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Pathways for energization of Ca in Mercury's exosphere

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ABSTRACT

We investigate the possible pathways to produce the extreme energy observed in the calcium exosphere of Mercury. Any mechanism must explain the facts that Ca in Mercury's exosphere is extremely hot, that it is seen almost exclusively on the dawnside of the planet, and that its content varies seasonally, not sporadically. Simple diatomic molecules or their clusters are considered, focusing on calcium oxides while acknowledging that Ca sulfides may also be the precursor molecules. We first discuss impact vaporization to justify the assumption that CaO and Ca-oxide clusters are expected from impacts on Mercury. Then we discuss processes by which the atomic Ca is energized to a 70,000 K gas. The processes considered are (1) electron-impact dissociation of CaO molecules, (2) spontaneous dissociation of Ca-bearing molecules following impact vaporization, (3) shock-induced dissociative ionization, (4) photodissociation and (5) sputtering. We conclude that electron-impact dissociation cannot produce the required abundance of Ca, and sputtering cannot reproduce the observed spatial and temporal variation that is measured. Spontaneous dissociation is unlikely to result in the high energy that is seen. Of the two remaining processes, shock-induced dissociative ionization produces the required energy and comes close to producing the required abundance, but rates are highly dependent on the incoming velocity distribution of the impactors. Photodissociation probably can produce the required abundance of Ca, but simulations show that photodissociation cannot reproduce the observed spatial distribution.

1. Introduction

Calcium was first detected in Mercury's exosphere by Bida et al. (2000) and was shown to be extremely energetic (Bida et al., 2000; Killen et al., 2005). Killen et al. (2005) derived a temperature of Mercury's calcium exosphere of >20,000 K based on the measured line profiles from ground-based observations. Observations by the MErcury Surface, Space ENvironment, GEochemistry, and Ranging (MESSENGER) spacecraft confirmed the energetic nature of the exospheric Ca and showed that it predominately originates in the equatorial dawn hemisphere (Vervack et al., 2010; Burger et al., 2012). Burger et al. (2014) modeled data obtained by the MESSENGER Ultraviolet and Visible Spectrometer (UVVS) during the primary and first extended missions, including data from March 18, 2011, through March 17, 2013. These data from portions of nine Mercury years showed that calcium is persistently ejected from the dawn equatorial region at speeds greater than Mercury escape velocity (4.25 km/s). The derived velocity distribution corresponds to a temperature $\sim$70,000 K based on the velocities required to populate the highest altitudes before the calcium is ionized. These energies are surprising because the previously proposed source processes (impact vaporization, photon-stimulated desorption, electron-stimulated desorption, and sputtering) produce much cooler ejecta (Killen and Ip, 1999; Killen et al., 2007). In a previous paper Killen et al. (2005) proposed that the hot Ca is the result of dissociation of Ca-bearing molecules. Killen and Hahn (2015) showed that the source rate for atomic Ca and its variation with Mercury's true anomaly angle derived by Burger et al. (2014) from MESSENGER observations is consistent with impact vaporization by the influx of interplanetary dust and, in addition, a cometary stream associated with Comet 2P/Encke. A follow-on paper that traced cometary dust under the influence of gravity and Poynting–Robertson drag (Christou et al., 2015) showed that the enhanced emission near true anomaly angle 25° is consistent with impacts due to a comet stream associated with Comet 2P/Encke. However, there has never been a study of the energization mechanisms that could be responsible for producing such extremely hot calcium vapor.

Although several processes have been discussed in the literature for ejection of surface-derived atoms into exospheres, none of these processes, including electron-stimulated desorption, photon-stimulated desorption, impact vaporization or sputtering, can produce an exosphere in excess of 70,000 K, and confined to the dawn equatorial hemisphere, as measured for the Ca exosphere

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at Mercury (e.g. Burger et al., 2014). We therefore propose a two-step process in which the initial process ejects calcium-bearing molecules and the second process produces highly energetic atomic Ca. The purpose of this paper is to discuss possible pathways for energization of atomic calcium.

To have escape velocity, the Ca fragment must have an energy of >3.77 eV. If the hot Ca in Mercury's exosphere is 70,000 K, then the average energy of the Ca atom must be 5.6 eV. We investigate the pathways by which neutral molecules containing Ca can be dissociated into energetic fragments and we investigate the excess energies for each proposed process. In addition to the fact that Ca in Mercury's exosphere is very hot, any mechanism must explain the additional observations that Ca is seen almost exclusively on the dawnside of the planet centered on the equator, and that its content varies seasonally, not sporadically.

We first discuss impact vaporization and justify our assumption that CaO and Ca-oxide clusters are the major calcium-bearing ejecta. We then discuss pathways for dissociation and energization of the fragments: (1) electron-impact dissociation of CaO molecules, (2) spontaneous dissociation of Ca-bearing molecules following impact vaporization, (3) dissociative ionization, and (4) photo-dissociation. We briefly discuss sputtering.

2. Impact vaporization producing Ca-oxide clusters

Killen and Hahn (2015) showed that the rate of impact-vaporization of Ca in Mercury's regolith by impacts of interplanetary dust and cometary dust, and its variation with true anomaly angle, are consistent with the observations (Burger et al., 2012, 2014). They did not discuss the physical state of the ejecta or pathways for energization of the calcium. In this paper we begin with the assumption that the initial vapor phase of calcium-bearing ejecta is CaO (e.g. Berezhnoy and Klumov, 2008). The equilibrium fraction of gas-phase Na-, K- and Ca-containing species released as a result of impact of a CI meteorite onto Mercury was calculated by Berezhnoy and Klumov (2008), assuming that the elemental composition of the mercurian regolith is a mixture of 90% plagioclase and 10% pyroxene by volume. At 3000 K, atomic Ca was found not to be a significant fraction of the gas-phase debris, rather $Ca(OH)_2$ dominates. At temperatures above 3750 K, CaO was found to dominate over atomic Ca and $Ca(OH)_2$. In addition to the equilibrium chemistry calculations of Berezhnoy and Klumov, laboratory experiments have been conducted using laser ablation to simulate high-energy impacts. $(CaO)_n$ clusters, where n can be 1 or more, were found (Ziemann and Castleman, 1992) and are shown to be possible precursor molecules for the hot Ca seen in Mercury's exosphere. In the remainder of this paper we assume that CaO is the initial form of the calcium ejecta, that it is ejected by impacts and that the initial fireball has a temperature >3750 K.

3. Processes producing hot calcium

3.1. Electron impact dissociation

CaO produced by impact vaporization at 4000 K has an energy of 0.3 eV, or a mean velocity of ~1.0 km/s. Having only one quarter of escape velocity it cannot directly escape, and most likely it sticks to the surface upon impact. Because CaO is highly reactive, the CaO will react with the surface minerals before the molecule is hit by another micrometeorite. Here we consider the possibility that CaO molecules produced by meteoritic impact are subsequently dissociated in the exosphere by electron impact.

The MESSENGER Energetic Particle Spectrometer (EPS) has sampled energetic electrons (10s of keV) at most Mercury longitudes and local times, and found that the largest burst events were either at high northern latitudes or near local midnight (Ho et al., 2012). Lower-energy events were seen near the equator at all longitudes but with the highest concentrations in the dawn–dusk sectors (Ho et al., 2015). These lower energy events may be related to the quasi-trapped population in the equatorial region found in simulations by Schriver et al. (2011). For both northward and southward IMF simulations, Schriver et al. (2011) show that electron fluxes can be as large as 10^9–10^{10} $cm^{-2}\,s^{-1}$ at some locations. On average, however, the observed electron flux is about 10^7 cm^{-2} (Ho et al., 2015).

For southward IMF, maximum precipitation fluxes in the Schriver et al. (2011) simulations tend to occur at the equator on the dawnside region, although there is also substantial precipitation in the northern hemisphere. Also for southward IMF, dayside reconnection occurs at lower latitudes over a broader region in longitude. When electrons pass through the reconnection region they tend to gain more energy with more spread in pitch and phase angle, which leads to a wider precipitation region in both latitude and longitude. The MESSENGER Fast Imaging Plasma Spectrometer (FIPS) detected MeV electrons during solar energetic events over the entire polar cap down to a latitude of 50° at midnight and again in the low latitude plasma sheet on the nightside of the planet (Gershman et al., 2015). They inferred from these measurements that the entirety of Mercury's polar caps are continuously bombarded by ~100 eV strahl solar wind electrons at fluxes of 10^7–10^9 $cm^{-2}\,s^{-1}$.

The electron impact dissociation cross sections of CaO were recently measured by Miles (2015) and are on the order of 0.4×10^{-16} cm^{-2} at 1 keV. This is similar to electron impact dissociation cross sections of other oxygen-bearing molecules by 100 eV electrons (McConkey et al., 2008). If CaO is produced by impact vaporization, a reasonable estimate of the column abundance of CaO, N(CaO), is about $2. \times 10^9$ cm^{-2} based on impact vaporization rates from Cintala (1992), using a calcium fraction of 0.035 in the regolith (Weider et al., 2015), assuming that all of the calcium is ejected as CaO (Berezhnoy and Klumov, 2008), and that its lifetime is the ballistic lifetime of the CaO molecule (760 s). Then the *e*-impact dissociation rate of CaO equals the production rate of Ca and is on the order of

$$\begin{aligned} &\frac{d(\mathrm{CaO})}{dt} = N(\mathrm{CaO})F(e)\sigma \\ &\frac{d(\mathrm{Ca})}{dt} \leqslant 2 \times 10^9 \times 10^9 \times 0.4 \times 10^{-16} \end{aligned} \tag{1}$$

where $F(e)$ is the electron flux and σ is the e-impact dissociation cross section. If $F(e)$ is between 10^7 electrons $cm^{-2}\,s^{-1}$ (background) and 10^9 (sporadic), using either the Ho et al. (2012) estimates for 100 eV to 1 keV electron flux or Schriver's et al. (2011) simulation results, the production rate of Ca by this process is ~80 atoms/cm^2/s. The Ca photoionization rate at 1 AU is 6.96×10^{-5} s^{-1} during normal (quiet) solar conditions (W.F. Huebner and J. Mukherjee, Photo rate coefficient database, 2011, http://phidrates.space. swri.edu). Over the course of a Mercury year, the Ca photoionization lifetime at Mercury varies between 23 and 52 min due to Mercury's changing heliocentric distance in its eccentric orbit. If the lifetime of neutral Ca is the photoionization lifetime, 1345 s at perihelion to 3107 s at aphelion, the column abundance of Ca would be <1×10^5 cm^{-2}. Thus using the most optimistic values, this result is 3 orders of magnitude too low compared with the observed Ca column abundance, 1.5×10^8 cm^{-2} (e.g. Killen et al., 2005). We do not expect that either the cross section or the electron flux is in error by orders of magnitude. Thus it is unlikely that electron impact dissociation is the cause of the hot calcium.