

METAL-SILICATE PARTITION COEFFICIENTS FOR SIDEROPHILE ELEMENTS

(Ni, Co, P, W AND Mo) AT 8, 15 AND 70 KB, 1300-1750°C. Kevin Righter¹, Michael J. Drake¹, and Greg Yaxley². ¹Lunar and Planetary Laboratory, University of Arizona, Tucson, AZ 85721; ²Research School of Earth Sciences, ANU, Canberra, Australia.

We report new metal-silicate partition coefficients for Ni, Co, and P at 70 kb (1650° - 1750°C), and Ni, Mo and W at 8 and 15 kb (1300-1400°C). These new partition coefficients are compared to previously reported 1 bar partition coefficients (at the same temperature and fO_2) to illustrate the effect of pressure on metal-silicate partition coefficients. All available metal-silicate partition coefficients for Ni, Co, P, Mo and W (M) are regressed against $1/T$, P/T , $\ln fO_2$ and X_S (mole fraction of sulfur in metallic liquid) to derive equations of the form, $\ln D(M) = a \ln fO_2 + b/T + cP/T + d + eX_S$, that can be used to predict $D(M)$ as a function of these intensive parameters.

Introduction: Experimental partitioning of siderophile elements between metal and silicate liquid at low temperatures (1300 - 1600°C) and 1 bar cannot account for the elevated siderophile element abundances in Earth's upper mantle [1]. Recent studies have shown the importance of high temperature partitioning behavior [2, 3], especially in light of high temperature magma ocean models of the early Earth [4]. In addition, several studies have reported high temperature and high pressure partition coefficients, illustrating the importance of pressure as well [5, 6, 7]. We have determined metal-silicate partition coefficients for several siderophile elements, and investigate the effect of pressure, temperature, fO_2 and S-content of metallic liquid on siderophile element partition coefficients.

Experimental: The 70 kb experiments were performed in a multi-anvil press, with a graphite furnace and a synthetic meimechite (alkali picritic lava) starting composition. Although no Ni or Co was added to the synthetic composition, the San Carlos olivine capsule has as much as 2580 ppm Ni and 135 ppm Co [8]. Both 70 kb experiments crystallized olivine (Fo₉₂₋₉₃), and small liquid metal blebs are in the glass. The 8 and 15 kb experiments were performed in a piston-cylinder apparatus, with a graphite furnace and BaCO₃ pressure medium. Samples of synthetic basalt (20% FeO) doped with 10% MoO₃ and 5% WO₃, were welded into Fe₆₄Ni₃₆ alloy tubing. These capsules were then sheathed in alumina tubes, to prevent reaction of the metal capsule with the graphite furnace, and W₅Re-W₂₆Re thermocouples monitored the temperature. Samples were quenched after 6 hrs. Phases produced in these experiments include olivine (Fo₃₀₋₄₀), silica, melt which quenched as glass, and iron molybdates in the MoO₃-doped experiments. The glass and the inner wall of the Fe-Ni capsule were analyzed to determine the partition coefficient for a given experiment; the innerwall of the capsule equilibrated with the silicate liquid in the capsule.

Calculation of oxygen fugacity: Knowledge of the oxygen fugacity in experimental runs is critical, because metal-silicate partition coefficients are strongly dependent on fO_2 . Oxygen fugacities are calculated using two different equilibria. The presence of olivine and free silica in the 8 and 15 kb runs allows calculation of fO_2 from the iron-quartz-fayalite (IQF) oxygen buffer, $Fe + SiO_2 + O_2 = Fe_2SiO_4$. Values of fO_2 were calculated using the program QUIF [9], with a_{Fe} determined from independent studies [10]; these are summarized in Table 1. The second equilibrium is the iron-wüstite (IW) oxygen buffer, $Fe + 1/2 O_2 = FeO$. This reaction is evaluated using values of a_{Fe} and X_{FeO} ($a=X$), and thermodynamic data for Fe, FeO and O₂ [11]. For pressures as high as 70 kb, thermal expansion and compressibility become significant in the volume change in this reaction and are included in the thermodynamic calculations, by use of the Murnaghan equation [12]. The calculated fO_2 's are also summarized in Table 1. In the discussion below, fO_2 will be discussed relative to the oxygen buffer IW at a specific temperature (e.g. $\Delta IW = -2.0$ refers to an oxygen fugacity two $\log fO_2$ units below the IW buffer at a specific temperature).

Results: The effect of pressure on the partitioning of Ni, Co, P, Mo and W can be evaluated by comparing the high pressure experimental results here, with those obtained by others [13, 14, 15, 16] at one bar. Regression of the available one bar partition coefficients against $\ln fO_2$ and T provides an expression for predicting a siderophile element partition coefficient (D) at any temperature and fO_2 . Our high pressure siderophile element partition coefficients are compared to the calculated one bar values in Fig. 1. For the 70 kb experiments, $D(Ni)$ and $D(Co)$ decrease with pressure, as observed in other studies [5, 6, 7]. For the 8 and 15 kb experiments, $D(W)$ and $D(Mo)$ clearly increase, while $D(Ni)$ decreases.

Discussion: Is there anywhere in P-T- fO_2 space where siderophile element partition coefficients satisfy simple metal-silicate equilibrium between the core and the mantle in the Earth? Combining these new results with previous studies, it is possible to evaluate the combined effect of P, T and fO_2 on partitioning behavior of Ni, Co, P, Mo and W. The partitioning of an element between metal and silicate liquid can be expressed in generalized form as: $MO_{X/2} = M^0 + x/4 O_2$. At equilibrium $\Delta G = \Delta H - T\Delta S + V\Delta P = -RT \ln K$. Since $K = (fO_2)^{x/4} (aM)/(aMO_{X/2})$, the above equation may be rewritten as: $\ln D(M) = a \ln fO_2 + b/T + cP/T + d$, where the constants a, b, c, and d are related to the stoichiometry of oxygen, $\Delta H/R$, $\Delta V/R$, and $\Delta S/R$, respectively. An

METAL-SILICATE PARTITION COEFFICIENTS: Righter et al.

additional term can be added for the mole fraction of sulfur (X_S) in metallic liquids, as the partitioning behavior of siderophile elements is affected by sulfur content of the metal. The resulting expression is then, $\ln D(M) = a \ln fO_2 + b/T + cP/T + d + eX_S$. These constants may be derived by regression of the available experimental $\ln D(M)$'s against T , P , X_S and $\ln fO_2$ (T in K, P in kb; Table 2). In this way, an expression predicting values for $\ln D(M)$ for each siderophile element may be derived. An example of how well these expressions can reproduce the experimental database is shown for $D(Ni)$ for solid metal/liquid silicate in Fig. 2 (5 kb experiments from [17]). Application of these expressions to simple metal-silicate equilibrium in Earth results in matches (to Earth's upper mantle) for two siderophile elements under certain P - T - fO_2 conditions, but not all five elements at once. For example, at 100 kb, 2300 K, $X_S = 0.15$ and fO_2 near IW, calculated Ni and Co abundances match those of the upper mantle, but P is too high, and Mo and W are too low. At 10 kb, 1600K, $X_S = 0.15$, and fO_2 near IW+1, calculated Mo and W values match those in the upper mantle, but Ni and Co are too low and P too high. These results indicate that either core formation involved several stages, or a mantle phase (e.g. magnesiowüstite or β -spinel) has fractionated some siderophile elements relative to others, since separation of the metal phase during core formation.

References: [1] Jones, J.H. and Drake, M.J. (1986) *Nature* 322, 221-228; [2] Murthy, V.R. (1991) *Science* 253, 303-6; [3] Capobianco, C.J. et al. (1993) *J.G.R.* 98, 5433-43.; [4] Ohtani, E. (1985) *P.E.P.I.* 38, 70-80; [5] Hillgren, V.J. et al. (1994) *Science* 264, 1442-45; [6] Walker, D. et al. (1993) *Science* 262, 1858-61; [7] Thibault, Y. and Walter, M.J. (1994) *Terra Nova Supp.* 6, p. 46; [8] Frey, F.A. and Prinz, M. (1978) *E.P.S.L.* 38, 129-176; [9] Lindsley, D.H. and Frost, B.R. (1992) *Amer. Mineral.* 77, 987-1003; [10] Schwartzenruber et al. (1991) In Phase Diagrams of Binary Nickel Alloys (ed. P. Nash), 110-132; [11] Knacke, O. et al. (1991) *Thermochem. prop. of inorg. subst.*, Springer-Verlag; [12] Fei, Y. and Saxena, S.K. (1986) *P.C.M.* 13, 311-24; [13] Hillgren, V.J. (1993) Ph.D. Thesis, U. of Arizona; [14] Capobianco, C.J. and Amelin, A. (1994) *G.C.A.* 58, 125-140; [15] Schmitt et al. (1989) *G.C.A.* 53, 173-186; [16] Newsom, H. and Drake, M.J. (1982) *G.C.A.* 46, 93-100; [17] Seifert et al. (1988) *G.C.A.* 52, 603-616. **Acknowledgment:** NASA Grant NAGW 3348

Table 1: Summary of experimental results

sample	D(Ni)	D(Co)	D(P)	D(Mo)	D(W)	P (kb)	T (°C)	logfO ₂	Δ IW
720	55.6	27.6	1.47	-	-	70	1750	-6.19	-0.85
724	61.4	25.5	1.60	-	-	70	1650	-6.80	-0.85
6	460	-	-	17.4	-	15	1300	-10.51	-0.07
10	612	-	-	-	3.5	8	1400	-9.75	-0.30
11	277	-	-	-	37.0	15	1300	-10.65	-0.19

Table 2: Regression coefficients for $\ln D(M)$ calculations

	# points	a ($\ln fO_2$)	b (1/T)	c (P/T)	d	e (X_S)	r ²
Ni (LM/LS)	40	-0.487	-22472	+48.06	+7.72	+7.75	0.990
Co (LM/LS)	21	-0.542	-22541	+71.67	+5.35	-2.44	0.962
Mo (LM/LS)	5	-1.138	-210489	-565.4	+112.5	-1.55	0.997
W (LM/LS)	6	-1.748	-199886	-192.1	+84.16	-10.12	0.917
Ni (SM/LS)	82	-0.442	-21139	-161.4	+9.90	-	0.986
Co (SM/LS)	27	-0.455	-22914	-235.8	+7.04	-	0.895
Mo (SM/LS)	10	-1.554	+226935	+302.4	-182.2	-	0.998
W (SM/LS)	26	-1.174	-66040	+406.1	+12.9	-	0.915

