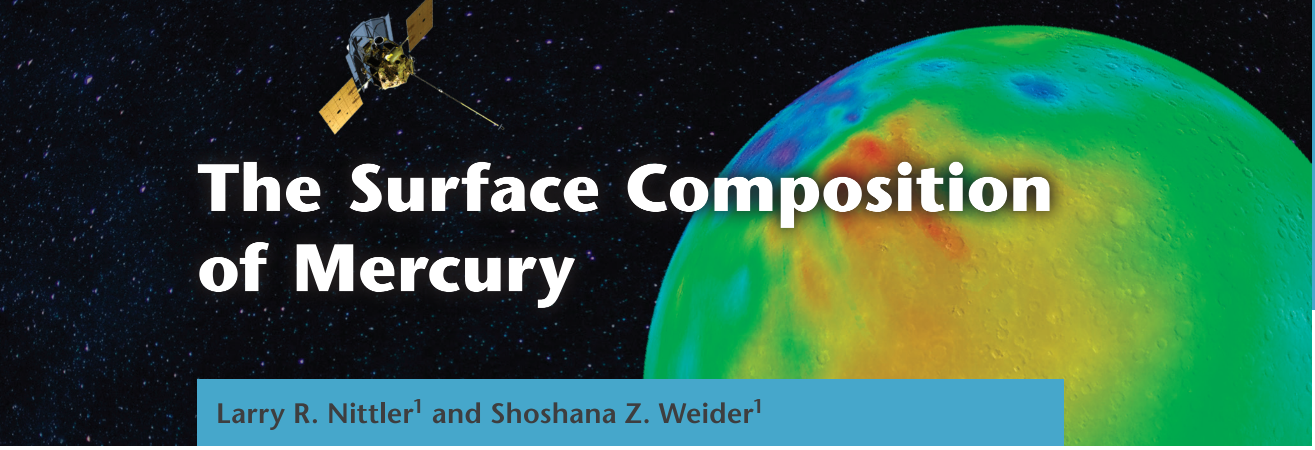

# The Surface Composition of Mercury

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**Geochemical data from *MESSENGER* have revealed details of Mercury's surface composition, showing that it differs from the other rocky planets in the inner solar system. For example, the planet's surface is enriched in S and C, and depleted in Fe, indicating that Mercury formed under much more reducing conditions than other planets. The surface is also enriched in Mg and depleted in Al and Ca. Observed elemental heterogeneities and percent levels of graphite suggest that Mercury underwent a magma ocean phase early in its history. These findings have important implications for understanding Mercury's origin and evolution.**

Keywords: Mercury, *MESSENGER*, geochemistry, remote sensing, surface composition, spectroscopy

## INTRODUCTION

Planets are born in disks of gas and dust as they circle and accrete around young stars. The bulk compositions of newly forming planets are shaped by several processes at a wide range of scales, from high-temperature dust condensation to large-scale collisions. Bulk composition is also a primary factor in determining the internal structure and geological history of a planet. As rocky planets differentiate, a dense core separates and is surrounded by silicate shells. The silicate surface forms and is subsequently modified by geological processes (e.g., volcanism and tectonics) and by impacts with other bodies. Therefore, determining the elemental composition of a rocky world can reveal crucial information about planetary formation and evolution.

As the innermost planet of our solar system, Mercury and its composition are of key importance for understanding its own origin and that of rocky worlds in general—both in our solar system and in the ever-increasing number of known extrasolar planetary systems. Prior to NASA's *MESSENGER* mission, however, little was known about the composition of Mercury. Mercury's anomalously high density indicated that its dense core, which is almost certainly dominated by Fe, makes up a much larger fraction of the planet's mass than the cores of the other terrestrial planets (i.e., Venus, Earth, and Mars) and the Moon. In contrast, measurements of reflected sunlight from Mercury's surface show that the silicates therein contain much less Fe than those at the surface of the other terrestrial bodies of the solar system. Measurements of Na, Ca, and K within Mercury's very tenuous atmosphere (its "exosphere") suggest that these elements are also present on the planet's surface.

Obtaining an improved understanding of Mercury's chemical composition was critical to addressing several of *MESSENGER*'s guiding scientific questions. The spacecraft was developed to carry multiple instruments that could be used to determine the planet's constituents. Here, we review these instruments, the scientific information they provided from the four years of *MESSENGER*'s orbital mission, and the new constraints on Mercury's surface composition. We also briefly outline how this knowledge of Mercury's surface composition can be used to study the bulk composition, origin, and geological evolution of this enigmatic innermost planet. For more details on these topics, we refer the reader to other articles in this issue and to the recent review by Nittler et al. (2018).

## MEASURING COMPOSITION FROM SPACE

The *MESSENGER* Gamma-Ray and Neutron Spectrometer (GRNS) detected high-energy photons (γ-rays) and neutrons that emanated from the planet's surface (Peplowski et al. 2012; Lawrence et al. 2013). As illustrated in Figure 1, γ-rays with characteristic energies are emitted during the decay of naturally occurring radioactive nuclei, including isotopes of K, U, and Th. Interactions between galactic cosmic rays (high-energy charged particles hurtling through space) and atomic nuclei in surface rocks release neutrons that, in turn, can interact with other nuclei to also produce characteristic γ-rays. By detecting and determining the energy of the γ-rays and neutrons, the GRNS sensors provided measurements of many important elements, including H, C, Na, Al, Si, S, Cl, K, Ca, Fe, Th, and U. The low signal-to-background ratios for both the γ-ray and neutron data, however, meant that it was only possible to obtain compositional measurements for Mercury's northern hemisphere, because *MESSENGER*'s highly eccentric polar orbit brought the spacecraft close to the planet over high northern latitudes.

The *MESSENGER* X-Ray Spectrometer (XRS) measured X-rays of characteristic energy that were emitted from Mercury's surface when surface atoms were irradiated by X-rays from the Sun's multimillion-degree coronal plasma (Nittler et al. 2011) (Fig. 1). This planetary, remote-sensing X-ray fluorescence method is analogous to the standard X-ray fluorescence laboratory technique, but the remote-sensing version involves a rapidly changing source (the Sun), nonconstant viewing geometry, low signal-to-noise ratios, and a lack of measurement standards. Nonetheless, as shown below, quantitative global mapping of several

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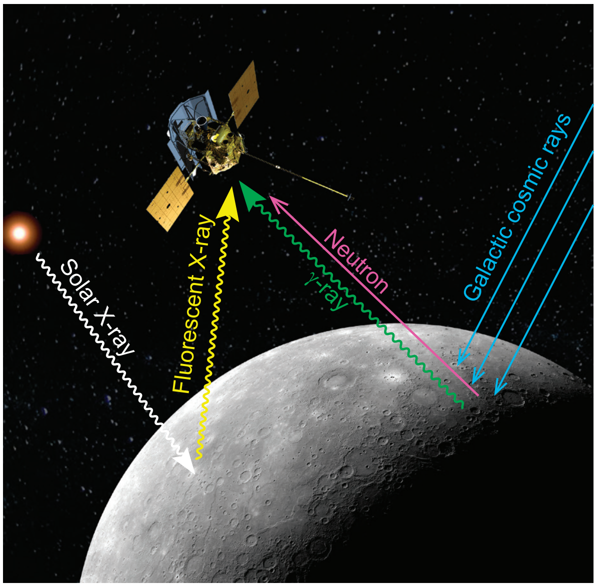


**FIGURE 1** *MESSENGER*'s X-Ray Spectrometer (XRS) and Gamma-Ray and Neutron Spectrometer (GRNS) instruments were used to obtain quantitative abundance estimates for several geochemically important elements in Mercury's surface. The XRS was used to measure fluorescent X-rays from the planet (yellow arrow) that were induced by interactions between irradiating solar X-rays (white arrow) and atoms at Mercury's surface. The GRNS detected γ-rays (green arrow) and neutrons (purple arrow) produced by either radioactive decay or interactions between galactic cosmic rays (blue arrows) and atomic nuclei. IMAGE CREDIT: NASA/JOHNS HOPKINS UNIVERSITY APPLIED PHYSICS LABORATORY/CARNEGIE INSTITUTION OF WASHINGTON

important rock-forming elements—including Mg, Al, Si, S, Ca and Fe—was achieved with the *MESSENGER* XRS. To detect elements heavier than Si, however, infrequent solar flares were required. The XRS maps of S, Ca, and Fe, therefore, do not have total global coverage. Unlike the GRNS, the XRS collected useful data in the southern hemisphere, albeit with much poorer spatial resolution than for the north (again because of the spacecraft's eccentric orbit).

In general (with the exception of elements measured directly from their radioactive decay), it is more difficult to calculate absolute elemental abundances from the *MESSENGER* GRNS and XRS data than to measure elemental (mass) ratios. Such ratios, therefore, are more often reported, and the *MESSENGER* results are normally provided as ratios of elements to Si. Silicon is a good choice because it is abundant, measured by both techniques, and it typically exhibits little heterogeneity on planetary surfaces. We also note that the XRS and GRNS probe to different depths in the surface (tens of µm versus tens of cm, respectively). The data analysis methods for both instruments also rely somewhat on modeling and uncertain inputs (e.g., atomic and/or nuclear physics data). As such, it is encouraging that the results from both instruments are generally consistent for those elements measured in common (Al, Si, S, Ca, and Fe).

## MERCURY'S SURFACE COMPOSITION

### *Volatile Elements on Mercury*

The wide range of temperatures experienced by planetary materials during their formation and evolution can lead to the fractionation of elements that are more volatile from those that are less so (those that are refractory). The volatile content of a planet can, thus, be an indication of formation conditions. For example, the Moon has a substantially lower volatile abundance than the Earth, which is taken as evidence for high-temperature lunar formation in a circumplanetary disk following a giant collision of a Mars-size impactor with the proto-Earth. Similarly, many pre-*MESSENGER* models of Mercury's formation predicted that the planet, or its building blocks, experienced very high temperatures and would be severely depleted in moderately volatile elements. Such elements (e.g., S, K, Na) are those that condense from the gas phase at temperatures between a few hundred and about one thousand Kelvin. The discovery of several moderately volatile elements at relatively high concentrations in Mercury's surface was, therefore, one of the biggest surprises from *MESSENGER*'s geochemical results.

Early in *MESSENGER*'s orbital mission, detections of γ-rays from the radioactive decay of $^{40}K$, $^{232}Th$, and $^{238}U$ were used to determine that Mercury's surface has, by weight, an average of ~1,300 ppm K, ~0.16 ppm Th, and ~90 ppb U (Peplowski et al. 2012; Nittler et al. 2018). These elements are particularly useful for elucidating Mercury's early conditions because they have different volatilities, but similar compatibilities, during silicate melting. Their relative abundances at the surface of a differentiated planet should, therefore, reflect that of its bulk silicate portion. Indeed, the ratio of moderately volatile K to refractory Th is commonly taken to be a sensitive tracer of bulk volatile contents. The *MESSENGER* results indicate that Mercury's relatively high volatile content is similar to that of Mars, although all rocky planets are somewhat depleted in moderately volatile elements compared with the Sun (FIG. 2). This interpretation of the K/Th ratio is complicated by the possibility of element fractionation during core formation (McCubbin et al. 2012), but the *MESSENGER* measurements provide additional evidence of Mercury's volatile enrichment. For example, GRNS data (Peplowski et al. 2014; Evans et al. 2015) revealed that both volatile Na and Cl are also abundant on Mercury's surface. Results for both elements show latitudinal variation: Na ranges from 2.6 wt% at the equator to ~5 wt% at high northern latitudes, whereas Cl varies from 1,200 ppm at the equator to 2,500 ppm at high northern latitudes. As with K/Th, Mercury's Cl/K ratio is similar to that of Mars (and to that of the Sun) (FIG. 2), which is strong evidence for Mercury's volatile enrichment.

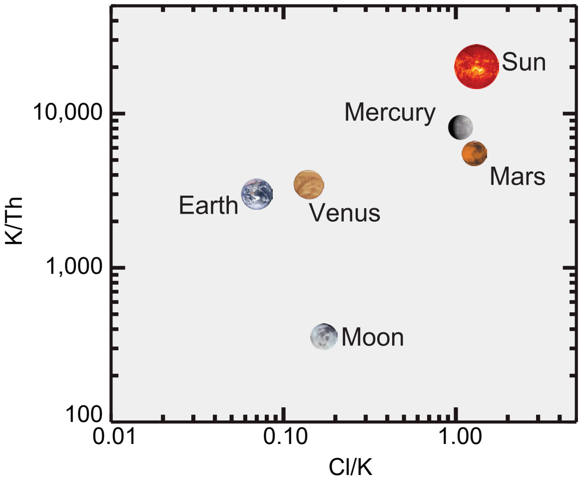


**FIGURE 2** The K/Th weight ratio of Mercury's surface as a function of its Cl/K weight ratio, as determined from *MESSENGER* Gamma-Ray and Neutron Spectrometer data (Peplowski et al. 2012; Evans et al. 2015). The Mercury results are shown in comparison with those of other inner solar system rocky bodies (Venus, Earth, the Moon, Mars) and the Sun.

In addition to the variations in Na and Cl abundance, the GRNS measurements revealed heterogeneities in the abundance of K across Mercury's northern hemisphere (Peplowski et al. 2012). It was hypothesized that thermal redistribution (via diffusion) of these elements could be responsible for these observations. That is, these moderately volatile elements could be transported from Mercury's hottest regions (reaching up to 700 K) to colder areas (e.g., the poles, with maximum temperatures <300 K) over geological timescales. Variations in the abundance of nonvolatile major elements (e.g., Mg) (Weider et al. 2015), however, correlate with those of the more volatile elements. Thermal effects, therefore, are unlikely to have been a major cause of the observed geochemical variations, albeit with one important exception. A marked decrease in the measured neutron flux at high northern latitudes is indicative of an increase in the abundance of H (Lawrence et al. 2013). Together with other lines of evidence, these GRNS data have been used to infer the presence of substantial water-ice deposits within permanently shadowed polar impact craters (Chabot et al. 2018). These ice deposits most likely formed via gradual redistribution of water molecules to the cold traps in the craters. It is likely that the water was delivered via comet and/or volatile-rich asteroid impacts.

Another surprise from the early *MESSENGER* orbital observations was the discovery of S (a moderately volatile element) at weight percent concentrations in Mercury's surface (Nittler et al. 2011; Evans et al. 2012). Mercury's surface has an average of ~4 wt% S, which is an order of magnitude greater than Earth's typical crust (<0.1 wt% S). The high S abundance is additional evidence of Mercury's high volatile content, but, more importantly, it has implications for understanding the planet's redox conditions (discussed in more detail below).

## Nonvolatile Major Elements on Mercury

The *MESSENGER* XRS and GRNS data show that Mercury's major-element surface composition is markedly different from that of the Earth and Moon (Nittler et al. 2011, 2018). In addition to its unusually high S abundance, Mercury has, on average, higher Mg/Si and lower Al/Si and Ca/Si ratios compared with typical terrestrial and lunar crustal rocks (Fig. 3). Mercury's average surface Fe abundance is 1–2 wt% (Evans et al. 2012; Weider et al. 2014), which is lower than the average for Earth's crust (4–8 wt%). Reflectance spectroscopy results constrain the amount of oxidized Fe (FeO) on Mercury's surface to <1 wt% (Murchie et al. 2015). Mercury's surface Fe must, therefore, be present in a reduced form (as a metal and/or sulfide).

The relatively high Mg/Si ratio, as well as the low Al/Si and Fe/Si ratios, are evidence that Mercury's crust did not form as a lunar-like flotation crust dominated by plagioclase. There is a strong correlation between the Ca/Si and S/Si ratios measured by the XRS across the planet (Fig. 3B). This was originally interpreted as evidence for Ca-bearing sulfides (Nittler et al. 2011), but may just reflect mixing of compositional end-members. In fact, the only measurement that lies significantly away from the correlation trend is that of a large, bright pyroclastic deposit northeast of the Rachmaninoff impact basin (Weider et al. 2016). It is thought that the oxidation of sulfide species (via reaction with oxides in the magma or assimilated materials) during the ascent of magma in this pyroclastic eruption created S-bearing volatile species. The loss of these species could account for the anomalous Ca/S trend for the region (see Thomas and Rothery 2019 this issue).

The earliest *MESSENGER* orbital geochemical data indicated substantial heterogeneity on Mercury (Nittler et al. 2011; Peplowski et al. 2012), and four years of orbital data allowed elemental variations to be investigated in greater detail. In particular, maps of elemental ratios (e.g., Fig. 3A) and of neutron emission fluxes revealed the presence of "geochemical terranes," i.e., regions with compositions distinct from their surroundings (McCoy et al. 2018; Nittler et al. 2018). In some, but not all, cases, these terranes align with well-defined geological boundaries. There is no consensus on the exact definition or number of such terranes, but perhaps the most distinctive is the "high-Mg region," a large area in Mercury's western hemisphere that exhibits the highest Mg/Si, S/Si, Ca/Si, and Fe/Si ratios, and the lowest Al/Si ratios on the planet (Fig. 3A). At another compositional extreme, the interior volcanic plains of Mercury's largest confirmed impact feature, the Caloris basin, have a composition that is relatively rich in Al and poor in Mg, S, K, and

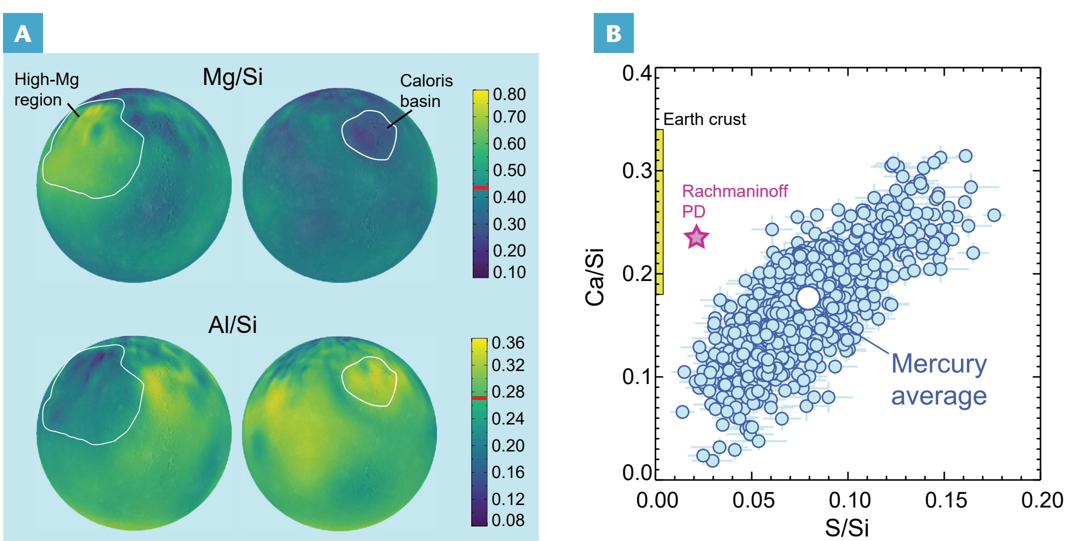


**Figure 3** (**A**) Maps of Mg/Si (upper) and Al/Si (lower) weight ratios across Mercury's surface in an orthographic projection, centered on –40°E (left) and 140°E (right) longitudes. The element-ratio maps are overlain on a base-map created from *MESSENGER* imagery. Red horizontal lines marked on the ratio scales indicate global averages. For comparison, Earth's crust has average Mg/Si and Al/Si ratios of ~0.08 and ~0.3, respectively. (**B**) Graph of Ca/Si as a function of S/Si for ~1,400 *MESSENGER* X-Ray Spectrometer measurements (blue circles). The yellow box indicates the range of these element ratios in Earth's crust and the purple star indicates the composition of a large pyroclastic deposit (PD on figure) near the Rachmaninoff basin. Data after Weider et al. (2016).

Fe. The large expanse of volcanic smooth plains at high northern latitudes is enriched in K, relative to Caloris, but exhibits at least two compositional terranes, one with very low Mg and Al abundances, and another with more intermediate composition and distinctive neutron flux.

On the basis of its extremely high Mg content, it was postulated that the high-Mg region could be the degraded remains of a very large impact basin that contains exposed mantle material (Weider et al. 2015). Subsequent studies, however, have shown that this interpretation is highly unlikely (Namur and Charlier 2017). It is more probable that the compositions of the high-Mg region and the other geochemical terranes primarily reflect variations in the degree of melting from chemically heterogeneous source regions in the mantle (discussed more below) and subsequent impact modification (Namur and Charlier 2017; McCoy et al. 2018).

### *Carbon on Mercury*

*MESSENGER*'s spectral reflectance measurements show that Mercury's surface is substantially darker than that of the Moon. The low surface abundances of Fe and Ti on Mercury, however, rule out ilmenite ($FeTiO_3$), which is the Moon's primary darkening phase, as a major component and the reason for the planet's low reflectance. Instead, modeling of Mercury's reflectance spectra has shown that a few weight percent C, in the form of fine-grained graphite, could be responsible for darkening the planet's surface (Murchie et al. 2015). Moreover, analysis of GRNS γ-ray data provided an average upper limit of ~4 wt% C for Mercury's surface (Peplowski et al. 2015), which is consistent with the reflectance modeling. Such an abundance is substantially higher than for other terrestrial bodies. For example, C makes up less than 0.2 wt% of Earth's crust.

In addition to the γ-ray data, *MESSENGER* neutron measurements were an invaluable part of identifying C as a major darkening phase on Mercury's surface. Carbon is a poor absorber of low-energy (<1 electron volt) neutrons, so variations in C abundance can lead to variations in the flux of these neutrons from the planet's surface. The darkest material on Mercury is known as "low-reflectance material." This material is heterogeneously distributed and thought to be excavated from depth in the crust by impact processes (Denevi et al. 2009). Towards the end of the *MESSENGER* mission, the spacecraft altitude was low enough for spatially resolved low-energy neutron measurements to be performed with the GRNS instrument. Measurements from three low-reflectance-material-enriched (to varying degrees) areas clearly indicated an increase in neutron flux compared with the immediate surroundings (Peplowski et al. 2016). These results were best explained by an enhanced C abundance (Fig. 4) in the low-reflectance material regions. The combined spectral, γ-ray, and neutron results provide convincing evidence that weight percent levels of C are present on Mercury, likely in the form of graphite. In addition, the most C-rich material appears to be endogenic and to have been exposed at the surface via impact excavation.

## IMPLICATIONS OF MERCURY'S SURFACE COMPOSITION

It was recognized early in *MESSENGER*'s orbital mission that the high S and low Fe contents of Mercury's surface are indicators of Mercury's formation under much more chemically reducing conditions than the other terrestrial planets (Nittler et al. 2011). Experimental work has shown that as the availability of O decreases in a planetary environment, less Fe and more S are partitioned into silicate melts (e.g., Namur et al. 2016a). Mercury's *MESSENGER*-derived surface composition (and, by extension, its mantle composition) is, therefore, evidence of formation from highly reduced starting materials, such as the asteroidal parent bodies of enstatite chondrite meteorites. Estimates of the O fugacity (the amount of O available to participate in chemical reactions) of Mercury's interior range from three to seven orders of magnitude below the iron–wüstite buffer, where the reaction $Fe + ½O_2 \rightarrow FeO$ obtains equilibrium (Zolotov et al. 2013; Namur et al. 2016a). These estimates are based on S-partitioning experiments (as a function of redox conditions). For comparison, the O fugacity of Earth's upper mantle is at least 100 times higher than the iron–wüstite buffer. In addition to Mercury's unusually large core, the planet also seems to have formed under much more reducing conditions than the other terrestrial

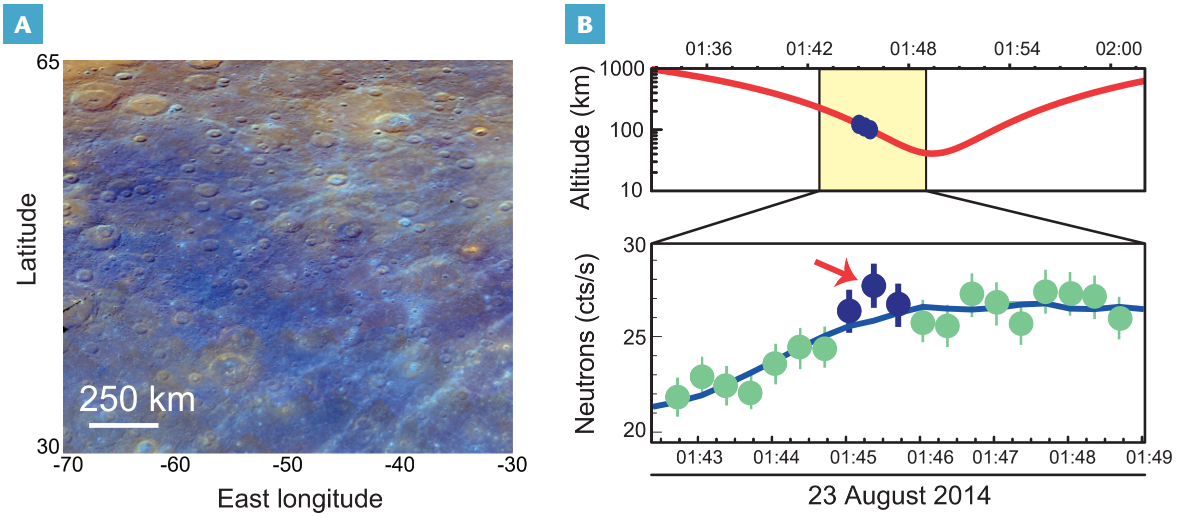


**Figure 4** (**A**) A region of Mercury enriched in low-reflectance material (dark blue in this enhanced-color representation, which is based on a mathematical treatment of *MESSENGER* color imagery). (**B**) Spacecraft altitude and low-energy neutron count rate for a portion of a *MESSENGER* orbit on 23 August 2014. The blue symbols indicate when the spacecraft was above the low-reflectance material area shown in 4A. The neutron counts (in counts per second) are higher for the low-reflectance material than expected from the average trend (blue curve) of values measured outside the low-reflectance material (green symbols) for the orbit. This indicates an enhanced abundance of carbon. Figures modified from Peplowski et al. (2016).

planets. Many of the geologic implications of this reduced chemistry are explored further by Cartier and Wood (2019 this issue).

The *MESSENGER* surface composition results have stimulated several recent experimental and/or theoretical studies aimed at determining the mineral assemblages that could be present on Mercury's surface, and better understanding the composition and geological evolution of the planet's thin silicate mantle (e.g., Stockstill-Cahill et al. 2012; Namur et al. 2016b; McCubbin et al. 2017; Namur and Charlier 2017; Vander Kaaden et al. 2017; McCoy et al. 2018). The results of these studies show that Mercury's surface is mainly dominated by FeO-poor pyroxene (enstatite) and olivine (forsterite), Na-rich plagioclase, and Mg–Ca–Fe-sulfide assemblages, with varying amounts of these minerals accounting for the variation among the planet's geochemical terranes. Although early results suggested similarities with terrestrial komatiites (Nittler et al. 2011), more recent work suggests that Mercury's surface rocks are better characterized as norites or boninites (e.g., Vander Kaaden et al. 2017). The elemental heterogeneity observed on the surface likely reflects both a chemically heterogeneous (layered) mantle, as well as variable-degree partial melts that produced the surface plains lava flows. Consideration of both the inferred mantle melting temperatures and the surface ages for different geochemical terranes provides evidence for strong secular cooling of the mantle prior to 3.7 Ga (Namur et al. 2016b).

By using mineralogies that were derived from melting experiments on Mercury's end-member compositions, Nittler et al. (2018) back-calculated the original composition of the mantle sources for Mercury's surface lavas. The results show that Mercury's bulk silicate composition is consistent with that of enstatite chondrite meteorites (once a Si-rich metallic melt has been subtracted from them). This indicates that Mercury's original silicate building blocks fall within the observed range of known planetesimal compositions in the inner part of the Sun's protoplanetary disk. Although enstatite chondrites are often cited as the best meteoritic analogs for Earth's precursor materials, this argument is largely made on isotopic grounds. Indeed, Earth is substantially less reduced than enstatite chondrites or Mercury (Cartier and Wood 2019 this issue).

The chemical heterogeneity of Mercury's mantle—as evidenced by the geochemical terranes—can be explained if Mercury went through a "magma ocean" phase early in its history (i.e., when at least its silicate portion would have been largely molten). Fractional crystallization in the magma ocean, followed by sinking and/or floating of different mineral phases, and subsequent convective overturn, could have given rise to the large-scale chemical variations that are observed. Although a feldspar-rich crust floating on a lunar magma ocean is the accepted explanation for the highly Al-rich nature of the lunar highlands, Mercury's highly reduced composition means that the mineralogies of its magma ocean and flotation crust would have been different (Vander Kaaden and McCubbin 2015; Cartier and Wood 2019 this issue). Given the low Fe content of Mercury's silicate portion, it is unlikely that there was a sufficient density contrast between plagioclase and the FeO-poor magma for a plagioclase-rich (Al-rich) crust to form, which is consistent with the *MESSENGER* surface composition results. In fact, only one phase—graphite—is thought to have been stable in the reducing conditions of Mercury's magma ocean and have a sufficiently low density to float (Vander Kaaden and McCubbin 2015). The observations of high C abundances within Mercury's low-reflectance material could be a chemical signature of this "exotic" primordial graphite flotation crust (Vander Kaaden and McCubbin 2015; Cartier and Wood 2019 this issue; Charlier and Namur 2019 this issue).

Mercury's bulk composition is a parameter of extreme importance in understanding the origin of the planet, but accurate estimates of this depend on the highly uncertain composition of its large metallic core. Cartier and Wood (2019 this issue) point out that Mercury's highly reduced state makes it likely that the core contains significant amounts of Si. However, our lack of a detailed understanding of how Mercury formed, as well as limitations in present elemental partitioning data, mean that a wide range of compositions are possible (Namur et al. 2016a; Nittler et al. 2018). Geochemical considerations and planetary interior models (based on geophysical measurements of Mercury's gravity field) have also led to the suggestion that Mercury's large Fe–Si-rich core is surrounded by a thin layer of FeS. Figure 5 shows a range of possible bulk Fe/Si and Mg/Si ratios for Mercury. These values are based on assumptions regarding the amount of Si and S in the core, and the possible presence of an FeS layer at the base of the mantle (Nittler et al. 2019). Although the estimated bulk Fe/Si ratio varies by a factor of eight (depending on the assumed core composition), this graph clearly illustrates Mercury's strongly anomalous composition among the terrestrial planets—a fact that has been recognized since its high density was discovered.

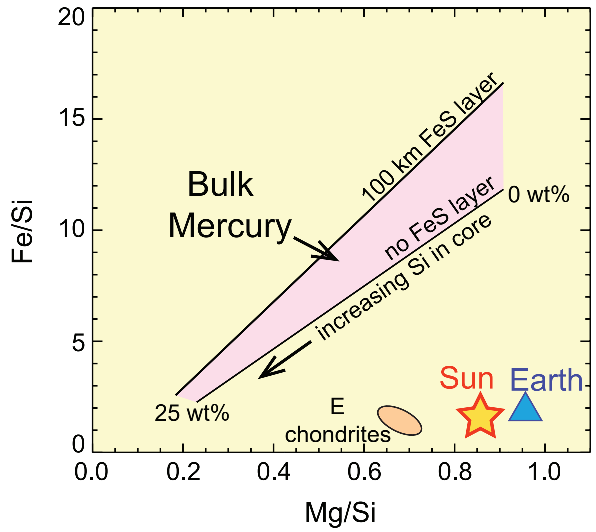


**Figure 5** The Fe/Si weight ratio as a function of Mg/Si ratio for the Sun, Earth, enstatite (E) chondrite meteorites, and Mercury bulk composition estimates. A wide range of bulk compositions for Mercury are possible, depending on how much Si is contained in the planet's metallic core and if there is an FeS layer at the base of the mantle. Modified from Nittler et al. (2018).

## OUTLOOK

The rich geochemical data sets returned by the *MESSENGER* spacecraft have revealed a volatile-enriched and highly chemically reduced planetary surface. After decades of data-poor speculation regarding Mercury's chemical nature, the most recent results from *MESSENGER* allow some prior models of Mercury's origin to be excluded (Ebel and Stewart 2018). The overall question of how Mercury obtained its anomalous, extremely metal-rich, composition, however, remains unanswered. The combined anomalous core size, volatile enrichment, and chemically reduced nature present a major challenge for modeling Mercury's formation and planetary accretion in the inner solar system. Looking forward to 2025, geochemical instruments onboard the European Space Agency/Japan Aerospace Exploration Agency *BepiColombo* mission will provide data that will build on the *MESSENGER* results and provide important new insights into the innermost planet's geochemical character, origin, and evolution. In particular, *BepiColombo* will allow high-resolution mapping of elemental abundances across Mercury's southern hemisphere, a region that has remained uncharacterized and/or unresolved in the *MESSENGER* data sets.

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