

PARTITIONING OF V, Cr, Mn, Co, Ni, AND Cu AMONG OLIVINE, SILICATE MELT AND SULFIDE MELT: IMPLICATIONS FOR CORE FORMATION IN THE TERRESTRIAL PLANETS. 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 the only geochemical record of the processes involved in core formation [1]. In the Earth's mantle, the moderately siderophile elements Ni, Co, and Cu are present in nearly chondritic ratios, despite very different metal/silicate partition coefficients [2,3]. The depletion patterns for V, Cr, and Mn are similar in the Earth and Moon, but do not correlate with the relative partitioning of these elements between metal and silicate [4-6]. Siderophile element depletion patterns inferred for the Eucrite and Shergottite parent bodies are distinct from the Earth and Moon, indicating differences in the core formation process [7,8]. Here we present experimentally-determined partition coefficients for V, Cr, Mn, Co, Ni, and Cu among coexisting olivine, ultramafic silicate melt, and sulfide melt over a range of oxygen and sulfur fugacity conditions, and use them to constrain the role of sulfide in producing the siderophile element depletions in the terrestrial planets. Our experiments suggest a resolution to the depletion of Mn relative to Cr and V found in the silicate portions of the Earth and Moon. The existence of Cr-rich spinel, a phase which retains Cr and V preferentially over Mn, at reducing conditions could significantly effect the bulk partition coefficients for these three elements during extraction of sulfide and metal.

Experimental and Analytical Methods. Experiments were performed at 1 atm in crucibles fabricated from San Carlos olivine (F₀₈₉₋₉₁), with f_{O_2} and f_{S_2} controlled by mixing CO₂, CO and SO₂ gases. The starting composition was a synthetic Monroe Township komatiite [9], doped with various combinations of FeS, NiO, CuO, Cr₂O₃, CoO and V₂O₅. Experiments were performed at 1350°C, with f_{O_2} ranging from 1 log unit below the fayalite-magnetite-quartz oxygen buffer (FMQ-1) to the iron-wüstite oxygen buffer (IW) and f_{S_2} ranging from 1.6 to 3.1 log units above to Fe-FeS sulfur buffer. Experimental run products were analyzed by electron microprobe at MIT and ion microprobe at Woods Hole Oceanographic Institute.

Results and Discussion. The sulfide melt/silicate melt and sulfide melt/olivine partition coefficients determined in our experiments are presented in Tables 1 and 2. Partition coefficients determined at FMQ-1 are relevant for conditions in the Earth's present-day upper mantle, while those at IW are appropriate for the reducing conditions under which core formation in the Earth may have taken place. At FMQ-1, V, Cr, and Mn are all incompatible in the sulfide melt, while our partition coefficients for Co and Ni overlap with those measured for immiscible sulfide melts occurring in natural mid-ocean ridge basalts [10]. At lower f_{O_2} , higher f_{S_2} conditions V, Cr, and Mn are all compatible in the sulfide, and the partition coefficients for

Table 1. Experimentally-determined sulfide melt/silicate melt partition coefficients.

Log f_{O_2}	Log f_{S_2}	$D_V^{Sif/Sil}$	$D_{Cr}^{Sif/Sil}$	$D_{Mn}^{Sif/Sil}$	$D_{Co}^{Sif/Sil}$	$D_{Ni}^{Sif/Sil}$	$D_{Cu}^{Sif/Sil}$
-7.9	-2.5	0.025	<0.01†	0.008	25	510	250
-10.2	-1.5	1.3	6.0	1.1	230	3800	1400

Table 2. Experimentally-determined sulfide melt/olivine partition coefficients.

Log fO ₂	LogfS ₂	D _V ^{Sif/Ol}	D _{Cr} ^{Sif/Ol}	D _{Mn} ^{Sif/Ol}	D _{Co} ^{Sif/Ol}	D _{Ni} ^{Sif/Ol}	D _{Cu} ^{Sif/Ol}
-7.9	-2.5	0.26	<0.02 [†]	0.01	14	80	2700
-10.2	-1.5	3.9	10.0	1.6	120	620	7100

[†]Cr concentration in sulfide melt below detection limit of electron microprobe.

Co, Ni, and Cr are larger by factors of ~5-10. Although the relative compatibility's of V, Cr and Mn in our experiments ($D_{Cr} > D_V > D_{Mn}$) are the same as those determined by Drake et al. [6] at slightly more reducing conditions, our partition coefficients are significantly larger. The fact that Cr is more compatible than V or Mn indicates that extraction of a sulfide from the mantle will lead to a depletion in Cr rather than Mn. However, our experimental charges contained Cr-rich spinel, even at the most reducing conditions. If fractionation of metal from silicate takes place continuously during accretion, as is currently favored by most models, pressures will be low enough for spinel to remain a stable phase. The presence of spinel means that Cr and V would be more strongly retained in the residue than Mn, leading to the observed depletion. It is possible to explain the Earth's nearly chondritic Ni/Cu ratio by extraction of a sulfide melt, due to the differences in the sulfide melt/silicate melt and sulfide melt/olivine partition coefficients, if the mantle undergoes high degrees (73%) of partial melting. However, this would lead to a significant fractionation of the Earth's Ni/Co ratio, which is known to be approximately chondritic. Extraction of a sulfide melt from a mantle with little (or no) melt present will lead to significant fractionation of Ni from Cu. None of the depletion patterns observed or inferred for the Earth, Moon, Eucrite parent body, and Shergottite parent body have characteristics expected for extraction of a sulfide melt under reducing conditions. The pattern for the Shergottite parent body, however, is qualitatively consistent with extraction of a sulfide melt from a silicate melt under more oxidizing conditions. There are no depletions in Mn and Cr, and the depletions in the moderately siderophile elements increase in the order Ni>Cu>Co. It is possible, therefore, that the sulfur-rich core inferred for Mars was extracted under conditions more oxidizing than those found in the early Earth.

References. [1] Jones and Drake, 1986, *Nature*, 322:221-228; [2] Jagoutz et al., 1979, *Proc. Lunar Planet. Sci. Conf.*, 10th, 2031-2050; [3] Schmitt et al., 1989, *Geochim. Cosmochim. Acta.*, 53:173-185. [4] Ringwood and Kesson, *The Moon*, 16:425-464; [5] Dreibus and Wänke, 1979, *Lunar Planet. Sci.*, 10:315-317; [6] Drake et al., 1989, *Geochim. Cosmochim. Acta.*, 53:2101-2111; [7] Dreibus and Wänke, 1980, *Z. Naturforsch.*, 35a:204-216; [8] Wänke and Dreibus, 1988, *Phil. Trans. R. Soc. London*, A325:545-557; [9] Kinzler and Grove, 1985, *Am. Min.*, 70:40-51; [10] Peach et al., 1990, *Geochim. Cosmochim. Acta.*, 54:3379-3389