PARTITIONING OF U, TH AND K BETWEEN METAL, SULFIDE AND SILICATE, INSIGHTS INTO THE VOLATILE-CONTENT OF MERCURY. M. Habermann[1,2], A. Boujibar[3], K. Righter[3], L. Danielson[4], J. Rapp[4], M. Righter[5], K. Pando[6], D. K. Ross[4,7], R. Andreasen[5], B. Chidester[8], [1]Lunar and Planetary Institute, Houston, TX 77058 (myanh@uga.edu), [2]University of Georgia, Athens, GA 30609, [3]NASA Johnson Space Center, Houston, TX 77058, [4]Jacobs, NASA Johnson Space Center, Houston, TX 77058, [5]University of Houston, Dept. of Earth and Atmospheric Sciences Houston, TX 77204, [6]UTC– Jacobs JETS Contract, NASA Johnson Space Center, Houston, TX 77058, [7]UTEP-CASSMAR, El Paso TX 79968, [8]University of Chicago, Dept. of the Geophysical Sciences, IL 60637.

Introduction: During the early stages of the Solar System formation, especially during the T-Tauri phase, the Sun emitted strong solar winds, which are thought to have expelled a portion of the volatile elements from the inner solar system [1]. It is therefore usually believed that the volatile depletion of a planet is correlated with its proximity to the Sun. This trend was supported by the K/Th and K/U ratios of Venus, the Earth, and Mars [2]. Prior to the MESSENGER mission, it was expected that Mercury is the most volatile-depleted planet. However, the Gamma Ray Spectrometer of MESSENGER spacecraft revealed elevated K/U and K/Th ratios for the surface of Mercury, much higher than previous expectations [2,3].

It is possible that the K/Th and K/U ratios on the surface are not a reliable gauge of the bulk volatile content of Mercury. Mercury is enriched in sulfur and is the most reduced of the terrestrial planets, with oxygen fugacity (fO_2) between IW-6.3 and IW-2.6 log units [2,4]. At these particular compositions, U, Th and K behave differently and can become more siderophile or chalcophile [2, 5-11]. If significant amounts of U and Th are sequestered in the core, the apparent K/U and K/Th ratios measured on the surface may not represent the volatile budget of the whole planet. An accurate determination of the partitioning of these elements between silicate, metal, and sulfide phases under Mercurian conditions is therefore essential to better constrain Mercury's volatile content and assess planetary formation models.

Methods: Experiments were conducted using a piston cylinder at NASA Johnson Space Center (JSC) at 1 GPa and temperatures comprised between 1500 and 1700 °C. Starting compositions consisted of a mix of 50 wt% silicate and 50 wt% metal and sulfide powders with variable sulfur and silicon contents (8 to 30 wt% Si and 9 to 25 wt% S in metals) to vary oxygen and sulfur fugacities. Two series of starting compositions were used: either 2 to 3 wt% UO_2 and 2 to 3 wt% ThO_2, or 17 wt% K_2O in the silicate fraction. All other elements were added in proportions similar to those found in enstatite chondrites. fO_2 was calculated in a similar matter to that in [12] and was between IW-4.6 and IW-1.8. All K-rich and S-rich samples were dry-polished using boron nitride and alumina powders, whereas all other samples were polished using methanol. Major elements and K were analyzed with JEOL 8530F and Cameca SX100 electron microprobes at NASA JSC, whereas U and Th were analyzed with Laser Ablation ICP-MS at the University of Houston.

Results: All samples contain silicate, metal and sulfide melts in variable amounts. Orthopyroxene crystals and small fractions of U-Th-rich oxides are present in samples equilibrated at low temperatures (T<1700 °C). Partition coefficients of U, Th, and K between metal (or sulfide) and silicate melt were calculated and compared to previous data. They show an increasing siderophile character of U, Th and K with increasing S-content of metals and with decreasing fO_2. (Figure 1).

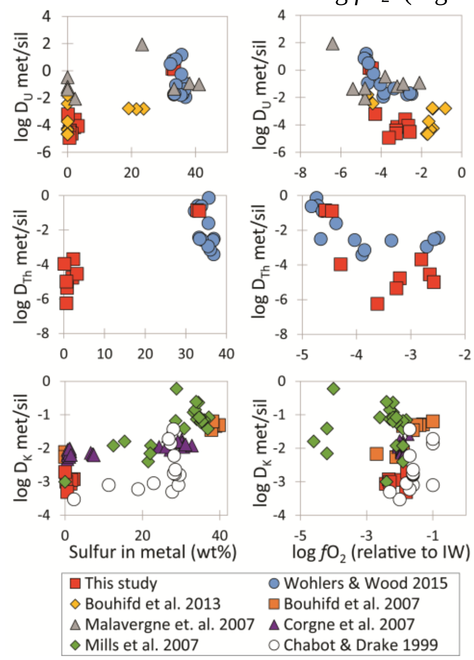

Figure 1: Experimentally determined partitioning coefficients of U, Th and K between metal and silicate as a function of the sulfur-content in metal and oxygen fugacity. Our data are reported with those from [5-11].

The calculated partition coefficients ($D^{met/sil}$) were combined with previously published ones [5-11] to derive equations that predict the partitioning of U, Th and K as a function of pressure (P), temperature (T), fO_2 and sulfur-content in metal/sulfide phases. Linear regression fits provide expressions in the form : log

($D^{met/sil}$)= a + b/T + c P/T + d fO_2 + e log(1-Xs), (where a, b, c, d, e are the fitted parameters and Xs is the mass fraction of sulfur in metals). For Th, all available data on its partitioning (this study and [11]) are obtained at pressures of 1 to 1.5 GPa. Because of this small variation of P, we ignored parameter c and fixed it to 0 in the regression fit. The resulting parameters are given in Table 1. They show that all U, Th, and K become more siderophile at high T, low fO_2 and high S-content. The effect of fO_2 and S-content are more pronounced for U and Th than for K, and S-content has a larger effect than fO_2 for all elements. In addition, pressure increases the affinity of U and K with metals.

	a	b (1/T)	c (P/T)	d (fO_2)	e (log(1-Xs))
U	-5.877	-470.2	198.4	-0.729	-12.19
Th	-3.026	-7338		-0.654	-14.24
K	-1.405	-3779	114	-0.212	-4.747

Table 1: Results of the linear regression fits (see text).

Implications for Mercury's volatile content: Using partitioning coefficients and K/U and K/Th ratios of Mercury's surface, measured by MESSENGER, we built a model that calculates the bulk planet's K/U and K/Th. We considered that the core and the mantle equilibrated at a pressure equivalent to Mercury's core/mantle boundary (5.5 GPa) [13] and a liquidus temperature calculated from the liquidus curve for chondrites (2230 K) [14]. Mass fraction of the core was fixed to 0.65, based on its gravity field [13]. U, Th and K are sufficiently incompatible elements to assume that they are only present in the crust and absent in the residual mantle. Hence, the concentrations of U, Th and K of Mercury's silicate fraction (X_{sil}) are considered equivalent to 10 % those measured on the surface [3], based on the average thickness of Mercury's crust[15]. The gravity field of Mercury [13] and the experimental constraints on Fe-S-Si alloy systems suggest the presence of a sulfide layer at the base of Mercury's mantle. We therefore calculated bulk element concentrations of the planet by varying the mass fraction of this layer using: $X_{bulk} = (0.65 * X_{sil} * D^{core}_X) + (f_{FeS\ layer} * X_{sil} * D^{FeS}_X) + ((1-0.65-f_{FeS\ layer})* X_{sil})$, where D^{FeS}_X and D^{core}_X stand for partition coefficients of element X (U, Th or K) between either the FeS layer (with 36 wt% S) and silicate or the S-poor core (with 2 wt% S) and silicate respectively, calculated using expressions predicting experimental $D^{met/sil}$ (see above). Figure 2 shows the resulting K/U and K/Th ratios for different fO_2 of core-mantle equilibration.

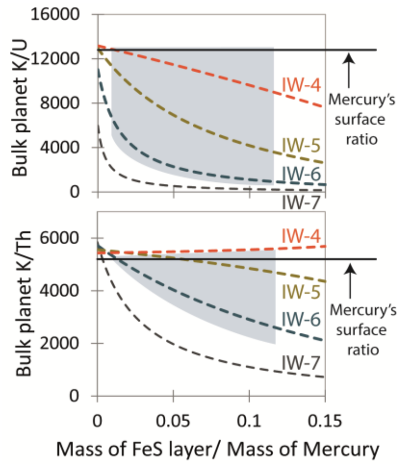

Figure 2: Calculated K/U and K/Th ratios for bulk Mercury as a function of the mass fraction of the sulfide layer at the base of the mantle, for different fO_2 (dashed curves). The gray areas represent Mercury's results for estimated ranges of sulfide layer thickness and fO_2 based on Mercury's gravity field [13] and Mercury's surface composition [2-4] respectively.

Using the estimated sulfide layer thickness from Mercury's gravity field and the estimated fO_2 range (IW-6.3 to IW-2.6) from sulfur and FeO abundances of the surface [2-4], we find that the minimum K/U and K/Th ratios are of 600 and 2003 respectively. These values are much lower than those measured by the MESSENGER spacecraft for the planet's surface (K/U=12800±4300 and K/Th=5200±1800) [3]. Therefore, these elevated ratios should not be interpreted as an enrichment of Mercury in volatile elements. Instead, they suggest low U- and Th-contents in the mantle and crust due to their early sequestration in Mercury's core and sulfide layer. Thus, Mercury's volatile inventory falls on the overall volatile depletion trend previously described by the other terrestrial planets [2]. Moreover, the presence of these radioactive elements in Mercury's core may have acted as major sources of energy, which can explain the relatively strong magnetic field and large volcanic plains.

References: [1] Albarède et al. (2009) *Nature, 461*, 1227-1233. [2] McCubbin et al. (2012) *GRL, 39*, L09202. [3] Peplowski, et al. (2011) Science, 333, 1850-1852. [4] Zolotov et al. (2013) *JGR, 118*, 138-146. [5] Chabot & Drake (1999) *EPSL 172*, 323-335. [6] Bouhifd et al. (2007) *PEPI 160*, 22-33. [7] Mills et al. (2007) *GCA, 71*, 4066-4081. [8] Corgne et al. (2007) *EPSL, 256*, 567-576. [9] Malavergne et al. (2007) *GCA, 71*, 2637-2655. [10] Bouhifd et al. (2013) *GCA, 114*, 13-28. [11] Wohlers & Wood (2015) *Nature, 520*, 337-340. [12] Boujibar et al. (2014) 46th LPSC, Abstract #2544. [13] Hauck II et al. (2013) *JGR Planets*, 118, 1204-1220. [14] Andrault et al. (2011) *EPSL 304*, 251-259. [15] Smith et al. (2012) *Science 336*, 214-217.