**HOLLOWS AS A SOURCE FOR MERCURY'S POLAR ORGANICS.** M.M. Sori[1], K.L. Laferriere[1], K.S. Burkman[1], J. Herring[1], A. Klidaras[1], H.T. Manelski[1], R.A. McGlasson[1], S.M. Menten[1], I.F. Pamerleau[1], and S.L. Pérez-Cortés[1]. [1]Purdue University, Department of Earth, Atmospheric, and Planetary Sciences (msori@purdue.edu).

**Introduction:** Mercury has deposits of water ice in permanently shadowed regions (PSRs) at both poles. These deposits are similar to PSR ice on the Moon, but important differences exist [e.g., 1]. Mercury's ice is thicker, purer, and in some places has surfaces with ~10-cm-thick carbon-rich organics. Understanding the cause of differences between deposits on Mercury and the Moon is critical in understanding the source, age, and physical properties of the ice. An exogenic mechanism has been hypothesized to explain some of the properties of Mercury's ices, where a single, recent impact delivers most of the water that comprises the deposits [e.g., 2]. Here, we instead consider whether an endogenic source can explain some of the observed properties of Mercury's polar deposits.

One surprising discovery from NASA's MESSENGER mission is that Mercury's crust is rich in moderately volatile elements [3, 4]. This geochemistry represents an important difference compared to the Moon and could lead to differences in polar deposits if volatiles can be effectively transported across the planet. One way in which volatiles are lost from the crust is through hollow formation. Hollows are surface features probably formed by volatile loss in the upper crust [5], though the composition of that material is debated [e.g., 6–8].

Here, we hypothesize that hollow formation naturally leads to the presence of carbon-rich organics on Mercury's polar ice deposits, one of the key differences in polar ice between Mercury and the Moon. First, we calculate the number of organic molecules expected to be created from hollows formation over the history of the polar ice deposits. Second, we numerically model the transport of these molecules across the planet, starting from the hollows. We find that if hollows are created from carbon-rich material, they are expected to deliver organic material 10s of cms thick to the PSRs, consistent with thickness constraints on the dark, organic material observed by MESSENGER [9].

**Volatile production:** We assume that hollows are created by irradiation of graphite-rich crust [10] that converts native carbon and solar wind hydrogen into methane [6]. We acknowledge other hypotheses for hollows formation exist [e.g., 7, 8], and our eventual conclusions will depend on this formation mechanism.

The total surface area of observed hollows is 57400 km$^2$, and the average depth of hollows is 47±21 m [11], leading to a total hollows volume of $2.7 \pm 1.2 \times 10^{12}$ m$^3$. However, this volume only represents the volume of hollows observable by MESSENGER. If there are hollows below the image resolution of MESSENGER or hollows were formed and later destroyed over the course of the last ~330 Myr that the polar ice deposits formed [12], this volume will lead to an underestimate of the number of methane molecules that could be delivered to the PSRs. We consider these issues below.

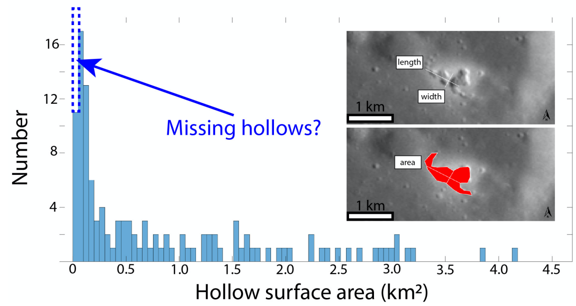


**Figure 1.** Histogram of surface areas across 137 representatively chosen hollows. A few hollows >4.5 km$^2$ are not shown for clarity. Inset shows example mapping of one hollow.

We mapped 137 hollows using the database of [11] and MESSENGER images, fitting them with polygons and calculating surface area. The distribution of surface areas is shown in Fig. 1. The distribution is well-fit by a power law, implying that there are many hollows that exist on Mercury that are too small to observe in current data. However, using the power law fit, we calculate that we are "missing" a total surface area of hollows of only ~1% of the current observed area. If hollow depth scales proportionally with hollow length, the missing volume is ~10$^9$ m$^3$, ~0.1% of the observed volume. Missing hollows are likely great in number, but small in volume.

We considered whether hollows could form in the past 330 Myr but become shallowed or destroyed by the present-day. Processes like viscous relaxation or volcanic infilling are unlikely to be significant in the past 330 Myr. We considered landscape diffusion, which has been quantified to be important on Mercury for km-scale topography [13]. We numerically modeled landscape diffusion and found that a typical hollow would take an order-of-magnitude longer than 330 Myr to lose half of its topographic relief. Therefore, we concluded that landscape diffusion will have only a minor effect on our estimated hollows volume.

Therefore, we used the total hollows volume that would form over the creation of the PSR deposits as the observed volume of $2.7 \times 10^{12}$ m$^3$. If hollows were entirely formed by the conversion of carbon-rich crust to methane, this number leads to $2.8\times10^{41}$ methane molecules.

**Volatile transport:** We calculated the thickness of an organic layer that would form in the PSRs, using our best estimate for the number of methane molecules produced by hollows. Two calculations that are simplistic but guided our intuition are as follows. If the molecules are uniformly distributed over the entire surface, each PSR would have an 0.08 m thick layer. If instead every molecule is transported to a PSR, each PSR would have a 29 m thick layer. The true answer is somewhere in between these end-members: methane molecules will be transported across the surface through the planet's exosphere, with some fraction landing in a PSR and some fraction lost from Mercury.

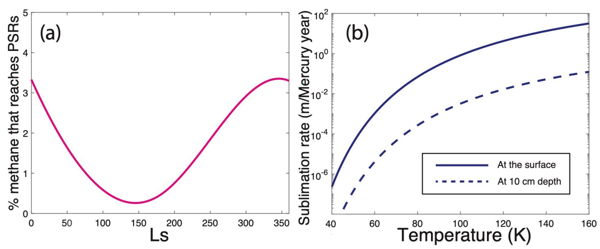


**Figure 2.** (a) Model results, showing how much hollow-sourced methane reaches PSRs over Mercury's orbit. (b) Methane sublimation rates at polar temperatures.

We conducted a volatile transport model of methane in an exosphere, with similar methods to previous work for water on Mercury [e.g., 14] and methane elsewhere [e.g., 15]. Our numerical model uses a Monte Carlo approach, simulating transport of 10,000s of molecules that begin at a hollow at different times of the year and move across the surface through ballistic "hops" until they are lost from the system or reach a PSR.

We calculated the fraction of methane expected to be lost to Jeans escape using Maxwell-Boltzmann probability distributions of molecule velocities as a function of temperature. Despite the high temperatures, we found that this loss mechanism is negligible. A molecule has a less than a one-in-a-billion chance of traveling faster the escape velocity of 4.3 km/s.

A more effective loss mechanism of methane on Mercury is photodestruction. Assuming that this process is dominated by dissociation by Lα radiation [16], we calculated that the photodestruction lifetime of methane at Mercury is 12441–28659 s (about 3–8 hours). We calculated the average time of flight for a methane molecule in Mercury's exosphere to be 190±40 s, implying a 1–3% chance of being photodissociated in a typical "hop". We find that a typical methane molecule experiences tens of hops before reaching a PSR, so this photodestruction probability becomes significant.

We found that 98.3% of methane molecules are lost from Mercury, and 1.7% of hollow-generated molecules reach a PSR. This fraction is less than but comparable to the fraction of water on Mercury that makes it to a PSR before being lost [14]. The fraction varies across a Mercury year because the process is temperature-dependent (Fig. 2a). By combining this result with our nominal calculation of $2.8\times10^{41}$ methane molecules produced by hollow formation and previous estimates of PSR surface area, we found that 50 cm of solid methane would be expected to be deposited in the PSRs.

**Discussion:** If ice deposits on Mercury were emplaced relatively quickly 100s of Ma as suggested [12, 17], then the 50 cm of methane would largely form atop the PSR ice. If this methane is efficiently converted into less volatile hydrocarbons as proposed [18], this thickness matches very well with observations [9] that suggest thickness of carbon-rich material ~10 cm.

For the conversion to be efficient, the radiolytic chemistry that produces dark compounds cannot be rapidly outpaced by sublimation. This condition is not viable everywhere, but is realistic for the coldest PSRs where mean temperatures are as low as 50 K [19] and some uppermost material is irradiated quickly enough to decrease sublimation rates of underlying ice by orders of magnitude (Fig. 2b), but still allow galactic cosmic rays to penetrate ~10 cm deep [18].

**Conclusions:** The formation of hollows and Mercury's unusual geochemistry provide an endogenic source of volatiles to the planet's polar ices. This process can plausibly explain a critical difference between ice on Mercury and the Moon – the presence of dark, organic-rich material on some deposits on Mercury. This idea does not preclude the exogenic delivery of the bulk of Mercury's water from a recent impact. Our hypothesis can be tested by ESA's and JAXA's BepiColombo mission, especially by determining chemistry involved in hollow formation.

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