OXYGEN DEPLETION ON THE SURFACE OF MERCURY: EVIDENCE OF SILICON SMELTING?

F. M. McCubbin[1], K. E. Vander Kaaden[1], P. N. Peplowski[2], A. S. Bell[3], L. G. Evans[4], L. R. Nittler[5], J.W. Boyce[1], L. P. Keller[1], T. J. McCoy[6], [1]NASA Johnson Space Center, Mailcode XI2, 2101 NASA Parkway, Houston, TX 77058, USA. [2]The Johns Hopkins University Applied Physics Laboratory, Laurel, MD 20723, USA. [3]Institute of Meteoritics, Department of Earth & Planetary Sciences, University of New Mexico, Albuquerque, NM 87131, USA. [4]Computer Science Corporation, Lanham-Seabrook, MD 20706, USA. [5]Department of Terrestrial Magnetism, Carnegie Institution of Washington, DC 20015, USA. [6]Department of Mineral Sciences, National Museum of Natural History, 10th and Constitution Aves. NW, Smithsonian Institution, Washington, DC 20560, USA (francis.m.mccubbin@nasa.gov).

Introduction: The MErcury Surface, Space ENvironment, GEochemistry, and Ranging (MESSENGER) spacecraft collected data that provided important insights into the structure, chemical makeup, and compositional diversity of Mercury. The X-Ray Spectrometer (XRS) and Gamma-Ray Spectrometer (GRS) onboard MESSENGER provided the first detailed chemical analyses of Mercury's surface. Among the many discoveries included several surprising characteristics about the surface of Mercury, including elevated S abundances (up to 4 wt%), low Fe abundances (less than 4 wt%), and relatively low O abundances (O/Si ratio of 1.40±0.03) [1–3].

The surface chemistry as determined by MESSENGER has been used to identify up to nine distinct geochemical terranes on Mercury [4–5]. Numerous modeling and experimental efforts have been undertaken to infer the mineralogy and petrology of mercurian lavas and surface materials. However, all of these efforts have presumed valence states for each of the elements according to the following: Si^{4+}, Ti^{4+}, Al^{3+}, Cr^{2+}, Fe^{2+}, Mn^{2+}, Mg^{2+}, Ca^{2+}, Na^+, K^+, S^{2-}, Cl^-. Based on these valence assignments, cations are charged balanced with the anions O^{2-}, S^{2-}, and Cl^- and the compositions are recast in terms of oxides, sulfides, and chlorides. Based on these assumptions, the geochemical terranes that have been identified on Mercury yield O/Si wt. ratios ranging from 1.61 to 1.84, which is substantially higher than the preliminary O/Si ratio of 1.40±0.03 determined by the MESSENGER GRS [2]. We have re-evaluated the O/Si ratio using the entire MESSENGER dataset to reassess its implications for the geochemistry of Mercury.

Results: The analysis of the O/Si ratio determined here leverages the methodology of [2] as well as the independent analysis techniques of [6]. We have also revised our analysis of the 6129-keV O gamma-ray peak to exclude contributions from the neighboring 6111-keV Cl gamma ray [7], which was not taken into account by [2]. Our revised, northern-hemisphere-average O/Si abundance for Mercury is 1.2±0.1. The error represents the one-standard-deviation statistical uncertainties in the measurement, as well as systematic uncertainties associated with various background cor-

rections. We investigated the possibility of spatially varying O/Si abundance ratios by binning GRS data acquired at high-northern latitudes (e.g. primarily northern volcanic plains material), mid-northern and equatorial latitudes (primarily intercrater plains), and specifically within the "high-Mg region" as defined by MESSENGER X-Ray Spectrometer data [4]. We observed no differences for either of these spatial regions at the one-standard-deviation level. These results confirm that the valence assignments of elements overestimate the surface abundance of O on Mercury by approximately 11.6–15.9 wt%. To make up for the O deficit, it requires that some of the elements measured by GRS and XRS are not bonded to O^{2-}, S^{2-}, or Cl^-, implying that these elements either comprise metallic phases, carbides, or (less likely) they are bonded to other anions like F^- or N^{3-}. Regardless, the O/Si value that has been measured on the surface of Mercury is either a primary (i.e. magmatic) or secondary (e.g., degassing or space weathering) feature, so we consider both possibilities.

Is the O/Si ratio primary or secondary? If the O/Si ratio is primary, we can use the geochemical behaviors of the elements in magmatic systems to determine which elemental valences have been improperly assigned. Fe and Ti are unlikely to play much of a role in making up for the O deficit due to their low abundances at Mercury's surface. In fact, Si is the only major rock-forming element measured on Mercury (Si, Mg, Al, Ca, Na) that is near the stability field of both its oxidized (SiO_2) and metallic (Si^0) forms (with respect to fO_2), so we have modeled the compositions of the lithologic portions of the nine geochemical regions assuming that there is a mixture of metallic Si and SiO_2 to make up for the calculated O deficit. The resulting compositions indicate 12.6–17.9 wt% metallic Fe-Si and 82.1–87.4% SiO_2-depleted, MgO-rich silicate melt compositions. In fact, some of the bulk silicate compositions of the nine geochemical terranes project into the periclase-forsterite region along an MgO-SiO_2 join. Consequently, the melting temperature required to produce such silicate compositions do not lend credence to the possibility of the O/Si depletion being a primary geochemical feature of mercurian lavas and surface

materials. For this reason, we do not favor a primary origin for the O/Si ratio of Mercury's surface.

What process has altered the O/Si ratio? By attributing the low O/Si ratio of Mercury's surface to a secondary process, we are limiting the process to one that either adds metal/carbides to the surface or one that causes the loss of oxygen from the surface. However, we will only consider O-loss processes. Of the processes that can cause the loss of O, we consider space weathering and magmatic degassing (from lavas or impact melts).

Space weathering can result in the reduction of FeO to Fe-metal. Although space weathering has been listed as one potential mechanism to explain the O/Si depletion on Mercury [8], there is insufficient Fe in the surface materials to make up the entire deficit of O and there is a paucity of evidence to support the formation of Si-, Mg-, Ca-, Al-, or Na-rich metallic phases among the many space weathering studies of planetary materials from airless bodies. Consequently, we will not consider space weathering further.

The next process we consider is loss of O from a silicate melt by degassing; however, under reducing conditions options are limited because the partial pressure of O_2 at mercurian fO_2 is exceedingly low and H_2O would be a very minor vapor species favoring H_2 [9–10]. Nevertheless, recent studies have provided evidence for abundant graphite in Mercury's crust [11–14], which can react with melt-species to form CO:

$$2C_{graphite} + SiO_{2melt} \longleftrightarrow 2CO_{gas} + Si^0_{metal} \qquad (1)$$
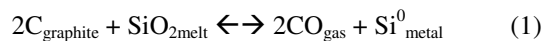
In a system with graphite and silicate melt, whether or not this reaction should proceed to the right depends on the partial pressure of CO. Figure 1 illustrates the pressure-dependence of CO on the fO_2 of the G-CO buffer relative to the Si-SiO$_2$ buffer as a function of temperature. Based on these calculations and liquidus temperatures for mercurian lavas of ~1320–1360 °C [15–17], confining pressures of more than 100 millibars of CO are needed to prevent the formation of Si metal in the presence of graphite. Given that the lavas are erupting essentially into a vacuum on the surface of Mercury, build-up of CO pressure as well as the amount of CO production would be a function of 1) degassing efficiency, which includes the kinetics of reaction (1) and the kinetics of bubble nucleation, and 2) the efficiency with which the degassed CO dissipates into the vacuum. Given that Mercury is still very dark (i.e., graphite is likely present) and still has enough O such that 55–75% of the Si is hosted by silicates, reaction (1) did not proceed to completion. However, as discussed above, conversion of SiO_2 to Si metal would increase the Mg/Si ratio of the silicate melt (Mg/Si ratio of the melt

increased by a factor of 1.5-2.2), which in turn, would increase the temperature of the solidus, resulting in crystallization and possibly quenching of the lavas.
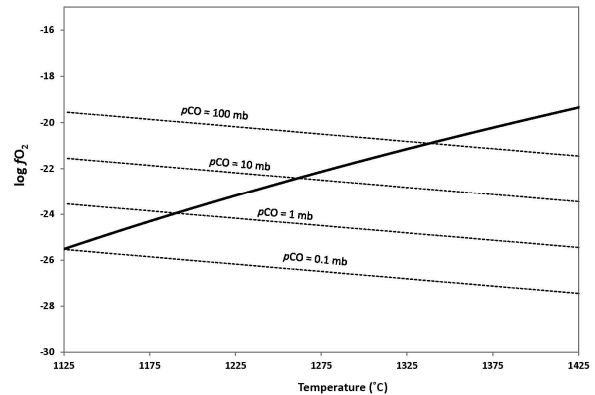

Figure 1. Plot of oxygen fugacity (fO_2) vs temperature (T). Dashed lines represent the fO_2 of the GCO buffer at specified partial pressures of CO. The solid black line represents the fO_2 of the Si-SiO$_2$ buffer. Thermodynamic data for the calculations obtained from JANAF tables [18]

Conclusion: The low O/Si ratio measured by GRS is likely the result of a secondary process, possibly related to magmatic degassing of CO in a process similar to industrial smelting. Although natural smelting processes have occurred on Earth (e.g., Disko Island, Greenland) and on asteroidal parent bodies (e.g., ureilite parent body), this process is unique on Mercury because, instead of Fe, it produced metals of typically lithophile elements like Si. This process is the natural consequence of magmatic processes on an airless body with graphite-bearing, low-FeO lavas. Mercury continues to demonstrate ways in which it represents a geochemical endmember in our solar system.

References: [1] Nittler et al. (2011) *Science* 333, 1847–1850. [2] Evans et al. (2012) *JGR-Planets* 117, E00L07. [3] Weider et al. (2014) *Icarus* **235**, 170–186. [4] Weider et al. (2015) *EPSL* 416, 109–120. [5] Vander Kaaden et al. (2017) *Icarus*, in press. [6] Peplowski et al. (2015) *MAPS* 50, 353–367. [7] Evans et al. (2015) *Icarus* 257, 417–427. [8] McCoy et al (in revision) in Mercury as Revealed by MESSENGER, editors S. Solomon, L. Nittler L., and B. Anderson, Cambridge University Press. [9] McCubbin et al. (2012) *GRL* 39, L09202. [10] Zolotov et al. (2013) *JGR-Planets* 118, 1–9. [11] Peplowski et al. (2015) *Planetary and Space Science* 108, 98–107. [12] Murchie et al (2015) Icarus 254, 287–305. [13] Vander Kaaden and McCubbin (2015) *JGR-Planets* 120, 1–15. [14] Peplowski et al. (2016) *Nature Geoscience* 9, 273–276. [15] Vander Kaaden and McCubbin (2016) *GCA* 173, 246–263. [16] Sehlke and Whittington (2016) *JGR-Planets* 120, 1924–1955. [17] Namur et al. (2016) *EPSL* 439, 117–128. [18] Chase (1998) J. Phys. Chem. Reference Data, Monograph 9.