

Origin and stability of lunar polar volatiles

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Abstract

Temperature regime at the LCROSS impact site is studied. All detected species in the Cabeus crater as well as CH₄ and CO clathrate hydrates except H₂, CO, and CH₄ are stable against evaporation at the LCROSS impact site. CO and CH₄ can be chemisorbed at the surface of the regolith particles and exist in the form of clathrate hydrates in the lunar cold traps. Flux rates of delivery of volatile species by asteroids, micrometeoroids, O-rich, C-rich, and low-speed comets into the permanently shadowed regions are estimated. Significant amounts of H₂O, CO, H₂, H₂S, SO₂, and CO₂ can be impact-produced during collisions between asteroids and O-rich comets with the Moon while CH₃OH, NH₃ and complex organic species survive during low-speed comet impacts as products of disequilibrium processes. C-rich comets are main sources of CH₄, and C₂H₄.

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1. Introduction

The possible existence of water ice in permanently shadowed regions near the lunar poles was considered by Watson et al. (1961) and Arnold (1979). Ice-like radar echoes were detected there by the Clementine-Deep Space Network bistatic experiment (Nozette et al., 2001), but subsequent radar study of south pole of the Moon are consistent with the ice being present only as disseminated grains in the lunar regolith (Campbell et al., 2006). Based on Lunar Prospector neutron flux data Feldman et al. (2000) estimated the mass of water ice to be 2×10^{11} kg in the south pole region, and its mass fraction as about 1.5% in the south polar caps.

The possibility of polar volatiles other than water ice has been considered theoretically by Sprague et al. (1995) for

the case of S-bearing species, Reed (1999) for the case of Hg, and Duxbury et al. (2001) for the case of clathrates. However, only active impact experiments and sample return missions from the lunar cold traps are able to give more detailed information about the chemical composition of lunar polar volatiles. During active Lunar Crater Observation and Sensing Satellite (LCROSS) impact experiment several volatile compounds including H-, C-, N-, S-bearing species were detected in the Cabeus crater near the south pole of the Moon (Colaprete et al., 2010; Gladstone et al., 2010). Properties of the LCROSS impact-produced cloud were studied by Hurley (2011). According to Lunar Reconnaissance Orbiter (LRO) Lunar Exploration Neutron Detector (LEND) data the LCROSS impact site inside the Cabeus crater demonstrates the highest hydrogen concentration in the lunar south polar region, corresponding to about 0.5–4 wt.% of water ice (Mitrofanov et al., 2010).

In this paper we re-evaluate comet hypothesis of the origin of lunar polar volatiles (Shevchenko, 1999) based on new data from LCROSS impact experiment and consider the thermal stability of volatile compounds detected in the Cabeus crater.

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2. Temperature regime and thermal stability of volatiles at the south pole of the Moon

2.1. Description of used model

To calculate the lighting conditions and temperature of the lunar surface we used data from Lunar Orbiter Laser Altimeter (LOLA) (PDS, 2012), working on board the LRO spacecraft. The data were taken with step of 0.05° for latitude and with step of 0.5° for longitude. The investigated part of the lunar surface was divided into areas and for each area we have determined on the basis of altimeter data the height, the slope angle and the orientation of the area with respect to other areas. To investigate the illumination regime for each area we determined the azimuths and the angular heights of all the surrounding areas in order to get real picture of the horizon. The temperature of any element of the surface was calculated in accordance with approach previously described by (Carruba and Corradini, 1999; Vasavada et al., 1999):

$$T_j = [(F_3 + (1 - a) \times [F_2 + F_4 + F_5]) / \varepsilon \times \sigma]^{1/4}, \quad (1)$$

where a is the albedo of the surface assumed to be 0.11 (Braden et al., 2011), $\varepsilon = 0.95$ is the coefficient of radiation (Greenhagen and Paige, 2006). F_2 is the flux of solar radiation which drops on the illuminated element of the surface, F_3 is the lunar heat flux estimated as 0.016 W/m^2 (Langseth et al., 1976), F_4 is the reflected flux from the other illuminated elements of the surface calculated in accordance with (Ueno et al., 1991), and F_5 is the flux of infrared radiation that drops on the element j calculated in accordance with (Ueno et al., 1991). The approach of (Ueno et al., 1991) does not take into account the thermal flux from the neighboring elements of the surface but we can neglect this flux due to low thermal conductivity of the lunar regolith, about $10^{-2} \text{ W m}^{-1} \text{ K}^{-1}$ (Langseth et al., 1976). We also neglect influence of the solar wind while solar wind particles are able to penetrate to permanently shadowed craters and change the chemical composition of lunar polar volatiles (Zimmerman et al., 2011).

2.2. Areas of thermal stability and masses of deposits of volatile species at the south pole of the Moon

The spatial resolution of obtained temperature maps is about 1.5 km. Maximal temperatures in the Cabeus crater were estimated during “summer” lunar day, when illuminations are maximal. Permanently shadowed region is located at the north part of the Cabeus crater. Maximal day-time surface temperature at the LCROSS impact site is about 37 K, this value is in agreement with observations (Hayne et al., 2010), while the night-time surface temperature is about 20 K (see Fig. 1).

Several volatile compounds such as CO, H₂, Ca, Hg, Mg (Gladstone et al., 2010), H₂O, H₂S, NH₃, SO₂, C₂H₄, CO₂, CH₃OH, CH₄, OH (Colaprete et al., 2010), and Na (Killen

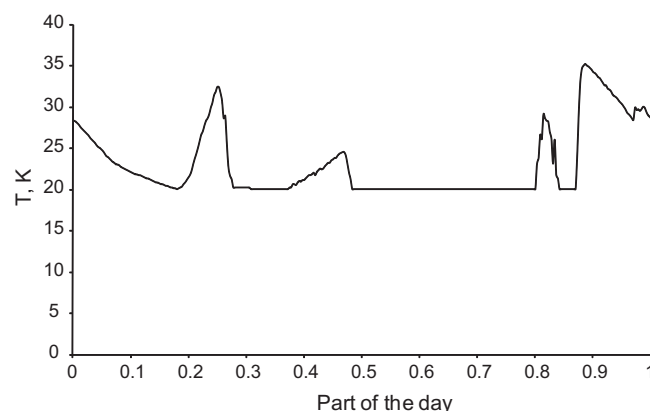


Fig. 1. Temperature regime at the LCROSS impact site in the Cabeus crater.

et al., 2010) were detected during the LCROSS impact experiment in the Cabeus crater.

It is adopted that species are stable on the surface against thermal evaporation if the evaporation rate is less than 10^{-10} cm/year (Zhang and Paige, 2009). The evaporation rates of surface volatile species as a function of temperature were calculated according to approach of (Schorghofer and Taylor, 2007). Volatility temperatures at 2 cm depth were calculated assuming that evaporation rates of volatile species at 2 cm depth is in 530 times less than at the surface in accordance with (Schorghofer and Taylor, 2007). Obtained results of estimations of surface and subsurface volatility temperatures and calculations of areas of thermal stability are presented at Table 1. Areas of thermal stability of volatile species are estimated also from Fig. 2 of (Paige et al., 2010). Subsurface temperature regime favors survival of subsurface polar volatiles; evaporation rate of subsurface volatiles is significantly lower than that of volatiles at the surface. Both factors lead to increasing of areas of thermal stability of subsurface ice deposits in comparison with that of surface volatiles (Siegler et al., 2011). Calculated volatility temperatures for pure surface volatiles are low limits because physical and chemical interactions with other volatiles and regolith are not considered. OH-containing minerals are stable against thermal vaporization even in the equatorial regions of the Moon at day-time temperatures of about 350 K (Pieters et al., 2009). Comparing temperature regime of the crater Cabeus with volatility temperatures of detected species shows that H₂, CO, and CH₄ are unstable against thermal vaporization. It is therefore reasonable to consider possibility of the existence of such volatile species as H₂, CO, and CH₄ in the Cabeus crater as not pure solids in the cold traps, but as chemisorbed at the surface of the regolith particles or in the form of clathrate hydrates.

Masses of deposits of volatile species at the south pole of the Moon were estimated assuming that depth of such deposits is 1 m, areas of existence of these deposits are equal to areas of thermal stability of these species in the cold traps at 2 cm depth (Paige et al., 2010), and mass fraction of species in areas of its thermal stability is the same as

Table 1
Volatility temperatures and areas of thermal stability of volatile species at the south pole of the Moon.

Compound	Surface volatility temperature (K)	Volatility temperature at 2 cm depth (K)	Area of regions of thermal stability at the surface (km ²) (model) ¹	Area of regions of thermal stability at the surface (km ²) (Diviner data) ¹	Area of regions of thermal stability at 2 cm depth (km ²) (model) ¹	Area of regions of thermal stability at the surface (km ²) (this work) ²
CO	16.8 ⁵	18.9 ⁵	0	0	0	0
CH ₄	22 ³	25 ³	0	0	0	0
CO-5.75H ₂ O	33.4 ³	36.5 ³	0	0	350	500
C ₂ H ₄	40 ⁵	44.6 ⁵	800	0	4500	900
CH ₄ /H ₂ O	41.8 ³	46.5 ³	1300	0	6100	1430
H ₂ S	47.8 ⁵	53.7 ⁵	3900	140	13500	4600
CO ₂	53.4 ³	59.5 ⁵	7800	1400	21400	8600
NH ₃	63 ⁵	70.4 ⁵	18300	6700	39000	20100
SO ₂	70.5 ⁵	78.3 ⁵	29000	13000	53000	32000
CH ₃ OH	90 ⁵	100 ⁵	59000	37000	100000	63000
H ₂ O	100.8 ⁵	112.7 ⁵	70000	53000	133000	72000
Hg	132 ⁶	148 ⁶	90000	90000	300000	90000
S	181 ± 7 ⁷	202 ± 8 ⁷	126000	130000	349000	130000
Na	226 ⁸	256 ⁸	190000	190000	349000	188000
Mg	303 ⁹	342 ⁹	349000	349000	349000	349000
Ca	378 ± 12 ¹⁰	426 ± 14 ¹⁰	349000	349000	349000	349000

References to studies of temperature regime: 1 – regions above 80° (Paige et al., 2010), 2 – this work for the case of vicinities of the crater Cabeus, 3 – regions above 80° (Zhang and Paige, 2010).
References to vapor pressure data: 3 – (Zhang and Paige, 2010), 4 – (Lunine and Stevenson, 1985), 5 – (Fray and Schmitt, 2009), 6 – (Huber et al., 2009), 7 – (Ferreira and Lobo, 2011), 8 – (Schins et al., 1971), 9 – from (Moser et al., 1998), 10 – (Brutti et al., 2001).

in the LCROSS impact site. It is assumed that evaporation rate of about 10^{-3} cm/s is required for sublimation of volatiles from LCROSS impact site; it corresponds to vapor pressure of about 10^{-5} bar. This value of vapor pressure achieves at 105 K for CO₂, 215 K for H₂O, 315 K for Hg, 380 K for S, 700 K for Mg, and 870 K for Ca while temperature of grains of the lunar regolith excavated by LCROSS impact to the exosphere and heated by direct solar light is about 300 K. Water ice evaporates from the LCROSS impact-produced cloud with mass of about 3150 kg (Colaprete et al., 2010). Mass fractions of CH₄, C₂H₄, H₂S, CO₂, NH₃, SO₂, CH₃OH, and H₂O in the regolith were estimated from (Colaprete et al., 2010) and assuming that CO, CH₄, C₂H₄, H₂S, CO₂, NH₃, SO₂, CH₃OH, H₂O, Hg, and S should be released from 50,000, 40,000, 35,000, 30,000, 25,000, 15,000, 12,000, 4000, 3150, 3000, and 2000 kg of regolith, respectively, based on relative volatility of these species. Mass fractions of Hg, CO and H₂ were estimated from masses of H₂ and CO in the LCROSS plume (Gladstone et al., 2011) while H₂ should be released from 250,000 kg of regolith (Hurley et al., 2012). Let us note that we use value of mass of regolith for CO in 3.6 times less than (Hurley et al., 2012) because CO is not so extremely volatile in comparison with H₂. Estimated masses of volatiles in the lunar cold traps are presented at Table 2.

3. Origin of lunar polar volatiles

3.1. Origin of metal atoms delivered to the lunar exosphere by the LCROSS impact

Several elements such as Na, K, Ca, Mg already detected at the Cabeus crater have lunar origin because these elements are abundant on the Moon and at typical velocities of collisions between celestial bodies and the Moon the target-to-impactor mass ratio is high, about 10–50 (Cintala, 1992). Thus, only volatile elements such as H, C, N, and Hg which are almost absent on the Moon can be delivered to the cold traps by impactors.

Na and K atoms can be released from the surface by UV solar photons and can migrate toward the lunar poles by its ballistic hops above the surface. Detection of Mg, Ca, and Hg in the LCROSS impact experiment can be explained that atoms of these elements like Na and K atoms can migrate toward the lunar poles. Atoms of Mg, Ca, and Hg may be released from the lunar surface in the equatorial regions by high-energetic processes such as micrometeoroid bombardment. The maximal temperature in the LCROSS impact site is about 1000 K (Hayne et al., 2010), it is high enough for thermal evaporation of Na, Mg, and Ca deposits (see Section 2.2). Vapor pressure above MgO and CaO reaches 10^{-5} bar at about 2000 and 2100 K, respectively, while evaporation occurs in the form of Ca, Mg, O₂, and O (Jacobson, 1989). Vapor pressure above Na₂O reaches 10^{-5} bar at about 1050 K while evaporation occurs in the form of Na, NaO₂, and O₂ (Steinberg and Schofield,

1991). Temperature in the LCROSS impact-produced cloud is about 1000 K (Hayne et al., 2010), it is not sufficient for evaporation of Mg, Ca, and, possibly, Na from the silicates. Thus, Mg and Ca were delivered to the LCROSS impact-produced cloud and presented in the polar regolith mainly in the form of atoms while Na could be presented in Na-bearing silicates in the polar regolith. Based on constants of reactions between CaO, MgO and H₂O, CO₂ (NIST, 2012) and estimating temperature and pressure in the LCROSS impact-produced cloud from (Hurley, 2011) it was found that chemical reactions with participation of Mg-, and Ca- bearing species are too slow for significant changes of the chemical composition of Mg-, Ca- bearing species in the cloud. If Mg and Ca were released to the LCROSS impact-produced plume mainly in the form of molecules then these molecules can be quickly destroyed by solar photons because photolysis lifetimes of Mg- and Ca-bearing species are quite short, about 10 s; MgO and CaO photolysis leads to formation of photolysis-generated metal atoms with excess energies of about 0.5 eV (Berezhnoy, 2010). However, the quality of Mg and Ca observations (Hurley et al., 2012) is not high enough for careful estimation of velocities of Mg and Ca atoms and fraction of hot photolysis-generated Mg and Ca atoms in the LCROSS impact-produced cloud.

3.2. Sources of lunar polar volatiles

Big amounts of volatiles are delivered to the Moon by low-speed short-period comets (Berezhnoy et al., 2003). However, volatile-rich asteroids are also important sources of lunar polar volatiles (Ong et al., 2010). Let us consider other types of impactors. Average velocity of collisions of interstellar comets with the Moon is about 70 km/s. For such high-speed impacts the amount of cometary material captured by the Moon is very low, about 10⁻³ (Ong et al., 2010). Thus, interstellar comets are just minor sources of lunar polar volatiles because the frequency of collisions of such comets is lower than that of short-period comets and the amount of cometary matter captured after impacts of high-speed interstellar comets is lower than that after impacts of low-speed short-period comets. To explain mass of hydrogen at the poles of the Moon (Feldman et al., 2000) about 100 impacts of 20 km/s mini-comets per year are required. This frequency of impacts is unrealistically high. Thus, mini-comets are just minor sources of lunar polar volatiles.

Solar wind is considered as a main source of hydrogen-containing species such as H₂, OH, and H₂O at the poles of the Moon (Crider and Vondrak, 2002). However, the content of other volatile elements such as N, C, and S is very small as in the solar wind as in the equatorial lunar regolith. For example, in the solar wind S/H, N/H, and C/H ratios are equal to 2.6 × 10⁻⁵, 4.2 × 10⁻⁵, and 3.5 × 10⁻⁴, respectively (von Steiger et al., 2000). Thus, solar wind cannot be considered as an important source of S-, N-, and C-containing species in the cold traps.

Outgassing of lunar interiors was studied by Fegley (1991), but outgassing rate is still poorly known.

3.3. Chemistry and physics of impact processes

Let us consider the behavior of H-, C-, N-, and S- bearing species detected in the Cabeus crater during collisions between comets and volatile-rich asteroids with the Moon. Impact flux F of volatile species to the cold traps can be estimated as

$$F(i, j) = F_{\text{imp}}(i, j)F_{\text{ret}}(i, j)F_{\text{mass}}(i, j)F_{\text{cap}}(i, j), \quad (2)$$

where i is the number of considered mechanism of delivery, j is the number of studied compound, F_{imp} is the impact flux, F_{ret} is the retaining fraction of the impact-produced cloud captured by the Moon, F_{mass} is the mass fraction of considered species in the impact-produced cloud after quenching of chemical reactions, F_{cap} is the capture probability of considered species. Impact flux and retaining mass fraction of volatile-rich asteroids to the Moon are assumed to be 1.5 × 10⁸ kg/year and 17%, respectively (Ong et al., 2010). Impact flux and retaining mass fraction of O-rich comets are assumed to be 1.2 × 10⁷ kg/year and 6.5%, respectively (Ong et al., 2010). Impact flux and retaining mass fraction of degassed C-rich comets are assumed to be the same as for O-rich short-period comets.

The behavior of volatiles in the impact-produced cloud is determined by the elemental composition of impactors because the Moon is almost dry. The elemental composition of O-rich short-period comets is assumed to be that of the comet Halley (Delsemme, 1988). The elemental composition of volatile-rich asteroids is assumed to be that of CM chondrites (Lodders and Fegley, 1998). Inactive degassed C-rich comets can be modeled by substantial removal of water molecules from the comet Halley. However, during degassing of comets other volatile species such as CO, CO₂, and CH₄ evaporate. For this reason existence of comets with extremely low O/C ratio, less than 0.6 is still in doubt. The elemental composition of C-rich comets is assumed to be that of dust of comet Halley (Krueger, Kissel, 1987). The elemental composition of sporadic meteoroids is assumed to be that of CI chondrites (Lodders and Fegley, 1998).

The quenching theory was already applied for study of chemical processes during collisions between comets and the Moon (Berezhnoi and Klumov, 1998; Berezhnoy et al., 2003). Namely, the initial temperatures and pressures in the impact-produced vapor cloud are so high that typical time scales of chemical reactions are shorter than the hydrodynamic time scale and the chemical composition of such a cloud is in equilibrium. During expansion of the cloud into vacuum temperatures and pressure are rapidly decrease while chemical time scales increase. Quenching of the chemical composition of impact-produced cloud occurs when chemical time scales are comparable with hydrodynamic time scale.

Table 2
Origin of volatile species at the poles of the Moon. Content of species detected at the LCROSS impact-produced plume, in comets, and impact-produced cloud at the quenching of chemical reactions is given in units of number of molecules normalized to water content assumed to be equal to 100%.

Compound	Content in the LCROSS plume	Mass fraction in polar regolith (wt.%)	Mass in the cold traps at the south pole (kg)	Content in comets	Photolysis lifetime (s ¹)	Main sources	O-rich comets (kg/year ²)	Asteroids (kg/year ²)	C-rich comets (kg/year ²)	Low-speed comets (kg/year)	Micrometeoroids (kg/year ³)
H ₂ ⁴	600 ⁵	0.05	4 × 10 ⁸	Product of photolysis	6.7 × 10 ⁶	Asteroids, O-rich comets	3 × 10 ⁴	6 × 10 ⁴	7 × 10 ³	–	10 ⁴
H ₂ O	100	5.6	10 ¹³	100	8.3 × 10 ⁴	Asteroids	10 ⁵	2 × 10 ⁶	4 × 10 ⁻³	2 × 10 ⁴	10 ⁵
OH ⁴	0.03 ⁶	–	–	Product of photolysis	5 × 10 ⁴	Photolysis	2 × 10 ⁻³	5 × 10 ⁻²	10 ⁻¹⁰	–	10 ⁴
CO	15 ⁵	0.08	5 × 10 ⁸	2–20 ⁷	1.3 × 10 ⁶	Comets, asteroids	2 × 10 ⁵	2 × 10 ⁵	2 × 10 ⁵	2 × 10 ³	7 × 10 ³
CO ₂	2.17 ⁶	0.04	2 × 10 ¹⁰	5–10 ⁹	5 × 10 ⁵	Asteroids	10 ⁵	1.5 × 10 ⁶	0.02	4 × 10 ³	7 × 10 ⁴
CH ₃ OH	1.55 ⁶	0.1	2 × 10 ¹¹	0.2–6 ⁸	8.3 × 10 ⁴	Low-speed comets	2 × 10 ⁻⁷	2 × 10 ⁻⁸	4 × 10 ⁻⁸	4 × 10 ²	5 × 10 ⁻⁷
CH ₄	0.65 ⁶	0.003	2 × 10 ⁸	0.2–1.5 ⁷	1.3 × 10 ⁵	C-rich comets	10 ⁻²	2 × 10 ⁻⁴	2 × 10 ⁴	70	2 × 10 ⁻⁷
C ₂ H ₄	3.12 ⁶	0.02	2 × 10 ⁹	0.3 ⁸	2.1 × 10 ⁴	C-rich comets	10 ⁻⁹	10 ⁻¹³	10 ⁴	60	10 ⁻¹⁶
H ₂ S	16.75 ⁶	0.2	4 × 10 ¹⁰	0.12–0.6 ⁷	3.1 × 10 ³	Asteroids	5 × 10 ³	10 ⁵	0.02	30	0.2
SO ₂	3.19 ⁶	0.2	10 ¹¹	0.1 ¹⁰	4.8 × 10 ³	Asteroids	3	2 × 10 ⁴	10 ⁻¹⁸	30	4 × 10 ³
S ¹¹	<0.6 ⁵	< 0.3	<2 × 10 ¹²	Product of photolysis	10 ⁶	Meteoroids	0.05	4	3 × 10 ⁻⁷	–	4 × 10 ⁵
NH ₃	6.03 ⁶	0.07	5 × 10 ¹⁰	0.1–1.6 ⁹	5.6 × 10 ³	Low-speed comets	0.2	0.1	0.01	60	10 ⁻³
N ₂ ⁴	Undetected	–	–	0.02 ¹²	10 ⁶	Asteroids, meteoroids	3 × 10 ⁴	4 × 10 ⁴	2 × 10 ³	–	10 ⁴
Hg ¹³	0.6 ⁵	0.4	10 ¹²	10 ⁻⁶	–	Comets	20	3	20	3	0.2

References and remarks: 1 – for quiet Sun at 1 AU according to Huebner et al. (1992); 2 – quenching of the chemical composition of impact-produced cloud occurs at $T_q = 1200$ K and $P_q = 0.03$ bar; 3 – quenching of the chemical composition of impact-produced cloud occurs at $T_q = 3000$ K and $P_q = 10$ bar; 4 – impact flux to the whole Moon is given, capture of delivered species by the cold traps is not considered; 5 – quenching of the chemical composition of impact-produced cloud occurs at $T_q = 3000$ K and $P_q = 10$ bar; 6 – ratios given by Gladstone et al. (2011) are normalized to water content assumed to be equal 5.6 wt.% (Colaprete et al., 2010); 7 – (Colaprete et al., 2010); 8 – (Crovissier, 2007); 9 – (Altwegg et al., 1999); 10 – (Kim et al., 1997); 11 – photoionization lifetime is given, impact flux from meteoroids was calculated at assumption that all atoms of sulfur produced during photolysis of S-bearing species reach the cold traps; 12 – (Wyskoff et al., 1991), 13 – Hg content in comets is assumed to be 3 ppm.

Let us assume that quenching temperature T_q for the case of collisions between comets and volatile-rich asteroids with the Moon is the same as for collision between comet Shoemaker-Levy 9 with Jupiter, about 1200 K (Berezhnoi et al., 1996). For initial temperature and pressure in the impact-produced cloud, about 10,000 K and 10,000 bar (Berezhnoy, 2010), and $\gamma = 1.2$ it corresponds to quenching pressure P_q equal to about 0.03 bar. Quenching parameters of chemical composition of clouds produced during collisions of meteoroids with the Moon are assumed to be 3000 K and 10 bar (Herzog et al., 2009). At the time of quenching of the composition of impact-produced cloud H_2O , CO, H_2 , H_2S , and CO_2 molecules are abundant as for impacts of O-rich comets as for impacts of asteroids while SO_2 is abundant only for impacts of volatile-rich asteroids (see Fig. 2). However, for impacts of O-rich comets and asteroids the content of other species such as CH_4 , C_2H_4 , CH_3OH , and NH_3 is very low in comparison with the observed values at the LCROSS impact-produced plume (see Fig. 2). Other species such as CO, CH_4 , and C_2H_4 can be delivered to the atmosphere of the Moon by C-rich comets (see Fig. 3).

For the case of low-speed impacts temperature in the impact-produced cloud is too low for full destruction of complex organic compounds contained in comets and at

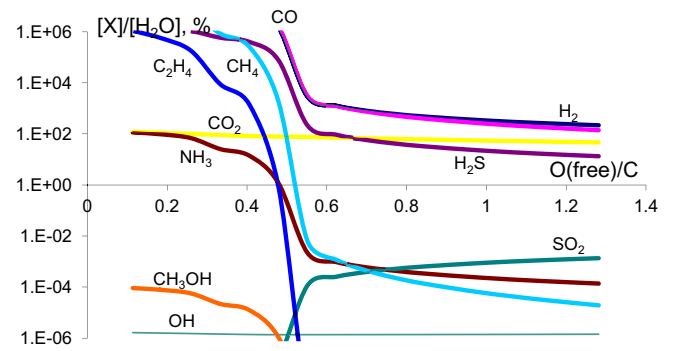


Fig. 3. Equilibrium content of species detected at the LCROSS impact site normalized to H_2O content at 1200 K and 0.03 bar versus O(free)/C ratio in impacting comets. The O(free) value is the amount of oxygen atoms which are not connected with Mg, Si, Al, Fe, Ca, Na atoms. The elemental composition of comets is assumed to be that of the comet Halley (Delsemme, 1988). The O(free)/C ratio in the comet Halley is 1.3. Decreasing of O(free)/C ratio is performed by removing of H_2O molecules from the elemental composition of the comet Halley.

such impacts these species can survive. Based on study of survival of amino acids during low-speed 10 km comet impacts on Earth (Pierazzo and Chyba, 1999) it is assumed that fraction of surviving species of cometary origin is equal to 1, 0.1, 10^{-2} , and 10^{-3} for the case of 7, 11, 15, and 20 km/s impacts, respectively. For this case about 5% and 15% of species originally presented in impactors are survived during impacts of near-Earth asteroids and short-period comets, respectively. Taking into account content of considered species in comets (see Table 2), velocity distribution of low-speed comet impacts (Jeffers et al., 2001), and its retaining factors (Ong et al., 2010) impact fluxes of species captured by the Moon and survived during low-speed comet impacts were estimated. Content of volatile species in asteroids is unknown. If content of considered species in asteroids is in 30 times lower than that in comets than comets are main sources of species for the case of low-speed impacts.

3.4. Capture of temporal impact-produced atmosphere in the cold traps

After an impact temporal atmosphere is formed over the whole Moon during about 2×10^4 s (Berezhnoy et al., 2003). At typical height scale of temporary impact-produced atmosphere of about 100 km and cross sections of photolysis of considered species of about 10^{-17} cm^{-2} (Huebner et al., 1992) photolysis lifetimes of molecules decreases with increasing column density at column densities greater than 10^{10} cm^{-3} corresponding to masses of atmosphere greater than 10^9 kg or diameters of impactors greater than about 200 m. Without taking into account adsorption of solar photons by photolyzed species molecules at impact-produced lunar atmosphere are stable against photolysis at column densities greater than 10^{13} cm^{-3} (Berezhnoy et al., 2003). For the case of Martian atmosphere molecules are stable against photolysis at

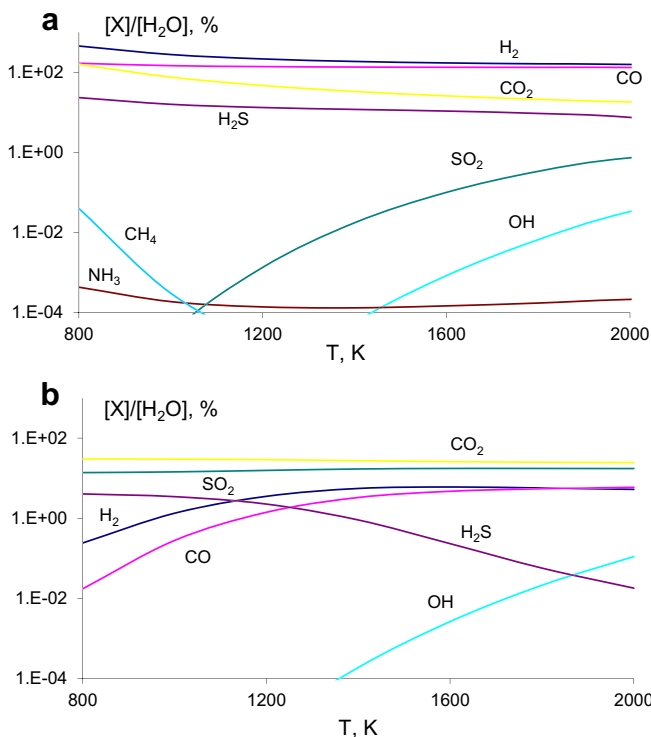


Fig. 2. Equilibrium content of species detected in the crater Cabeus during adiabatic cooling of impact-produced vapor cloud. Water vapor content is assumed to be equal to 100%. Initial temperature is 10,000 K, initial pressure is 10,000 bar, $\gamma = 1.2$. The elemental composition of the vapor cloud is assumed to be that of the comet Halley for the case (a) (Delsemme, 1988), and mixture of equal masses of CI chondrites and ferroan anorthosites (Lodders and Fegley, 1998) for the case (b).

column densities greater than 10^9 cm^{-3} (Fox and Dalgarno, 1979). Majority of volatiles are delivered by biggest impacting asteroids and comets with typical diameters of about 20–100 km (Ong et al., 2010), such impactors can produce temporal atmosphere with surface column density of about 10^{16} cm^{-3} . For this reason it was assumed that dense impact-produced atmosphere protects species against photolysis.

Ratio of typical time of capture of temporal atmosphere in cold traps t_d and lifetime of atmosphere t_a (assuming that it is determined by photolysis and products of photolysis escape the Moon) can be estimated in accordance with (Berezhnoi and Klumov, 1998) as

$$t_d/t_a \sim (S_m/S_{tr})d_c/t_{ph}v, \quad (3)$$

where $S_m = 3.8 \times 10^7 \text{ km}^2$ is the total area of the lunar surface, S_{tr} is the area of cold traps assumed to be equal to area of thermal stability of species at 2 cm depth (Paige et al., 2010), $d_c \sim 1 \text{ km}$ is the characteristic depth of permanently shadowed craters, t_{ph} is the photolysis lifetime taken from (Huebner et al., 1992), $v \sim 300 \text{ m/s}$ is the thermal velocity of species at 200 K. Based on estimated t_d/t_a ratio capture probabilities were estimated as unity for CO_2 , CH_3OH , H_2O , and S; about 0.7 for CO, CH_4 , and NH_3 ; about 0.4 for SO_2 and C_2H_4 ; and 0.2 for H_2S . These estimations are upper limits of values of capture probabilities because photolysis of species below the exobase level, which may be important for 100 m – 1 km impactors, was not taken into account.

During photolysis of impact-produced molecules in the temporal atmosphere preferable escape of atomic and molecular hydrogen into space occurs due to its low masses and high velocities, it leads to depletion of hydrogen content in species captured by lunar cold traps in comparison with that in the impact-produced cloud at the time of quenching.

For the case of smaller impactors collisional atmosphere is not produced. Transition from collisionless to collisional atmosphere occurs at column densities of about 10^8 cm^{-3} and mass of atmosphere of about $5 \times 10^6 \text{ kg}$ (Vondrak, 1974). During micrometeoroid bombardment temporary impact-produced collisional atmosphere is not produced and photolysis of species in the lunar exosphere must be taken into account. Based on measurements of terrestrial cosmic dust flux impact flux of sporadic meteoroids is assumed to be $2 \times 10^6 \text{ kg/year}$ (Love and Brownlee, 1993). The retaining fraction F_{ret} is estimated with usage of Maxwell velocity distribution function at 3000 K. For the case of micrometeoroid bombardment capture probabilities of species to the cold traps were estimated in accordance with (Berezhnoy et al., 2003) as

$$F_{cap} \sim ct_{ph}S_{tr}/t_{mig}S_m, \quad (4)$$

where $c \sim 1$ is the capture probability of molecules during their collisions with the surface of cold traps, t_{mig} is the mean duration of hops. Using Eq. (5) capture probabilities to cold traps at the south pole of the Moon are estimated as

2×10^{-3} for H_2S , 5×10^{-3} for C_2H_4 , 7×10^{-3} for NH_3 , 0.015 for CH_4 and SO_2 , 0.03 for CO, 0.3 for H_2O , 0.4 for CH_3OH , 0.45 for CO_2 , and about unity for S and Hg. In fact capture probabilities increase with increasing mass of atmosphere impactors at the transition case between two ultimate regimes described by Eqs. (3) and (4). Fluxes of species of different origin to the cold traps estimated in accordance with adopted mass fluxes, retaining factors, chemical composition of the impact-produced cloud at the time of quenching of chemical reactions, and capture probabilities are given at Table 2.

4. Discussion and conclusion

The LCROSS impact experiment gives us information about existence of volatile species in the Cabeus crater considered as one of the coldest lunar polar craters. Stability of these species against evaporation is studied; areas of thermal stability of studied species at the south pole of the Moon are estimated.

Comparison of estimated masses of deposits of lunar polar volatiles and its flux rates shows that considered sources of majority of lunar polar volatiles can deliver required amounts of volatiles to the poles of the Moon for 10^4 – 10^6 year. It means that only small fraction of delivered volatiles survives during existence of the cold traps (about 10^9 year). Maximal required delivery time, about 10^8 – 10^9 year, is estimated for Hg, CH_3OH , and NH_3 . Hg can be delivered to the poles from the upper layers of lunar regolith during meteoroid bombardment (Reed, 1999). Molecular nitrogen is the main nitrogen-bearing compound for almost all studied sources of volatiles. Formation of NH_3 molecules from implanted protons and nitrogen atoms in the cold caps upon action of ionization radiation is possible; this mechanism is already discussed by Colaprete et al. (2010). Our estimates of flux rates of molecular nitrogen show that amounts of nitrogen of asteroid's and cometary origin are comparable while isotopic studies show that chondritic micrometeoroids are main sources of non-solar nitrogen on the Moon (Füri et al., 2012). Methanol can be formed also during reactions at the surface of cold grains of the polar regolith.

Asteroids are main sources of H_2 , H_2O , CO, CO_2 , and H_2S while O-rich comets are responsible for delivery of H_2 and CO. C-rich comets are main sources of CO, CH_4 , and C_2H_4 . Low-speed comets deliver NH_3 , CH_3OH , and complex organic species originally presented in comets while meteoroids deliver elemental sulfur to the poles of the Moon. Estimation of the isotopic composition of lunar polar ices will be useful for determination of the main sources of polar volatiles because each considered source has unique isotopic composition.

Thermodynamic calculations of equilibrium chemical composition of impact-produced cloud at the time of quenching of chemical reactions, about 3000 K and 10 bar, formed after impact of micrometeoroids in cold traps shows that main impact-produced species are H_2O ,

H₂, CO, CO₂, HSOH, SO, SO₂, H₂S, and N₂ while other species such as NH₃, C₂H₄, CH₃OH, and CH₄ can be destroyed during such impacts. For this reason preferable survival of NH₃, C₂H₄, CH₃OH, and CH₄ is possible in subsurface layers better protected from meteoroid bombardment in comparison with surface.

Different sources are responsible for delivery of simple molecules such as H₂O, CO₂, and SO₂ and complex organic molecules to the poles of the Moon. Progress in our knowledge about sources of lunar polar volatiles can be achieved after delivery of samples of lunar polar deposits to Earth. Further study of thermal regime and remote sensing mapping of polar deposits are required for careful estimation of amount and spatial distribution of lunar polar volatiles.

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