EXPERIMENTAL PARTITIONING OF TC, MO, RU, AND RE IN FE-NI-S AT 60 kBAR. C. Lazar and D. Walker, Lamont-Doherty Earth Observatory, and Department of Earth and Environmental Sciences, Columbia University, Palisades NY 10964, clazar@ldeo.columbia.edu, dwalker@ldeo.columbia.edu

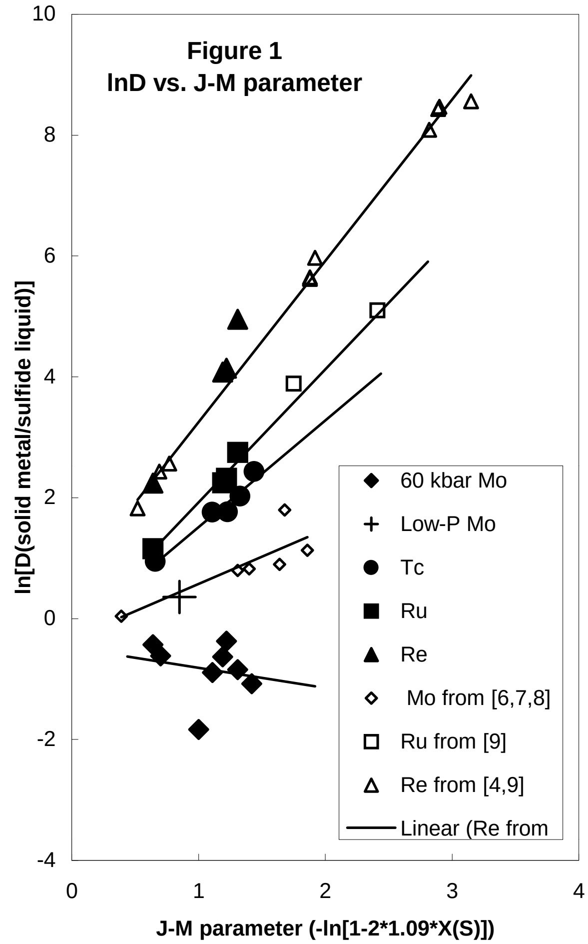
Introduction: The detection of faint $^{98}Ru/^{101}Ru$, $^{99}Ru/^{101}Ru$, and/or $^{97}Mo/^{96}Mo$ anomalies in some iron meteorites would imply that active Tc was present during asteroidal differentiation and that it was fractionated from Ru and/or Mo [1,2,3]. In the absence of experimental determination of Tc partitioning during the crystallization of Fe-Ni-S melts, Re partitioning has been used as an analog for Tc partitioning. We present new evidence that Tc behaves very much like the more modestly-siderophile Ru than highly-siderophile Re, and that Tc is substantially more siderophile than Mo. We also demonstrate a pressure effect in the partitioning of Mo in Fe-Ni-S. Our results place constraints on the creation of Tc-induced isotopic anomalies during asteroidal core evolution.

Methods and analysis: Our experimental methods are essentially identical to those of [4]: multi-anvil techniques in sintered MgO capsules in inverted temperature gradients with percent-level dopings of the siderophile elements of interest. Runs were pressurized to 60 kbar, sintered overnight at 800°C, and heated to run temperature (950°-1325°C) for 6-72 hours. The product was a layer of Fe-Ni alloy overlying a quenched region of sulfide and metal dendrites. Electron probe analyses were performed at 20-25kV and 50-75nA. Mo was analyzed using its Lβ line to avoid Lα interference with S Kα; Fe, Ti, Ni, S, O by Kα; Tc, Ru, Re by Lα. A Tc standard was hot-pressed from powder after reduction by Ti in a silica tube. A theoretical count rate for pure Tc was determined by interpolation of the pure count rates of the elements which flank it on the periodic table. Using the ratio of measured count rate to theoretical pure count rate, we calculated the percent of Tc in the standard to be roughly 80 wt%, with 15-16%Ti, 3-4%Si, and ~1%O determined by direct analysis using the preliminary Tc abundance in the standard.

The sulfide composition was analyzed in raster mode under the assumption that the spatial averaging of many local dendrite+antidendrite compositions statistically recreates the equilibrium composition of the once-homogenous sulfide liquid. The metal was analyzed using point mode in order to maximize spatial resolution at the metal-sulfide interface.

Results: Partition coefficients are tabulated in Table 1 and plotted in Figure 1 versus the Jones-Malvin parameter [5], -ln(1-2αX(S), where α=1.09 in the Fe-Ni-S system.

Although there have been some published reports of D(Mo) [6,7,8] and D(Ru) [9], no previous study of the partitioning of Tc between solid metal and sulfide liquid has been published in the geochemical literature, presumably because of the complications associated with obtaining and handling this radioactive element. Data for Ru includes two points published in [9]; data for Re includes seven points from [9] and three points from [4]. There is good agreement between this study and previous work for Ru and Re. Given that the previous Ru studies and some Re studies [9] were performed at low pressure, Jones-Malvinian pressure-independence of siderophile element partitioning is supported for Ru and Re.



The data for Mo at 60 kbar in Table 1 and Figure 1 differ significantly from previous experiments. In the present study, all the partitioning is in favor of the sulfide liquid, giving D(Mo)<1. Furthermore the slope of the D(Mo) variation in Figure 1 is negative, suggesting chalcophile behavior. Previous studies have all given D(Mo)>1 and variations with the J-M parameter showing a positive slope. We were concerned that this anomaly arose because of the differences in analytical procedures used by the various studies to avoid the Mo Lα overlap with the S Kα X-ray emission line. Consequently we performed an experiment with the evacuated silica tube procedures of Liu and Fleet [6] using our Ni-bearing compositions. The cross in Figure 1 shows that our low-pressure experiment (LW1) is in excellent agreement with the low-pressure experiments of Liu and Fleet [6] so that analytical artifacts are not the cause of the unprecedented behavior seen in our 60 kbar data. Likewise Ni-free [6] vs Ni-bearing compositional issues are not at the root of the discrepancy because both our 60 kbar and silica tube experiments are Ni-bearing. A pressure effect on Mo partitioning appears to be the residual hypothesis capable of explaining the unusual behavior of Mo at 60 kbar which is divergent from all previous low-pressure experimental results and which is divergent from conventional positive-sloped Jones-Malvin systematics. Mo-sulfide speciation at high pressure rather than S-avoidance at low pressure would explain the results, but further observations are required for verification. At typical core S contents of roughly 10%, this pressure effect exerts only a minor influence on Mo partitioning because D(Mo) approaches 1 at low S content. At any pressure, Tc is considerably more siderophile than Mo.

Table 1: Partitioning data

	X(S)	*error*	*D(Mo)*	*error*	*D(Re)*	*error*
BB751	0.218	0.0031	0.65	0.03	9.43	0.24
BB753	0.231	0.0037	0.54	0.02	--	--
BB755	0.29	0.0009	0.16	0.03	--	--
BB756	0.348	0.0006	0.34	0.06	--	--
BB757	0.307	0.0013	0.41	0.04	--	--
BB758	0.335	0.0009	0.43	0.02	142	16
BB759	0.319	0.0023	0.53	0.03	59.2	2.7
BB760	0.323	0.0039	0.69	0.05	63	5
LW1	0.2631	0.0055	1.43	0.2		
	X(S)	*error*	*D(Tc)*	*error*	*D(Ru)*	*error*
BB763	0.338	0.0014	7.59	0.19	--	--
BB764	0.307	0.0024	5.82	0.24	--	--
BB765	0.325	0.0029	5.84	0.19	--	--
BB766	0.221	0.0073	2.57	0.15	--	--
BB767	0.35	0.0011	11.4	0.48	--	--
BB751	0.218	0.0031	--	--	3.18	0.11
BB758	0.335	0.0009	--	--	15.7	0.9
BB759	0.319	0.0023	--	--	9.47	0.4
BB760	0.323	0.0039	--	--	10.2	0.5

Because D(Tc)/D(Mo) is always significantly greater than 1, Tc/Mo fractionation would occur within the core itself during crystallization. Tc enrichment of the solid phase could generate Mo isotopic anomalies in the solid if crystallization occurred before Tc became extinct. A core-mantle fractionation of Tc from Mo to create isotopic anomalies is not specifically required in the way it is for some other short-lived isotopic systems. However because Tc behaves very much like Ru (rather than Re), Ru isotopic anomalies are not expected to arise from rapid crystallization of asteroidal cores. Minimal Tc-Ru fractionation occurs even when Tc is still extant. This is consistent with a recent study [10] which reduces an earlier claim of Ru isotopic anomalies in iron meteorites. If Ru anomalies are present, however, they would most easily arise through some fractionation process other than core crystallization, such as core-mantle fractionation.

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