EXPERIMENTAL METHODS

Figure 1 depicts a schematic of the high-pressure apparatus intimately attached to the UHV chamber. Pyrite samples attached to the end of the transfer probe were withdrawn from the UHV environment into an intermediate pressure cell that was evacuated by a turbomolecular pump to $10^{-7}$ Pa. The transfer probe slid through Teflon seals so that the intermediate cell was never directly exposed to the UHV chamber. Once the sample was within the intermediate cell and isolated from UHV by a gate valve the pressure of the UHV chamber was increased to 1 bar with dry nitrogen. A mechanical pincer was used to transport the sample to the reaction cell. After well-controlled heating was achieved by pressing a current through the Ta backing of the pyrite crystal. Sample temperatures were monitored with a type-K thermocouple that was spot-welded to the top edge of the sample holder.

Experiments were conducted in an integrated ultra-high vacuum/high-pressure apparatus. In short, samples could be scrutinized with surface science techniques, transferred to a reaction cell, exposed to liquid or gas, and transferred back to UHV for further analysis. At no time during this process was the sample exposed to the ambient atmosphere.

UHV was obtained with cryogenic and turbomolecular pumps and the typical working base pressure of the UHV chamber was $6 \times 10^{-7}$ Pa. X-ray photoelectron data were obtained with unmonochromatized MgKα radiation (1253.6 eV) as the excitation source and double pass cylindrical mirror analyzer (CMA, pass energy of 25 eV). 2p<sup>3/2</sup> and 2p<sup>1/2</sup> contributions to each S 2p doublet used to fit spectra in this contribution have been constrained by a 2:1 peak area ratio, 1.8 eV separation, and 1.5 eV FWHM.

Experimental observation is due to a higher concentration of under-coordinated Fe in the outermost surface of FeS<sub>2</sub> (111), relative to FeS<sub>2</sub> (100). The structure of a surface plays a key role in determining its ability to facilitate heterogeneous chemistry. Often this dependence of reactivity on structure can be quite dramatic. The rate of ammonia formation from its elements on an Fe catalyst, for example, can vary over an order of magnitude depending on the structure of the outermost surface of that metal exposed to the reactant gas (Strongin et al. 1987). One might make the argument that the dependence of structure and reactivity for an alloy or mineral is even more complex in that different crystallographic planes of these types of materials not only expose different geometries, but also different atomic compositions. With regard to mineral chemistry, we argue here that it is important to develop the structure-reactivity relationships, because the geometric structure and atomic composition of a mineral surface is expected to play a major role in its interaction with the environment. Certainly, understanding this relationship is required for the accurate modeling of mineral surface reactivity.

Research presented here addresses the effect of surface structure on the oxidation of pyrite. Pyrite can occur in 85 different crystal forms (Dana 1903). Most natural pyrite, however, occurs in one of three crystal forms {001}, {111}, and {210} (Murowchick and Barnes 1987). Here we examine surface reactivity between the (100) and (111) crystal faces that dominate the {001} and {111} forms, respectively. Our X-ray photoelectron spectroscopy (XPS) results show that the oxidation of the outermost surface of the (111) crystallographic plane in a H<sub>2</sub>O or H<sub>2</sub>O/O<sub>2</sub> environment proceeded to a further extent than on the (100) plane.

**ABSTRACT**

The interaction of atomically clean (100) and (111) crystallographic planes of FeS<sub>2</sub> with H<sub>2</sub>O vapor, O<sub>2</sub>, and a H<sub>2</sub>O/O<sub>2</sub> mixture was investigated. A combined high pressure/ultra-high vacuum (UHV) apparatus allowed the surfaces to be reacted at environmentally relevant pressures and studied with X-ray photoelectron spectroscopy (XPS) without exposure to the atmosphere. Neither surface exhibited significant reaction in pure O<sub>2</sub>. Exposure of FeS<sub>2</sub>(111) to H<sub>2</sub>O vapor resulted in significant oxidation, but under these same experimental conditions FeS<sub>2</sub>(100) exhibited a much smaller amount of oxidation. It is suspected that on FeS<sub>2</sub>(100), H<sub>2</sub>O only reacted on nonstoichiometric regions (i.e., defects). Both surfaces showed substantial reaction in H<sub>2</sub>O/O<sub>2</sub>. The amount of FeS<sub>2</sub>(100) and FeS<sub>2</sub>(111) oxidation in the H<sub>2</sub>O/O<sub>2</sub> mixture was more than simply the sum of the reaction observed individually in pure O<sub>2</sub> and H<sub>2</sub>O. This result suggests that there is a synergy between H<sub>2</sub>O and O<sub>2</sub> in oxidizing pyrite. In all cases, the amount of oxidation that occurred on FeS<sub>2</sub>(111) was greater than on FeS<sub>2</sub>(100). We believe that this experimental observation is due to a higher concentration of under-coordinated Fe in the outermost surface of FeS<sub>2</sub>(111), relative to FeS<sub>2</sub>(100).

**INTRODUCTION**

The structure of a surface plays a key role in determining its ability to facilitate heterogeneous chemistry. Often this dependence of reactivity on structure can be quite dramatic. The rate of ammonia formation from its elements on an Fe catalyst, for example, can vary over an order of magnitude depending on the structure of the outermost surface of that metal exposed to the reactant gas (Strongin et al. 1987). One might make the argument that the dependence of structure and reactivity for an alloy or mineral is even more complex in that different crystallographic planes of these types of materials not only expose different geometries, but also different atomic compositions. With regard to mineral chemistry, we argue here that it is important to develop the structure-reactivity relationships, because the geometric structure and atomic composition of a mineral surface is expected to play a major role in its interaction with the environment. Certainly, understanding this relationship is required for the accurate modeling of mineral surface reactivity.

Research presented here addresses the effect of surface structure on the oxidation of pyrite. Pyrite can occur in 85 different crystal forms (Dana 1903). Most natural pyrite, however, occurs in one of three crystal forms {001}, {111}, and {210} (Murowchick and Barnes 1987). Here we examine surface reactivity between the (100) and (111) crystal faces that dominate the {001} and {111} forms, respectively. Our X-ray photoelectron spectroscopy (XPS) results show that the oxidation of the outermost surface of the (111) crystallographic plane in a H<sub>2</sub>O or H<sub>2</sub>O/O<sub>2</sub> environment proceeded to a further extent than on the (100) plane.

We studied (100) and (111) planes of natural pyrite from Longrono, Spain, and Turkey, respectively. Samples were typically 2 mm thick plates with areas close to ~1 cm<sup>2</sup>. All samples used began as “as-grown” surfaces.

**EXPERIMENTAL METHODS**

Samples for study were prepared by a combination of ion bom-