IRRADIATION OF FeS: IMPLICATIONS FOR THE LIFECYCLE OF SULFUR IN THE INTERSTELLAR MEDIUM AND PRESOLAR FeS GRAINS.

L.P. Keller[1], M. J. Loeffler[2], R. Christoffersen[3], C. Dukes[4], Z. Rahman[3] and R. Baragiola[4]. [1]ARES, Robert M. Walker Laboratories for Space Science, Mail Code KR, NASA Johnson Space Center, Houston, TX 77058, [2]Astrochemistry Laboratory, NASA Goddard Space Flight Center, Mail Code 691, Greenbelt, MD 20771, [3]Jacobs ESCG, Houston, TX 77058, [4]Univ. of Virginia, Laboratory for Atomic and Surface Physics, Charlottesville, VA 22904 (Lindsay.P.Keller@nasa.gov).

Introduction. Fe(Ni) sulfides are ubiquitous in chondritic meteorites and cometary samples where they are the dominant host of sulfur. Despite their abundance in these early solar system materials, their presence in interstellar and circumstellar environments is poorly understood. Fe-sulfides have been reported from astronomical observations of pre- and post-main sequence stars [1, 2] and occur as inclusions in *bona-fide* circumstellar silicate grains [3, 4]. In cold, dense molecular cloud (MC) environments, sulfur is highly depleted from the gas phase [e.g. 5], yet observations of sulfur-bearing molecules in dense cores find a total abundance that is only a small fraction of the sulfur seen in diffuse regions [6], therefore the bulk of the depletion must reside in an abundant unobserved phase. In stark contrast, sulfur is essentially undepleted from the gas phase in the diffuse interstellar medium (ISM) [7-9], indicating that little sulfur is incorporated into solid grains in this environment. This is a rather puzzling observation unless Fe-sulfides are not produced in significant quantities in stellar outflows, or their lifetime in the ISM is very short due to rapid destruction. The main destruction mechanism is sputtering due to supernova shocks in the warm, diffuse ISM [10]. This process involves the reduction of Fe-sulfide with the production of Fe metal as a by-product and returning S to the gas phase. In order to test this hypothesis, we irradiated FeS and analyzed the resulting material using X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM).

Methods and Samples. For the irradiation experiments, synthetic FeS was irradiated with 4 keV He^+ to a total fluence of 2.3×10^{18} He^+/cm^2. Details of the sample preparation, irradiation conditions and surface analysis are described in [11]. We prepared vertical cross-sections from the irradiated sample using the JSC FEI Quanta600 focused ion beam (FIB) instrument. The specimen surface was protected by layers of electron beam deposited C and Pt followed by an ion-deposited Pt layer to avoid damage during the milling process. We obtained imaging, diffraction and chemical data from the sections using the JSC JEOL 2500 field-emission STEM equipped with a Noran thin window energy-dispersive X-ray (EDX) spectrometer. Quantitative element maps were acquired by rastering a 1 nm incident probe whose dwell time was minimized to avoid beam damage and element diffusion during mapping. Successive image layers were acquired and combined in order to achieve ~1% counting statistics for Fe and S.

Results and Discussion. XPS analysis of the irradiated sample shows that S is preferentially sputtered from the surface with a concomitant reduction of Fe^{2+} to Fe metal [11]. The XPS data are sensitive to a depth of ~3 nm and show that the S/Fe atomic ratio is reduced to ~0.5. TEM observations of the FIB sections show a distinct 2-3 nm thick layer on the uppermost surface of the sample that is nanocrystalline and Fe-rich (Fig. 1). High angle annular darkfield images are consistent with this thin Fe-rich layer consisting of Fe-metal. There appears to be little noticeable amorphization or significant structural change in the host troilite below the Fe-metal layer; in high resolution TEM images, the structural details of the host troilite extend up to the base of the Fe metal layer (Fig. 1). Additional HRTEM studies are underway to investigate the defect density in the troilite as a function of depth.

Quantitative chemical maps from the FIB sections show a S-depleted layer that extends to a depth of ~10 nm (Fig. 2). The Fe/S ratio increases from 1 in the deeper undamaged material to a maximum of ~6 at the surface (Fig. 3). We also detect minor oxygen at the surface indicating that the sample has partly oxidized from atmospheric exposure after the irradiation and XPS measurements and prior to the TEM analyses. SRIM [12] calculations show the maximum ion-deposited atomic collision energy (E_d) occurs at a depth of ~6.5 nm, in excellent agreement with the 8-10 nm width of the chemically and microstructurally altered layer in the sample. Our previous work [13] on 1 MeV Kr irradiation of troilite and pyrrhotite showed these phases remained crystalline up to an experimentally-practical maximum E_d value of 140 keV/nm^3. These results confirm the extreme radiation tolerance of the troilite crystal structure against amorphization, especially relative to silicates like olivine and pyroxene that undergo complete amorphization at $E_d = 40$-50 keV/nm^3. The results also show, however, that troilite is not immune to chemical (and associated microstructural) changes occurring in an actively-sputtered near-surface zone.

Conclusions. Irradiation of FeS with 4 keV He^+ results in preferential sputtering of S and the formation of a thin 2-3 nm, compact Fe metal layer that armors the surface. The zone of S loss extends to a depth of ~8-10 nm. Despite this S loss, the FeS in the depleted

region retains its crystallinity and shows no sign of incipient amorphization. The experimental data indicate this microstructure develops rapidly and reaches an equilibrium state on the order of ~10^4 years [11] and so is predicted to be a common feature in preaccretionally irradiated sulfides from meteorites and IDPs. The nanocrystalline microstructure of the putative irradiated surface alteration of pyrrhotite reported by [14] is not observed in our experiments.

FeS is a highly radiation resistant mineral, far more resistant than the typical silicates in meteoritic materials (e.g. olivine). Circumstellar (CS) silicates survive passage through the ISM, processing in the protoplanetary disk and incorporation into parent bodies. Based on our experimental results, CS Fe sulfides should be as abundant as CS silicates. The fact that current astronomical data indicates they are not is a paradox that may point to a gap in current astronomical methods for recognizing ISM sulfide grains. Alternatively, the paradox may reflect issues with the inferred S abundance in the ISM and/or the extent of the S depletion from the gas phase.

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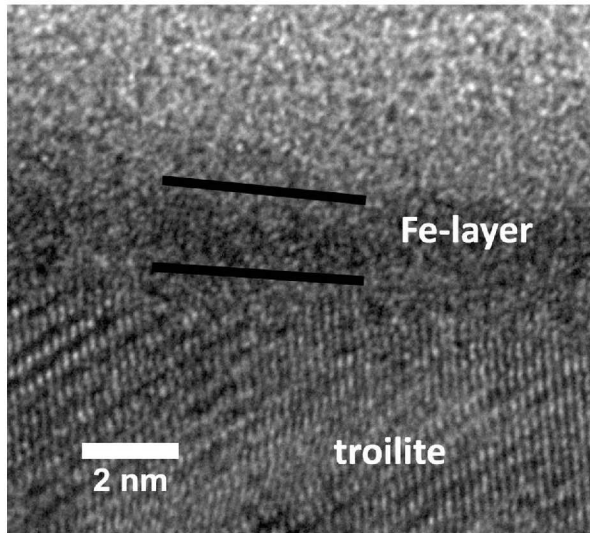

Figure 1. A HRTEM image of irradiated FeS showing the Fe metal layer on the uppermost surface. Note that the troilite lattice fringes extend to the base of the Fe metal layer.
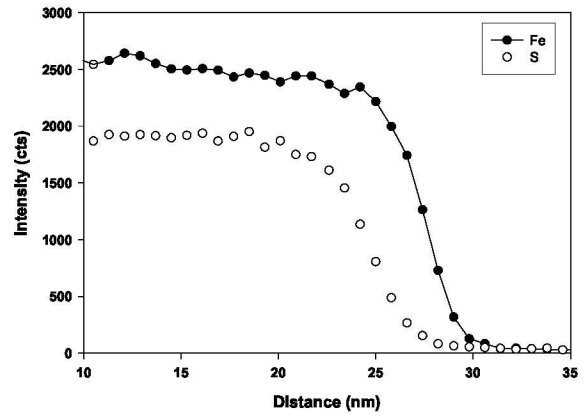

Figure 2. Line profiles for Fe and S from the core of the FeS grain through the irradiated rim. The S depletion extends to a depth of ~10 nm.
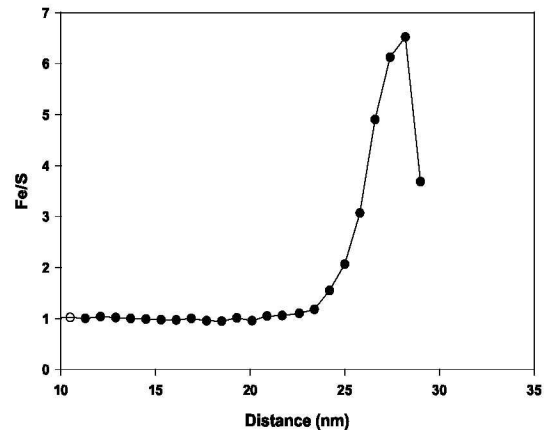

Figure 3. The Fe/S atomic ratio from the line profiles in Figure 2 showing the pronounced Fe enrichment at the irradiated surface.