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SIDEROPHILE ELEMENTS IN THE UPPER MANTLE OF THE EARTH: NEW CLUES FROM METAL-SILICATE PARTITION COEFFICIENTS: A. Holzheid, A. Borisov, H. Palme. MPI für Chemie, Saarstrasse 23, D- 6500 Mainz, Germany

New, precise data on the solubilities of Ni, Co and Mo in silicate melts at 1400°C and fO_2 from IW to IW-2 are presented. The results suggest NiO, CoO as stable species in the melt. No evidence for metallic Ni or Co was found. Equilibrium was ensured by reversals with initially high Ni and Co in the glass. Mo appears to change oxidation state at IW-1, from MoO_3 to MoO_2. Metal-silicate partition coefficients calculated from these data and recent data on Pd [1] indicate similar partition coefficients for Pd and Mo at the conditions of core formation. This unexpected result constrains models of core formation in the Earth.

EXPERIMENTAL METHODS. All experiments were conducted in a gas mixing furnace. A PtRh-Pt thermocouple and a ZrO_2 solid electrolyte oxygen sensor were employed for measuring temperature and oxygen fugacities. $CO_2/H_2/N_2$ gas mixtures were used for most of the experiments.

Silicate starting materials close to anorthite- diopside eutectic composition (48.8 wt% SiO_2, 22.7% CaO, 14.4% MgO, 14.1% Al_2O_3) were inserted into loops of pure Co, Ni and Mo- metal with a maximum diameter of 2.5 mm. Samples were equilibrated at constant temperature (1400°C) and constant run duration (50 h). Ni, Co and Mo- loops were simultaneously included in the run. Samples were quenched by withdrawal from the furnace. After separation from the loops glass samples were polished to remove possible metal contamination and were then analysed by instrumental neutron activation analysis (INAA). Repeated analyses of bulk samples and several individual pieces showed homogeneity of Co, Ni and Mo- distribution in silicate melt. A reversed experiment (AD 14*) with initially high Co and Ni content in the glass confirmed the attainment of equilibrium.

RESULTS AND DISCUSSION. Experimental conditions and results of measurements are presented in Table 1. Analytical uncertainties are below 10%. Figure 1 shows the dependence of Ni, Co and Mo solubilities on oxygen fugacity. Slopes for Ni and Co are close to 0.5 (Ni=0.48±0.02, Co=0.54±0.01), implying NiO and CoO as stable species in silicate melt. From olivine/melt partition data [4] inferred a significant fraction of metallic Ni below IW-0.3 and metallic Co below IW-2. Metallic Ni in silicate melts below IW was also postulated by [3]. No evidence for the presence of metallic Ni and Co was found in the silicate melt within the range of conditions of the present experiments (at least as low as IW-2.2). The Mo species in the silicate melt appear to change from MoO_2 at reducing conditions to MoO_3 at oxidizing conditions, alternatively a significant change of the activity coefficient of MoO_2 (γ_{MoO2}) must be considered.

In Fig. 1 we have also plotted recent data on the solubility of Pd in silicate melt of the same composition as that used here [1]. These data were obtained at 1350°C. Extrapolation to 1400°C would result in a 5% increase of solubilities [1]. The Pd-results and the partition data on Ni, Co and Mo reported here are extrapolated to lower oxygen fugacities into a region were planetary core formation is expected to occur (FeO in silicate from 20% to 1%). The two lines for the extrapolated Mo and Pd data in Fig. 1 intersect in this region. Metal/silicate partition coefficients derived from solubilities probably show a similar behaviour, as the activity coefficient of Pd in Fe-metal (γ_{Pd} = 0.4, see [1]) is only about a factor of two lower than that of Mo (γ_{Mo} in Fe- metal is assumed to be one). Since D_{Pd} is decreasing with increasing temperature [1] and D_{Mo} probably increasing (expected from MoO_2 in melt) the Pd and Mo- metal/silicate partition coefficients could be similar at even higher fO_2 than indicated in Fig. 1. In a global mantel/core equilibrium such as envisioned by [5], the residual silicate mantle would have similar, or even higher CI- normalized abundances of Mo compared to Pd, depending on the temperature extrapolation. Mo is generally considered a moderately siderophile element (together with W, P and Ge) and Pd a highly siderophile element (similar to Ir, Os and Au). Upper mantle abundances of moderately siderophile elements (Mo) are, however, more than a factor of ten above the abundances of highly siderophile elements (Pd). In the inhomogeneous accretion model [7] upper mantle abundances of moderately siderophile elements are established by addition of oxidized material that is later affected by removal of a small amount of Ni-rich metal modifying moderately siderophile elements and removing, more or less completely, the highly siderophile elements. This would occur at rather oxidizing conditions where the difference between D_{Pd} and D_{Mo} is much higher (Fig. 1). The late veneer (late accretional spike) would then provide the required amount of highly siderophile elements in the upper mantle. The amount of Mo associated with the late veneer is low, 7 ppb vs. 59 ppb in the present upper mantle [6].

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Table 1. Experimental results of solubility of Ni, Co and Mo in silicate melts and calculated Fe-metal/liquid silicate partition coefficients at T=1400°C and variable oxygen fugacities

Run	#	log pO2	IW	Ni solub. [ppm]	Ni s.d. [%]	Ni D (M/S) [w.r.]	Co solub. [ppm]	Co s.d. [%]	Co D (M/S) [w.r.]	Mo solub. [ppm]	Mo s.d. [%]	Mo D (M/S) [w.r.]
AD 13	1	-9.4	IW+0.1	1699	8	840	26677	5	35			
AD 12	2	-9.6	IW-0.1	1615	5	884	21990	5	43	4183	5	411
AD 7	3	-10.0	IW-0.5	841	7	1697	12673	5	74	1129	5	1522
AD 10	4	-10.3	IW-0.8	672	5	2124	9322	5	101	548	5	3135
AD 6	5	-10.6	IW-1.1	434	5	3288	6206	5	151	223	5	7705
AD 1	6	-10.6	IW-1.1	410	5	3481	6179	5	152	196	5	8766
AD 8	7	-10.8	IW-1.3	350	5	4078	4728	5	198	83.2	5	20659
AD 11	8	-10.9	IW-1.4	337	6	4235	4243	5	221	69.2	5	24830
AD 5	9	-11.1	IW-1.6	279	7	5115	3392	5	277	40.0	6	42923
AD 9	10	-11.3	IW-1.8	224	5	6371	2709	5	346	34.5	5	49746
AD 14	11	-11.4	IW-1.9	160	9	8920	2377	5	395	21.6	6	79694
AD 14 *	12	-11.4	IW-1.9	178	6	8018	2430	5	386			
AD 2	13	-11.6	IW-2.1	156	6	9149	1850	5	507	15.2	9	113115
AD 3	14	-11.7	IW-2.2	164	7	8702	1535	5	611	11.3	7	151920

*-reversal; solub.-solubility; s.d.-standard deviation; w.r.-weight ratio; D(M/S) are calculated from D(M/S)=1/[X(metal)×γ(metal, in Fe-metal alloy)], X(metal)= mole fraction of the total amount of metal in silicate melt, γ_{Ni} =0.736 (see [2]), γ_{Co} =1.124 (see [2]), γ_{Mo} =1 (assumed)

Fig.1: Solubilities of siderophile elements in silicate melt