

**COBALT AND NICKEL PARTITIONING INTO PLANETARY OLIVINE.** R. E. Dwarzski<sup>1,2</sup> and C. D. K. Herd<sup>2</sup>, <sup>1</sup>Oberlin College, OCMR 793, Oberlin, OH 44074 ([rachel.dwarzski@oberlin.edu](mailto:rachel.dwarzski@oberlin.edu)), <sup>2</sup>Lunar and Planetary Institute, 3600 Bay Area Blvd., Houston, TX 77058 ([herd@lpi.usra.edu](mailto:herd@lpi.usra.edu)).

**Introduction:** Secondary Ion Mass Spectrometry (SIMS) has enabled trace analysis of transition-series elements in olivine in martian, terrestrial and lunar basalts [1,2,3]. Two of the elements of interest are Ni and Co, which partition differently into planetary olivine, despite being present as divalent cations and having similar effective ionic radii in octahedral coordination [4].

The partitioning of a trace element into a mineral (expressed as its D value) varies with temperature, pressure, oxygen fugacity, and melt composition; all of these are variables which change depending on planetary setting. Herd et al. [1] compared Co, Ni, and Mn concentrations in lunar, martian, and terrestrial basaltic olivine. They noted differences in the behavior of Co in olivine between the planetary suites, specifically, that in martian olivine, Co increases as Ni decreases (tracking crystallization), in spite of its compatibility in olivine ( $D_{Co} \sim 3$ ; [3]). The apparent incompatibility of Co was attributed to differences in the rate of change of  $D_{Co}$  during igneous evolution, similar to the explanation of [3] for the behavior of Co in Apollo 12 olivine. Herd et al. [1] postulated that the rate of change of  $D_{Co}$  depends on oxygen fugacity, which would explain the difference between Co partitioning in martian and lunar olivine.

Accordingly, we have carried out experiments with the goal of examining the effects of oxygen fugacity, temperature and melt composition on the partitioning of Co and Ni in olivine, in order to better understand the behavior of these elements in planetary basalts.

**Experimental Details:** In this study, we grew olivine crystals using two compositions: the “Eg” composition, representing the Lithology A groundmass of the martian meteorite EET 79001[5], and a composition similar to that of the Sioux County eucrite meteorite, provided by John Jones. Both were doped with one weight percent each of CoO and NiO.

Experiments were performed at one atmosphere in Deltech furnaces in the experimental petrology laboratory at the Johnson Space Center (JSC). The oxygen fugacity in this lab is controlled by mixing CO and CO<sub>2</sub>, using a ZrO<sub>2</sub> sensor in a calibration furnace, and is accurate to  $\pm 0.2$  log units [6]. We ran experiments at a range of oxygen fugacities, from 0.5 log units above the Iron-Wüstite (IW) buffer to IW +3, representing the range of oxygen fugacity observed in the lunar and martian basalts [7,8] and overlapping with that of the more reduced terrestrial basalts. Tempera-

tures were determined with a type-B thermocouple calibrated against the melting point of gold.

Experiments were carried out using a Re loop to mitigate iron loss. The Eg charges underwent a homogenization period for one hour at 1350°C prior to dropping the temperature at a rate of 1000°C per hour, to run at temperatures of 1290°C, 1270°C, 1250°C, and 1230°C. Experimental setup for the eucrite composition was identical to that of Eg, except that we used a single run temperature (so far) of 1180°C. All runs were held at temperature for times ranging from 24 hours to 89 hours, and were quenched in air.

**Analytical Approach:** Polished thin sections of the charges were made. They were then analyzed using the Cameca SX-100 electron microprobe (EMP) at JSC, with an accelerating voltage of 20kV and a beam current of 20nA. Core to rim traverses were made whenever possible. Back-scattered electron images were also collected to examine textures and to look for compositional zoning.

**Observations:** Zoning in Ni from core to rim was observed in most runs. Ni varied systematically from higher in the cores to lower at the rims. Therefore, we used rim concentrations when calculating D values. Fe, Mg, and Co are constant from core to rim in the olivine crystals, reflecting differences in diffusion rates of these elements, as noted by [3]:  $Mn > Fe = Mg > Co > Ni$ .

Metal blebs were observed in all of the runs, but are most common, and largest, at lower oxygen fugacity. These blebs have been observed previously in experiments that use Re wire (Musselwhite, personal communication). While the blebs consist mainly of Ni, Re, and Co, with small amounts of Fe, their presence did not hinder our analysis and we were able to obtain valid D values.

**Results & Discussion:** D values determined from this study are consistent with known relationships between  $D_{Co}$  and  $D_{Ni}$  [3] and  $D_{Co}$  and  $D_{Mg}$  [9].  $D_{Co}$  is approximately 3, in agreement with previous work [3]. D values are presented graphically in Figure 1. Results demonstrate that oxygen fugacity has very little effect on  $D_{Co}$  or  $D_{Ni}$ . The largest effect is temperature (Figure 1); as temperature decreases, the D values of both nickel and cobalt increase. A comparison of D values from Eg and the eucrite indicates that the effect of temperature is greater than the effect of bulk composition. Further experiments with the eucrite composition, and a lunar basalt composition, are underway to ad

dress the effects of bulk composition on Ni and Co partitioning in olivine.

Figure 2 is a plot of Co/Ni ratio versus Mn in planetary olivine, with experimental results shown for comparison. Experimental data from IW + 1 (not shown) is artificially high due to the preferential uptake of Ni by the Re blebs at lower oxygen fugacity. The trends in experimental data from IW + 2 and IW + 3 (where Re blebs are fewer) parallel the trends of the natural samples, particularly the Apollo 12 lunar basalt suite. Therefore, we have reproduced the trends seen in the natural samples, and done so at a range of oxygen fugacities.

The experimental results are supported by revised estimates for oxygen fugacity in the EET 79001 (Lithology A) and Dar al Gani 476 martian basalts, which show no systematic change in slope in Co/Ni vs. Mn with changing oxygen fugacity (Fig. 2). Analytical data for Ni, Co and Mn in olivine in EET 79001 (Fig. 2) are derived from zoned olivine in the xenocryst assemblage; this assemblage yields an oxygen fugacity of QFM - 2.8 ( $\pm 0.5$ ), based on the compositions of the earliest olivine, orthopyroxene and chromite, following the procedure of [10] and using the data of Goodrich [11]. This is equivalent to IW + 0.7, and is 1 log unit more reducing than the groundmass of Lithology A [8]. The oxygen fugacity of Dar al Gani 476 is  $\sim$ IW + 1 [10].

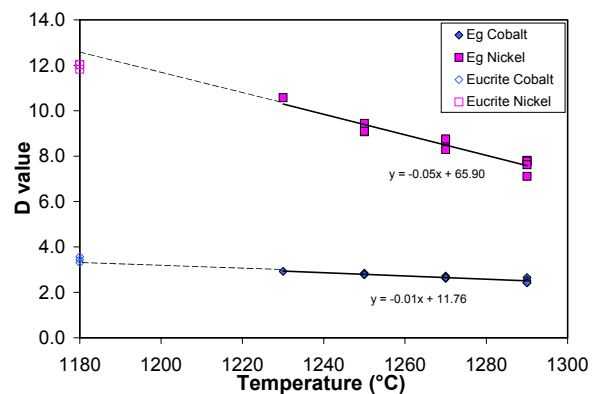
Although we have ruled out oxygen fugacity as a major influence on Ni and Co partitioning in olivine, the range in slope in Co/Ni vs. Mn for the martian basalts remains unexplained. Olivine in the lherzolithic shergottites has undergone magmatic and/or subsolidus re-equilibration in terms of Fe and Mg, which has likely also affected the trace elements [1]. As noted, Mn and Co diffuse more rapidly than Ni. However, diffusion of Mn would result in a steepening of the slope, in contrast to the shallowing observed in the slopes of DaG 476 and EET 79001 olivine, relative to the Apollo 12 olivine and experimental data.

Previously, [1] considered all of the terrestrial olivine data as a single trend; in fact, there is variation in Co, Ni and Mn between terrestrial suites, but very little within a given suite (Fig. 2). The range of olivine compositions (in terms of Mg#) in a given terrestrial suite is not nearly as large as in a given martian basalt or in the Apollo 12 suite, which precludes a direct comparison of olivine in terrestrial basalts with olivine in lunar and martian basalts.

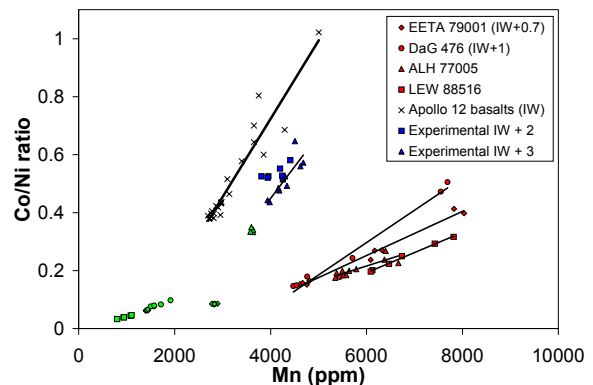
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**Figure 1.** D values for Ni and Co as a function of temperature. Multiple points at each temperature represent runs at different oxygen fugacities.



**Figure 2.** Co/Ni ratio vs. Mn in planetary olivine, with results of experiments. Terrestrial data shown in green, with MORB (diamonds), IAB (circles), Archean (squares) and CFB (triangles). Data sources as in [1].