EFFECT OF OXYGEN FUGACITY ON PARTITIONING OF Ni AND Co BETWEEN OLIVINE AND SILICATE MELT: IMPLICATIONS FOR EUCRITE PARENT BODY EVOLUTION

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Partitioning of nickel and cobalt between olivine and silicate melt has been determined in the system olivine-albite-anorthite-CaO at 1350 °C and 1 atm over the oxygen fugacity range from one log unit above Nickel-Nickel Oxide (NNO+1) to two log units below the Iron-Quartz-Fayalite (IQF-2) buffers (fO2 = 10-5.5 to 10-12.6). These conditions span the range relevant for crystal/liquid processes in terrestrial planets and meteorite parent bodies. There is no effect of oxygen fugacity on DOl/glsNi over the range of fO2 from 10-5.5 to 10-9. Upon metal saturation (fO2 < 10-10.3) the partition coefficient decreases by a factor of 1.8 and DOl/glsNi changes from 6.8 at log fO2 of -9 to 3.8 at log fO2 of -10.3. Partition coefficients for Co are constant (DOl/glsCo = 2.8) over the range of fO2 from 10-6.6 to 10-10.6. The Co partition coefficient decreases upon metal saturation to a value of 1.65 at log fO2 of -12.2. These changes in Ni and Co partitioning behavior may indicate that Ni and Co are present in a mixed valence state in the silicate melt under metal saturated conditions.

Accurate knowledge of the partitioning behavior of siderophile elements between silicate minerals, silicate melt and metal is a prerequisite for developing realistic models of the chemical evolution of planetary interiors. The majority of experimental studies on partitioning of Ni and Co between olivine and silicate melt have been concerned with the effect of silicate melt composition on partitioning behavior and there are several models that account for the effects of melt (or olivine) compositional variation on partitioning [1,2,3,4]. An effect of variable oxidation state on partitioning has been proposed on the basis of Ni variations observed in olivines in terrestrial layered intrusions [5] and in terrestrial lavas [6]. Several investigators have studied the effects of variable fO2 on Ni olivine/melt partitioning [7,8,9]. The early study of Mysen and Kushiro [7] showed an increase of DOl/glsNi as a function of decreasing fO2. At the most reducing conditions (IQF-0.5 at 1275 °C) DOl/glsNi = 18 and at the most oxidizing conditions (NNO-2.4 at 1275 °C) DOl/glsNi = 4. Ehlers and Grove [8] and Steele et al. [9] show the opposite effect: a decrease of DOl/glsNi as a function of increasing fO2. The reason for the discrepancy in [7] is that these authors used Pt wire loops as containers and a beta-track method for determination of Ni concentration.

Experimental Experiments were conducted at 1350 °C on a Fo86-Ab-"An" composition [following 1,4], corresponding to a natural barred olivine chondrule composition from an ordinary chondrite [10].

Synthetic analog of barred olivine chondrule (wt. % components)

<table>
<thead>
<tr>
<th>Forsterite</th>
<th>Fayalite</th>
<th>Albite</th>
<th>0.65 Anorthite + 0.35 CaO</th>
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<tbody>
<tr>
<td>54.8</td>
<td>12.7</td>
<td>27.0</td>
<td>5.5</td>
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For investigating a wide range of oxidation states, one needs a container that will not interact with the bulk sample as fO2 changes. The PtFe alloy loop technique, commonly used at 1 atm, would require fabrication of a new metal alloy composition for each oxygen fugacity and each silicate melt composition. We overcame the container problem by using crucibles fabricated from San Carlos olivine (Fo89,91) single crystals. At 1350 °C composition Fo86-Ab consists of Fo96 olivine and high-MgO, low-Al2O3 liquid, and therefore there exists little potential for Fe-Mg exchange between the melt and crucible. Chemical analyses were performed on a four spectrometer JEOL model 733 electron microprobe at an accelerating potential of 15 kV and a sample current of 10 nA for the major elements and up to 200 nA for the Ni and Co trace element analyses. Counting times

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were 10 - 40 sec for the major elements (Mg, Si, Al, Fe, Na, Ca) and 200 - 1000 sec for Ni and Co. The data are predominantly "synthesis" but a reversal indicates the duration of the synthesis experiments was sufficient for equilibrium to be approached.

Results The partition coefficients (D_{Dol/gls}^{Ni} and D_{Dol/gls}^{Co}) are defined as the weight ratio of NiO or CoO in olivine to NiO or CoO in melt. The experimental results for Ni and Co are shown below on D_{Dol/gls} versus log_{10}f_{O2} plots. Error bars are 2 sigma and are based on counting statistics. The abrupt change in D_{Dol/gls}^{Ni} and D_{Dol/gls}^{Co} corresponds with metal saturation. The low values of D_{Dol/gls}^{Ni} observed in the metal saturated experiments are not the result of uncompensated nonideality in either liquid or olivine. We suggest that the change in partitioning behavior is a result of the change of the valence of Ni and Co in the melt. In the metal saturated experiments there has been a significant decrease in Ni^{2+} and Co^{2+} and an increase in Ni^{0} and Co^{0}. We measure these elements as oxides, and can not distinguish valence state. We have no way of predicting the proportion of Ni as Ni^{0} (or Co as Co^{0}) in any of our experiments. It may be that these elements exist in the liquid phase in both the 2+ and 0 state, regardless of metal saturation. Our observation of a precipitous drop in D_{Dol/gls} reflects a change in the amount of Ni^{0} and Co^{0}, rather than its sudden appearance as a melt species.

Implications Eucrite meteorites are samples of basaltic melts that were produced by partial melting of the eucrite parent body. The extent of melting and the proportion of metal phase are questions that have been addressed by major and trace element studies. Newsom [11] and Hewins and Newsom [12] develop a model to set limits on the amount of melting and the weight fraction of metal that was residual in the eucrite parent body (EPB) in the source of eucrite basalts. The Ni and Co data for olivine available as a result of our study provide an estimate of from 9 to 16 % melting with residual metal present. The values of melt % overlap with the range of estimates of 5 to 15 % based on major element [13] and rare earth element [14] data on eucrite basalts.