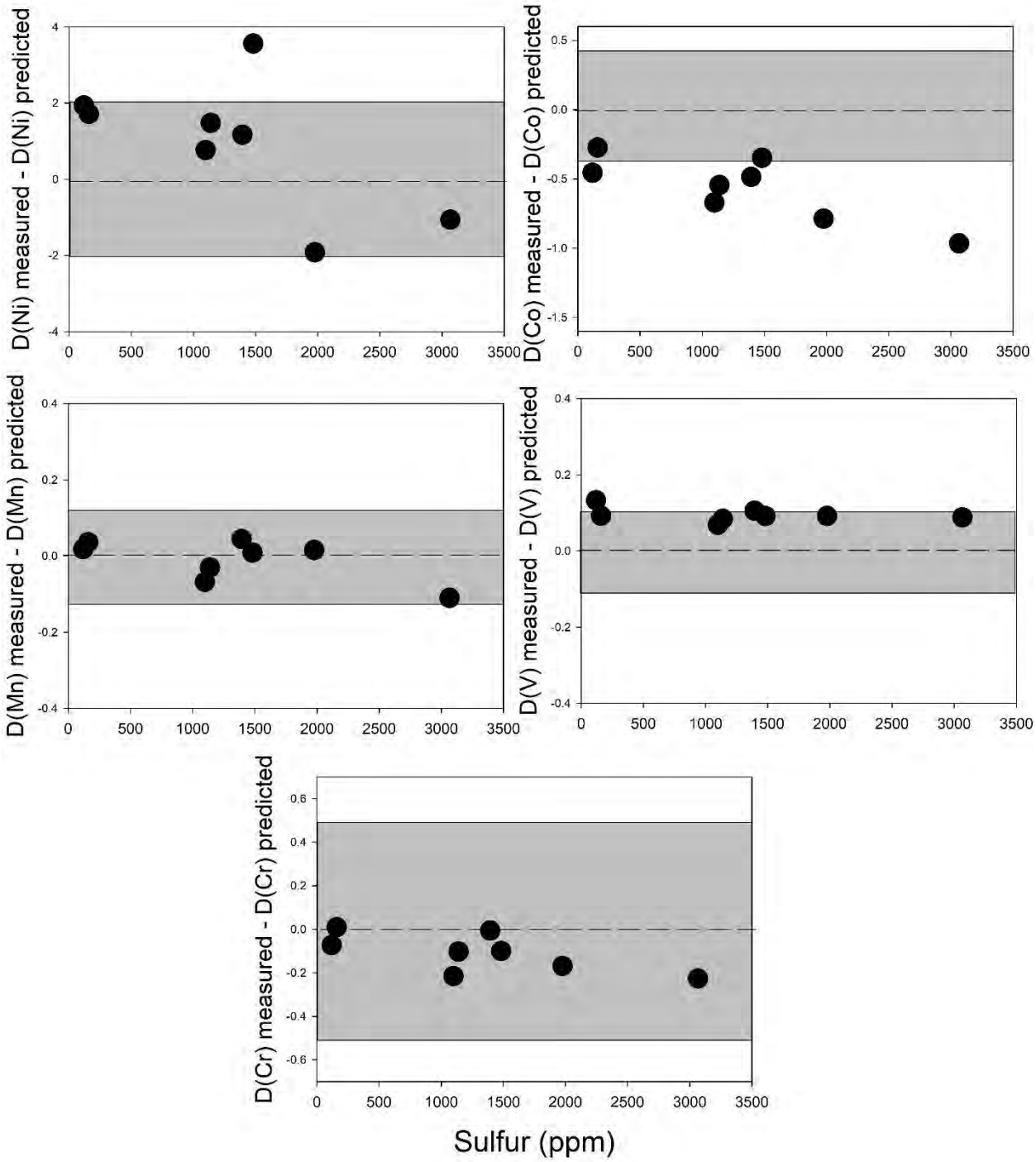

Table 1: Run conditions, electron microprobe and SIMS analyses of glass (all experiments at 0.75 GPa, with olivine and glass)

Run#	Starting	11	14	16	17	22	27	28	29
T (°C)		1500	1475	1475	1475	1450	1450	1450	1475
S added		2000	2000	1000	0	2000	0	1000	3000
% melt		98	93	88	98	85	88	83	86
n		13	12	12	10	12	13	14	12
SiO_2	49.9	46.81(40)	49.14 (20)	49.69(17)	49.24(43)	50.26(21)	49.74(30)	51.00(24)	50.31(36)
TiO_2	0.532	0.55(3)	0.55(3)	0.59(1)	0.51(1)	0.67(2)	0.62(3)	0.64(3)	0.62(2)
Al_2O_3	5.17	6.26(12)	6.62(30)	7.14(43)	6.24(6)	7.25(9)	7.03(14)	7.49(13)	7.49(10)
Cr_2O_3	0.659	0.65(3)	0.66(2)	0.67(2)	0.65(3)	0.68(2)	0.68(3)	0.63(2)	0.69(2)
FeO	17.3	16.83(19)	16.84(20)	16.55(30)	16.41(9)	16.70(17)	16.62(23)	16.59(16)	16.69(19)
MnO	0.481	0.45(4)	0.46(3)	0.49(4)	0.46(4)	0.42(3)	0.45(3)	0.48(2)	0.50(5)
MgO	18.7	17.58(32)	15.26(51)	14.82(58)	17.57(14)	12.87(12)	15.33(13)	12.65(19)	13.43(10)
CaO	6.83	6.98(13)	7.33(21)	7.76(17)	6.94(11)	7.98(6)	7.77(7)	8.17(9)	7.96(8)
Na_2O	0.651	0.70(3)	0.69(4)	0.78(3)	0.67(4)	1.30(5)	0.71(3)	0.79(3)	0.80(3)
K_2O	0.0156	0.024(14)	0.030(13)	0.028(10)	0.025(12)	0.030(13)	0.035(12)	0.038(11)	0.025(13)
P_2O_5	0.29	0.34(5)	0.34(7)	0.36(5)	0.32(4)	0.36(3)	0.33(4)	0.35(4)	0.36(4)
S (ppm)	-	1394(185)	1481(232)	1139(179)	160(131)	1977(267)	119(130)	1098(134)	3066(218)
Cr (ppm)	-	4416(203)	4487(125)	4556(166)	4468(202)	4664(130)	4621(176)	4330(166)	4710(142)
Mn (ppm)	-	3473(305)	3563(198)	3795(276)	3532(337)	3266(211)	3467(257)	3745(186)	3866(374)
Total	100.529	97.45(37)	98.22(45)	99.12(36)	99.08(53)	98.92(34)	99.35(44)	99.06(30)	99.50(46)
NBO/T	-	1.67	1.47	1.42	1.58	1.33	1.71	1.28	1.33
V (SIMS)	-	182(9)	188(10)	192(10)	187(10)	207(11)	201(10)	202(10)	192(10)
Co (SIMS)	-	437(22)	401(20)	385(19)	510(25)	316(16)	447(22)	358(17)	300(15)
Ni (SIMS)	-	71.0(4.0)	56.5(2.8)	56.7(2.8)	56.7(2.8)	39.7(2.0)	51.0(2.5)	43.1(2.2)	54.0(2.7)

Table 2: Olivine EMPA and SIMS analyses

Run#	11	14	16	17	22	27	28	29
n	11	11	13	11	11	13	15	15
SiO_2	39.13(10)	39.22(17)	39.21(15)	38.90(7)	38.75(9)	38.69(20)	38.45(26)	38.43(24)
Cr_2O_3	0.37(1)	0.38(1)	0.40(2)	0.38(1)	0.43(1)	0.40(1)	0.39(2)	0.39(2)
FeO	14.72(10)	16.08(24)	16.14(58)	14.77(6)	17.08(44)	15.82(26)	16.04(98)	15.43(74)
MnO	0.32(1)	0.34(1)	0.35(1)	0.32(1)	0.35(2)	0.34(1)	0.37(2)	0.35(2)
MgO	44.60(14)	44.08(29)	44.00(35)	44.31(11)	43.03(43)	44.03(22)	43.76(83)	44.41(67)
CaO	0.17(1)	0.17(1)	0.19(1)	0.18(1)	0.19(1)	0.18(1)	0.17(1)	0.17(1)
NiO	0.049(7)	0.066(12)	0.054(8)	0.044(8)	0.027(10)	0.047(9)	0.047(9)	0.042(10)
CoO	0.063(5)	0.081(7)	0.072(6)	0.087(5)	0.062(8)	0.081(6)	0.080(8)	0.051(5)
Total	99.43(27)	100.43(25)	100.41(39)	98.99(16)	99.91(14)	99.59(17)	99.30(14)	99.26(19)
Si	0.990	0.989	0.989	0.990	0.987	0.984	0.982	0.979
Cr	0.007	0.008	0.008	0.008	0.009	0.008	0.008	0.008
Fe^{2+}	0.312	0.339	0.340	0.314	0.364	0.336	0.343	0.329
Mn	0.0068	0.0073	0.0075	0.0068	0.0075	0.0073	0.0079	0.0076
Mg	1.683	1.657	1.655	1.681	1.634	1.669	1.666	1.687
Ca	0.0047	0.0046	0.0051	0.0050	0.0051	0.0050	0.0047	0.0046
Ni	0.0010	0.0013	0.0011	0.0009	0.0006	0.0010	0.0010	0.0009
Co	0.001	0.002	0.001	0.002	0.001	0.002	0.002	0.001
Total	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
Fo	83.8(1)	82.4(3)	82.3(6)	83.6(1)	81.2(5)	82.6(3)	82.3(1.1)	83.1(9)
Mg #	84.4(1)	83.0(3)	82.9(6)	84.2(1)	81.8(5)	83.2(3)	83.2(3)	83.7(9)
V (SIMS)	41.0(4.0)	41.1(4.1)	41.0(4.0)	40.8(4.1)	45.8(4.6)	49.4(5.0)	40.2(4.0)	41.9(4.2)
Co (EMPA)	493(25)	636(32)	563(28)	686(34)	486(24)	635(32)	629(31)	399(20)
Ni (EMPA)	386(19)	521(26)	423(21)	343(17)	214(11)	369(18)	367(18)	331(16)

Table 3: D and K_d values

Run #	**27**	**28**	**22**	**17**	**16**	**14**	**29**	**11**
Temp	1450	1450	1450	1475	1475	1475	1475	1500
S (ppm)	0	1000	2000	0	1000	2000	3000	2000
D V	0.25(3)	0.20(3)	0.22(3)	0.22(3)	0.21(3)	0.22(3)	0.22(3)	0.23(3)
D Cr	0.60(4)	0.62(4)	0.63(4)	0.58(4)	0.60(4)	0.58(4)	0.57(4)	0.57(4)
D Mn	0.76(9)	0.77(9)	0.83(9)	0.70(8)	0.71(8)	0.74(8)	0.70(8)	0.71(8)
D Fe	0.95(2)	0.97(2)	1.02(2)	0.90(2)	0.98(2)	0.96(2)	0.92(2)	0.87(2)
D Co	1.42(14)	1.76(18)	1.54(15)	1.35(14)	1.46(15)	1.59(16)	1.33(13)	1.13(12)
D Ni	7.24(73)	8.52(85)	5.39(55)	6.05(61)	7.46(75)	9.22(92)	6.13(63)	5.44(60)
D Mg	2.87(5)	3.46(5)	3.34(5)	2.52(5)	2.97(5)	2.89(5)	3.31(5)	2.54(5)
K_d (V-Mg)	0.085(10)	0.058(10)	0.066(10)	0.086(10)	0.072(10)	0.076(10)	0.066(10)	0.088(10)
K_d (Cr-Mg)	0.20(3)	0.18(2)	0.19(2)	0.23(3)	0.20(2)	0.20(2)	0.17(2)	0.22(3)
K_d (Mn-Mg)	0.26(3)	0.22(3)	0.25(3)	0.28(3)	0.24(3)	0.26(3)	0.21(2)	0.28(3)
K_d (Fe-Mg)	0.33(1)	0.28(1)	0.31(1)	0.36(1)	0.33(1)	0.33(1)	0.28(1)	0.35(1)
K_d (Co-Mg)	0.49(6)	0.51(5)	0.46(5)	0.53(6)	0.49(5)	0.55(6)	0.40(5)	0.44(5)
K_d (Ni-Mg)	2.52(26)	2.46(25)	1.61(17)	2.40(25)	2.51(26)	3.19(32	1.85(20)	2.14(22)

Table 4: Regression results for D(olivine/melt): D = a D(Mg) + b NBO/T + c ΔFMQ + d (S ppm) + e

Element	a	b	c	d	E	N	Std error	Studies
Ni	3.23(19)	-1.29(43)	-	-	-1.78(1.09)	82	1.00	2,3,4,5,6,7
Co	0.805(38)	-0.182(85)	-	-	-0.124(219)	69	0.20	2,3,4,5,7
Co (with S)	0.495(67)	-0.311(91)	-	-0.0000824 (253)	0.843(267)	117	0.23	1,2,3,4,5,7,8
Mn	0.206(6)	0.045(12)	-	-	0.0689(319)	121	0.054	2,3,4,9
V	-0.0619(123)	-0.0140(58)	-0.0398(29)	-	0.199(33)	116	0.051	2,7,9
Cr	-0.0448(578)	0.262(29)	-0.0404(139)	-	-0.0752(167)	113	0.252	2,4,9,10

1 – Gaetani and Grove, 1997; 2 – Tuff and O'Neill, 2010; 3 – LeRoux et al., 2011; 4 – Longhi et al., 2010; 5 – Herd et al., 2009; 6 – Filiberto et al., 2009; 7 – Elardo et al., 2011; 8 – this study; 9 – Mallmann and O'Neill, 2013; 10 – Hanson and Jones, 1998.