

SIMULTANEOUS EXPERIMENTAL DETERMINATION OF METAL-SILICATE PARTITIONING OF W, Mo, Ru, Pt AND Pd USING NATURAL ABUNDANCES, ELEVATED P-T AND ISOTOPIC TRACERS.

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Introduction: Experimental studies have shown that moderately siderophile elements (MSE), and some highly siderophile elements (HSE) are characterized by greatly reduced siderophilic tendencies under high P and T conditions [1-5]. Consequently, the relatively high abundances of MSE and HSE in the terrestrial mantle have been interpreted by some as evidence for metal-silicate segregation under high P-T conditions, most likely at the bases of transient magma oceans that periodically formed as the Earth grew by accretion. Of particular importance has been the observation that abundances of MSE, such as W and Mo, can be well explained by high P-T processes [2]. The ability of high P-T processes to account for HSE abundances has been much more highly debated [1,5-6]. Some studies have shown that certain HSE, such as Pt, may be in abundances consistent with high P-T metal-silicate segregation [e.g., 5]. Because the HSE appear to be in approximately chondritic relative abundances, metal-silicate D values would have to converge to relatively low, nearly common values for some appropriate set of conditions. However, other studies have concluded that high P-T conditions do not reduce the siderophilic nature of at least some HSE, such as Os and Ir [6-7]. If the latter is true, HSE abundances in the mantle must have been established by another process, such as late accretion [8]. Yet even if late accretion was the process that dominated HSE (and possibly MSE abundances), lowered D values for some elements, could potentially account for apparent suprachondritic Ru/Ir and Pd/Ir in the terrestrial primitive upper mantle [9].

A key to resolving this issue is the determination of metal-silicate D values for multiple MSE and HSE under identical conditions at elevated P-T appropriate to magma ocean conditions. Few studies have attempted this [e.g., 7]. An additional problem with experimental studies has been the observation that HSE-rich nuggets can form in the silicate portions of experimental charges. Whether the nuggets are indigenous to the silicate in which they are found, or represent bits of the associated metal has been highly debated. The interpretation can highly affect the D values determined [5].

Yokoyama et al. [6] devised a method to consider metal-silicate partitioning of Os using natural abundances and an isotopic contrast between the metal (iron meteorite) and silicate (komatiitic basalt) phases present in a charge. The new approach allowed

mathematical extrapolation of data for three or more chunks of silicate from each charge, to metal-nugget-free compositions, where the isotopic composition would match that of the initial silicate. Here we use the same approach for W, Mo, Ru, Pt and Pd. In order to use the isotopic extrapolation approach, a synthetic metal was created with isotopically modified MSE and HSE. Chunks of the silicate portions of charges were then spiked with different enriched isotopes of these elements, and measured by isotope dilution.

Methods: Preparation of isotopically-distinct metal batches was accomplished by 4 hour fusions of metal starting ingredients at 10 kbar, 1550°C in MgO capsules contained within a graphite tube heated in a BaCO₃ pressure-transmitting cylinder in a ¾" WC piston-cylinder compound pressure vessel, manufactured by Rockland Research. The WC vessel core was end-loaded with 200 tons force on a 2" circular area of contact with the pressure distribution plates top and bottom. Sample pressurization was performed with a ¾" WC cylindrical piston driven into the pressure vessel from below by a 5" ram holding 290 bars of oil pressure. Heating of the graphite tube was accomplished by passing a ~400 A current at ~4 VAC delivered from an SCR-controlled primary 208 V power source through a 40:1 step-down transformer.

Metal starting ingredients were high purity Fe and Ni powders from Aesar and Fisher respectively. These powders were combined in a 9:1 weight ratio by manually blending with a nonmagnetic spatula on a large sheet of glazed weighing paper and subsequent shaking in a glass bottle. This Fe₉Ni₁ stock mixture was subsequently combined with 1.5-3.9 mg each of siderophile element spikes of unnatural isotopic composition: ⁹²Mo, ¹⁰⁴Ru, ¹⁹⁸Pt, ¹¹⁰Pd, and ¹⁸⁴W. The spikes were weighed into an Al foil envelope at UMD, the envelope was closed and sent to LDEO, where it was added to 1.5 gm charges of Fe₉Ni₁ in MgO capsules for insertion into the piston-cylinder apparatus. Once pressurized, the charge, #67, was heated to 1000 °C for 17 hours to sinter closed the MgO pore space in the capsule. After sintering, the charge was raised to 1550°C for 4 hours. This temperature was sufficient to achieve fusion of the Fe₉Ni₁ + SE alloy. Quenching of the charge was performed by cutting the power. The initial rate of temperature drop was about 100 °C/s, so that solidification temperatures should have been achieved in about 5 seconds. The quench metal showed few structures optically besides the Al₂O₃ re-

mains of the Al foil envelope and the odd MgO stringer from the capsule walls.

Because of chemical heterogeneity identified via microprobe analysis, a second fusion-dilution step at 1550 °C, 10 kbar, for 4 more hours was performed to make product #68. The isotope dilution analysis of product #68 is given in Table 1 along with the value expected from weights added and dilutions. Pt and Ru agree with their expected values to within 20%. Pd is depleted by ~ 2 , instead of being at the expected value as in #67. Mo and W are present in excess of their expected values, Mo by ~ 4 , in contrast to the ~ 2 depletions seen by electron microprobe in #67. It is possible that these deviations from expectation reflect imperfectly homogeneous distributions of the SE tracers in #67. Also, the isotopic compositions of the SE tracers in #68 suggest that there may also be a component of contamination in Mo, W, Ru, and Pt because the isotopic ratios found are not those of the spike.

	observed	expected
Fe %	90	90
Ni %	10	10
Mo ppm	25	5.7
Ru ppm	10	12
Pd ppm	14	25
W ppm	15	10
Pt ppm	5	4.5

~ 10 mg of metal #68 were then combined with ~ 100 mg of the komatiitic basalt 91117 used by [5]. This combined charge, #69, was run using the same $\frac{1}{2}$ " protocols as [6] at 1450 °C, 10 kbar, for 1.4 hours in an attempt to observe the isotopic/compositional systematic previously observed for Os on a more extensive palate of SE. Additional equilibrations done for longer times and at higher temperatures, 2000 °C, have been completed and await analysis.

Silicate chunks from #69 were separated from the charge, were ground in an agate mortar and pestle, spiked with ^{182}W , ^{100}Mo , ^{99}Ru , ^{194}Pt and ^{105}Pd , then digested in a 1:2 mixture of concentrated HCl and HNO_3 in sealed carius tubes. These elements were separated from the matrix and one another using standard anion exchange procedures. Isotopic analysis was achieved using the *Thermo Element 2* ICP-MS at UMD.

Results: Elemental concentrations and isotopic compositions obtained for initial experiment #69 are provided in Table 2. Averaged metal-silicate concentration ratios for Mo and W are ~ 200 and ~ 40 , respectively. The blank comprises $>50\%$ of the Mo signal, so we do not consider the results for Mo to be robust. The isotopic compositions of W in the silicate fractions show a negative correlation with concentration, so these initial results suggest W metal-silicate equilibration was approached, but with minor W nugget formation. Extrapolated D values would be only marginally higher than 40. Ruthenium concentrations in the silicates were similar to starting material. If equilibrated with metal, results would be consistent with a D value of $\sim 10^4$. However, measured $^{104}\text{Ru}/^{101}\text{Ru}$ ratios were lower than natural, consistent with a minor isobaric interference. Palladium abundances were ~ 10 to 100 times lower than the starting material, but $^{110}\text{Pd}/^{106}\text{Pd}$ ratios were also lower than natural. Data for both Ru and Pd were compromised by high blank contributions, so additional refinement will be required before high quality partitioning data can be generated. Results for Pt show relatively high concentrations in the silicate (similar to starting materials) and $^{198}\text{Pt}/^{195}\text{Pt}$ that are also similar to the natural, starting material. If it is assumed metal-silicate equilibration occurred, a D value of ~ 220 is obtained, similar to some prior studies [5].

Conclusions: The first results of this new approach to measure metal-silicate D values at natural abundance levels shows promise, but also some measurement problems. Results for Ru and Pd are consistent with relatively high D values, whereas D values for Pt and the MSE appear to be much lower.

References: [1] Righter K. and Drake M. J. (1997) *EPSL* 146, 541-553. [2] Righter K. and Drake M. J. (1999) *EPSL* 171, 383-399. [3] Li J. and Agee C. B. (1996) *Nature* 381, 686-689. [4] Drake M. J. (2000) *GCA* 64, 2363-2370. [5] Cottrell E. and Walker D. (2006) *GCA* 70, 1565-1580. [6] Yokoyama et al. (2009) *EPSL* 279, 165-173. [7] Brenan J. and McDonough W. F. (2009) *Nature Geosci.* 2, 798-801. [8] Chou C.-L. (1978) *Proc. Lunar Planet. Sci. Conf. 9th*, 219-230. [9] Walker R. J. (2009) *Chem. Erde* 69, 101-125.

Table 2. Abundances and isotopic compositions of MSE and HSE in metal and silicate from experiment #69.

Sample	W (ppb)	2 σ	Mo (ppb)	2 σ	Ru (ppb)	2 σ	Pd (ppb)	2 σ	Pt (ppb)	2 σ	$^{184}\text{W}/^{183}\text{W}$	$^{92}\text{Mo}/^{85}\text{Mo}$	$^{110}\text{Pd}/^{106}\text{Pd}$	$^{104}\text{Ru}/^{101}\text{Ru}$	$^{198}\text{Pt}/^{195}\text{Pt}$
69NM1	543	33	353	122	0.690	0.08	0.19	0.13	9.91	0.79	1.90	0.991	1.60	0.159	0.175
69NM2	445	32	103	200	0.949	0.17	1.20	0.18	8.44	0.15	2.48	0.956	0.87	0.185	0.229
69NM3	439	28	220	166	0.940	0.14	2.23	0.15	8.52	0.14	2.54	0.959	1.26	0.220	0.244
69Metal	15700	930	25160	6610	9070	183	13650	344	2086	87	24.63	4.371	65.19	65.15	18.94
91117 natural					0.957		11.7		9.96		2.14	0.932	1.093	0.4420	0.2147