

INFLUENCE OF VARIABLE OXYGEN AND SULFUR FUGACITY ON PARTITIONING OF Ni, Cu AND Cr AMONG OLIVINE, SILICATE MELT AND SULFIDE MELT. Glenn A. Gaetani and Timothy L. Grove, Dept. Earth, Atmospheric and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, Mass 02139

Introduction. The absolute and relative abundances of siderophile elements in the silicate mantles of terrestrial planets provide constraints on the conditions under which their metallic cores segregated [1]. It has been recognized for nearly thirty years that the siderophile abundances in the Earth's upper mantle are inconsistent with simple metal/silicate equilibrium [2]. It has been suggested that a light element, such as S, dissolved in an FeNi metallic liquid may have affected the distribution of siderophile elements during segregation of the core [3,4]. Here we report the results of experiments designed to determine the influence of variations in the fugacities of oxygen (f_{O_2}) and sulfur (f_{S_2}) on the partitioning of Ni, Cu and Cr among coexisting olivine, silicate melt and sulfide melt. Our experimental results indicate that at a constant temperature the partition coefficients for Cu and Cr between sulfide melt and silicate melt increase as the ratio of f_{O_2} to f_{S_2} decreases. The sulfide melt/silicate melt partitioning behavior of Ni at low f_{O_2} /high f_{S_2} conditions is complicated by composition-related variations in the solubility of NiS in the silicate melt. The olivine/silicate melt partition coefficient for Cr increases with decreasing f_{O_2}/f_{S_2} ratio, while Ni becomes less compatible in olivine relative to silicate melt.

Experimental and Analytical Methods. Experiments were performed at 1 atm in crucibles fabricated from San Carlos olivine (Fo₈₉₋₉₁), with f_{O_2} and f_{S_2} controlled by mixing CO₂, CO and SO₂ gases. Starting compositions were a CaO-MgO-Al₂O₃-SiO₂-FeO-Na₂O analog for a chondrule from an ordinary chondrite (Fo86) [5] doped with FeS and NiO, and a synthetic Monro Township komatiite (KOM) [6], containing Cr₂O₃, doped with FeS, NiO, and CuO. Experiments were performed at a single temperature, with f_{O_2} ranging from 1 log unit below the fayalite-magnetite-quartz (FMQ) oxygen buffer to the iron-wüstite (IW) oxygen buffer and f_{S_2} ranging from 1.7 to 2.7 log units above to FeFeS sulfur buffer. Experimental run products were analyzed by electron microprobe. Analytical conditions for trace elements were 15 kV accelerating potential and a beam current of 200 nA with counting times ranging from 250 to 700 s, depending on concentration of the trace element.

Results and Discussion. Table 1 reports the sulfide melt/silicate melt partition coefficients ($D_i^{sf/sil}$) determined experimentally for high f_{O_2} /low f_{S_2} and low f_{O_2} /high f_{S_2} conditions.

Table 1. Sulfide melt/silicate melt partition coefficients for Ni, Cu and Cr.

Experiment	T (°C)	Log f_{O_2}	Log f_{S_2}	$D_{Ni}^{sf/sil}$	$D_{Cu}^{sf/sil}$	$D_{Cr}^{sf/sil}$
Fo86-8s	1350	-7.9	-2.5	570	—	—
Fo86-10s	1350	-10.2	-1.5	2000	—	—
KOM-1s	1350	-7.9	-2.5	540	270	<0.01‡
KOM-3s	1350	-10.2	-1.5	510	910	44

‡ Cr concentration in sulfide melt below detection limit of electron microprobe.

The sulfide melt/silicate melt partition coefficients for both Cu and Cr increase as the f_{O_2}/f_{S_2} ratio decreases. Further, the solubility of both elements decreases in the silicate melt, Cu by a

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factor of 12 and Cr by a factor of 6. The partitioning behavior of Ni appears to be more complicated. Experiments performed on the Fo86 composition show a factor of 3.5 increase in $D_{\text{Ni}}^{\text{sf/sil}}$, while Ni partitioning between sulfide melt and komatiite appears to be insensitive to the changing conditions. Table 2 reports the olivine/silicate melt partition coefficients measured in our experiments, along with the concentrations of nickel (Ni^{sil}) and sulfur (S^{sil}) dissolved in the silicate melt and the value of $D_{\text{Ni}}^{\text{ol/sil}}$ predicted from the composition of the silicate melt in a S-free system [8].

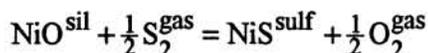
Table 2. Olivine/silicate melt partition coefficients for Ni, Cu and Cr.

Experiment	Ni^{sil}	S^{sil}	$D_{\text{Ni}}^{\text{pred}\dagger}$	$D_{\text{Ni}}^{\text{ol/sil}}$	$D_{\text{Cu}}^{\text{ol/sil}}$	$D_{\text{Cr}}^{\text{ol/sil}}$
Fo86-8s	0.102	0.031	7.9 ± 0.9	7.5 ± 0.2	—	—
Fo86-10s	0.006	0.080	7.1 ± 0.9	4.0 ± 0.4	—	—
KOM-1s	0.068	0.073	6.7 ± 0.9	6.74 ± 0.06	0.10	0.65
KOM-3s	0.014	0.155	6.1 ± 0.8	0.94 ± 0.02	‡	3.4

† Olivine/silicate melt partition coefficient predicted using the expressions of Kinzler et al. [8].

‡ Cu concentration in olivine below detection limit of electron microprobe.

The most striking results for olivine/silicate melt partitioning are the anomalously low $D_{\text{Ni}}^{\text{ol/sil}}$ values obtained at low f_{O_2} /high f_{S_2} conditions, while at high f_{O_2} /low f_{S_2} conditions the observed partition coefficients are within uncertainty of the predicted values. Selective retention of Ni in the silicate melt relative to olivine is attributable to the existence of NiS species in the silicate melt [9,10]. The deviation of the observed $D_{\text{Ni}}^{\text{ol/sil}}$ from the predicted values can be used to estimate the NiS/NiO ratio of the silicate melts at low f_{O_2} /high f_{S_2} conditions (0.78 for Fo86-10s and 5.4 for KOM-3s). If we then consider the sulfide melt/silicate melt exchange reaction:



and calculate simple Nernst distribution coefficients for the two sulfide melt/silicate melt pairs, we obtain similar values (3,700 for FO86 and 3,100 for KOM). Further, the estimated NiO concentrations of the two silicate melts are similar (0.004 for FO86 and 0.003 for KOM) despite significant differences in total Ni. The difference in NiS solubility between the Fo86 and KOM compositions may be due to differences in the degree of polymerization of the silicate melt, as Fo86 has a higher ratio of network formers to network modifiers. It therefore appears that at extremely reducing conditions, when the fugacity of sulfur is high, the NiS content of the silicate melt may have a significant effect on observed partition coefficients for both olivine/silicate melt and sulfide melt/silicate melt pairs. This implies that it is necessary to know something about the composition of the silicate melt, in addition to the ambient conditions, in order to model the evolution of siderophile elements in the mantles of terrestrial planets.

References. [1] Jones and Drake, 1986, *Nature*, 322:221-228; [2] Ringwood, 1966, *Geochim. Cosmochim. Acta*, 30:41-104; [3] Arculus and Delano, 1981, *Geochim. Cosmochim. Acta*, 45:1331-1343; [4] Brett, 1984, *Geochim. Cosmochim. Acta*, 48:1183-1188; [5] Ehlers et al., 1992, *Geochim. Cosmochim. Acta*, 56:3733-3743; [6] Kinzler and Grove, 1985, *Am. Min.*, 70:40-51; [8] Kinzler et al., 1990, *Geochim. Cosmochim. Acta*, 1255-1265; [9] Naldrett, 1989, *Magmatic Sulfide Deposits*, p. 36; [10] Gaetani et al., 1993, *EOS*, 74:337-338.