**SULFUR-DEPLETED COMPOSITION OF MERCURY'S LARGEST PYROCLASTIC DEPOSIT: IMPLICATIONS FOR EXPLOSIVE VOLCANISM AND SURFACE REFLECTANCE ON THE INNERMOST PLANET.**

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**Introduction:** Multispectral reflectance data from Mercury's surface returned by the MErcury Surface, Space ENvironment, GEochemistry, and Ranging (MESSENGER) spacecraft during its three flybys and orbital mission have revealed 51 sites interpreted to be pyroclastic deposits (PDs) formed through explosive volcanism [1, 2]. These deposits have relatively high albedo, steep or "red" slopes of spectral reflectance versus wavelength, and diffuse borders that surround irregularly shaped rimless pits, thought to be the source vents. The presence of the PDs indicates that the source magmas had substantial volatile contents [1], although the specific volatile phases are unknown. From a spatially resolved, targeted X-Ray Spectrometer (XRS) measurement, we report the chemical composition of the largest PD on Mercury, located northeast of Rachmaninoff basin. We have determined that this deposit has a similar major-element composition to surrounding materials with the notable exception of sulfur, which is strongly depleted. This result suggests that S is a dominant volatile species driving explosive volcanism on the planet, and that sulfides may play a role in darkening much of Mercury's surface.

**NE Rachmaninoff Pyroclastic Deposit:** The NE Rachmaninoff PD, ~71 km in radius (Fig. 1), is centered at 36.0°N, 63.4°E, ~430 km to the northeast of the ~290 km-diameter Rachmaninoff basin [1, 3]. It is one of only five identified PDs that are not contained within a known impact crater. The central vent has an approximately elliptical shape, with a long axis of ~37 km, a short axis of ~22 km, and a depth of ~2.4 km [2], making it the largest identified PD source vent. The material that surrounds the NE Rachmaninoff vent, with reflectance among the highest on the planet, is diffusely distributed and mantles the underlying terrain, which indicates that it was emplaced as a more or less laterally continuous deposit of pyroclastic origin.

**XRS Data:** Although the XRS has now obtained near-global coverage in measurements of Mg, Al, and Si [4–6], coverage for S, Ca, and Fe is sparser because solar flares are required to produce measureable X-ray fluorescence (XRF) from these elements [5–7]. During MESSENGER's second extended mission, we have initiated targeted XRS observations whereby the spacecraft is rotated to keep the instrument's field of view centered on specific sites, for periods of up to tens of minutes. The goal of these measurements is to increase the chance of observing the sites during solar flares and hence obtain high-quality chemical data for regions of high scientific importance.

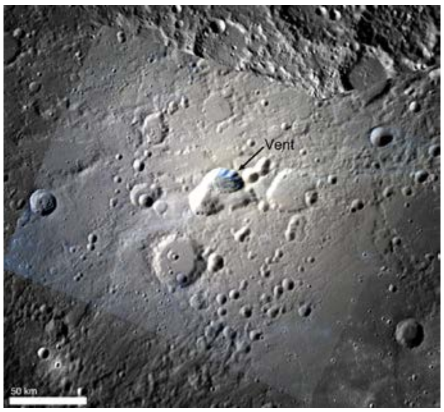

Figure 1. MESSENGER color image of NE Rachmaninoff PD, shown with 1000, 750, 430 nm in red, green, and blue, respectively, on a monochrome base map.

On 14 December 2013, a large solar flare occurred during a targeted XRS observation of the NE Rachmaninoff PD, from which a strong XRF signal was measured. Footprints of the four XRS spectral integrations with the highest XRF signals are outlined on a color image of Mercury in Fig. 2a. These XRS spectra were analyzed to obtain major-element ratios following our standard techniques [4, 5, 7]; results are shown in Table 1.

**Results and Discussion:** Global XRS measurements during MESSENGER's orbital mission have revealed that Mercury's crust is Mg- and S-rich and Fe-poor [4, 5, 7]. Smooth volcanic plains typically have lower Mg/Si, S/Si, and Ca/Si, but higher Al/Si, ratios than the older intercrater plains and heavily cratered terrain (IcP-HCT) [Table 1; 5]. Ca/Si and S/Si are strongly correlated in all XRS data, with an average global Ca/S ratio of ~2.5. The measured Mg/Si, Al/Si, and Ca/Si ratios of the NE Rachmaninoff PD are similar to those of nearby materials (*e.g.*, Fig. 2b) and are typical of values observed in the IcP-HCT [5]. The Fe/Si ratio of 0.062 is similar to the planet's mean value measured by XRS [7], although the latter is based primarily on data from the southern hemisphere. In strong contrast, the S/Si ratio of 0.02 (Fig. 2c) is among the lowest values observed anywhere on Mercury. The Ca/S ratio of 10.5 is much higher than the value determined from other XRS measurements.

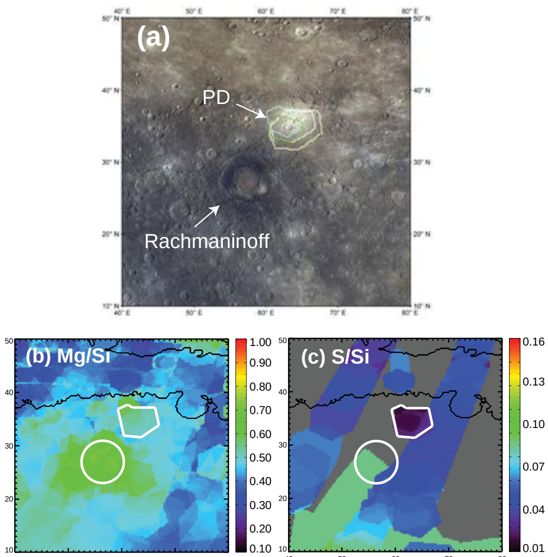


Figure 2. (a) Color image of Mercury for the region surrounding the NE Rachmaninoff impact basin and nearby PD. Polygons indicate outlines of footprints for XRS spectra used in chemical analysis of the PD. (b) Mg/Si and (c) S/Si maps of same region; white circle and polygon indicate Rachmaninoff basin and XRS measurement footprint of PD, respectively. Black lines indicate outlines of northern volcanic plains.

The low S/Si and high Ca/S ratios measured for the NE Rachmaninoff PD, coupled with the typical Mg/Si, Al/Si, Ca/Si and Fe/Si ratios, indicate that the bright materials that dominate the XRS footprint are depleted in S, relative to other locations on the planet. The most straightforward explanation for this anomaly is that the explosive volcanism that produced this deposit was largely driven by S volatilization and that the deposited materials experienced substantial degassing. If the source magma originally had a Ca/S ratio typical of Mercury crustal materials and a bulk Si abundance of ~25 wt%, the measured S/Si ratio corresponds to a loss of ~1.5 wt% of S from the deposited material. It has been estimated [1] that the radial extent of this PD would require an $S_2$ abundance of ~3.7 wt% in the magma, which is consistent with our result. Further work is needed to assess whether decompression of S-rich magmas on Mercury would be sufficient to produce this amount of volatilized S, or if oxidation of the magma by crustal materials would be required [8].

Immature surfaces on Mercury are measurably darker than those on the Moon [9], indicating the possible presence of a ubiquitous "darkening agent" to account for Mercury's low reflectance. Inhomogeneous distribution of this agent has also been invoked to explain reflectance differences across Mercury [10], although the chemical nature of the darkening materials remains a matter of speculation. The low S content we observe associated with the PD material (with among the highest reflectance on Mercury) supports sulfides as a key darkening phase on Mercury [11,12]. The highest measured S/Si ratios on the planet are associated with a region of high Mg/Si [6, 13] that includes substantial low-reflectance material (LRM), lending further support to sulfides as darkening agents, although a spatially resolved S measurement of the LRM associated with Rachmaninoff itself (Fig. 2) would be desirable to test this idea further.

**Table 1. Chemical composition of the NE Rachmaninoff PD determined from XRS observations.**

| | NE Rachmaninoff PD[a] | IcP-HCT[b] | Northern Plains[b] |
|---|---|---|---|
| Mg/Si | 0.53±0.01 | 0.57±0.18 | 0.34±0.13 |
| Al/Si | 0.25±0.01 | 0.22±0.08 | 0.26±0.07 |
| S/Si | 0.023±0.003 | 0.09±0.03 | 0.06±0.02 |
| Ca/Si | 0.215±0.005 | 0.19±0.04 | 0.15±0.04 |
| Fe/Si | 0.062±0.006 | - | - |
| Ca/S | 10.5 | 2.1 | 2.5 |

[a]Statistical 1-σ errors. [b]From [5]; errors represent standard deviations of different measurements.

**References:** [1] Kerber L. et al. (2011) *Planet. Space Sci., 59*, 1895-1909. [2] Goudge T. A. et al. (2013) *JGR Planets*, submitted. [3] Prockter L. M. et al. (2010). *Science, 329*, 668–671. [4] Nittler L. R. et al. (2011). *Science, 333*, 1847–1850. [5] Weider S. Z. et al. (2012) *JGR, 117*, E00L05. [6] Nittler L. R. et al. (2013) *LPS, 44*, abstract 2458. [7] Weider S. Z. et al. (2013) *Icarus*, submitted. [8] Zolotov M. Y. (2011) *Icarus, 212*, 24–41. [9] Braden S. E. and Robinson M. S. (2013) *JGR Planets, 118*,1903-1914. [10] Denevi B. W. et al. (2009) *Science, 324*, 613–618. [11] Blewett D. T. et al. (2013) *JGR Planets, 118*, 1013–1032. [12] Helbert J. et al. (2013) *EPSL,369-379*, 233-238. [13] Weider S. Z. et al. (2014) *LPS, 45*, this volume.