Laboratory simulations of sulfur depletion at Eros

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Abstract

The X-ray spectrometer of the Near-Earth Asteroid Rendezvous (NEAR) mission discovered a low abundance of sulfur on the surface of asteroid Eros, which is seemingly inconsistent with the match of the overall surface composition to that of ordinary chondrites. Since troilite, FeS, is the primary sulfur-bearing mineral in ordinary chondrites, we investigated the hypothesis that sulfur loss from surface FeS could result from ‘space weathering’ by impact of solar wind ions and micrometeorites. We performed laboratory studies on the chemical alteration of FeS by 4 keV ions simulating exposure to the solar wind and by nanosecond laser pulses simulating pulsed heating by micrometeorite impact. We found that the combination of laser irradiation followed by ion impact lowers the S:Fe atomic ratio on the surface by a factor of up to 2.5, which is consistent with the value of at least 1.5 deduced from the NEAR measurements. Thus, our results support the hypothesis that the low abundance of sulfur at the surface of Eros is caused by space weathering.

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1. Introduction

The Near-Earth Asteroid Rendezvous (NEAR) mission’s year-long orbital study of Asteroid 433 Eros revealed fascinating new information about the asteroid (Veverka et al., 2000; Robinson et al., 2001; Thomas et al., 2001; Veverka et al., 2001a, 2001b). Among the new findings are the presence of a complex regolith with very low color contrast, a population of craters depleted in small sizes, an abundance of boulders and flat regions (“ponds”) without structure down to the 1.2 cm resolution level and, when compared to the reflectance of the constituent minerals assumed to be on the surface, Eros appears darker, redder, and with attenuated mafic absorption bands in the near infrared. The latter characteristics are typical effects of exposure of minerals to “space weathering” by solar radiation and micrometeorite impact (Clark et al., 2001, 2002). The NEAR data taken by the visible-near infrared spectrometer and the X-ray/Gamma-ray Spectrometer (X/GRS) suggest that the surface of Eros best matches an ordinary chondrite (McCoy et al., 2001; McFadden et al., 2001), consistent with Earth-based, near-infrared observations (Murchie and Pieters, 1996; Kelley et al., 2001). However, the NEAR XRS data show a striking mismatch between Eros and ordinary chondrites: the surface appears to be strongly depleted in sulfur (McCoy et al., 2001; Nittler et al., 2001; Trombka et al., 2001). This is evidenced by an upper limit of 0.05 for the S:Si weight ratio, measured on the surface of Eros, in contrast to ratios of 0.075–0.165 in ordinary chondrites (Nittler et al., 2001).

The short attenuation length of the X-rays detected by XRS implies that the elemental composition is obtained only from a shallow depth. Values of ~3.4, ~5.5 and 95 µm for Si, S, and Fe, respectively, are estimated from tabulated cross sections (Henke et al., 1993), assuming the asteroid regolith has a composition similar to olivine but with a lower density of 1.7 g/cm³. Since the range of grain size on Eros is 50–100 µm (Li et al., 2004), the shallow XRS sampling depths mean that all of the information obtained from XRS is likely to originate from the top layer of grains on the surface. However, regolith turnover by meteorite impact implies that sulfur depletion probably extends to grains located much deeper in the regolith.

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Sulfur in chondrites is primarily bound in the form of troilite (FeS). Due to a relatively high volatility, sulfur can be preferentially removed from troilite by the two primary space weathering mechanisms considered active on the Moon and asteroids: sputtering by solar wind ions and impact vaporization by micrometeorites (Chapman, 2004). Sulfur depletion by sputtering (Trombka et al., 2000; Killen, 2003; Kracher and Sears, 2005) has been considered previously using a first order description of the phenomenon where the sputtering rate is assumed to be constant. As we will show later, ion irradiation indeed sputters sulfur preferentially from FeS, but its removal rate decreases with time as sulfur is removed. The alternative mechanism of sulfur depletion during impact vaporization by micrometeorites has also been considered (Burbine et al., 2001; Killen, 2003; Kracher and Sears, 2005), with widely different estimates of the degree of chemical alteration.

Here we address experimentally whether the extent of sulfur depletion on Eros revealed by XRS can be explained by ion irradiation and/or micrometeorite impact. We irradiated troilite (FeS) with 4 keV He$^+$ ions typical of the solar wind and nanosecond laser pulses that mimic the fast-pulsed heating that accompanies micrometeorite impact. During irradiation, we monitored the atomic S:Fe ratio with X-ray photoelectron spectroscopy and ion scattering spectroscopy and, after the experiment, examined the irradiated surface with electron microscopy.

2. Experimental procedures

2.1. Sample preparation and analysis

Synthetic iron sulfide (FeS) rods were obtained from the Alfa Aesar company. To prepare powder samples, the rods were cleaved, crushed with an agate mortar and pestle, and sieved to obtain grain sizes between 45–125 µm, the range of the reported average particle size on Eros (Li et al., 2004). Next, we pressed the powder with ~3000 psi into a disk inside a 10-mm aluminum ring placed in between two stainless steel disks, similar to the technique used by Sasaki et al. (2001). Since leaving the sample in air for a day or more produces detectable amounts of sulfur oxides on the surface, for every experiment we prepared a fresh sample using the method above and placed it in vacuum within ~15 min after crushing the powder.

The pressed samples were mounted on a copper holder and transferred into an ion-pumped ultra-high vacuum chamber with a base pressure of 5–10 $\times$ 10$^{-9}$ Torr (Fig. 1). For surface analysis, we used the sample manipulator to position the sample at the focus of the electron energy analyzer and to orient it so that it could be irradiated with ions and illuminated with X-rays at the same time. For laser irradiation we positioned the sample normal to the incident laser beam. All irradiations and chemical analysis were performed without removing the samples from vacuum.

Surface analysis of the troilite was done before, during and after irradiation using two techniques: X-ray photoelectron spectroscopy (XPS) and Ion Scattering Spectroscopy (ISS). XPS is a widely used surface analysis method, which gives both elemental abundance and chemical information. In this technique, irradiation of the surface with X-rays (in our case Al–K X-rays of energy $E_{\text{X-ray}} = 1486.6$ eV) ejects electrons into vacuum with a kinetic energy ($E_k$) given by

$$E_k = E_{\text{X-ray}} - E_B - \phi,$$

where $E_B$ is the electron binding energy with respect to the Fermi level, and $\phi$ is the work function of the spectrometer. The energy distribution (spectra) of photoelectrons is measured with double pass cylindrical-mirror electron energy spectrometer (Dukes et al., 1999) and is given as number of counts vs binding energy. The spectra show a continuous background on which photoelectron and Auger peaks are superimposed. The escape depth of the electrons analyzed by XPS depends on their kinetic energy; it is 2–3 nm for the Fe-2p and S-2p electrons in
troilite (Seah and Dench, 1979). The relative area of the photoelectron peaks is used together with sensitivity factors (see below) to obtain elemental composition, whereas the precise value of the electron binding energy gives information on the chemical state of the element (Moulder et al., 1992).

For these XPS measurements, the spectrometer was operated in fixed transmission mode at a 200 eV pass energy for survey spectra and 40 eV for high resolution spectra, providing energy resolutions of 3.2 and 0.6 eV, respectively. The ultimate energy resolution of the XPS spectra is limited by the width of the Al-K X-ray line, 0.85 eV FWHM. Survey spectra were measured in ~5 min, while the more detailed spectra took ~30 min.

To obtain absolute ratios of S:Fe in our XPS measurements, we measured the relative sensitivity factors for pure iron and sulfur, using an iron sheet and sulfur powder pressed into a flat pellet. To prevent sulfur from outgassing in the chamber, we cooled the sample holder down to 200 K before introducing the sulfur. The surface of both samples was cleaned by sputtering with 4 keV Ar⁺ ions. To obtain the relative sensitivity factors for iron and sulfur, we maintained the same incident X-ray intensity on both samples and determined the areas of the Fe-2p (~700–740 eV) and the S-2p (150–175 eV) photoelectron peaks. Then we obtained the sensitivity factors relative to O-1s (a standard practice) by measuring the intensity of the O-1s photoelectrons from a condensed ice film under the same conditions. The sensitivity factors relative to O-1s were Fe-2p = 2.54 and S-2p = 0.29, within 10%.

In addition to XPS, the composition of the topmost layer of the sample was studied with Ion Scattering Spectroscopy (Brongersma et al., 2007). In this technique, low energy ions (~1 keV) are incident on the surface, and the spectrometer is used to measure the energy spectra of ions backscattered at a specific angle. In this low energy regime, the backscattered ions result from elastic binary collisions with atoms in the outermost surface layer, and thus their energy is given by energy and momentum conservation:

\[ E_{\text{ion}} = E_0 \left( \cos \theta \pm \sqrt{A^2 - \sin^2 \theta} \right)^2 / (1 + A)^2, \]

where \( E_0 \) is the incident ion energy, \( A = m_2 / m_1 \), and where \( m_1, m_2 \) are the masses of the projectile and target atoms, respectively. The scattered ions are detected with our CMA by switching the polarity of the spectrometer with respect to that used to analyze electrons. The backscattering angle of interest, \( \theta \), is selected by a slit in a rotating drum (Fig. 1). In our experiments, we used 1 keV He⁺ ions and \( \theta = 150^\circ \). The ISS energy spectra were taken in <5 min using the same parameters as in the survey spectra for XPS. The He⁺ flux was low enough that, during this time, it did not produce detectable compositional changes in the surface, as determined by ISS and by XPS. In this work we used ISS mainly to identify the elements that are in the outermost surface layer.

In addition to surface analysis, during irradiation we also monitored the molecules ejected from the surface with a quadrupole mass spectrometer aimed at the sample. After completing all irradiation and analyses, we removed the sample and imaged its surface ex situ using a JEOL 6700 field-emission scanning electron microscope.

### 2.2. Ion irradiation

A low energy (0–5 kV) ion gun was used to irradiate the sample surface. It is differentially pumped and thus during experiments the chamber pressure remained in the mid 10⁻⁸ Torr range, where the mean free path of residual gas in the chamber is low enough that it does not affect the trajectory of the projectiles or of the sputtered particles. Ion irradiation was done with 4 keV He⁺ and Ar⁺ rastered uniformly over the sample surface analyzed by XPS. The average ion incidence angle was ~45 degrees to the average sample surface, and varied locally at each grain. We measured the ion current density before (~4 x 10¹³ ions/cm²) and after each experiment with a Faraday cup and found it to be stable within ~5%.

The use of He⁺ ions should be adequate to simulate He²⁺ solar wind ions. It has been argued (Kracher and Sears, 2005) that a higher charge state can enhance sputtering, based on measurements on highly charged heavy ions that carry keV potential energy. However, there is neither experimental evidence nor a theoretical justification for a charge state dependence of sputtering yields for ions of such low charge state.

#### 2.3. Laser irradiation

The traditional method to simulate micrometeorite or hypervelocity dust impacts in the laboratory is to accelerate silicate grains, which mimic interplanetary dust, with an electrostatic accelerator and collide them with the desired surface. Another technique to simulate micrometeorite impacts, more suitable for uniform irradiation over macroscopic areas, is the use of high-energy pulses from a nanosecond laser (Yamada et al., 1999; Sasaki et al., 2001; Brunetto et al., 2006). This method has been successful in producing the rapid melting and vaporization that is thought to occur in micrometeorite impacts (Sasaki et al., 2001). Furthermore, it has been shown that ns-pulsed laser irradiation alters reflectance spectra of silicates and meteorites in a manner that is consistent with the hypothesis of space weathering (Sasaki et al., 2001). The justification of using ns-pulsed lasers to mimic dust impacts has been made by comparing thermoionic plasma emitted from samples that were impacted by accelerated dust and laser beams (Kissel and Krueger, 1987), normalized to the deposited power density (W/cm²). These authors found that, above the laser ablation threshold, similar ion mass spectra and absolute yields are obtained when the power density of the laser beam is ~100 times lower than that for dust impact, as a result of the different efficiency of conversion of impact energy to temperature (Sugita et al., 2003). With this in mind, we estimate that the UV laser used in our experiments (~10⁻¹⁸ W/cm²) is roughly equivalent to a 1–20 μm particle (2 g/cm³) traveling ~10–15 km/s (appropriate for Eros; Killen, 2003). On impact, this is equivalent to a power density of 10¹⁰ W/cm² assuming the energy is deposited over an area given by the cross section of the dust particle, and a depth of 3 particle diameters. We note that even micrometeorite impacts as slow as 0.05 km/s can produce a thermionic plasma and, hence, vaporization (Smith and Adams, 1973).
Laser irradiations were made with a GAM excimer laser that emits 10 ns pulses at 193 nm (ArF) at 1 Hz. The laser beam entered the analysis chamber through a quartz-fused silica window and was imaged to a 0.5 mm² spot on the sample; each pulse had an energy fluence of 0.7 J/cm². The beam was rastered uniformly across the sample with mirrors actuated by a motion control system synchronized to the laser.

3. Results

The comparison of XPS spectra of troilite before (virgin) and after irradiation with 4 keV He⁺ and Ar⁺, as well as laser pulses, show notable differences (Fig. 2): sulfur increases with laser irradiation and decreases with ion impact, while C and O impurities decrease with both types of irradiation. Analysis of the energies of the S-2p and Fe-2p photoelectron peaks shows that the oxygen impurity is mainly bound to iron and not to sulfur [the peak of S bonded to oxygen at $\sim$169 eV is very weak (Fig. 2, bottom)]. This is consistent with the studies of Jones et al. (1992) and Pratt et al. (1994) on pyrrhotite (Fe₁₋ₓS, $x < 0.25$).

ISS spectra, giving information only of the outermost atomic surface layer, is shown in Fig. 3 for samples before and after irradiation with 4 keV He⁺. Iron and sulfur, which has not been found as an impurity in other studies in our laboratory, are present in the initial spectra indicating that the common air-borne surface contaminants (C and O impurities) do not cover the entire surface.

Fig. 4a gives the S:Fe atomic ratio vs irradiation fluence from the XPS and ISS measurements, where the ISS data have been scaled so that the ratio at zero fluence matches the XPS data. The similarity of the two sets of fluence dependencies, in spite
of the different depth information in ISS and XPS, indicates that the alteration by ion impact is relatively uniform for depths less than \( \sim 3 \) nm. The same conclusion results from the constancy of the ratio of Fe-2p (\( \sim 700 \) eV) and Fe-3p (55 eV) peak intensities, which, because of their different energies, also sample different depths: 2.1 nm vs 3.6 nm (Seah and Dench, 1979).

Fig. 4a shows that the S:Fe ratio increases at low He\(^{+}\) fluences as the initial surface contaminants are removed, suggesting that those contaminants are not uniformly distributed but are preferentially bound to the sulfur. We note that in addition to the XPS and ISS measurements, we also observed that the flux of sputtered sulfur, measured by the mass spectrometer, initially increased at low ion fluences and subsequently decreased. The initial increase in the S:Fe ratio was not seen in the Ar sputtering experiments, because at the lowest irradiation fluence shown in Fig. 4b, Ar already removed the contaminants due to its \( \sim 15 \) fold larger sputtering yield. In both cases, the final S:Fe ratio, obtained by extrapolating the fit of a single-exponential decay to high fluences, is \( 0.55 \pm 0.05 \).

We used TRIM to calculate sputtering yields (Ziegler and Biersack, 2006) to convert the fluence dependence into a depth scale: 7 (100) nm removed by \( 10^{17} \) He (Ar)/cm\(^2\). However, Fig. 4 does not represent a depth distribution of the S:Fe ratio for the unirradiated (or laser irradiated) solid. This is because the instantaneous surface composition is affected by preferential sputtering (for 4 keV He impact, the sputtering yield of S is \( \sim 15\% \) higher than that of Fe) and surface segregation. This segregation is a result of defects and radiation enhanced diffusion over the maximum ion penetration depth (Kelly, 1989). For our experiments at 45\(^o\) incidence, the maximum depth is \( \sim 80 \) (\( \sim 10 \)) nm for 4 keV He (Ar) (Ziegler and Biersack, 2006).

A different behavior is observed under laser irradiation. Fig. 4b shows the Ar\(^{+}\) fluence dependence of the S:Fe ratio for FeS samples with and without irradiation by 100 laser pulses (total 70 J/cm\(^2\)). The initial (zero ion fluence) S:Fe ratio increases from \( \sim 1.0 \pm 0.2 \) to about 1.8 \( \pm 0.2 \) after one laser pulse and does not increase with further laser irradiation. Ion irradiation of laser impacted samples decreases the S:Fe ratio by a factor of 2 after \( 10^{16} \) ion/cm\(^2\), at which \( \sim 4 \) nm of the surface is removed. This dramatic drop indicates that sulfur enrichment is limited to this shallow depth.

Further ion irradiation after laser processing lowered the S:Fe ratio to \( \sim 0.40 \pm 0.04 \), indicating that even though repeated laser pulses do not alter the surface composition, they deplete sulfur below the surface, causing lower S:Fe ratios at high ion fluences. After irradiation we removed the samples and examined them with the scanning electron microscope. Fig. 5 shows micrographs of an unirradiated sample and one that has been ablated with 100 laser pulses to a total fluence of 70 J/cm\(^2\). The unirradiated sample presents small grains of FeS, which have adhered to larger grains during the sieving process. The high-resolution images show that the surface of
the grains is fairly smooth. The laser irradiated sample shows
grains with smooth edges, and the absence of small particles.
High-resolution images show surface ripples typical of laser ablated
materials, which indicate surface melting and rapid cooling (Foltyn, 1994).

4. Discussion

4.1. Irradiation effects

The laser experiments, that simulate pulse heating during micrometeorite impact, show that sulfur segregates to the surface of troilite. This is consistent with the thermal surface segregation of sulfur observed in ordinary chondrites subject to heating above 500 °C (Launera et al., 1997); high temperatures are needed to achieve sufficiently high rates of diffusion in iron sulfide (Fry et al., 1979). As shown in Fig. 4, the excess sulfur is in a thin surface layer that can be easily removed by a subsequent impact or by sputtering.

The decrease of the S:Fe ratio at the outermost surface layer upon ion irradiation, as revealed by ISS, demonstrates the preferential sputtering of the surface sulfur. The XPS data show that the sulfur depletion region extends at least 3 nm deep (the XPS sampling depth) but most likely continues through the whole ion penetration depth (Kelly, 1989). This depletion below the layer that contributes to sputtering can be explained by radiation driven diffusion, where defects generated by each ion enhance the segregation of sulfur to the surface, even in the absence of macroscopic heating. Our results for changes of surface composition by ion irradiation are consistent with a body of evidence on surface alteration of other types of multi-element targets; for example, preferential sputtering of sulfur is also seen in ion irradiation of FeS2 (Nikzad et al., 1992; Chaturvedi et al., 1996). The similar equilibrium (high fluence) S:Fe ratio we obtain for different types of ions, is consistent with previous findings that equilibrium concentrations achieved through ion irradiation are generally independent of the mass of incident projectile (Liu et al., 1978).

4.2. Application to Eros

Our experiments test the effect of space weathering on the sulfur abundance on Eros’ surface, under the assumption that S is only in the form of troilite and that the concentration of troilite is in the range found in ordinary chondrites. This concentration can be inferred from the S:Si ratio, which is in the range 0.075–0.165 in weight (Nittler et al., 2001). There are two reports of S:Si weight ratios on Eros from XRS data: 0.014 ± 0.017 (McCoy et al., 2001) and <0.05 (Nittler et al., 2001). This implies that the abundance of S on Eros is reduced by a factor of at least 0.075/0.05 = 1.5 or 0.075/0.031 = 2.4, from the two interpretations of the XRS data. Our measurements show a maximum depletion of 1.82 ± 0.17 for ion irradiation alone and 2.5 ± 0.25 for laser impact followed by ion irradiation. However, the sulfur depletion by the solar wind will be limited to the penetration depth of the ions, ~0.2 μm (Bradley, 1994), which is only a few percent of a typical grains size and of the sampling depths of the NEAR XRS instrument. Therefore, the solar wind by itself cannot be the source of the sulfur depletion in the regolith observed by NEAR.

On the other hand, micrometeorite impact will produce transient heating that will enhance diffusion and bring sulfur from depths greater than the ion range to the surface of the grain where it will segregate, as seen in our laser simulations and other heating experiments (Launera et al., 1997). In addition, regolith turnover by meteorite impact brings grains to the surface where they are impacted by ions and micrometeorites; the time for this turnover depends on depth. From lunar studies, a layer as thick as the XRS information depth of a few microns is turned over a few times in 10^4 years (Horz et al., 1991), during which impact heating produces sulfur sublimation and the surface segregation mentioned above.

The time needed to sputter the segregated surface layer can be estimated from the measurements of Fig. 4a. There we see that a He+ fluence of ~1.5 × 10^18 ions/cm^2 suffices to reduce the surface concentration of S to an equilibrium level. Since the flux of solar wind He at 1.34 AU—the current location of Eros—is ~4 × 10^9 ions/cm^2 s, the depletion time by sputtering will be about 10^5 years, or of the order of the turn over time for the few micron depth sampled by the XRS on NEAR. Hence, sulfur depletion on Eros to the upper limits of concentration reported by XRS can occur on times scales on the order of 10^4–10^5 years by combined micrometeorite and solar wind impact. These times are much smaller than the 3–50 million years estimate for the formation time of Eros regolith (Korycansky and Asphaug, 2004).

Based on these arguments we conclude that space weathering is a plausible mechanism for sulfur depletion on Eros. For completeness, we must consider that the XRS data does not exclude a much smaller sulfur concentration that would require other explanations. A number of physical processes have been proposed including partial melting and physical sorting. Partial melting during the formation of the asteroid could have caused the sulfur to evaporate or move from the surface into the interior (Nittler et al., 2001; McFadden et al., 2005), but it should also have affected the relative concentration of Cr, Mn, and Ni, which was not observed (Foley et al., 2006). The idea of physical sorting is based on the assumption that grains containing troilite are differentiated in size or weight with the other grains in the regolith. A variety of processes have been postulated that could remove these grains with different physical properties from the surface (Asphaug et al., 2001; Nittler et al., 2001; Robinson et al., 2001; Kracher and Sears, 2005). However, there is not enough information on the regolith that would allow evaluating the hypothesis that grains containing troilite have different properties from other grains in the regolith.

We note that the processes described here will occur also on other small airless bodies. In fact, sulfur depletion has been detected on the Itokawa asteroid (T. Okada, private communication). In addition, our results may help explain the low S:Fe ratios observed in some of the cometary dust captured by the STARDUST mission (Zolensky et al., 2006).

Finally, while the space weathering effects will also occur on the Moon and Mercury, it is important to note that the sig-
significant gravity of those bodies will cause most of the ejected sulfur to return and coat the surface. We note that a large S enhancement has been observed on the rim of lunar grains (Keller and McKay, 1993).

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**References**


