	Experiment title: Valence and spin states of iron in silicate perovskite and post-perovskite with 75% FeSiO3	Experiment number: ES-144
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Report:

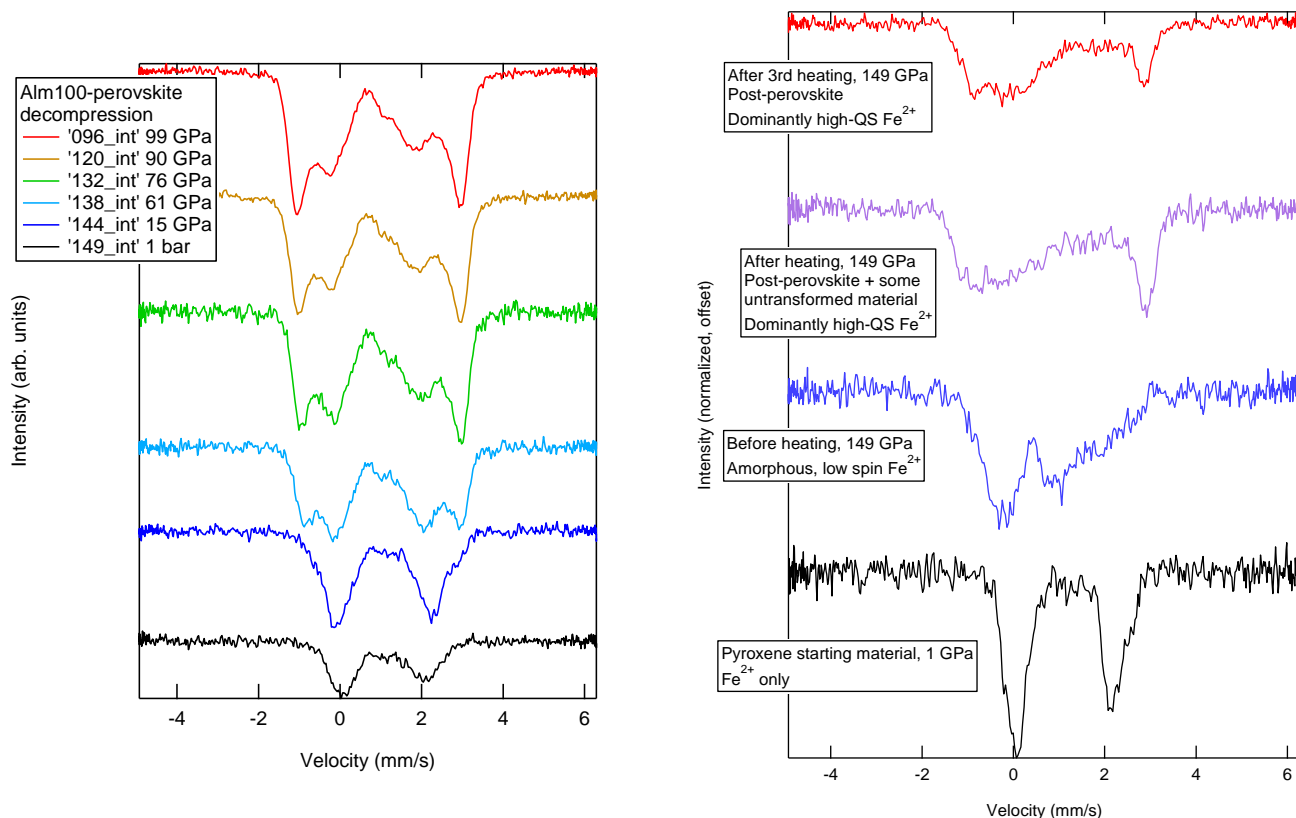
The oxidation and spin states of Fe in mantle phases have important implications for the chemistry and physical properties of the mantle. The dominant phase of the lower mantle, (Mg,Fe,Al)(Fe,Al,Si)O₃ bridgmanite, and its high-pressure polymorph post-perovskite, can accommodate both Fe²⁺ and Fe³⁺. Previous studies have reported Fe³⁺/ΣFe ratio in Al-free bridgmanite ranging from 0-50%, with much higher Fe³⁺/ΣFe in Al-bearing compositions. In addition, transitions have been observed in one or both of these Fe species from high to intermediate or low electronic spin states. These observations are complicated by limited systematic constraints on the Mössbauer parameters as a function of valence state, spin state and site occupancy in these high-pressure phases.

We used energy-domain synchrotron Mössbauer spectroscopy (SMS) at ESRF beamline ID18 to examine spin and valence states of bridgmanite and post-perovskite synthesized from Fe²⁺-rich compositions with and without Al. For each composition, we measured SMS for both the starting material and synthesized phases at both ambient conditions and high pressures. Structures of synthesized phases were confirmed by X-ray diffraction. High-pressure phases were (or will be) decompressed to ambient conditions with SMS to follow structural or spin transitions and unambiguously confirm valence state at ambient conditions. This approach will resolve controversy in interpretation of previous studies of Fe in mantle silicates.

Data were obtained for:

- Fe²⁺, Al-bearing silicate glass (1 bar-91 GPa)
- Fe²⁺-rich clinopyroxene (1 bar-147 GPa)
- Fe²⁺, Al-rich bridgmanite (1 bar-100 GPa)
- Fe²⁺-rich bridgmanite (75 GPa)*
- Fe²⁺-rich silicate post-perovskite (150 GPa)*
- Fe²⁺-rich olivine and bridgmanite-oxide mixture (1 bar-50 GPa)
- Natural Fe²⁺-rich bridgmanite (125 GPa) and post-perovskite (160 GPa)

Selected spectra are shown in the figures below. In future beamtime, we will complete the starred experiments by measuring additional spectra over decompression to ambient conditions.



Bridgmanite was synthesized at 75-99 GPa and 2000-2500 K. Post-perovskite was synthesized at 149-160 GPa and 2500-3000 K. The observed quadrupole splitting (QS) and center shift (CS) are consistent with dominant Fe²⁺ for all compositions and do not show higher Fe³⁺/ΣFe with higher Al-content. The dominant doublet at lower mantle pressures exhibits QS=3.6-4.2 mm/s and CS=0.9-1.1 mm/s, similar to previous observations of high or intermediate spin Fe²⁺. A second high-spin Fe²⁺ doublet is observed at QS=2.2-3.3 mm/s and CS=0.8-1.2 mm/s. A minor high-spin Fe³⁺ doublet is fit to QS~1.2 mm/s and CS=0.3-0.5 mm/s. For the Al-bearing bridgmanite, ambient spectra before and after synthesis contain no more than ~10% Fe³⁺/ΣFe, indicating no disproportionation or oxidation of Fe²⁺. In contrast, previous studies of Al-bearing bridgmanite observed ~50% Fe³⁺/ΣFe. This difference may reflect the high Si-content of the starting material and balance of Al between the Si-site and Mg-site.

The results of these experiments have important implications for the effects of Al on oxidation potential of Fe in bridgmanite and the lower mantle oxygen fugacity. We are currently analyzing the spectra in detail. Preliminary results have been submitted in an abstract to the American Geophysical Union Fall Meeting, December 2014.