

METAL/SILICATE PARTITIONING OF P, Ga, AND W AT HIGH PRESSURES AND TEMPERATURES: DEPENDENCE ON SILICATE MELT COMPOSITION. Edward Bailey and Michael J. Drake, Lunar and Planetary Laboratory, University of Arizona, Tucson, Arizona 85721-0092, U.S.A. drake@lpl.arizona.edu

Introduction: The distinctive pattern of element concentrations in the upper mantle provides essential evidence in our attempts to understand the accretion and differentiation of the Earth (e.g., Drake and Righter, 2002; Jones and Drake, 1986; Righter *et al.*, 1997; Wänke 1981). Core formation is best investigated through use of metal/silicate partition coefficients for siderophile elements. The variables influencing partition coefficients are temperature, pressure, the major element compositions of the silicate and metal phases, and oxygen fugacity. Examples of studies investigating the effects of these variables on partitioning behavior are: composition of the metal phase by Capobianco *et al.* (1999) and Righter *et al.* (1997); silicate melt composition by Watson (1976), Walter and Thibault (1995), Hillgren *et al.* (1996), Jana and Walker (1997), and Jaeger and Drake (2000); and oxygen fugacity by Capobianco *et al.* (1999), and Walter and Thibault (1995). Here we address the relative influences of silicate melt composition, pressure and temperature.

Experimental Methods: All experiments were performed in a one half inch non-end-loaded piston-cylinder press at the University of Arizona, using a barium carbonate pressure medium. Experimental samples were prepared with a variety of silicate compositions to produce a wide range of silicate melt polymerization. Melt structure was quantified by calculating the ratio of nonbridging oxygens to tetrahedrally coordinated cations (Jaeger and Drake (2000) after Mills (1993)). Starting materials were prepared from powdered natural granite, granodiorite, andesite and ankaramite basalt. Each was mixed with 2-3 weight% each of WO_3 , Durango apatite (for P_2O_5), Ga_2O_3 and MoO_2 . In order to better cover the range of nbo/t these compositions represent, another “modified granite” sample was also prepared. This sample consisted of granite with approximately 10 wt % each of MgO and Fe_2O_3 . For each experiment approximately 0.02 g of the starting material was packed into a thick-walled, T-shaped Fe capsule weighing 0.2 g. The capsule provided the metal half of the partition couple, and its large mass ensured that the run products would not be oversaturated by any of the trace elements, an important consideration given their relatively high sum total concentration in the starting silicate compositions. The capsule was sealed prior to loading into the piston-cylinder press by compression in a desktop vice. The

capsule also fixed oxygen fugacity during experiments. Oxygen fugacity was calculated using the method of Capobianco *et al.* (1999), assuming that the activity of metallic iron was fixed at 1 by the capsule, and that all iron in the silicate was present as FeO .

We conducted a set of time series experiments to investigate how closely our experiments approach equilibrium. None of the experiments approached true equilibrium, but the more silicic compositions reached a homogenous melt composition after a few tens of hours with a diffusion profile in the metal dropping in concentration away from the glass-metal interface. The large mass of metal capsule served as an “infinite sink” for siderophile elements in the more fluid compositions but, again, a homogeneous silicate melt formed quickly. However, the concentration of the siderophile element in the melt continuously dropped with time. Runs as short as a few hours showed no detectable Mo in the silicate, so no Mo partitioning data were obtained. Partition coefficients were obtained by quenching and analyzing the glass and by extrapolating the metal composition to the glass-metal interface.

Analytical Techniques: Run products were analyzed by a CAMECA SX-50 electron microprobe with four wavelength dispersive spectrometers and a PAP ZAF correction program at the University of Arizona. Operating conditions were 15 kV accelerating potential, 40 nA sample current and 20-60 s count times on major elements; 25 kV accelerating potential, 200 nA sample current and 200 s count times on trace elements. Trace element concentrations in the metal phase at the metal-silicate boundary were estimated by extrapolation of analysis line-scans (Fig. 1). This was found to be unnecessary for estimation of boundary values in the silicate phase, which was homogeneous.

Results and Discussion: Results are presented in the Table. The silicate melt compositional dependences for Ga and W are in broad agreement with previous work. We confirm that partition coefficients are a stronger function of nbo/t for higher valence cations (P, W) than lower (Ga), e.g., Jaeger and Drake (2000), Walter and Thibault (1995). Our metal/silicate partition coefficients for Ga and W in LogD versus nbo/t space (Fig. 2) can plausibly be fit by trends of the same slope as those of Jaeger and Drake (2000). One explanation of this is that the higher pressure and tempera-

ture of the present work have offsetting effects. The same reasoning can be applied when comparing present results with those presented by Walter and Thibault (1995). Their data on W were collected at similar pressure and fO_2 conditions, but at the higher temperature of 2027 °C.

We find a small increase of LogD_{Ga} and LogD_W with temperature. The effect of pressure is too small to distinguish, and the observation that LogD_{Ga} and LogD_W values presented here are generally higher than in the 1 bar experiments of Jaeger and Drake (2000) is attributed to the temperature difference. We conclude, therefore, that temperature and silicate composition have a greater influence on partitioning than pressure, at least over the pressure range of this study.

Run	P(kb)	T(°C)	D	IW	nbo/t	P	Ga	W
28	10	1350	-1.66	1.3		-1.2		
45	10	1350	-1.89	0.41	0.7	0.4	1.9	
35	10	1350	-2.41	0.29	1.4	1		
47	20	1350	-1.72	1.16	-0.6	0.2	0.8	
86	20	1350	-1.51	1.06	-0.4	0.2	0.8	
84	20	1350	-2.20	1.45	-0.5	0.1	0.6	
96	20	1350	-2.36	0.23		0.5	2	
105	20	1350	-1.84	0.44	0.2	1.2	0.6	
56	20	1350	-1.94	0.41	0.9	0.5	1.6	
107	20	1350	-1.95	0.42	0.9	0.7	1.9	
106	20	1350	-2.09	0.28	0.5	0.4	1.7	
101	20	1350	-2.74	0.18		1		
102	20	1350	-3.01	0.16		0.8		
103	20	1350	-4.08	0.12	1.3	1.8		
29	10	1400	-2.15	1.35	-0.5	0.4	0.8	
44	10	1400	-2.47	0.4	1.3	0.7		
34	10	1400	-2.52	0.39		0.5		
46	20	1400	-1.95	1.37	-0.3	0.2	0.8	
57	20	1400	-2.47	0.39	1.1	0.6	1.9	
30	10	1450	-2.62	1.41	-0.5	0.5	1	
43	10	1450	-2.94	0.4	1	0.7	1.8	
33	10	1450	-3.32	0.35	1.2	1		
38	10	1450	-3.53	0.25	1	1.1		
48	20	1450	-2.63	1.36	-0.2	0.5	1.1	
77	20	1450	-2.68	0.86		0.4	1.2	
81	20	1450	-2.60	1.07	0.2	0.6	1.4	
53	20	1450	-3.34	0.25	1.4	1.5		

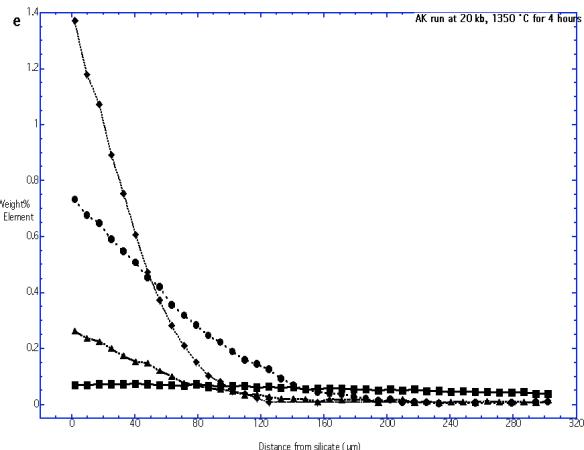


Fig 1. Typical compositional profile away from glass-metal interface. Symbols: W = closed diamonds. Ga = closed circled. P = closed squares.

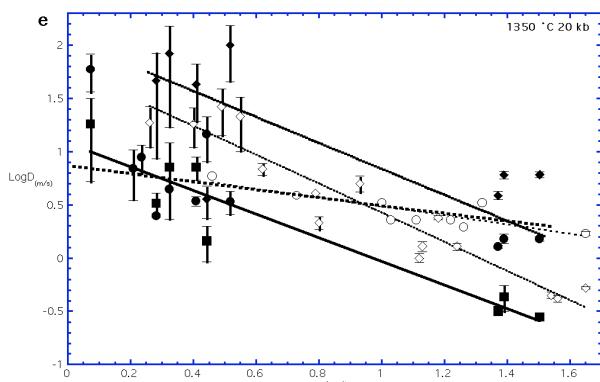


Fig 2. Metal/silicate partition coefficients as a function of nbo/t. Symbols: W = closed diamonds, this study; open diamonds, Jaeger and Drake (2000). Ga = closed circled, this study; open circles, Jaeger and Drake (2000). P = closed squares, this study.

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References: Capobianco *et al.* (1999) *Geochim. Cosmochim. Acta* **63**, 2667-2677; Drake and Righter (2002) *Nature* **416**, 39-44; Hillgren *et al.* (1996) *Geochim. Cosmochim. Acta* **60**, 2257-2263; Jaeger and Drake (2000) *Geochim. Cosmochim. Acta* **64**, 3887-3895; Jana and Walker (1997); Jones and Drake (1986) *Nature* **323**, 470-471; Mills (1993) *ISIJ International* **33**, 148-155; Righter *et al.* (1997) *Physics Earth and Planet. Int.* **100** 115-134; Walter and Thibault (1995) *Science* **270**, 1186-1189; Wänke (1981) *Phil. Trans. R. Soc. Lond. A* **303**, 287-302; Watson (1976) *Contrib. Mineral. Petrol.* **56**, 119-134.