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Cold-trapped organic compounds at the poles of the Moon and Mercury: Implications for origins

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[1] We have calculated evaporation rates for a range of organic compounds that may be cold-trapped at the poles of the Moon and Mercury. Organics vary widely in their volatilities and thus can be stable to evaporation at higher and lower temperatures than water. The detection of cold-trapped organics would point to volatile delivery by impacts, as comets and asteroids are the only plausible sources for organic molecules. The characterization of cold-trapped organics on both bodies may provide constraints on the thermal evolution of cold traps over time and the history of volatiles in the inner solar system. **Citation:** Zhang, J. A., and D. A. Paige (2009), Cold-trapped organic compounds at the poles of the Moon and Mercury: Implications for origins, *Geophys. Res. Lett.*, *36*, L16203, doi:10.1029/2009GL038614.

1. Introduction

[2] The notion that water ice may be cold-trapped at the lunar poles was first proposed by *Watson et al.* [1961]. Modeling results show that thermal conditions at the poles of both the Moon and Mercury are cold enough to permit the stability of water ice for extended periods [*Vasavada et al.*, 1999]. There is good observational evidence that water ice is cold-trapped within the permanently shaded regions of impact craters near the poles of Mercury [*Harmon and Slade*, 1992; *Paige et al.*, 1992; *Slade et al.*, 1992; *Harmon et al.*, 1994; *Vasavada et al.*, 1999; *Harmon*, 2007]. For the moon, the observational case for widespread ice is presently less definitive [*Margot et al.*, 1999; *Feldman et al.*, 2001; *Campbell et al.*, 2006; *Haruyama et al.*, 2008]. For both bodies, the source of the water (asteroids and comets, volcanism or solar wind [*Arnold*, 1979]) is not clear. In this paper, we explore the possibility that the permanently shadowed cold traps of the Moon and Mercury may contain organic compounds in addition to inorganic ices and explore the implications for origins.

2. Impact-Derived Organics

[3] We know that asteroids and comets are rich in organic compounds, and that these compounds are being delivered to all the planets in the inner solar system on a continuous basis [*Anders and Owen*, 1977; *Chyba*, 1987; *Anders*, 1989; *Chyba et al.*, 1990]. These include primary organics contained in the impacting body, as well as secondary organics that form due to chemical reactions after the impacting event, both of which are believed to be important in the origin of life on Earth [*Anders*, 1989]. Examination of Apollo lunar samples has found no evidence for amino acids at the $\geq$0.3 ppb level [*Brinton and Bada*, 1996], and background concentrations of organic compounds on the Moon and Mercury have not yet been observed or estimated. However, we have reason to believe that the delivery of organics to the Moon and Mercury by some impact scenarios is possible at least in principle.

[4] During hypervelocity impact events on airless bodies, primary exogenic organics are largely destroyed by shock heating [*Pierazzo and Chyba*, 2006]. However, the destruction of organics during impact events is not expected to be complete. High-resolution hydrocode simulations show that primary amino acid survival in cometary impacts at velocities of 15 km/sec may exceed 10% [*Pierazzo and Chyba*, 1999, 2002] with the survival probability increasing with decreasing impactor velocity, decreasing impactor mass, and increasing impactor incidence angle [*Pierazzo and Chyba*, 1999, 2002]. Impact velocity distributions from known Earth-crossing asteroids [*Olsson-Steel*, 1990] and known comets [*Olsson-Steel*, 1987] show that the most probable asteroid impact velocity on the Moon is 7 km/sec, and that cometary impact velocities can be as low as 13 km/sec [*Chyba*, 1991]. Asteroid impact velocities on Mercury are calculated to range from 15 to 80 m/sec [*Marchi et al.*, 2005]. Therefore on the basis of the results of the hydrocode simulations, we would expect at least some primary organics to survive and recondense on both bodies. The lowest possible impact velocity can be approximated by the escape velocity, which is 2.7 km/sec for the Earth-Moon system and 4.2 km/sec for Mercury. Thus, all things being equal, survival of impact delivered organics on the Moon is more likely than on Mercury.

[5] The absence of detectable organics in Apollo samples has been generally attributed to long-term thermal and ultraviolet decomposition of organics in the lunar environment [*Pierazzo and Chyba*, 2006]. However, as the Apollo samples all derive from near the lunar equatorial regions, where destruction mechanisms for most volatile species are likely to be highly effective, it might be expected that smaller impacts within dark, cold-trap regions – where ultraviolet and thermal decomposition is minimized – would have a higher probability for long-term preservation of organic materials. Organics deposited outside of cold traps should have an opportunity to randomly migrate into cold-traps by hopping along the surface as has been hypothesized for water [*Arnold*, 1979; *Butler*, 1997]. Since the bond energies for organics are similar to those of water, we would expect that the UV decomposition rates for most organics will be similar to that of water, so the theoretical framework that has been

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Table 1. Abundances of Major Organic Compounds in Meteorites and Comets

Meteorites[a]	
Compound Class	Concentration (ppm)
Amino acids	17–60
Aliphatic hydrocarbons	>35
Aromatic hydrocarbons	3319
Fullerenes	>100
Carboxylic acids	>300
Hydroxycarboxylic acids	15
Dicarboxylic acids and Hydroxydicarboxylic acids	14
Purines and Pyrimidines	1.3
Basic N-heterocycles	7
Amines	8
Amides (linear)	>70
Amides (cyclic)	>2
Alcohols	11
Aldehydes and Ketones	27
Sulphonic acids	68
Phosphonic acids	2
Comets[b]	
Compound	Abundance Relative to Water (%)
H_2O	100
CO	<1–40
CO_2	2–20
H_2CO	<1–5
CH_3OH	0.9–7
$HCOOH$	<0.2
CH_4	0.1–0.5
C_2H_6	0.2–2
$C_{14}H_{10}$	0.15
HCN	0.007–0.2
CH_3CN	0.01–0.02
NH_3	0.1–2
H_2CS	<0.1
H_2S	0.1–1.6
N_2	<1.5
Ar	<17

[a] From *Botta and Bada* [2002].

[b] From *Cottin et al.* [1999], *Ehrenfreund and Charnley* [2000], and *Task Group on Organic Environments in the Solar System* [2007].

established for the migration and cold-trapping of water and other inorganic compounds at the poles of the Moon and Mercury should also be applicable to organics.

3. Methods

[6] We have conducted a preliminary exploration of the thermal stability of major classes of potentially cold-trapped organic and inorganic compounds the poles of the Moon and Mercury. Table 1 shows published estimates for the abundances of organic compounds in meteorites and comets. From the top four most abundant classes of organic compounds in meteorites we created a list of most common or abundant compounds in each of the four classes from Table 1, aromatic hydrocarbons, fullerenes, carboxylic acids, and linear amides. We believe these complex organic compounds to also be representatives of comets [*Ehrenfreund and Charnley*, 2000].

[7] Vapor pressure data were collected from *Fegley and Lodders* [1998] and the CRC Handbook of Chemistry and Physics [*Lide*, 2007] in the 1Pa – 100kPa pressure range, and fit to the standard vapor pressure equation [*Fegley and Lodders*, 1998]:

$$P = Ae^{\frac{-B}{T}} \tag{1}$$

to obtain solid-vapor equilibrium pressure P as a function of temperature T, where A and B are fitted constants appropriate for each compound. In some cases, only liquid vapor pressure data were available, but we assume that they are similar to those of solids at the same temperatures. We have also included some representative inorganic ices and clathrates [*Fegley and Lodders*, 1998], as well as some representative volcanic gasses that have been proposed for the Moon and Mercury such as S, SO_2, CS_2, OCS [*Sprague et al.*, 1995; *Kerber et al.*, 2009] for comparison.

[8] With P, we can solve for the sublimation rate to vacuum using [*Watson et al.*, 1961],

$$E = P\sqrt{\frac{\mu}{2\pi RT}} \tag{2}$$

where E is the mass sublimation rate per unit area. To compare sublimation rates, we define volatility temperature (T_V) as the temperature at which the pure solid would evaporate to a vacuum at a rate of 1 mm per billion years assuming a bulk density of 1 g cm^{-3}. Our calculated sublimation rates are upper limits for pure surface volatiles, and do not take into account potential physical and chemical interactions with other volatiles or regolith materials. Our results should therefore be best interpreted in terms of relative rather than absolute volatility.

4. Results

[9] Figure 1 shows vacuum sublimation rates in meters per billion years plotted against absolute temperature for a range of potential cold-trapped volatiles and organics. Figure 2 shows calculated volatility temperatures as a function of molecular mass. The main trend for the organic compounds is that volatility increases roughly linearly with increasing molecular mass – as would be expected for van der Waals solids. The volatility of the C_{60} fullerene compound, which is not shown in Figure 1 and 2, also follows this trend. The organic compounds we investigated are roughly evenly divided between those that are more volatile than water, and those that are less. All the inorganic compounds we have investigated except sulfur have higher volatility than water.

5. Discussion and Implications for Cold Traps

[10] We currently have very little direct information regarding the nature and abundances of cold-trapped volatiles at the poles of the Moon and Mercury. In their original paper, *Watson et al.* [1961] considered a range of volatile species, but focused on water as the most likely to be cold-trapped because of its low vapor pressure and high cosmic abundance. Previously, *Hodges* [1980] proposed that there may be regions within lunar polar cold traps with temperatures low enough to trap ^{40}Ar, and *Sprague et al.* [1995] proposed that Mercury's polar radar features may be due to the cold-trapping of sulfur rather than water. Our results illustrate that

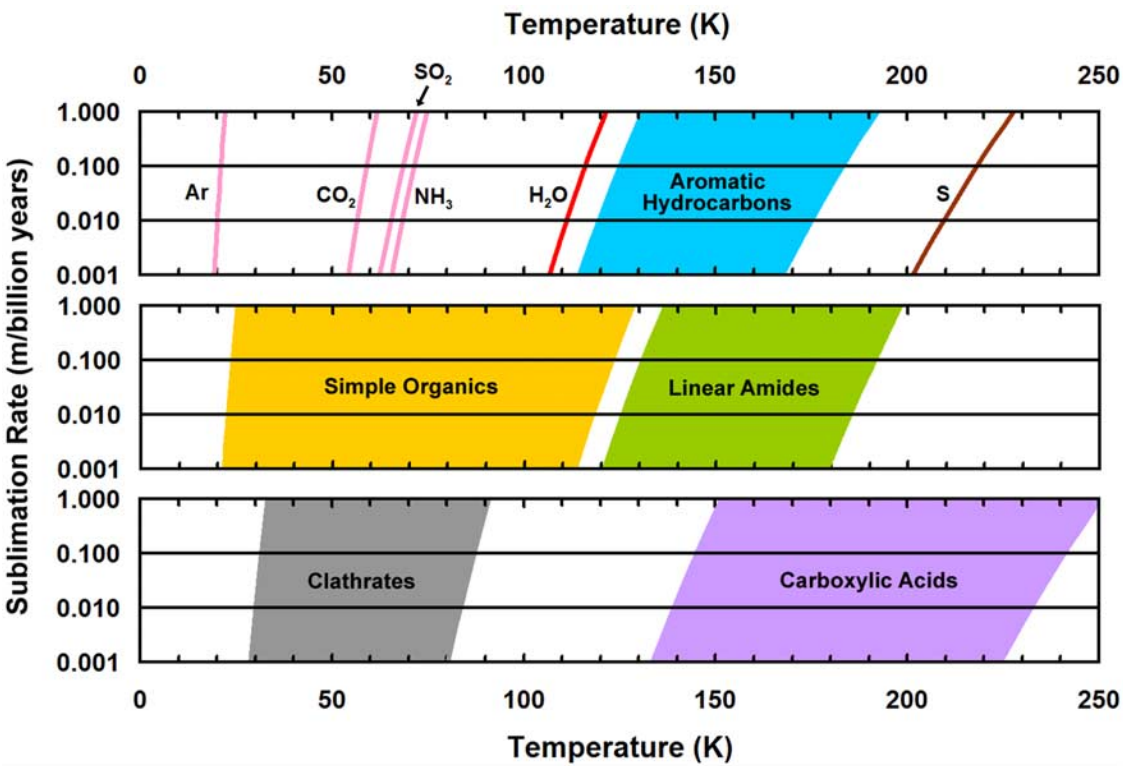

Figure 1. Calculated vacuum evaporation rates as a function of temperature for representative organic and inorganic compounds. The shaded areas show the range of evaporation rates calculated for the compounds shown in the figure legend. With the exception of sulfur, most inorganic volatiles are less volatile than water. Most simple organics and clathrates are also more volatile than water, whereas aromatic hydrocarbons, linear amides and carboxylic acids are less volatile than water. Very large molecules such as Fullerene (not shown on graph) are much less volatile than water.

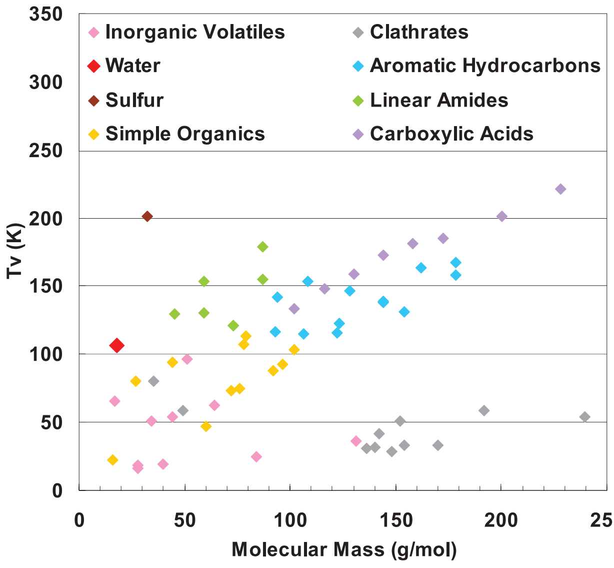

Figure 2. Volatility temperature (T_V) versus molecular mass for the organic and inorganic compounds described in Figure 1. T_V is the temperature at which the pure solid would evaporate to a vacuum at a rate of 1 mm per billion years.

there is a wide range of volatile organic and inorganic compounds that potentially could be cold-trapped. This suggests that the detection of these non-water volatiles could provide valuable additional information regarding volatile sources and cold-trap history.

[11] Table 2 shows a notional summary of potentially significant sources of cold-trapped volatile species. The multiplicity of potential water sources means that a positive detection of cold-trapped water may not necessarily shed light on its origin(s). Detection of cold-trapped sulfur for instance would point to volcanism and outgassing sources, whereas the detection of carbon dioxide would point to either volcanism and outgassing, or impacts. The detection of organics would point to impacts as they are the only plausible source, with the possible exception of organics synthesized in the cold-trap environments [*Lucey*, 2000].

[12] If cold-trapped organics are detected, then their distribution of volatilities should place constraints on the

Table 2. Significant Sources of Potential Cold-Trapped Volatile Species on Mercury and the Moon

Volatile Species	Volatility Relative to Water	Solar Wind	Volcanism and Outgassing	Impact
H_2O	-	X	X	X
S	Low		X	
Ar	High		X	
CO_2	High		X	X
Organics	Low-High			X

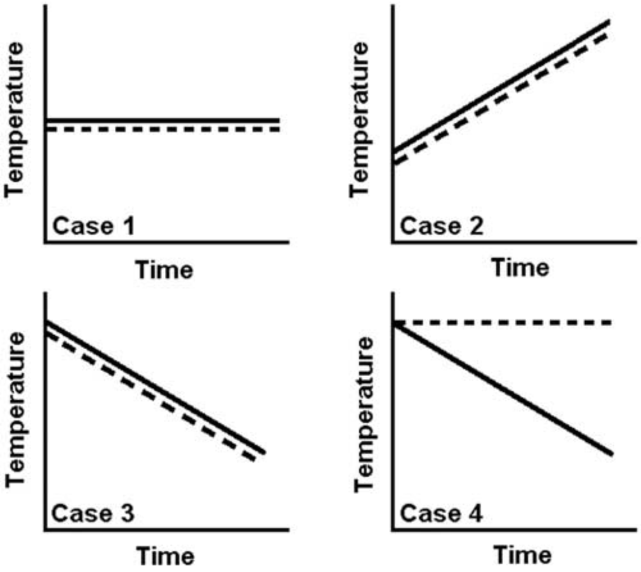

Figure 3. Four notional scenarios for the thermal evolution of a cold trap that contains organics. The solid line is T, the cold trap temperature, and the dotted line is T_V(min), the minimum volatility temperature of the cold-trapped organics.

thermal history of the cold trap in which they are found. At any given point in time, the distribution of organic volatilities within a cold trap can be characterized by T_V(min), which we define to be the volatility temperature of the most volatile organic compound present. If the temperature of a cold trap is T, then we would expect that all volatiles with $T_V < T$ to be unstable to evaporation. Thus, T_V(min) should generally be greater or equal to T. Figure 3 shows four notional scenarios for the thermal evolution of a cold trap that contains organics. In Cases 1 and 2, the temperature of the cold trap remains constant or increases over time and T_V(min) tracks T for both cases. In Cases 3 and 4, cold trap temperatures decrease over time. In Case 3, organics are being actively cold-trapped as temperatures decrease, and so T_V(min) also tracks T. In Case 4, organics are not being actively cold-trapped as temperatures decrease, so T_V(min) remains fixed as T decreases. This last scenario could provide information on the evolution of past cold trap temperatures relative to the rates of delivery of impact-derived organics. As illustrated in Figures 1 and 2, organics exhibit a wide range of volatilities that can be substantially less than or substantially greater than the volatility of water. Therefore, organics may be present in cold traps that are currently too warm to permit the present stability of water ice.

[13] The above discussion suggests the relative abundances of cold-trapped organics may contain information regarding the thermal histories of cold traps. However, fully interpreting measurements of the absolute abundances of cold-trapped organics, or any other cold-trapped volatile will require additional quantitative information regarding volatile sources or sinks over time.

6. Conclusions and Recommendations

[14] Based on the known composition of impacting bodies, and models for the survival of impact-derived organics, we believe that there is a reasonable expectation that volatile organic compounds are being delivered to polar cold traps on the Moon and Mercury. Primary and secondary organic compounds have a wide range of volatilities relative to water, and thus have the potential to be cold-trapped over a wide range of temperatures.

[15] In the future, we anticipate further remote sensing studies of the polar cold traps of the Moon and Mercury, as well as in-situ and sample return missions. Determining the abundance and distribution of cold-trapped water should be a major goal for future missions, but the detection and characterization of organics should also be a priority. Unlike water and most other inorganic volatiles, organics should only be derived from impact sources. Therefore, the positive detection of cold-trapped organics would provide immediate information regarding origins. In-situ and sample return missions have the potential to characterize the compositional distribution of cold-trapped organics in detail, and thus could provide information regarding cold trap thermal history as well as volatile sources. Complementary isotopic studies of cold-trapped organics and inorganic volatiles from returned samples have the potential to yield significant additional information regarding volatile sources. For instance, the D/H ratios of organics and water in meteorites, comets, and the D/H ratios of bulk planets and the solar wind are all distinct [*McKeegan and Leshin*, 2001; *Robert*, 2002].

[16] The Moon and Mercury have the potential to preserve information regarding conditions that existed during the early history of the solar system that have been largely erased on Earth. In one scenario, the cold traps may contain preserved records of ancient volatiles and organics that contributed to the formation of the Earth's oceans and atmosphere, and the origin of life on Earth. In another scenario, the cold traps may not contain any ancient volatiles, but instead contain only recently acquired volatiles that reflect current conditions in the modern solar system. The availability of definitive quantitative data regarding cold-trapped volatiles on the Moon and Mercury should allow us to address these, and possibly many other fundamental questions regarding solar system volatiles.

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