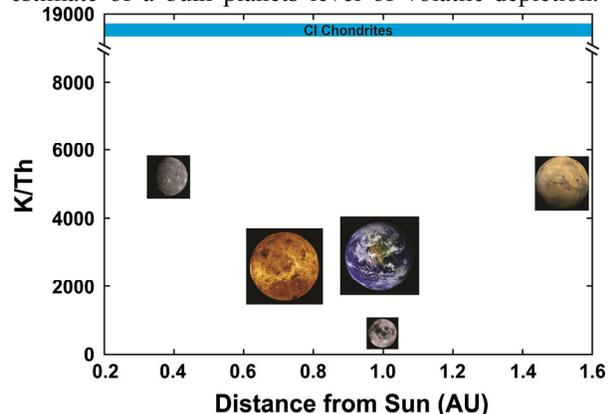


**IS MERCURY VOLATILE ENRICHED OR VOLATILE DEPLETED? NEW INSIGHTS FROM COMBINING MESSENGER X-RAY, NEUTRON, AND GAMMA-RAY SPECTROMETER DATA.** F. M. McCubbin<sup>1</sup>, M. A. Riner<sup>2</sup>, K. E. Vander Kaaden<sup>1</sup>, S. M. Elardo<sup>1</sup>, and C. K. Shearer<sup>1</sup> <sup>1</sup>Institute of Meteoritics, University of New Mexico, Albuquerque, NM 87131. <sup>2</sup>Hawaii Institute of Geophysics and Planetology, University of Hawaii, Manoa, Honolulu, HI ([fmccubbi@unm.edu](mailto:fmccubbi@unm.edu)).

**Introduction:** In planetary science, there are several important constraints that can reveal information regarding the formation, bulk chemistry, and evolution of a terrestrial planetary body. One of the most important and commonly used constraints are the ratios of moderately volatile large-ion lithophile (LIL) elements, such as K, Rb, and Cs, and refractory LIL elements such as Th, U, and some of the rare earth elements, which can provide important constraints regarding a planetary bodies relative volatile depletion (see [1] for more details). Importantly, LIL elements behave very incompatibly during partial melting, so LIL element ratios remain fairly constant from source to eruption during typical igneous processes, although some fractionation can occur during aqueous processes [2]. Consequently, the mean LIL element ratio of a terrestrial bodies surface is often used as a first-order estimate of a bulk planets level of volatile-depletion.

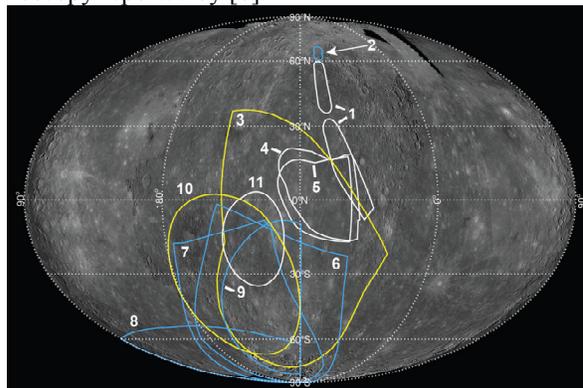


**Figure 1.** K/Th ratio of terrestrial bodies within the inner solar system plotted as a function of their distance from the Sun. Data for K/Th from [2-6]. Blue line represents CI chondrite.

The volatile depletion of a planet is typically believed to be correlated to temperature of formation, so it has commonly been assumed that the volatile depletion of the terrestrial planets would increase as their distance from the Sun decreased. However, recent results from the Gamma-ray spectrometer onboard MESSENGER indicate that Mercury has a relatively high K/Th ratio ( $5200 \pm 1800$  [6]), which means Mercury may be even more volatile enriched than Mars (Figure 1). This surprising result could dramatically for understanding volatile-depletion processes in the early solar system and solar nebula. In the present study, we integrate the K/Th ratio with other data being returned by the MESSENGER spacecraft, in particular data from the neutron absorption spectrometer and the X-

ray spectrometer (XRS), to re-examine volatile enrichment on Mercury.

**Composition of the Mercurian surface:** Elemental ratios for portions of the mercurian surface have been obtained from the X-ray spectrometer onboard MESSENGER from the regions outlined in Figure 2 below (adopted from [7]). If these ratios are averaged, and the average Si abundance of 25 wt.% is used (from [7]), the average composition of the surface highlighted in Figure 2 is:  $\text{SiO}_2 = 53.48$  wt%,  $\text{TiO}_2 = 0.56$  wt%,  $\text{Al}_2\text{O}_3 = 11.17$  wt%,  $\text{MgO} = 20.58$  wt%,  $\text{FeO} = 2.63$  wt%,  $\text{MnO} = 0.07$  wt%,  $\text{CrO} = <0.65$  wt%,  $\text{CaO} = 7.70$  wt%,  $\text{K}_2\text{O} = 0.14$  wt%, and  $\text{S} = 2.27$  wt%. The potassium value was obtained from Gamma-ray spectroscopy reported by [6].



**Figure 2.** Footprints sampled by MESSENGER's XRS to determine composition reported above (adopted from [7]).

The elemental abundances of Fe and Ti at Mercury's surface are fairly low, which is slightly surprising given the high neutron absorption observation from the neutron spectrometer on MESSENGER of  $45\text{-}81 \times 10^{-4} \text{ cm}^2/\text{g}$  [8-9]. The calculated neutron absorption cross section for the composition above is  $31 \times 10^{-4} \text{ cm}^2/\text{g}$  and ranges from from  $17\text{-}34 \times 10^{-4} \text{ cm}^2/\text{g}$  for the 11 individual footprints in Figure 2. If the absolute upper limits are used for the most highly neutron absorbing elements analyzed by XRS, the composition barely reaches the minimum neutron observation [according to 7]. Interestingly, it is presently unknown how much the super-neutron absorbing rare earth elements Sm and Gd are contributing to Mercury's neutron absorption observation. To understand why these elements may play a significant role, it is helpful to think of these elements in the context of a putative mercurian magma ocean (MMO).

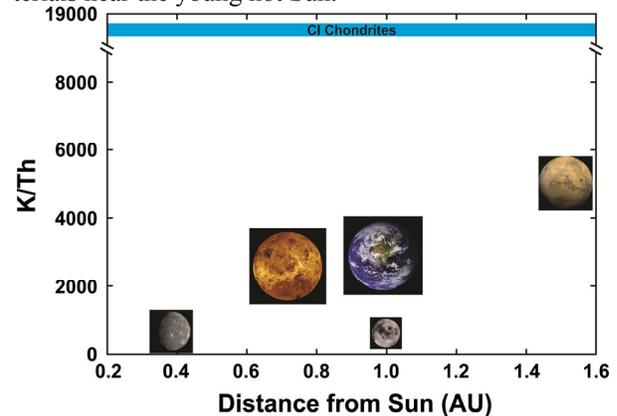
It has been postulated that during MMO crystallization, the Fe content of the liquid may not have been

sufficiently high to allow plagioclase flotation [10], which was responsible for the primary anorthositic crust on the Moon. This led [11] to postulate that the primary crust on Mercury may represent a foundering quench crust with the last late-stage liquid, analogous to lunar urKREEP, being perched just below the quench crust. Therefore, the present day surface of Mercury could have a substantial contribution from that late-stage magma-ocean material, which would be highly enriched in incompatible elements like the rare earth elements and potassium. If we calculate the amount of Sm and Gd required to reach the neutron absorption observation on Mercury from the average composition above, assuming a chondritic Sm/Gd ratio and assuming the isotopic abundance ratios for each element is the same as the Moon [after 8, 9], Sm and Gd would need to be enriched by approximately 60x chondrite (average surface composition of 11 and 15 ppm Sm and Gd, respectively). This is consistent with the amount of enrichment expected for the mercurian surface through magma ocean processes.

**MESSENGER data dichotomy? Neutrons vs Gamma-rays:** With the addition of 11 and 15 ppm Sm and Gd, we have found a way to comfortably match the neutron absorption observation on Mercury without using the absolute upper bounds for the other highly neutron absorbing elements Fe and Ti. However, a problem arises regarding the inferred volatile enrichment on Mercury. The amount of potassium on the mercurian surface is low compared to the concentration of rare earth elements. In fact, the resulting K/Gd ratio is approximately 90, which is very similar to values obtained for the Moon [3-4, 12]. Furthermore, the values for U and Th [6] are much lower than would be expected for the REE enrichment.

However, Mercury is a planet with a highly reduced interior, and elements that typically behave as lithophile elements will behave differently in an oxygen-starved system like Mercury. There is limited experimental data available that indicate U becomes chalcophile under highly reducing conditions consistent with 3-6 log units below the iron-wüstite oxygen buffer (i.e.,  $\Delta IW$  -3 to -6) [13-14]. Furthermore, these data indicate that K will continue to behave as a lithophile element at these conditions. Consequently, a significant portion of U and perhaps Th could have partitioned into the S-rich portion of the core during MMO crystallization. Nearly all K would have partitioned into the silicate portion and would then be enriched in the late-stage magma ocean liquid. If this was the case, it would imply that Mercury is actually volatile depleted. In fact, if the K/Th ratio is corrected based on this process, assuming a chondritic REE/Th ratio, the new K/Th value for Mercury would be <660 (Figure 3). This value is on the order of the K/Th values for the highly volatile-depleted Moon, and it would be consis-

tent with Mercury forming from volatile depleted materials near the young hot Sun.



**Figure 3.** K/Th ratio of terrestrial bodies within the inner solar system plotted as a function of their distance from the Sun with corrected K/Th for Mercury. Data from [2-6]. Blue line represents CI chondrite.

**Caveats and data gaps:** This model is not without significant gaps and caveats. The core-mantle boundary on Mercury is approximately 7-8 GPa, and experiments to understand the metal-silicate partitioning of lithophile elements like REE, U, Th, and K at highly reducing conditions are extremely limited. In fact, it is possible that the REE's would become chalcophile before U and/or Th, which would invalidate the methods used in the present study for correcting the K/Th ratio. In fact, the sulfide mineral oldhamite (CaS) is present in highly reduced chondrite and achondrite meteorites and has elevated U, Th, and REE [15], so additional experimental work is needed to determine the order in which elements become chalcophile as a function of decreasing  $fO_2$ .

This work is largely a thought experiment that has successfully demonstrated that we may not be able to conclude whether Mercury is a volatile-rich or volatile-depleted planet given the data set that is currently available. Better constraints on Fe, Ti, and the REE's would significantly aid in this effort. Furthermore, high pressure petrologic experiments could be conducted to determine the order in which lithophile elements lose their lithophile character as a function of decreasing oxygen fugacity in an S-rich system.

**References:** [1] McLennan (2003) *MAPS* 38, 895-904. [2] Taylor et al. (2006) *JGR Planets* 111(E3). [3] Lodders and Fegley (1998) *The Planetary Scientist's Companion* [4] Lucey et al. (2006) *New Views of the Moon* RiMG 60. [5] McDonough and Sun (1995) *Chem Geo* 120, 223-253. [6] Peplowski et al. (2011) *Science* 333, 1850-1852 [7] Nittler et al. (2011) *Science* 333, 1847-1850 [8] Lawrence et al. (2010) *Icarus*. 209, 195-209. [9] Riner et al. (2011) *EPSL* 308, 107-114. [10] Brown and Elkins-Tanton (2009) *EPSL* 286, 446-455. [11] Riner et al. (2010) *Icarus* 209, 301-313. [12] Warren (1998) *Workshop on Moon in transition: Apollo 14, KREEP, and evolved lunar rocks* [13] Malavergne et al. (2007) *GCA* 71, 2637-2655. [14] Malavergne et al. (2010) *Icarus* 206, 199-209. [15] Lodders and Fegley (1993) *EPSL* 117, 125-145.