XAS Investigations of Higher Oxidation States of Fe

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Introduction

Since the Viking missions of the 1970s, the existence of life on the surface of Mars has been doubted, in part because of the apparent absence of organic matter, which should have been delivered via meteorites and comets.[1] The absence of organic matter was postulated to be due to the chemical reactivity of the surface material. Results from the Viking experiments suggested the presence of a strong oxidant, or more likely, several strong oxidants, on the Martian surface.[1,2] Such oxidant(s) would be incompatible with organic matter, thus making the presence of life on the Martian surface unlikely. In the years since the Viking experiments, considerable effort has gone into the search for oxidants that can mimic the Viking results. However, no suggestions have emerged that are consistent with the Viking results.

One potential group of oxidants that curiously has been overlooked (considering the abundance of iron on the surface of Mars) is that of the higher oxidation states of iron, including Fe(IV), Fe(V), and Fe(VI). Fe(VI), in the form of ferrate [FeO_4^{2-}] salts, even though an extremely strong oxidant, is rather stable in alkaline solutions and as dry salts when incorporated with several cations. The formation of ferrate, as a purple by-product in some strongly alkaline solutions, was first described as early as 1702.[3] More recently, there has been interest in ferrates as an oxidizing agent for organic synthesis[4] and a material for rechargeable alkaline batteries of high capacity.[5] Additionally, a major feature of the NASA space program is the Mars Sample Return mission. When such samples are returned, it will be possible to obtain high-resolution Mossbauer, EPR, and XAFS spectra from them. The objectives of this study were 1) to investigate the application of XANES to detect a signature indicative of Fe in a 6+ valence state, and 2) to investigate the average local chemical environment about Fe in 2+, 3+, 4+, and 6+ valence states in both solid and liquid phases.

Methods

In this study, crystalline potassium ferrate was prepared by a previously described procedure.[4] Barium ferrate was prepared in a similar fashion, except that commercial bleach (sodium hypochlorite) was applied instead of potassium hypochlorite, and barium oxide was added at the last stage instead of potassium hydroxide. The Fe(6) solution used in this study was taken from the precursor solution before precipitation to the solid $BaFeO_4$ sample.

All XAFS measurements for these studies were performed at the Materials Research Collaborative Access Team (MRCAT) insertion device beamline.[6] The beamline optics and setup parameters for the Fe K-edge XAFS studies were as follows. The fluorescence signals from the Fe(2), Fe(3), and Fe(6) solutions were collected with a Lytle detector (argon fill gas), in the Stern-Heald configuration,[7] using a Mn(3) filter. The transmission and fluorescence signals were collected for the solid-phase samples. The incident ion chamber was filled with a free-flowing 90%:10% He:N_2 mixture. The transmission ion chamber was filled with 100% free-flowing N_2 gas. The Si (111) reflection of the double-crystal monochromator, running on the first harmonic of the beamline undulator, was used. The energy output of the monochromator was calibrated with an Fe foil with edge energy (7112 eV) set equal to the maximum of the first derivative of the transmission XANES data. The calibration of the monochromator was continuously monitored by measuring the scattered radiation through an iron foil into a reference ion chamber.[8] Linearity tests[9] on all samples indicated less than 0.5% nonlinearity for at least a 50% attenuation of the incident x-ray beam intensity. Tape mounts were not used for any samples in order to reduce the interactions between the oxidizing Fe(6) and the reducing organics in the tape adhesive. Rather, solution samples were contained in nonreacting polypropylene bags, and solids were pressed into a pellet and contained within customized airtight kapton film bags.

The theoretical $\chi(k)$ for all data were constructed using the program FEFF7.[10] The data were analyzed using the codes from the UWXAFS package.[11] The error analysis and the goodness-of-fit parameters were calculated by the fitting routine FEFFIT.[12] Additionally, to account for anharmonic effects, cumulant expansions[13] were used to fit the first-shell data for all solutions.

Additional information pertaining to the sample preparation, data analysis, and discussion of these XAFS results has been published previously.[14,15]

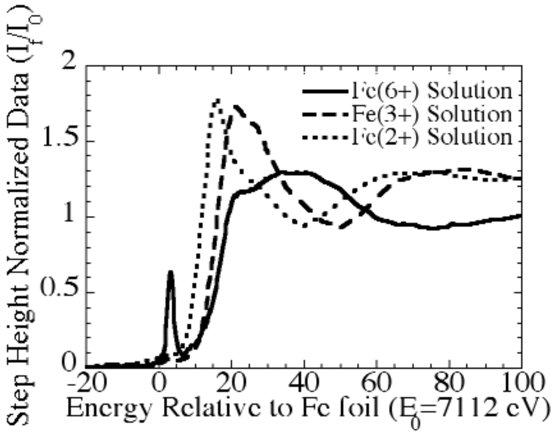

FIG. 1. Step height normalized Fe XANES data for Fe(2), Fe(3), and Fe(6) solutions.

Results And Discussion

Figure 1 shows the Fe XANES for solutions of single-phase Fe(2), Fe(3), and Fe(6). The relative energy shifts are consistent with previous studies indicating a 2-4 eV difference between edge positions for Fe(2) and Fe(3).[16] The XANES for the Fe(6) solution shows a well-defined pre-edge peak similar to that observed for Cr(6), consistent with tetrahedral coordination and *p-d* electron orbital mixing. Table I lists the Fe EXAFS fitting results for the samples measured in this study. Fitting results are consistent with

Table I. Results of first coordination shell fitting parameters for Fe EXAFS data from different Fe solutions and solids.

Sample	First Shell Oxygen CN	Radial Distance (Å)	σ^2 (Å^2)
Fe 6+ solution	3.9 ± 0.9	1.58 ± 0.01	0.007 ± 0.002
Fe 6+ mixed (3/6) solid Potassium ferrate	3.6 ± 0.6	1.63 ± 0.06	0.009 ± 0.002
Fe 6+ solid Barium ferrate	3.7 ± 0.8	1.61 ± 0.02	0.006 ± 0.001
Fe 3+ solution	6.3 ± 0.4	2.00 ± 0.01	0.008 ± 0.001
Fe 2+ solution	7.2 ± 1.2	2.10 ± 0.02	0.014 ± 0.004
Fe 4+ mixed (3/4/6) solid	6.1 ± 2.2	1.80 ± 0.02	0.010 ± 0.006

tetrahedral coordination of oxygen to iron for Fe(6) and octahedral [or greater coordination for Fe(2)] of oxygen to iron for Fe(4) and Fe(3).

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