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Production of a Biomimetic Fe^(I)-S Phase on Pyrite by Atomic-Hydrogen Beam-Surface Reactive Scattering

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Abstract

Molecular beam-surface scattering and X-ray absorption spectroscopic experiments were employed to study the reaction of deuterium atoms with a pyrite, FeS₂ (100), surface and to investigate the electronic and geometric structures of the resulting Fe-S phases. Incident D atoms, produced by a radio frequency plasma and expanded in an effusive beam, were directed at a pyrite surface held at various temperatures from ambient up to 200 °C. During exposure to the D-atom beam, D₂S products were released with a thermal distribution of molecular speeds, indicating that the D atoms likely reacted in thermal equilibrium with the surface. The yield of D₂S from the surface decreased approximately exponentially with exposure duration, suggesting that the surface accessible sulfur atoms were depleted, thus leaving an iron-rich surface. This conclusion is consistent with X-ray absorption measurements of the exposed surfaces, which indicated the formation of a layered structure, with elemental iron as the outermost layer on top of a formally Fe^(I)-S phase as an intermediate layer and a formally Fe^(II)-S₂ bulk pyrite layer at lower depths. The reduced Fe^(I)-S phase is particularly remarkable because of its similarity to the catalytically active sites of small molecule metalloenzymes, such as FeFe-hydrogenases and MoFe-nitrogenases.

Introduction

Biological iron-sulfur clusters¹ provide well defined examples of highly evolved catalytic systems that are capable of carrying out kinetically challenging small molecule activation reactions, such as nitrogen reduction to ammonia or reversible hydrogen uptake and evolution in nitrogenases^{2–4} and hydrogenases,^{5–8} respectively. The promise of developing novel catalytic systems that mimic the reactivity of metalloenzymatic active sites which are composed of abundant Fe and S components has already fueled intense synthetic,^{9,10} spectroscopic,¹¹ and structural research.¹² In addition to their technological potential,^{13–15} iron-sulfur systems, including particles and minerals,¹⁶ have also been implicated as the catalytic component in the chemical evolution of the building blocks of life.^{17–20}

As a first step in the investigation of mineral surface defects as functionally analogous and structurally related biomimetic systems, we have explored the surface modifications created by molecular beams of hydrogen atoms (in their deuterated form) on the (100) surface of pyrite (FeS₂). Formally, pyrite is composed of low spin ferrous iron (Fe^(II)) and persulfide (S₂^{2–}) ions. The Fe^(II) and S₂^{2–} ions can be considered as a reduced form of the ferric (Fe^(III)) ion and the oxidized form of two sulfide ions, respectively. The latter are the common biological forms of iron and sulfur ions. The reduced metal and oxidized ligand is a remarkable chemical pairing that has the potential to promote redox reactions. These ions

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are organized in a simple cubic structure, with roughly octahedral coordination for the Fe^(II) ions and tetrahedral coordination around each of the S atoms of the persulfide ions. The lattice parameter of the pyrite crystal is 5.42 Å, with Fe-S and S-S bonds of 2.26 Å and 2.14 Å, respectively.²¹ Although Fe in pyrite is typically more reduced than Fe in the biological systems, atomic hydrogen has the potential to reduce the Fe sites further and thus create surface sites that mimic the catalytically active form of Fe in metalloenzymes, such as FeFe-hydrogenases.²² The use of molecular beam techniques allows for energetically controlled and systematic creation and probing of surface defects. Such techniques provide the ability to bombard a surface with atoms or molecules of known composition, directionality, and kinetic energy. Products that scatter from a temperature-controlled surface may be detected as a function of their mass, velocity, and scattering angle. The observed scattering behavior may be used to infer details about gas-surface energy transfer and reactions, as well as chemical and physical transformations on the surface.

We used field emission scanning electron microscopy (FE-SEM), atomic force microscopy (AFM), and X-ray absorption spectroscopy (XAS) to evaluate the surface after exposure to molecular beams. XAS measurements at the Fe K-edge (energy range of 7–8 keV) were employed to evaluate changes at the atomic scale with respect to both geometric and electronic structures from Extended X-ray Absorption Fine Structure (EXAFS) and X-ray Absorption Near-Edge Structure (XANES) analyses, respectively. In order to probe various depths of the surface, we employed three detection methods. The most commonly used transmission setup was used to gain information about the structure of the bulk for powder samples. Fluorescence detection with an approximate escape path of about 200 Å provided information about the intermediate layer between the bulk and the top surface. Electron-yield detection with a shallow escape depth of about 10 Å is highly surface sensitive and provides information about the top molecular layer of a surface.²³ The combined application of three complementary detection methods and employment of both EXAFS and XANES allowed us to uncover structural details of hydrogen-atom-modified pyrite surfaces, which showed a remarkable relevance to small molecule activation catalysis in biological systems.

Experimental Methods

Beam-surface scattering experiments were carried out with the use of a crossed molecular beams apparatus (see Fig. 1).^{24–26} An effusive beam containing D atoms and a supersonic beam containing N₂ molecules were directed at pyrite surfaces, which were mounted at the center of rotation of a rotatable mass spectrometer detector. Products that scattered from a sample surface were monitored with this detector. A spinning slotted disk (“chopper wheel”) was placed in front of the detector in order to modulate the products and thus allow their velocity distributions to be determined by the time-of-flight method. The chopper wheel had three 1.5 mm wide slots and rotated with a frequency of 150 Hz. The distance from the chopper wheel to the electron bombardment ionizer was 29 cm.

A 40 W radio-frequency (13.56 MHz) plasma was used to produce deuterium atoms from a mixture of D₂ in Ar, with a mole ratio of approximately 1:4, respectively, and a total pressure of ~150 mTorr. The addition of Ar to the D₂ gas was needed for the production of a stable plasma. The partially dissociated mixture was expanded through a 0.5 mm dia. orifice to form an effusive beam containing D atoms, D₂ molecules, and Ar atoms. The effusive beam from the plasma source was characterized with the use of the mass spectrometer detector, allowing mole fractions of the various beam components to be estimated: D(0.21), D₂(0.04), and Ar(0.75). No evidence for ions in the beam was observed. Beam velocity distributions were fit to a Maxwell-Boltzmann distribution, and the translational temperatures were determined to be 550 K for D, 505 K for D₂, and 450 K for Ar. The beam was directed at sample surfaces at normal incidence. The distance from the orifice to the

surface was typically 18 mm. The flux of D atoms at the surface was estimated to be $\sim 10^{15}$ atoms $\text{cm}^{-2} \text{s}^{-1}$. D atoms were used instead of H to allow unambiguous assignment of reaction products. Control experiments were conducted with the use of an effusive beam produced with pure Ar gas in the plasma source.

A second beam was used for some of the experiments. This was a supersonic beam that was formed by expanding a mixture of 1% N_2 seeded in H_2 , with a stagnation pressure of ~ 640 Torr, through a pinhole of 125 μm diameter. The nozzle of this source was held at room temperature, yielding N_2 molecules with a nominal translational energy of 17 kcal mol^{-1} . The supersonic beam passed through a 2 mm dia. skimmer, 11.5 mm from the nozzle orifice, before entering the main scattering chamber. The beam was further collimated by a 1.4 mm dia. aperture, 30.0 mm from the skimmer. The distance from the second aperture to the surface was 56.1 mm, and the diameter of the N_2 beam at this position was 3.3 mm.

The samples were cut from natural single crystal pyrite cubes (Logrono, Spain) that were purchased from Ward's Natural Science. The as-received (100) faces of the pyrite samples were used. As the samples are naturally grown, there are macroscopic striations on the surfaces. Native oxides on the sample surfaces were removed by dipping the samples in a 1 M HCl solution for 5 min at room temperature, followed by a rinse with deoxygenated water. After cleaning, samples were immediately mounted on a sample manipulator in the main chamber of the molecular beam apparatus, and the chamber was evacuated to a base pressure of 2×10^{-7} Torr. Mounting of the sample was carried out by pressing the surface of the sample against a square stainless steel rim, with a 9×9 mm window, using a copper backing plate. With this setup, the sample was heated with the use of a cylindrical heater inserted into a hole in the copper plate, and the sample temperature was monitored with a type-K thermocouple that was screwed onto the stainless steel mount. The sample temperature could be held at any temperature from room temperature to slightly above 200 $^{\circ}\text{C}$. Samples were typically changed between exposures to the D-atom beam, as it was usually desirable to start with a pristine surface.

Time-of-flight (TOF) distributions were collected with the use of the chopper wheel. These are number density distributions as a function of time, $N(t)$, and these distributions may be integrated by summing $N(t)/t$ to obtain integrated flux.²⁵ Most TOF distributions were collected with mass-to-charge ratios, m/z , of 28 (N_2^+) and 36 (D_2S^+). The TOF distributions were generally collected with fixed incidence and detection angles. For the N_2 beam, the incidence angle was 45° with respect to the surface normal, and for the effusive (D-atom) beam, the incidence angle was 0° (normal incidence). The detection angle was 45° from normal, such that the total included angle for N_2 inelastic scattering was 90° and the total included angle for reactive scattering to produce D_2S was 45° .

In addition to detecting scattered products, post-exposure characterization was carried out on the sample surfaces. Surface morphology was characterized by field emission scanning electron microscopy (FE-SEM) using a Zeiss Supra 55VP Field Emission Scanning Electron Microscope and by atomic force microscopy (AFM) using a Digital Instruments NanoScope Dimensions atomic force microscope operated in contact mode. X-ray absorption spectroscopic techniques were used to investigate the chemical changes on the surfaces that were exposed to D and Ar atoms. XAS measurements were carried out at beamlines 7-3 and 4-3 of the Stanford Synchrotron Radiation Light Source (SSRL) under storage ring (SPEAR 3) conditions of 3 GeV energy and 200–120 mA current. BL7-3 is a 20-pole, 2 T Wiggler beam line equipped with a Si(220) downward reflecting, double-crystal monochromator. Data were collected in the energy range of 6900–8000 eV using an unfocused beam. Samples were mounted on a sample paddle at 45° relative to the incident beam and the 30-element Ge array detector with a Soller slit and a Mn (Z-1) filter. The energy windowing of

the detector was carefully adjusted to minimize the fluorescence signal due to scattering and other non-Fe K α emission sources. The beamline parameters were optimized at 8000 eV. Transmission experiments were carried out for reference pyrite powder ground and mixed with BN in an optimal composition for transmittance measurements as determined by using the SAMPLE4 program of EXAFSPAK.²⁷ BL4-3 is a 20-pole, 2.0 T Wiggler beam line with a liquid nitrogen-cooled, Si(111) double-crystal monochromator. Fe K-edge spectra were collected using an unfocused beam in a He-purged beam path with Lytle fluorescence and electron yield detectors. The incident photon energy was calibrated to the spectra of iron foil at the first inflection point of 7112 eV, which was estimated from the energy position of the first maximum of the first derivative along the rising edge. The data normalization including calibration and background subtraction was carried out using our Automated Data Reduction Protocol (ADRP)²⁸ and SixPACK²⁹ for XANES and EXAFS, respectively.

Results and Discussion

Figure 2A shows a representative TOF distribution of D₂S molecules ($m/z = 36$) that scattered from a near pristine pyrite surface after D atoms collided with it. In this TOF distribution, the raw signal can be fit with a curve that is derived from a Maxwell-Boltzmann distribution of product translational energies at the surface temperature of 100 °C.²⁵ This observation indicates that D₂S products desorb in thermal equilibrium with the surface. It is thus likely that the incident D atoms adsorbed on the surface and came into thermal equilibrium before or during the reaction to produce D₂S.

At the atomic level, the D atom may be trapped at an iron site or directly at a sulfur site. Reaction of a formally Fe^(II) site with a D atom can result in either formation of a formally Fe^(I) site and a D⁺ ion, or an Fe^(III) site with a bound D⁻ (hydride) ligand. Given that D₂S is the observed product, the reduced Fe site is more likely as the D⁺ ion needs to migrate to a nearby S atom and leave its electron behind on the Fe site. Direct hydrogenation of the persulfide ligand could result in reduction of the S-S bond order and formation of S₂D²⁻ radical anion. As indicated from an earlier study,¹⁶ creation of the (100) surface may cleave the persulfide bond, leaving behind a S⁻ radical anion. This relaxes to a terminal sulfide by oxidizing the adjacent Fe center. Reaction of a D atom with a dangling sulfide S is expected to result in a reduced Fe site coordinated by a sulfhydryl SD⁻ ligand. The arrival of the second D atom would provide further reduction of the formally Fe^(I) site or reduction of another Fe^(II) site and consequently after D⁺ migration the complete cleavage of the S-S bond and formation of the D₂S product.

The time dependence of D₂S product intensity calculated from integrating $N(t)/t$ over the flight time at $\theta_f = 45^\circ$ is shown in Fig. 2B.²⁵ Notably, in the first few minutes, the D₂S signal increases and then decreases, roughly exponentially, with exposure time. The initial increase can be attributed to sputtering or reactive scattering of exogenous contaminants from the surface that the acid wash and deoxygenated water rinse was unable to remove. Also, a thin layer of contamination may initially be present because the samples were transferred through air after cleaning and prior to their being mounted in the vacuum chamber. The decreasing D₂S signal indicates that the *in situ* generated fresh surface reacted with the beam of D atoms and clearly shows the depletion of surface accessible S atoms.

We used inelastic scattering with a supersonic beam of 17 kcal mol⁻¹ N₂ molecules to investigate the development of surface roughness as D atoms eroded the surface to produce D₂S. TOF distributions of N₂ collected after various durations of D-atom exposures are shown in Fig. 3A. The TOF distributions were collected for 22 minutes (200,000 pulses through the chopper wheel), with incidence (θ_i) and final (θ_f) angles of 45°. In each case, the TOF distribution of inelastically scattered N₂ was collected after a fresh pyrite surface was

exposed to the effusive D-atom beam for the indicated period of time and then the exposure was stopped. The TOF distributions for inelastically scattered N_2 typically exhibit two components, which can be described in terms of two limiting cases of thermal desorption (TD, slower component at longer flight times) and direct inelastic (IS, faster component at shorter flight times).^{25,26} In the TD process, the N_2 molecules desorb with a Maxwell-Boltzmann distribution of velocities corresponding to the surface temperature, perhaps after becoming momentarily trapped on the surface. In the IS process, the N_2 molecules scatter directly, after one or a few bounces, and only lose a fraction of their incidence kinetic energy on the surface. As seen in Fig. 3A, the IS component has a maximum at a flight time near 200 μs , and the TD component has a maximum near 400 μs . Before D-atom exposure, the IS component dominates, but as the D atoms bombard the surface for longer times, the IS component decreases and the TD component becomes dominant. The relative contributions of the IS and TD components to the scattered flux have been determined by standard means,^{25,26} and the ratio of TD to IS scattering is shown in Fig. 3B. After a small decrease resulting from removal of contaminants (see above), the ratio increases rapidly. The rise in the dominance of the TD component is consistent with an increasing surface roughness, which leads to enhanced multiple-bounce scattering at the surface and drives the N_2 molecules into thermal equilibrium with the surface. The increased surface roughness with D-atom exposure has been confirmed by FE-SEM and AFM of the exposed pyrite samples. FE-SEM and AFM images for pyrite surfaces exposed to D-atoms for 0, 5, and 270 minutes are shown in Fig. 4. These images clearly reveal surface roughening on a nanometer-size scale.

The potential effect of Ar atoms, which accompanied the D-atom beam, was investigated with an effusive beam produced from running the plasma source with pure Ar. Fresh pyrite samples were exposed to the pure Ar beam for various durations, and after a given duration, the exposure was stopped and a TOF distribution of inelastically scattered N_2 was collected (11 minutes, 100,000 pulses of the chopper wheel), in a manner analogous to that described above for exposures to the D-atom beam (which contained a mixture of D atoms, D_2 , and Ar). The TOF distributions of inelastically scattered N_2 are presented in Fig. 5. In contrast to the results with the D-atom beam, there is no visible change in the shape of the N_2 TOF distributions with exposure time. Therefore, the surface does not roughen when exposed to Ar alone. We thus conclude that Ar plays no role in the reaction at the surface or in the development of surface structure. These observations have also been confirmed by XAS measurements (see below), which show identical spectra for the control pyrite and the Ar-exposed pyrite surfaces. The surface roughness caused by exposure of pyrite to the D-atom beam, which also contained Ar, must therefore be the sole result of reactions of D atoms with the surface.

In order to obtain atomic-level information about both the electronic and geometric structures of the modified pyrite surfaces, we carried out X-ray absorption spectroscopic investigations at the Fe K-edge using different detection methods that probed the pyrite surface at various depths. Figure 6 summarizes two sets of XANES spectra of structurally well defined reference compounds of iron oxides and sulfides. The inset in Figure 6A illustrates the origin of spectral features as the Fe 1s core electrons are being excited into unoccupied Fe 3d and Fe 4p orbital-based bound states, giving rise to weak electric quadrupole and strong electric dipole allowed pre-edge and rising-edge transitions, respectively. As a result of the considerable difference in the Fe effective nuclear charges, the rising-edge features of more reduced $Fe^{(II)}$ compounds are shifted to lower energies relative to the more oxidized $Fe^{(III)}$ compounds. In Fig. 6A, the rising edge inflection point of magnetite (7124.7 eV) with a formal oxidation state of $Fe^{2.66+}$ is located proportionally in between those of the formally $Fe^{(II)}O$ (7118.9 eV) and $Fe^{(III)}_2O_3$ (7127.4 eV) spectra. The analogous rising-edge inflection points of the corresponding sulfides, seen in Fig. 6B, are

located at 7117.8 eV and 7126.7 eV for freshly precipitated $\text{Fe}^{\text{(II)}}\text{S}$ and $\text{Fe}^{\text{(III)}}_2\text{S}_3$ samples. The sensitivity of these XANES measurements to the effective oxidation state of the Fe centers is well demonstrated by the difference between the pyrite ($\text{Fe}^{\text{(II)}}\text{S}_2$) and $\text{Fe}^{\text{(II)}}\text{S}$ spectra. Due to the presence of the S-S bond of persulfide ligand in pyrite, the S atoms cannot donate as much electron density to the Fe sites as in the case of the dianionic sulfide in $\text{Fe}^{\text{(II)}}\text{S}$ and thus the Fe sites remain effectively more oxidized as reflected by the rising-edge position at 7118.4 eV. The effective oxidation state of the Fe in pyrite is slightly higher than in ferrous sulfide precipitate. The same trend is valid for comparing the rising edge inflection points of the spectra of $\text{Fe}^{\text{(II)}}\text{S}$ (7117.8 eV) and $\text{Fe}^{\text{(II)}}\text{O}$ (7118.9 eV). Due to the higher electronegativity of O than S in addition to the less favorable overlap of Fe 3d and O 2p vs. S 3p orbitals, the metal-ligand bonding in oxides is generally less covalent than in sulfides and thus the Fe will be effectively more oxidized in $\text{Fe}^{\text{(II)}}\text{O}$ as reflected by the approximately +1 eV shift of the rising edge.

Figure 7 summarizes the XANES data collected in fluorescence detection mode for pyrite (100) surfaces as a function of exposure time (Fig. 7A) and surface temperature (Fig. 7B) at constant room temperature and 4 hours exposure time, respectively. Significant spectral changes were only observed on surfaces that were held at elevated temperatures when they were exposed to D atoms. For these samples, the rising edge was shifted toward lower energies and differences were observed in the post-edge energy region (above 7120 eV). The former corresponds to the appearance of more reduced Fe sites than those in pyrite, while the latter is an indication of changes in the atomic structure of the Fe sites.

Much more dramatic differences between samples that were exposed at different temperatures can be observed in the spectra shown in Figs. 8A and 8B, which were collected in electron-yield detection mode. These spectra conclusively show the appearance of a highly reduced Fe phase as well as a complete change in the radial distributions of atoms around the Fe absorbers. The considerable difference between the fluorescence and electron-yield data is the result of the different probe depths of these detection methods. The approximate escape depth for fluorescence radiation is about 200 Å, while it is only about 10 Å for the electron-yield.²³ Thus, Figs. 7 and 8 are indicative of the formation of layered Fe/S phases on the top of bulk pyrite that vary in the degree of reduced state of Fe. Based on the depletion of surface accessible S atoms observed in Fig. 2, the top layer is expected to be fully reduced metallic Fe.

The full energy range XAS spectrum in Fig. 9A, collected in electron-yield mode, and the Fourier-transformed EXAFS region in Fig. 9B above the ionization threshold of the Fe 1s core electrons (approximate Fe 1s core ionization energy position indicated by a dashed line in Fig. 9A) allow for the unambiguous assignment of the top layer. It is the same layer as the outer layer of metallic iron powder. In addition to the bulk metallic iron, we anticipate a thin passivating layer of iron oxide, resulting from exposure to air upon sample removal from the vacuum chamber where the exposures were conducted. Note that the XAS data were collected with the samples in air.

While this passivating layer is an artifact in our measurements, it is useful because it preserves the interfacial layer between the bulk pyrite and the top layer of metallic iron. Figure 10 provides a first glimpse into the electronic structure of this interfacial layer, which was probed by fluorescence detection. In comparison to the metallic Fe and the bulk pyrite, the effective iron oxidation state of this layer is in between that of $\text{Fe}^{\text{(II)}}$ and $\text{Fe}^{(0)}$. While the crossing of spectra for the metallic Fe and pyrite at 7117, 7122, and 7133 eV offers a likely possibility for isosbestic points, no combination of these two spectra can reproduce the XANES of the interfacial layer. We tentatively assign the formal oxidation state of this intermediate layer to $\text{Fe}^{\text{(I)}}$ with formal stoichiometry of Fe_2S . The findings from Fe K-edge

XANES and EXAFS analysis thus reveal layered Fe-S phases of the D-atom modified pyrite surface. A pictorial summary is shown in Fig. 11.

The presence of a reduced Fe-S phase is remarkable because of its catalytic implications. The catalytically active site of FeFe-hydrogenase, the H-cluster,³⁰ containing a complex Fe-S cluster can adopt formal oxidation states that are similar to the observed reduced intermediate surface layer of pyrite. The H-cluster is one of the most active catalytic centers for the reversible evolution and uptake of H₂ at close to diffusion limited rates.^{31, 32} Furthermore, the catalytically active Fe-S cluster of nitrogenase, FeMo-co undergoes three or four electron reduction before the N₂ substrate can bind and then it is reduced to NH₃ with concomitant H₂ formation. Although experimentally not yet shown, it is plausible from electron counting that one or perhaps more Fe sites of the FeMo-co cluster reach low valence, reduced Fe sites during the catalytic cycle. One of the inhibitors of biological nitrogen fixation and hydrogen uptake/evolution reactions is CO, which also prefers to bind to reduced or metallic Fe sites, as opposed to oxidized Fe(II) or Fe(III) sites. The analogy of the electronic structure of the reduced Fe-S phase to the biologically relevant and important catalytic conversion of small, inert molecules, such as N₂ and H₂, makes the reduced Fe-S phase a highly promising catalytic system.

In addition to possible technological implications, the discovery of a unique Fe^(I)₂S phase is relevant to the NASA Astrobiology Institute's Mission (Roadmap Objective 3 and 7,³³) as it relates to the interfacial processes between exposed Fe-S containing rocks of the lithosphere and activated molecules from the atmosphere. It is likely that H₂O, CH₄, and H₂ molecules of the Hadean atmosphere could provide a considerable source of simple radicals under highly ionizing ultraviolet radiation and hence the exposed mineral surfaces might have undergone modifications to generate reduced metal sites that were desirable for activation of other atmospheric molecules such as N₂, NO, CO/CO₂, etc. Formation of a reduced Fe-S phase that may be an active catalytic surface is a credible scenario for prebiotic amino acid formation from simple molecules, such as N₂, H₂O, and CO₂.

Conclusion

From combined beam-surface scattering and X-ray absorption spectroscopic experiments we have demonstrated that a pyrite surface may react with deuterium (or hydrogen) atoms to produce volatile D₂S, leaving a roughened and reduced surface. We found that D atoms react with a pyrite surface at elevated temperatures (100 °C and above) and produce D₂S product with a thermal distribution of speeds. The yield of D₂S decreases exponentially with exposure time suggesting the depletion of surface accessible S atoms. The inelastic scattering dynamics of N₂ on modified surfaces indicated that the surface became significantly rougher during the exposure, which was also in agreement with post-exposure characterization by FE-SEM and AFM. From control experiments using an Ar beam, we unambiguously assigned the source of the increased nanoscale surface roughness as the chemical reaction of D with S atoms and consequently the formation of a surface rich in metallic iron. Notably, the rougher surface has a larger surface to volume ratio, which is an important factor in heterogeneous catalysis. Atomic scale characterization of the surfaces using Fe K-edge X-ray absorption spectroscopic measurements concluded that the top surface of the modified samples is identical to that of the metallic Fe. The intermediate layer beneath this top layer and above the bulk pyrite has been determined to contain a previously unknown reduced Fe-S phase, which tentatively was assigned as amorphous Fe^(I)₂S. This reduced Fe-S phase is likely to be catalytically active, thus suggesting further studies of its utility and providing insight into potentially important steps in the prebiotic formation of amino acids.

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Figure 1. Pictorial diagram of the molecular beam apparatus, configured for beam-surface scattering experiments.

Figure 2.

(A) Representative time-of-flight distribution of scattered D_2S product detected at a final angle, θ_f , of 45° when D-atoms bombarded a pyrite surface with an incidence angle, θ_i of 0° , with the surface temperature held at $100^\circ C$. (B) Integrated intensity of D_2S signal as a function of exposure time to the D-atom beam, with $\theta_i = 0^\circ$ and $\theta_f = 45^\circ$.

Figure 3.

(A) Time-of-flight distributions of inelastically scattered N_2 , with $\theta_i = \theta_f = 45^\circ$, collected after the D-atom exposure durations indicated. Each exposure began with a pristine pyrite sample. (B) Intensity ratio of thermal desorption (TD) to inelastic scattering (IS) obtained from the time-of-flight distributions in (A).

Figure 4.

(A₁ – C₁) FE-SEM images of 2 μm × 2 μm regions of a pristine pyrite surface and pyrite surfaces exposed for 5 and 270 minutes to the D-atom beam. The surface temperature was 100 °C. (A₂ – C₂) AFM images of the same samples in A₁ – C₁. For A₂ and B₂, the image size is 5 μm × 5 μm and the *z* scale is 60 nm. For C₂, the image size is 20 μm × 20 μm, and the *z* scale is 300 nm. RMS roughnesses are 4 nm (A₂), 14 nm (B₂), and 100 nm (C₂).

Figure 5.

(A) Time-of-flight distributions of inelastically scattered Ar, with $\theta_i = \theta_f = 45^\circ$, collected after the exposure durations indicated. Each exposure began with a pristine pyrite sample. (B) Intensity ratio of thermal desorption (TD) to inelastic scattering (IS) obtained from the time-of-flight distributions in (A).

Figure 6. Reference Fe K-edge X-ray absorption near-edge spectra of reference (A) iron oxides and (B) sulfides..

Figure 7.

Fe K-edge X-ray absorption near-edge spectra collected in fluorescence yield mode for pyrite (100) exposed to the D-atom beam for the indicated durations at (A) room temperature and (B) elevated temperatures.

Figure 8.

Fe K-edge X-ray absorption near-edge spectra collected in electron yield mode for pyrite (100) exposed to the D-atom beam for the indicated durations at (A) room temperature and (B) elevated temperatures.

Figure 9. Fe K-edge extended X-ray absorption fine-structure analysis of the electron yield data of the 4-hr-exposed pyrite (100) sample: (A) in energy space and (B) in momentum (k) space.

Figure 10. Comparison of the K-edge X-ray absorption near-edge spectra for metallic Fe and a pyrite (100) surface that was exposed to the D-atom beam for 4 hr while being held at 200 °C.

Figure 11. Pictorial illustration of the layered Fe-S phases of a pyrite (100) surface that has been reduced by exposure to the D-atom beam at elevated temperatures of 100 – 200 °C.