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Ices on Mercury: Chemistry of volatiles in permanently cold areas of Mercury's north polar region

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ABSTRACT

Observations by the MESSENGER spacecraft during its flyby and orbital observations of Mercury in 2008–2015 indicated the presence of cold icy materials hiding in permanently-shadowed craters in Mercury's north polar region. These icy condensed volatiles are thought to be composed of water ice and frozen organics that can persist over long geologic timescales and evolve under the influence of the Mercury space environment. Polar ices never see solar photons because at such high latitudes, sunlight cannot reach over the crater rims. The craters maintain a permanently cold environment for the ices to persist. However, the magnetosphere will supply a beam of ions and electrons that can reach the frozen volatiles and induce ice chemistry. Mercury's magnetic field contains magnetic *cusps*, areas of focused field lines containing trapped magnetospheric charged particles that will be funneled onto the Mercury surface at very high latitudes. This magnetic highway will act to direct energetic protons, ions and electrons directly onto the polar ices. The radiation processing of the ices could convert them into higher-order organics and dark refractory materials whose spectral characteristics are consistent with low-albedo materials observed by MESSENGER Laser Altimeter (MLA) and RADAR instruments. Galactic cosmic rays (GCR), scattered UV light and solar energetic particles (SEP) also supply energy for ice processing. Cometary impacts will deposit H_2O, CH_4, CO_2 and NH_3 raw materials onto Mercury's surface which will migrate to the poles and be converted to more complex C–H–N–O–S-containing molecules such as aldehydes, amines, alcohols, cyanates, ketones, hydroxides, carbon oxides and suboxides, organic acids and others. Based on lab experiments in the literature, possible specific compounds produced may be: H_2CO, HCOOH, CH_3OH, HCO, H_2CO_3, $CH_3C(O)CH_3$, C_2O, C_xO, C_3O_2, C_xO_y, CH_3CHO, $CH_3OCH_2CH_2OCH_3$, C_2H_6, C_xH_y, NO_2, HNO_2, HNO_3, NH_2OH, HNO, N_2H_2, N_3, HCN, Na_2O, NaOH, CH_3NH_2, SO, SO_2, SO_3, OCS, H_2S, CH_3SH, even B_xH_y. Three types of radiation processing mechanisms may be at work in the ices: (1) Impact/dissociation, (2) Ion implantation and (3) Nuclear recoil (hot atom chemistry). Magnetospheric energy sources dominate the radiation effects. Total energy fluxes of photons, SEPs and GCRs are all around two or more orders of magnitude *less* than the fluxes from magnetospheric energy sources (in the focused cusp particles). However, SEPs and GCRs cause chemical processing at greater depths than other particles leading to thicker organic layers. Processing of polar volatiles on Mercury would be somewhat different from that on the Moon because Mercury has a magnetic field while the Moon does not. The channeled flux of charged particles through these magnetospheric cusps is a chemical processing mechanism unique to Mercury as compared to other airless bodies.

1. Introduction

A surprising result from ground-based and spacecraft observations of Mercury is that water ice and other volatiles appear to be hiding in permanently-shadowed regions (PSRs) near Mercury's poles. The Sun's heat cannot reach into these shadowed areas

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because of Mercury's low obliquity. Polar ices never see direct sunlight because at such high latitudes, solar photons cannot reach over the crater rims. Only scattered light will reach them. The craters maintain a permanently cold environment for the ices to persist and so their temperatures can stay at < 100 K for many centuries. (Obliquity is currently at ∼0° from its orbital plane). Thermal model results show that in these polar craters, temperatures are cold enough to inhibit sublimation of water ice and other ices for longer than a billion years (Paige et al., 2013). Radar backscatter images from Earth-based observations show that Mercury's PSR's have unusually high radar backscatter cross sections suggesting the presence of thick, relatively pure water ice deposits (Slade et al., 1992; Black et al., 2010; Harmon, 2011; Cremonese et al., 2010; Solomon 2011). Indications of water ice are also seen in data from the MESSENGER neutron spectrometer (Lawrence et al., 2013). MESSENGER Laser Altimeter (MLA) and Dual Imaging System (MDIS) observations show that the surfaces of the Mercury's north polar PSR regions are uniformly covered by dark material of unknown composition in regions where subsurface water ice is thermally stable (Neumann et al., 2013; Chabot et al., 2012, 2014). These instruments have also observed bright surface material in the permanently shadowed region of Prokofiev crater where thermal models predict the presence of thermally stable surface water ice (Neumann et al., 2013; Paige et al., 2012, 2013; Chabot et al., 2012, 2014).

Observations suggest that the composition of the dark surface material in Mercury's PSR's is distinctly different from that of typical Mercury silicate regolith. MLA reflectance measurements at 1064 nm wavelength show that the normal albedo of this material is ∼ 0.04, which is half the normal albedo measured in adjacent non-PSR regions (Neumann et al., 2013). MDIS images illuminated by scattered sunlight obtained at visible wavelengths show that the coverage of the dark material within the PSR's is extremely uniform and that the boundaries of the dark deposits conform closely to those of the permanently-shadowed regions (Chabot, 2014). See Fig. 1. Thermal model results show that the bi-annual maximum surface temperatures of MLA-dark deposits in the north polar region are ∼175 ± 50 K (Paige et al., 2013). These temperatures are distinctly higher than the expected thermal stability temperature for exposed pure water ice of ∼100 K (Watson et al., 1963). Paige et al. (2013) hypothesized that the dark material covering Mercury's PSR's is rich in a low-albedo organic material. Similar material is observed covering the surfaces of comets as well as asteroids and primitive outer solar system bodies (Johnson, 1991a; Mumma and Charnley, 2011). Paige et al. (2013) calculated that the ice deposit would disappear on time scales of tens of thousands of years if not thermally protected by a ∼10-cm-thick layer of overlying ice-free material. They state that the volatile organic material delivered to Mercury via cometary or asteroidal impacts may become cold-trapped in the permanently-shadowed regions along with water ice and ultimately become exposed at the surface as a sublimation lag deposit. The spatially organized state of Mercury's polar deposits suggests that they are geologically young and are being actively maintained by ongoing processes in Mercury's PSR's. However, the actual composition of this dark material and their origin remains a mystery.

Darkening of the surface material at 1064 nm is not unambiguously a detection of organics. However, a covering of organic material provides a solution for the issue of water ice stability. Thermal models show that water ice will be unstable in many of the radar-observed ice-rich areas unless buried (Paige et al., 2013) implying that these deposits were buried on timescales faster than the time it would take for the ice to sublimate: about 1800 years kg^{-1} m^{-2} at 130 K, or 3.5 years per kg^{-1} m^{-2} at 150 K. If the original material creating both the bright and dark deposits arrived simultaneously (from comet origin), complex organics could quickly create a lag

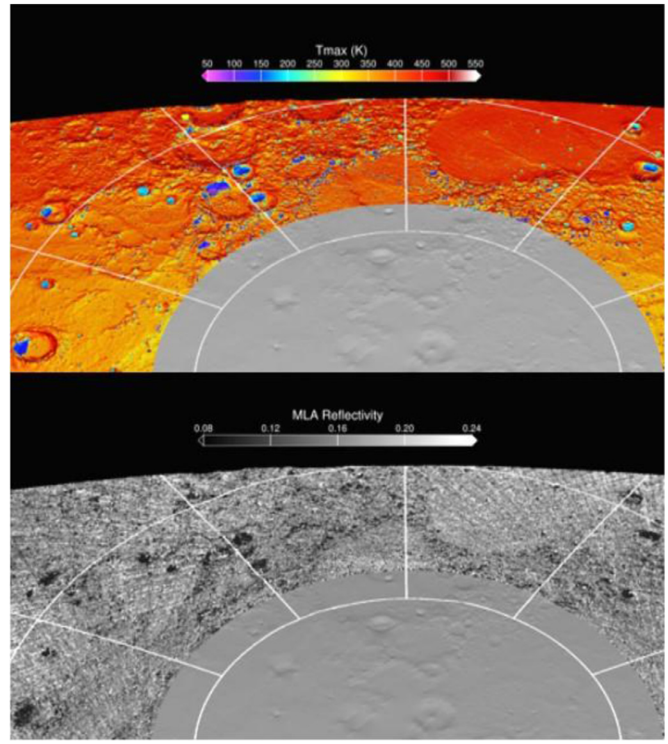

Fig. 1. (Upper) Calculated Bi-annual maximum temperature from Paige et al. (2013) for the North Polar region of Mercury. (Lower) MLA reflectance from same region showing "dark" material in areas remaining below ∼350 K, and "bright" material in areas remaining below ∼100 K. Data for the gray circle about the pole has not yet been published.

deposit of material burying the water ice below. This would occur from evaporation of the underlying water ice, leaving less volatile organic materials to accumulate. Radar absorption properties of low-density macromolecular organic carbonaceous materials are typically less lossy than low-density silicate soils expected in Mercury surface materials and so can be distinguished. Organic-rich materials overlying ground ice deposits, or organic macromolecular materials present in minor concentrations within ice deposits, are not inconsistent with the radar observations. (Paige et al., 2013). The dark material is more likely to be the product of chemical and radiation processing of icy volatile materials via energy deposition from the variety of sources available to Mercury's surface. This type of processing can yield crusty high-molecular weight organic materials that could act as a covering of the solid water ice below and thereby stabilize it against sublimation.

In this paper, we describe chemical and radiolysis processes that may be occurring in Mercury's polar regions where permanently frozen icy volatiles residing in cold traps are converted into dark refractory organics by energy input from many sources. Mercury's polar magnetospheric space environment sets it apart from that of other airless bodies in the solar system including the Moon and we propose that its unique properties may explain the present existence of abundant dark organics persisting in the polar regions on Mercury.

2. Magnetospheric particle precipitation near Mercury's poles

The first reconnaissance of Mercury was done by the Mariner 10 spacecraft during its 1974–1975 flybys. Its particles and fields measurements were the first indication that Mercury has a significant dipole magnetic field that is strong enough to deflect solar wind ions (Ness et al., 1974; Ness et al., 1975; Slavin, 2004). The MESSENGER spacecraft flyby and orbital data from its mission