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#### Supporting Online Material

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# Radioactive Elements on Mercury's Surface from MESSENGER: Implications for the Planet's Formation and Evolution

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The MESSENGER Gamma-Ray Spectrometer measured the average surface abundances of the radioactive elements potassium (K,  $1150 \pm 220$  parts per million), thorium (Th,  $220 \pm 60$  parts per billion), and uranium (U,  $90 \pm 20$  parts per billion) in Mercury's northern hemisphere. The abundance of the moderately volatile element K, relative to Th and U, is inconsistent with physical models for the formation of Mercury requiring extreme heating of the planet or its precursor materials, and supports formation from volatile-containing material comparable to chondritic meteorites. Abundances of K, Th, and U indicate that internal heat production has declined substantially since Mercury's formation, consistent with widespread volcanism shortly after the end of late heavy bombardment 3.8 billion years ago and limited, isolated volcanic activity since.

Measurements of the surface composition of Mercury offer a special window into the epoch of planet formation in the inner solar system. Mercury likely preserves a more complete record of early crustal formation than do Venus, Earth, or Mars, each of which experienced extensive and prolonged resurfacing and near-surface alteration since earliest crustal formation. The MESSENGER spacecraft, in-

serted into orbit about Mercury on 18 March 2011, carries a suite of instruments designed for elemental and mineralogical remote sensing. We report abundances of radioactive elements on the surface of Mercury that we determined from measurements with MESSENGER's Gamma-Ray Spectrometer (GRS).

The MESSENGER GRS measures 0.25- to 9-MeV gamma rays originating from isotope-specific gamma-ray emission from the surface (*I*). The two sources of gamma-ray emission are natural radioactive decay of unstable elements (e.g., K, Th, U) and excitation of stable elements (e.g., Si, O, Fe, Ti, S, Ca) by incident galactic cosmic rays. This work focuses on measurements of the elemental abundances of K, Th, and U through the detection of gamma rays emitted during the decay of the naturally occurring radioactive isotopes <sup>40</sup>K, <sup>232</sup>Th, and <sup>238</sup>U. MESSENGER's highly eccentric orbit, combined with the altitude dependence of the gamma-ray signal, limits GRS compositional measurements to the region northward of  $\sim 20^\circ$  S latitude. GRS compositional data nonetheless cover a variety

of geologic terrain types, including heavily cratered terrain and smooth plains (2, 3). The data discussed here were acquired at low altitudes ( $< 2000$  km) during the first Mercury sidereal day ( $\sim 59$  Earth days) of orbital operations (4). To improve the statistical significance of the results, the low-altitude data were summed to create a single data set covering the measured region. The resulting GRS measurements of surface elemental abundances therefore should be regarded as representative values for this region.

Count rates of gamma rays emanating from the surface are obtained by fitting the peaks of interest in the gamma-ray energy spectra (Fig. 1) for the summed low-altitude measurements and correcting for the background gamma-ray count rates derived from a summed high-altitude ( $> 14,000$  km) data set. These count rates have been compared, for each spectral peak, to count rates in the detector derived from calculated surface gamma-ray fluxes to determine the elemental abundance required to account for the measured signal (4). The average surface abundances of radioactive elements on the surface of Mercury north of  $\sim 20^\circ$ S are  $1150 \pm 220$  parts per million (ppm) K,  $220 \pm 60$  parts per billion (ppb) Th, and  $90 \pm 20$  ppb U. The quoted errors represent the 1-SD statistical uncertainties of the measurements, as well as the systematic uncertainties introduced during the conversion of measured count rates to surface elemental abundances.

Ratios of the moderately volatile incompatible element K to the refractory incompatible elements Th and U provide insights into the volatile inventory of planetary bodies. In contrast, the absolute abundances of these elements can vary appreciably over a planetary surface as a result of variations in melt generation and crustal emplacement and modification processes. Mercury's K/Th ratio is  $5200 \pm 1800$ , a value comparable to those for the other terrestrial planets, which range from 2000 to 7000 (5, 6). By contrast, the lunar K/Th value (360) is an order of magnitude lower (7), indicative of the depletion of lunar volatiles relative to those of Earth. Mercury's K/Th ratio indicates that the planet's volatile budget relative to refractory elements is similar to that of the other terrestrial planets.

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This finding is supported by the high abundance of S measured by MESSENGER's X-Ray Spectrometer (8).

The K/Th ratio for Mercury, which can be regarded as a representative value for the mea-

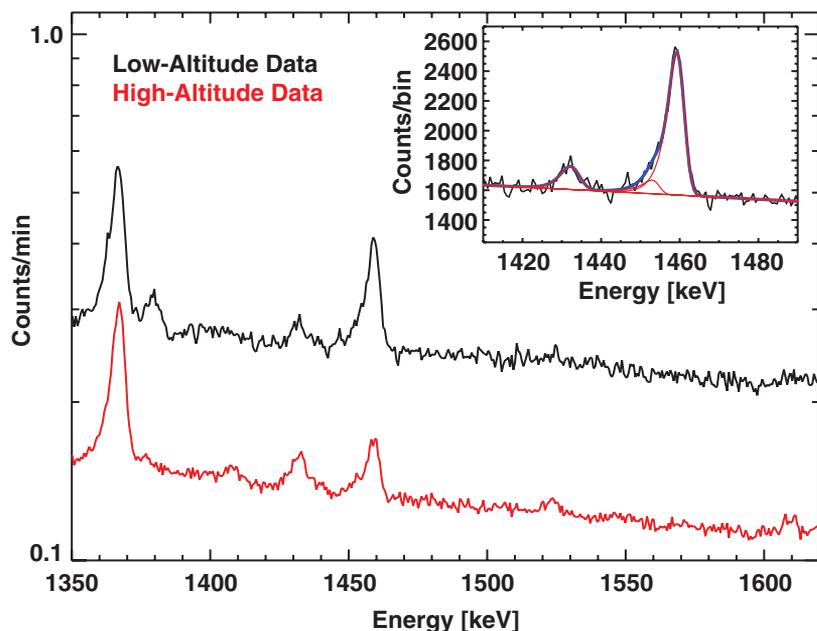
sured region, is most similar to that of Mars, where 95% of measured surface K/Th values are between 4000 and 7000 (Fig. 2) (6). The absolute abundances of K and Th for Mercury are in the range measured for martian meteor-

ites, whose values are a factor of 3 to 4 lower than for the martian surface. This difference reflects the origin of the meteorites from mantle material depleted in incompatible elements, consistent with the conclusion that the higher values on the surface are at least partially the result of igneous processes (9). The lower concentrations of K and Th on the surface of Mercury relative to Mars suggest differences in the magmatic and crustal evolution of the two planets.

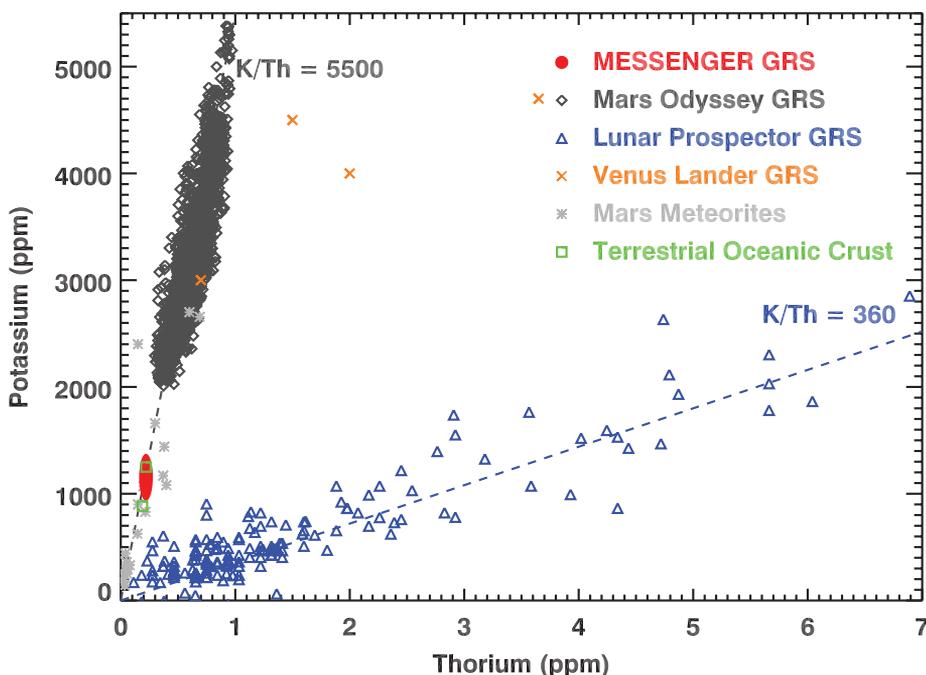
A number of physical and chemical models have been proposed for the formation and early evolution of Mercury, each of which predicts a different present-day bulk silicate composition for the planet (10). Hypotheses proposed to explain the unusually high metal-to-silicate ratio of Mercury (11) also carry predictions for the ratios of volatile to refractory elements that can be tested against the K, Th, and U abundances measured by MESSENGER. Evaporation models (12) invoke preferential vaporization of much of Mercury's outer silicate shell in a high-temperature (2500 to 3500 K) solar nebula. This process would have left the crust and upper mantle strongly depleted in volatiles, with marked depletions in K. Uranium would also be depleted, owing to formation of the volatile  $\text{UO}_3$  (13), resulting in a highly fractionated Th/U ratio of  $\sim 1000$  (10). The observed K abundance and Th/U ratio of  $2.5 \pm 0.9$  do not support such a high-temperature process. Likewise, the measured K abundance is inconsistent with the giant impact hypothesis, in which one or more impacts removed Mercury's early crust and upper mantle to yield a planet with a high metal-to-silicate ratio (14). Recent simulations suggest that the collisions necessary to prevent reaccretion of ejected material would have subjected the entire planet to high temperatures and would have led to substantial loss of volatiles (15).

In contrast to models that invoke heating of Mercury after formation, other proposed models suggest formation directly from high-temperature nebular condensates [e.g., (16)]. Such models predict a composition of metallic Fe and Fe-free silicates, consistent within uncertainties with observations (17, 18), and chondritic relative abundances of Th and U ( $\sim 0.300$  and  $\sim 0.080$  ppm, respectively) (10), similar to the measured GRS abundances. However, such models also predict a volatile-depleted bulk silicate planet with minimal K and S (8), contrary to measured K and S (8) abundances.

The indication of modest Fe concentrations in silicates on the surface of Mercury (17, 18) led to models in which refractory and volatile condensates mixed during accretion (19). As the innermost planet, Mercury would have incorporated material that on average formed closer to the Sun and was more enriched in refractory materials than the other terrestrial planets. These models predict bulk silicate compositions with chondritic Th/U and subchondritic K/Th ratios (10), although the precise compositions

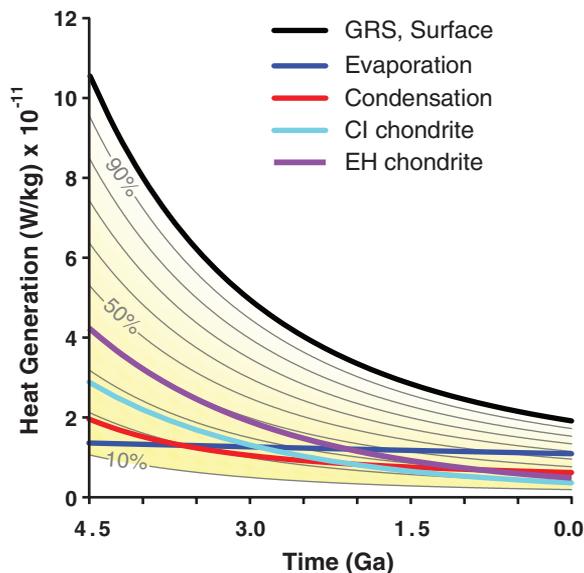


**Fig. 1.** A comparison of the high- and low-altitude summed gamma-ray spectra in the region of the 1461-keV K gamma-ray peak. (Inset) The fit to the low-altitude data; the 1434-, 1454-, and 1461-keV peaks are included in the fit.



**Fig. 2.** A comparison of K versus Th abundances for Mercury (the 1-SD ellipse is indicated in red) with those for Mars ( $\sim 500$  km spatial resolution) as measured by the Mars Odyssey Gamma-Ray Spectrometer (6, 9) and martian meteorites [e.g., (5)], the Moon ( $\sim 500$  km spatial resolution) as measured by the Lunar Prospector Gamma-Ray Spectrometer (7), Venus as measured by gamma-ray spectrometers on Soviet Venus landers, and terrestrial oceanic crust (5).

**Fig. 3.** Heat generation per unit mass in the bulk silicate fraction of Mercury over the past 4.5 billion years. The solid black line corresponds to a composition identical to that of the uppermost crust of Mercury's northern hemisphere as measured by GRS. Yellow shading indicates the range of heat generation in the bulk silicate portion of the planet if K, Th, and U fractionated fully into the magma during partial melting for melt fractions variously equal to 10 to 100% at 10% intervals (gray contours). Predictions from the evaporation (0 K, 400 ppb Th, 0 U) and condensation (0 K, 120 ppb Th, 30 ppb U) models are included, as well as formation from CI chondrite (550 ppm K, 29 ppb Th, 8 ppb U) and EH chondrite (840 ppm K, 30 ppb Th, 9 ppb U) material (12).



depend on the end-members assumed, and magmas derived from partial melting of material of bulk composition have somewhat higher K/Th ratios. A variant on the refractory-volatile mixing models is the formation of Mercury from chondritic materials, particularly those with high metal-to-silicate ratios, such as the CB chondrites. Models of the present-day bulk silicate composition of Mercury resulting from accretion of metal-rich chondrites [e.g., (20)] predict Th/U and K/Th ratios of  $\sim 3.5$  and  $\sim 4300$  (10), respectively, similar to the GRS Th/U value of  $2.5 \pm 0.9$  and consistent with the K/Th value of  $5200 \pm 1800$ . Given the relative incompatibility of K, U, and Th, surface compositions derived from melting of the bulk interior are likely to have comparable ratios. Thus, the composition of Mercury might be best represented by a chondritic composition with a substantially greater inventory of volatiles than previously postulated.

Measurements of K, Th, and U on the surface of Mercury provide constraints on the planet's interior history, because the radiogenic isotopes of these elements are the primary long-lived source of internal heat generation. Among the manifestations of Mercury's thermal evolution are its history of volcanism (8), its dynamo-generated magnetic field (21, 22), and the history of global cooling as recorded in surface tectonic features (23). GRS measurements indicate that heat production at 4 billion years ago was about four times larger than at present. The substantial decline in heat production (Fig. 3) with time is consistent with evidence for the widespread emplacement of volcanic smooth plains deposits near or shortly after the end of late heavy bombardment and only limited, isolated centers of volcanism since that era (3).

The inference that Mercury's internal magnetic field arises from a dynamo in the plan-

et's liquid outer core [e.g., (22, 24)] requires that there be a mechanism within the core to drive the convective motions needed to convert rotational energy to magnetic energy. One suggestion has been that U may have fractionated into the core if accretion and planet-wide differentiation occurred under highly reducing conditions (23) and that heat from the decay of U could have driven core convection. However, Mercury's Th/U ratio of  $2.5 \pm 0.9$ , similar to or slightly less than that of chondritic meteorites, is inconsistent with such a proposal.

Widespread contractional tectonic features on Mercury's surface accommodated an average surface strain equivalent to a 1- to 2-km reduction in the planet's radius over the past 4 billion years (Gy) (25). Most models for Mercury's internal thermal history predict greater contraction over that time interval (26). The evaporation model for Mercury's formation, because of its prediction that the bulk silicate portion of the planet lost most of its K and U, provided a possible explanation for the limited contraction given that internal heat production dominated by Th would have declined by only 22% over 4 Gy (Fig. 3). The measured K/Th and Th/U ratios, however, are inconsistent with this model. To further relate GRS measurements to Mercury's history of cooling and contraction, it is necessary to understand the degree to which K, Th, and U in the bulk silicate portion of the planet are concentrated in the crust. Because those elements partition into the melt during silicate partial melting, the crustal enrichment depends strongly on the typical melt fractions in the source regions of magmas on Mercury (Fig. 3). The Mg/Si, Al/Si, and Ca/Si ratios of Mercury's surface materials (8) are consistent with compositions similar to those of terrestrial volcanic rocks derived from high degrees ( $\sim 20$  to 30% or more) of partial melting (27), implying

that substantial heat production was retained in Mercury's mantle and may have served to slow global cooling and contraction.

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