EVIDENCE FOR COORDINATION AND REDOX CHANGES OF IRON IN SHOCKED FELDSPAR FROM SYNCHROTRON microXANES.

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Introduction: Shock modification of feldspar has been documented and experimentally reproduced in many studies since the recognition of maskelynite in Shergotty (1). Experimentally shocked feldspar samples have been well studied using chemical and crystallographic techniques (2-4). The crystallographic, site-specific characterization of major and minor elements is less well documented. We present early x-ray absorption (XAS) spectral data for a suite of albitite samples (5,6) that were experimentally shocked at pressures between 17 and 50 Gpa.

Method: The experimental shock methods are described by [7]. The samples are about 98-99% fine grained albite with minor muscovite, zircon and Y-rich phosphate. Synchrotron microXANES spectra were acquired using the x-ray microprobe at the National Synchrotron Light Source beamline X26A using the methods of [8] and Fe^{3+} and Fe^{2+} feldspar end members for calibration.

Several XANES spectra were acquired on 15x20 μm spots on each of 6 small chips of shocked albitite that were impregnated with epoxy and polished.

Table 1: Sample pressures and selected spectra.

Sample	Gpa	$Fe^{3+}/\Sigma Fe$	NSLS ID
3315	17	0.75-0.99	629.032
3311	25.5	0.62-0.77	608.102
3312	29	0.65-0.70	608.104
3319	34.8	0.62-0.69	629.033
3320	44.6	0.62-0.65	629.035
3316	50	0.40-0.65	629.036

Results: The Fe content of the albite is very low, (400-1000 ppm), but there is sufficient Fe present to permit usable XANES spectra to be obtained with approximately 2 hour counting times for each spectrum. In Figure 1, XANES spectra of 5 of the 6 shocked samples are similar except for changes in their pre-edge features. Because the Fe content of this feldspar is very low, secondary fluorescence of adjacent muscovite by the scattered x-ray beam must be avoided. This was a problem in our earlier work on shocked anorthosites [9] where impurities were ubiquitous and such contamination was generally unavoidable. The main edge shapes of the spectra in Figure 1 provide a check for interference by muscovite, as the main edge shape of muscovite shows clear subpeaks that are absent in these spectra. The data *in this study* are therefore believed to be pure feldspar spectra. The main edge of the 50 Gpa spectrum is shifted ~1-2eV toward lower energy than the others.

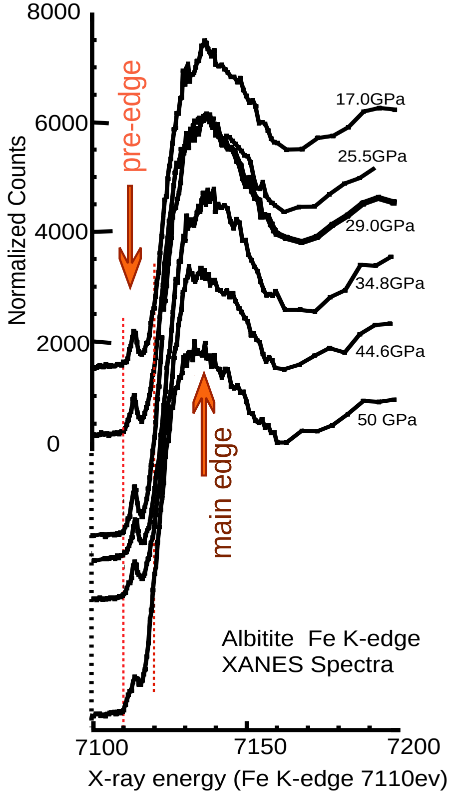

Figure 1: Fe K-edge XANES spectra for shocked albitite. Spectra are separated vertically to show features of individual spectra.

Results from two different analytical sessions are consistent with a significant decrease in the *apparent* $Fe^{3+}/\Sigma Fe$ with increasing shock pressure (0.8-1.0 at 17 Gpa to 0.4-0.65 at 50 Gpa.). (Figure 2). However, the detailed structure of the pre-edges from the albitite reveals that Fe coordination is also changing as a function of pressure (Figure 3).

Fe usually occurs in albite as Fe^{3+} substituting for Al in tetrahedral (IV) coordination.

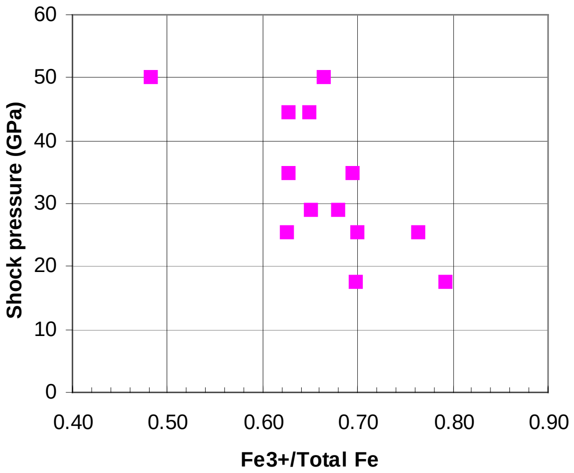

Figure 2: Variation of *apparent* $Fe^{3+}/\Sigma Fe$ with shock pressure for spectra in nsls608 session.

A typical XANES spectrum (background corrected) of $^{IV}Fe^{3+}$ is shown above the shocked albitite spectra in Figure 3 for comparison. This IV pre-edge envelope has an intense near-Gaussian shape, consistent with the asymmetrical distribution of oxygen atoms around ^{IV}Fe. When Fe enters a more symmetrical octahedral (VI) site, the typical XANES pre-edge envelope has a broad low intensity shape (Bottom spectrum in Figure 3 provides example of $^{VI}Fe^{2+}$).The observed peak broadening and decrease in overall pre-edge intensity as shock pressure increases are consistent with a change in Fe^{3+} coordination from IV to VI with pressure. At the highest pressure (50 GPa) the enhanced shoulder to the peak envelope at ~7112 eV may be the result of either increasing $^{IV}Fe^{2+}$ OR $^{VI}Fe^{3+}$ & Fe^{2+}. The overall broadening in all spectra is strongly suggestive of coordination changes. In addition, the shift of the 50 Gpa main edge spectrum toward lower energy is consistent with shock-induced reduction of the original Fe^{3+} in the albite.

Discussion: The apparent reduction of Fe and changes in the coordination of the Fe in feldspar can be used as indicators of shock intensity (at a submillimeter scale) in natural samples. Nanophase metal in shock-melted lunar agglutinates is well known as is the increasing coordination number of elements such as Si with increasing static pressure.

The present (preliminary) data are suggestive that both reduction and coordination chage can be observed directly in shocked feldspar from meteorites and other shocked materials, although further measurement will need to be done to elucidate the relative roles of redox and coordination changes

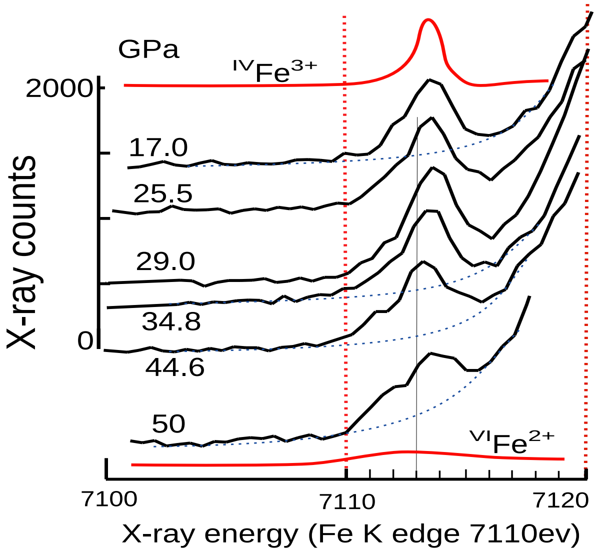

Figure 3: Details of albitite pre-edges with typical $^{IV}Fe^{3+}$ and $^{VI}Fe^{2+}$ for comparison.

Distinguishing the relative importance of *in situ* reduction and coordination changes of the Fe requires further spectral data and measurements on a variety of shocked feldspars containing more Fe. The most significant changes appear to be occurring at the highest shock pressures and perhaps reflect the change from shock-disordered feldspar (maskelynite) to shock-melted feldspar. Breaking the tetrahedral Fe bonds of the albite, as a result of melting, permits more complete reorganization of the Fe sites to octahedral coordination as might be expected in very high pressure regimes. The formation of higher symmetry octahedral Fe as a result of shock melting is in stark contrast to the decreasing symmetry (from VI to V and IV) of transition metals in many melts formed by high temperature melting.

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