Journal of
Synchrotron
Radiation

ISSN 0909-0495

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Recent attention has been given to a reexamination of results from the early Viking missions to Mars that suggested the presence of one or more strong oxidants in Martian soil. Since Fe is one of the main constituents of the Martian surface and Fe(VI) is known to be a highly reactive, strong oxidant, we have made XANES and EXAFS measurements of Fe(II), Fe(III), Fe(IV), and Fe(VI) in solid and solution forms. Results from these studies indicate a preedge XANES feature from Fe(VI) samples similar to that commonly seen from Cr(VI) samples. Results of first shell analysis indicate a linear relationship between the Fe-O bondlength and Fe valence state.

Keywords: astrobiology, biosignature, biogeochemistry, environmental science, XAFS

1. Introduction

Since the Viking missions of the 1970's, 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 (Klein, 1978). 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 (Klein, 1978; Zent and McKay, 1994). 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 (Stahl, 1715). More recently, there has been interest in ferrates as an oxidizing agent for organic synthesis (Delaude, and Laszlo, 1996) and a material for rechargeable alkaline batteries of high capacity (Licht, Wang, and Ghosh, 1999). 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. These experiments have been performed to investigate the feasibility of using the XAS technique for the study of Fe and its valence states in samples from 1) the proposed NASA Mars soil sample return mission and 2) Astrobiology and biogeochemistry investigations of "life in extreme environments" here on earth where the valence state of Fe can be indicative of different biogeochemical and life processes.

2. Methods

In this study, crystalline potassium ferrate was prepared by a previously-described procedure (Delaude and Laszlo, 1996). 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. Results from other characterization studies (Tsapin et al, 2000; Kopelev, Perfiliev, and Kiselev, 1992) of the solid samples described in this paper indicate 1) a pure phase $BaFeO_4$ Fe(6) sample, 2) a mixed $KFeO_2$ / K_2FeO_4 [50 % Fe(3) / 50% Fe(6)] sample, and 3) a mixed $KFeO_2$ / K_2FeO_3 / K_2FeO_4 [20% Fe(3) / 35% Fe(4) / 45% Fe(6)] sample. 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 beam line (Segre *et al.* 2000). The beams line 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 (Stern and Heald, 1979), utilizing 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 beam line undulator, was utilized. 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 (Cross, 1999). Linearity tests (Kemner *et al.* 1994) 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 (Zabinski *et al*., 1995.) The data were analyzed using the codes from the UWXAFS package (Stern, et al. 1995). The error analysis and the goodness-of-fit parameters were calculated by the fitting routine FEFFIT (Newville, 1994). Additionally, to account for anharmonic effects, cumulant expansions (Bunker, 1983) were used to fit the first shell data for all solutions. Quoted error bars in the fitted variables include correlations of the fitted variables as well as systematic errors from the experimental XAFS measurement. The error bars do not include errors introduced due to inaccurate determination of the relative amounts of different Fe valence states in the solids by other experimental methods. In order to reduce the number of fitting parameters determined during a fit, for the mixed-valence solids, the relative percentages of each phase were held at the values determined by other measurements already discussed. Results of first shell analysis of the EXAFS data are listed in Table I. Only the results for the specified components of the mixed-valence solids are listed here. Results for the other components of the mixed-valence solids were consistent with the single phase results listed in Table I.

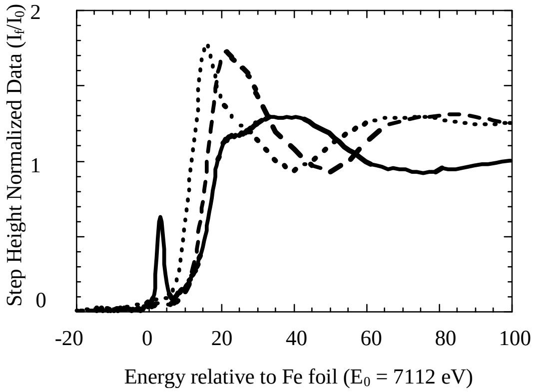

Figure 1
Step height normalized Fe XANES data for Fe(2), Fe(3), and Fe(6) solutions. Full line – Fe(6+) solution; dashed line – Fe(3+) solution; dotted line – Fe(2+) solution.

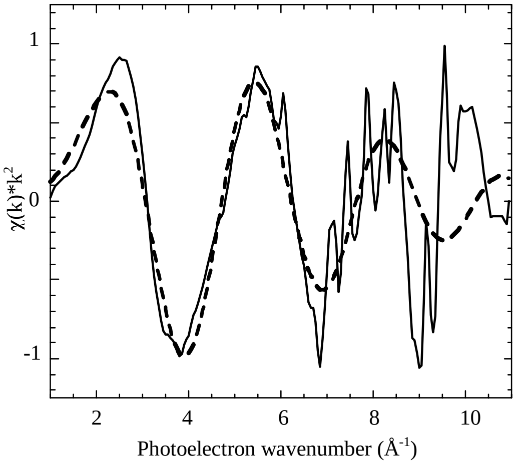

Figure 2
Illustration of quality of k^2 –weighted $\chi(k)$ data from Fe(6) solution (solid line) and fit to Fourier filtered first coordination shell data (dashed line).

Table 1
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

3. 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) (Waychunas, et al. 1983). 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. Because the number of unoccupied electron orbitals for Cr(6) and Fe(6) are 10 and 8 respectively, one would expect the amplitude of the pre-edge peak to be slightly larger for Cr(6) ions in solution than it is for Fe(6) ions in solution. The intensity of the step-height normalized pre-edge feature for Cr(6) is typically ~1. Thus, the amplitude of the pre-edge peak for Fe(6) would be expected to be slightly less than 1. Although this is only a crude and qualitative observation and near neighbor distortions of Fe-O and Cr-O distances have been shown to be important effects in determining the amplitude of such pre edge peak amplitudes (Waychunas et al., 1983), our experimentally measured amplitude of 0.64 is in agreement with these approximations. Presently, studies of additional Fe(6) compounds are underway to determine a more quantitative explanation of this observed pre-edge feature.

Figure 2 shows the quality of the Fe(6) solution EXAFS and the fit to the first shell frequency from the Fe-O coordination. Table I lists the Fe EXAFS fitting results for the samples measured in this study. Fitting results are consistent with 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). Figure 3 illustrates a linear fit (R=0.995) to the Fe-O bondlength results versus iron valence. These results indicate that the Fe-O bondlength is linearly related to the different valence states of iron regardless of whether the Fe is four- or six-fold coordinated.

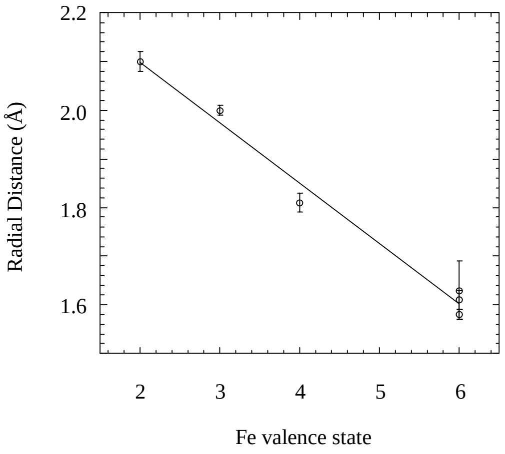

Figure 3
Plot of average Fe-O bondlength versus iron valence state and linear fit of the data.

Attempts were made to fit a higher coordination shell for the liquid Fe(6) sample data. Results from the analysis of the EXAFS data indicate the presence of an atom in the second coordination shell around the iron. However, because of the limited range of high quality data available for analysis, the identity of the atom could not be definitely determined. Equally good fits result with an Fe-Fe (indicative of a diferrate entity in the solution) distance of 2.58 Å or an Fe-Na (indicative of the counter ion from the sodium hypochlorite used to produce the ferrate solution) distance of 2.47 Å.

4. Conclusions

Results from these experiments indicate that Fe XANES is a good method for identifying the presence of Fe(6) in a sample. It has been shown that, for the samples measured in this study, the Fe-O bondlength is linearly related to the iron valence regardless of the Fe-O coordination number (consistent with valence–dependent ionic radii tables). Although Fe XAFS has been shown to be a powerful technique for investigating systems with Fe(2) and Fe(3), it now has been demonstrated that it is also a powerful technique for investigating systems where Fe(4) or Fe(6) may exist. This may prove to be very powerful for investigating biogeochemical systems in extreme environments such as alkaline lakes where the pH is typically greater than 10, a required condition for the presence of solvated Fe(6). Finally, XAFS investigations of Fe(6) may also be valuable when studying US DOE high-level waste tanks where the pH values typically greatly exceed 10.

Support was provided by the U.S. Department of Energy's Office of Biological and Environmental Research NABIR program and Argonne National Laboratory LDRD funds. Use of MR-CAT sector at the APS was supported by the U.S. Department of Energy, Basic Energy Science, Office of Science, under contract No. W-31-109-ENG-38. This work was performed, in part, under contract with NASA, grant 100483.344.50.34.01 and was supported by the DRDF grant 100656-00888.

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Received 31 July 2000 • Accepted 21 December 2000