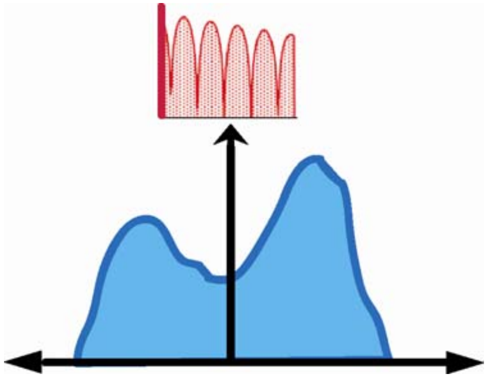
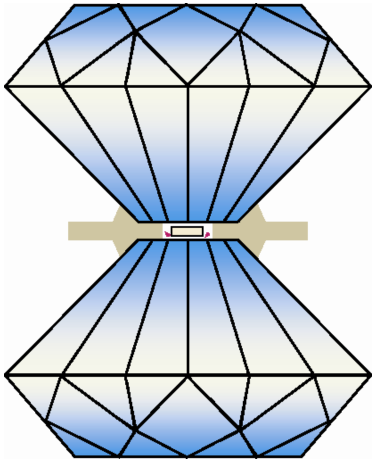
Iron valence, lattice distortion, and spin crossover in $(Mg,Fe)SiO_3$ perovskite: A synchrotron Mössbauer spectroscopy study to 120 GPa

Jennifer M. Jackson





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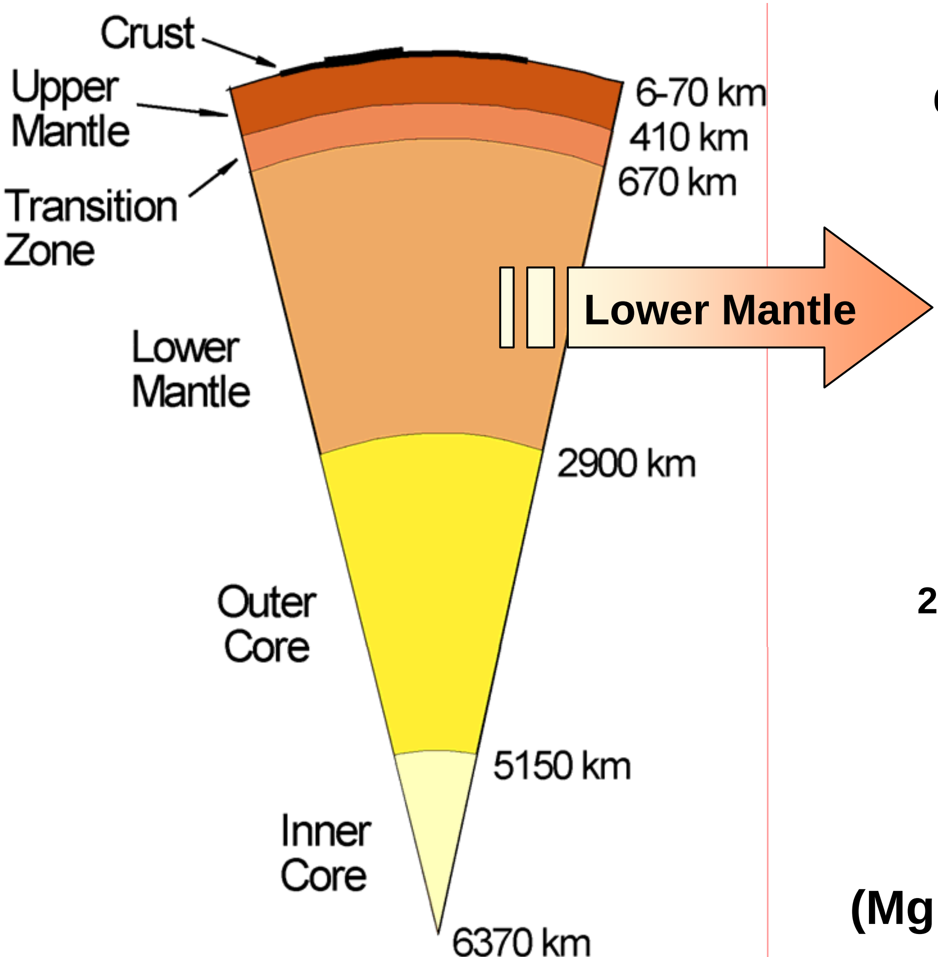
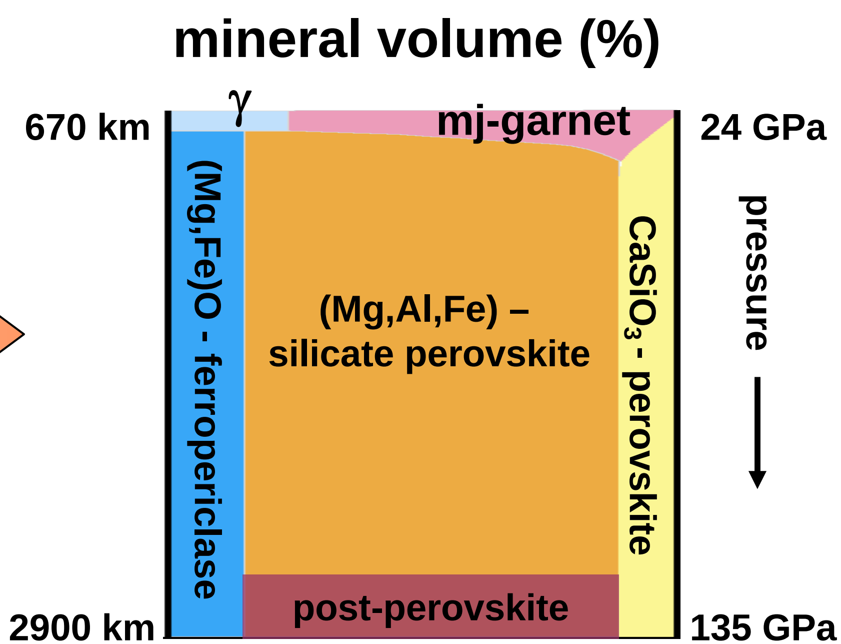
Earth's lower mantle (simplified)





(Mg,Al,Fe)-silicate perovskite occupies almost 50% of Earth's volume

Motivation for electronic structure measurements of *Iron* in magnesium-silicate perovskite

The physical and chemical properties of Mg-silicate perovskite largely control the properties of the bulk mantle

Iron is present at concentration levels of only about 2 atomic% (or less) in Mg-silicate perovskite

Electronic charge states of iron (e.g., Fe^{2+} and Fe^{3+}) and spin state (high-spin or low-spin) may affect:

- **Charge balance and equilibrium defect concentration**
- **Presence of metallic iron**
- **Rheology, solubility of volatiles, partitioning of major and trace elements, and transport properties**
- **Elasticity**

Outline of presentation

- Motivation for studying the electronic structure of iron-bearing magnesium silicate perovskite
- **Experimental details:**
  - **Sample description**
  - **Synchrotron Mössbauer spectroscopy (*SMS*)**
- ***SMS* Results & Discussion for (Mg,Fe)SiO_3 – perovskite**
  - **Iron valence fractions**
  - **Quadrupole splitting (lattice distortion)**
  - **Spin crossover**
- **Conclusions & Future Directions**

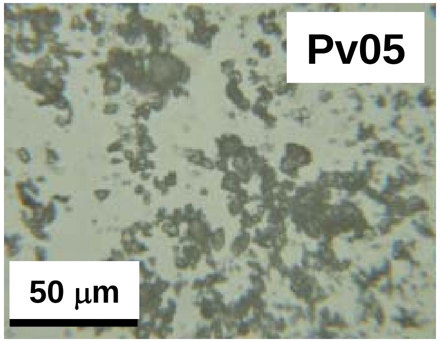
Description of $(Mg,Fe)SiO_3$ perovskite samples and preparation

Synthesis:
Synthetic $(Mg_{0.95}Fe_{0.05})SiO_3$ (Pv05) and $(Mg_{0.90}Fe_{0.10})SiO_3$ (Pv10) orthopyroxene structure with 92% ^{57}Fe enriched

Re capsules in a multi-anvil at 26 GPa and 1873 K (Pv05) and 1923 K (Pv10) (see Fei et al. 1994).

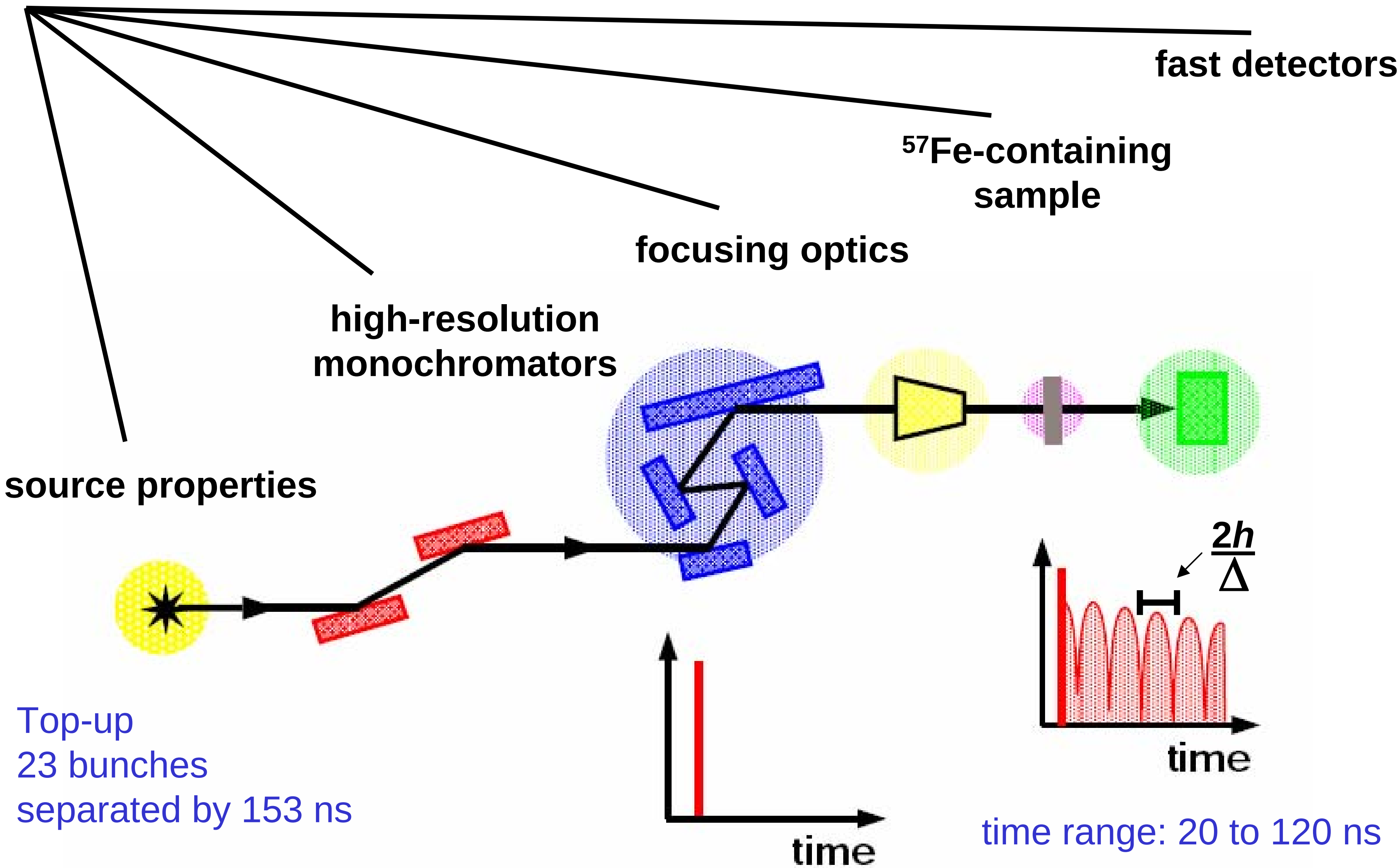
Pv10 experiments to 75 GPa:
- **Dilute! (~2 atomic %Fe)**
- **small sample: ~$40 \times 50 \times 50\ \mu m^3$**

Pv05 experiments to 120 GPa
- **Dilute! (~1 atomic %Fe)**
- **small sample: ~$10 \times 50 \times 50\ \mu m^3$**



Powder XRD confirmed the perovskite structure (*Pbnm*)

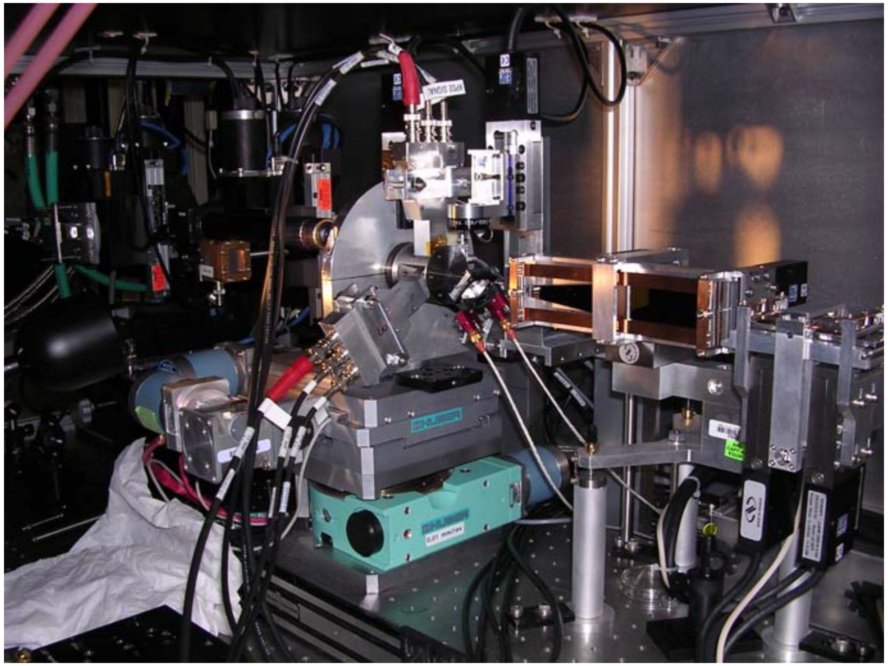
Synchrotron Mössbauer spectroscopy (schematic set-up)



Top-up
23 bunches
separated by 153 ns

time range: 20 to 120 ns

Synchrotron Mössbauer Spectroscopy
Set-up at sector 3-ID



Nuclear Resonant X-ray Scattering
Beamline 3-ID, APS

X-ray bandwidths:

- 2.2 meV, Pv10 (Toellner 2000)
- 1.0 meV, Pv05

KB mirrors: 6 x 6 μm^2 at FWHM

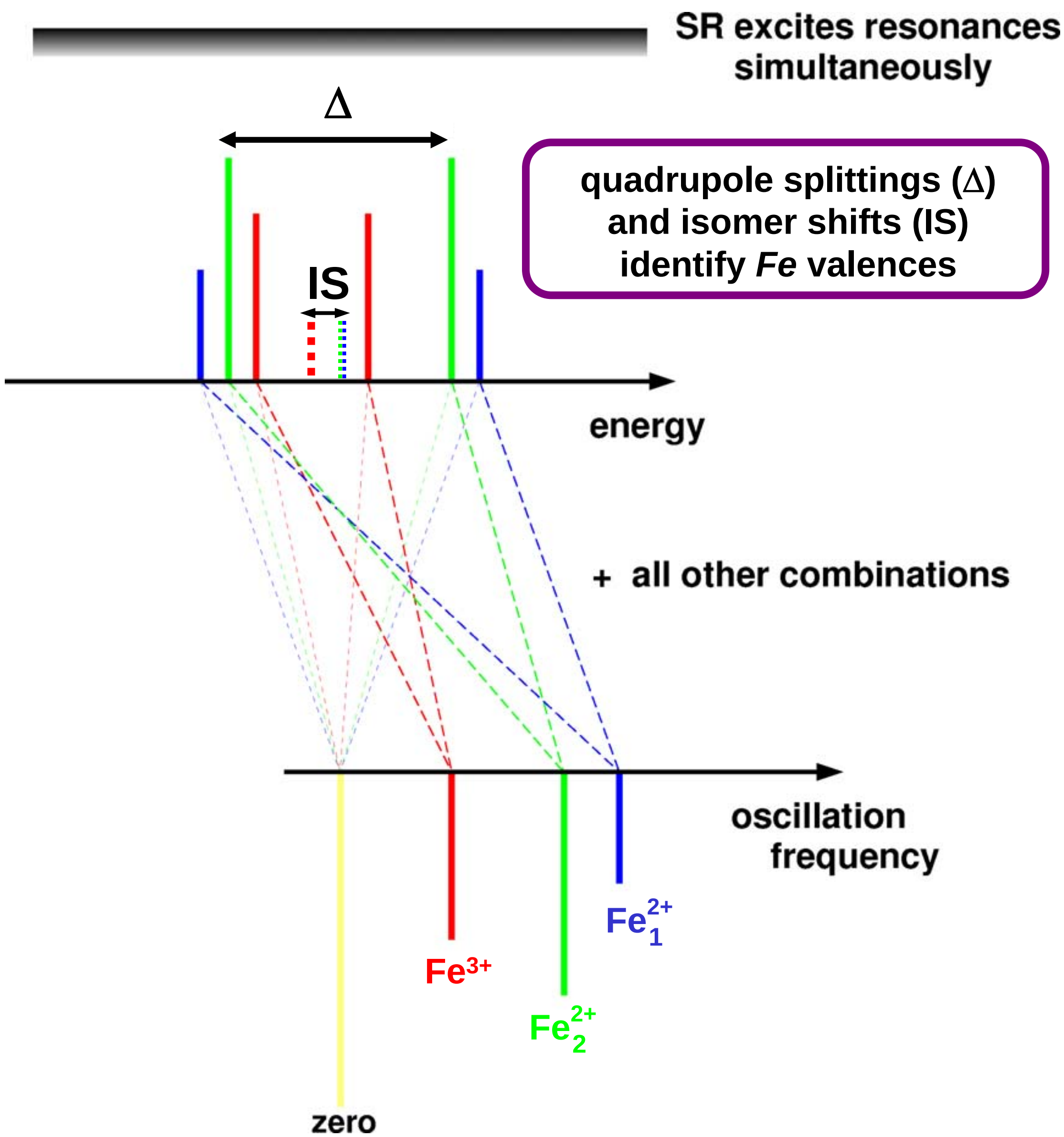
- higher flux (10^9 ph/s)
- Increased sensitivity
- Effects of pressure gradients reduced

14.4125 keV resonance of the ^{57}Fe isotope

Spectral flux density (2×10^{16} ph/s/eV/mm^2) is up to **10** orders of magnitude higher than conventional MBS

Permits high P-T measurements in a reasonable time

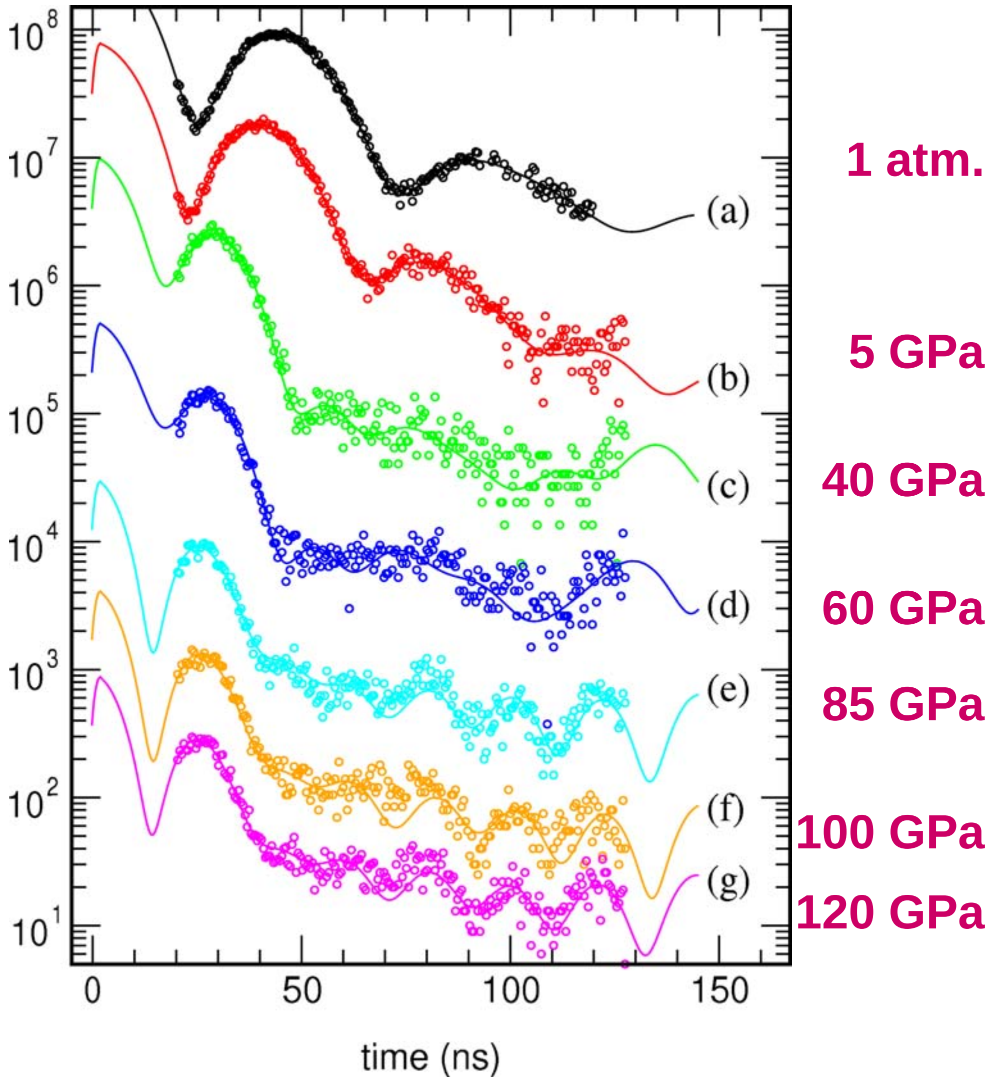
Origin of the time oscillations for silicate perovskite



quadrupole splitting (Δ):
A splitting of the excited nuclear state caused by an electric field gradient

isomer shift (IS):
A shift of the nuclear states caused by the electron density in the nuclear volume

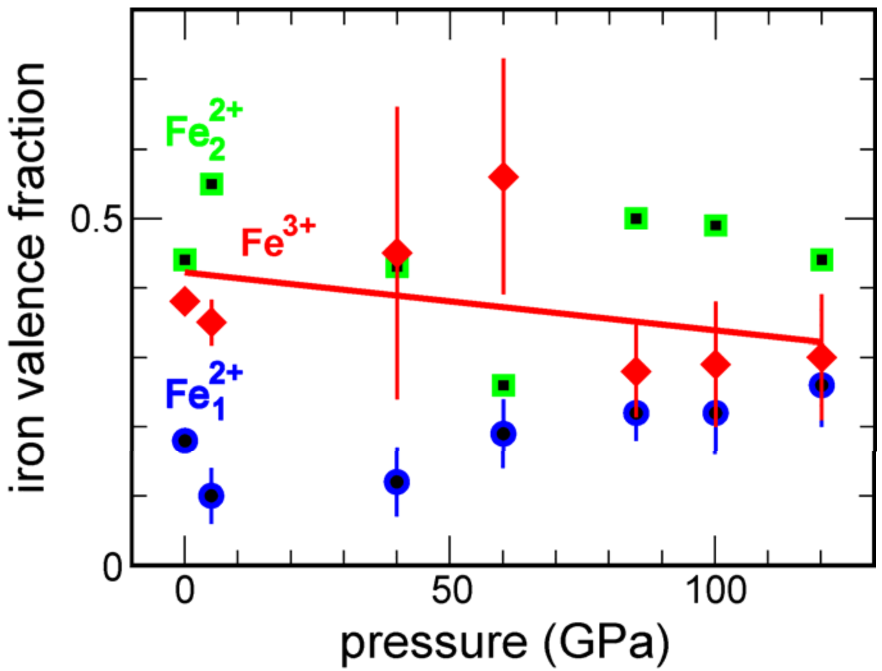
Time spectra for $(Mg_{0.95}Fe_{0.05})SiO_3$ perovskite



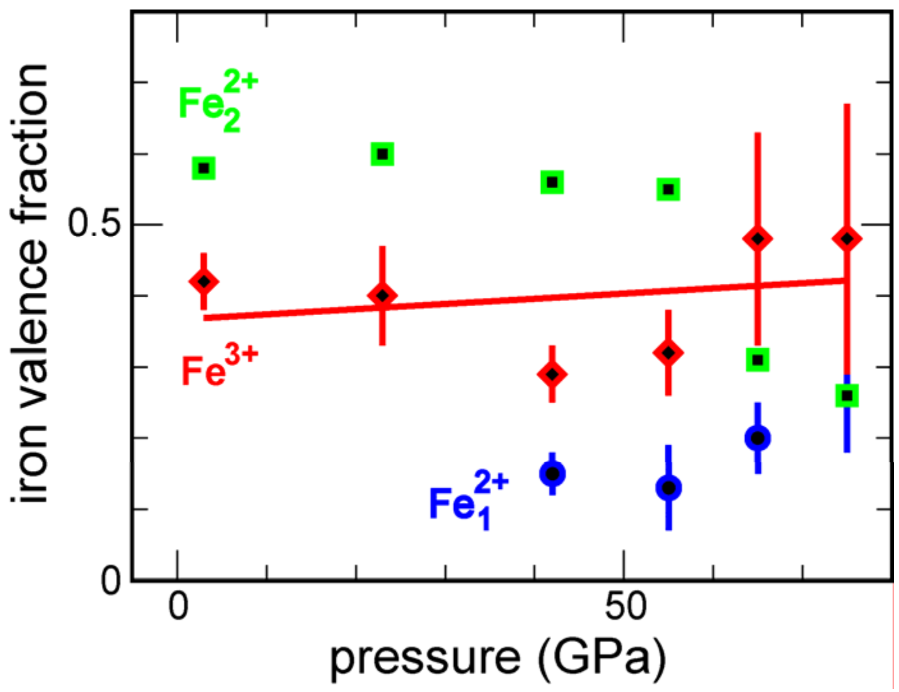
(Jackson *et al.* Am.Min., 90, 2005)

Iron valence fraction results to 120 GPa for (Mg,Fe)SiO_3 perovskite

$(Mg_{0.95}Fe_{0.05})SiO_3$

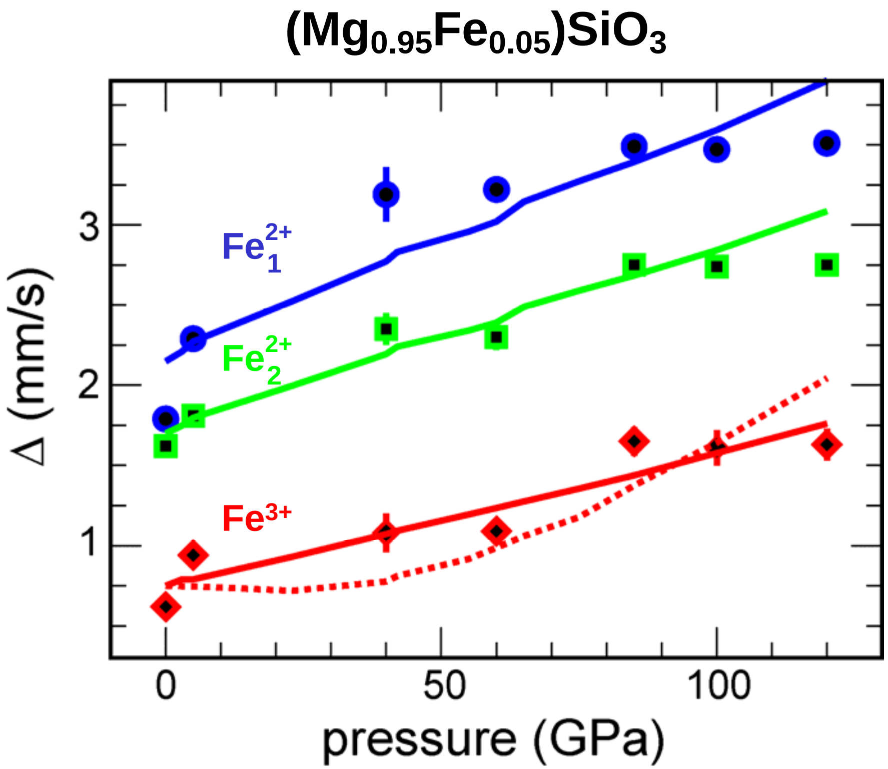


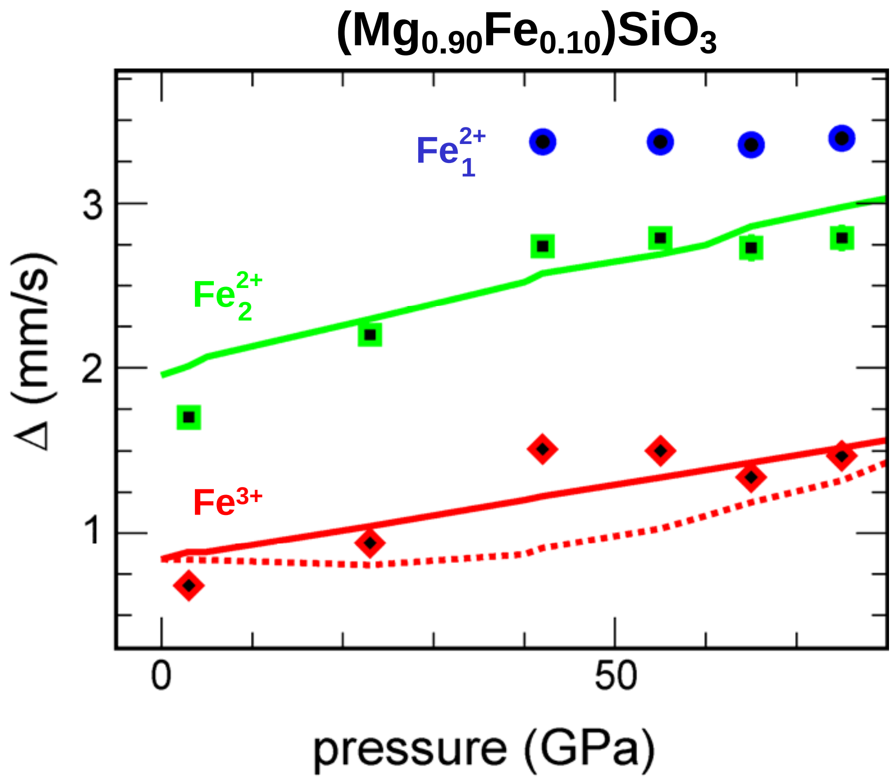
$(Mg_{0.90}Fe_{0.10})SiO_3$



metallic iron was not detected

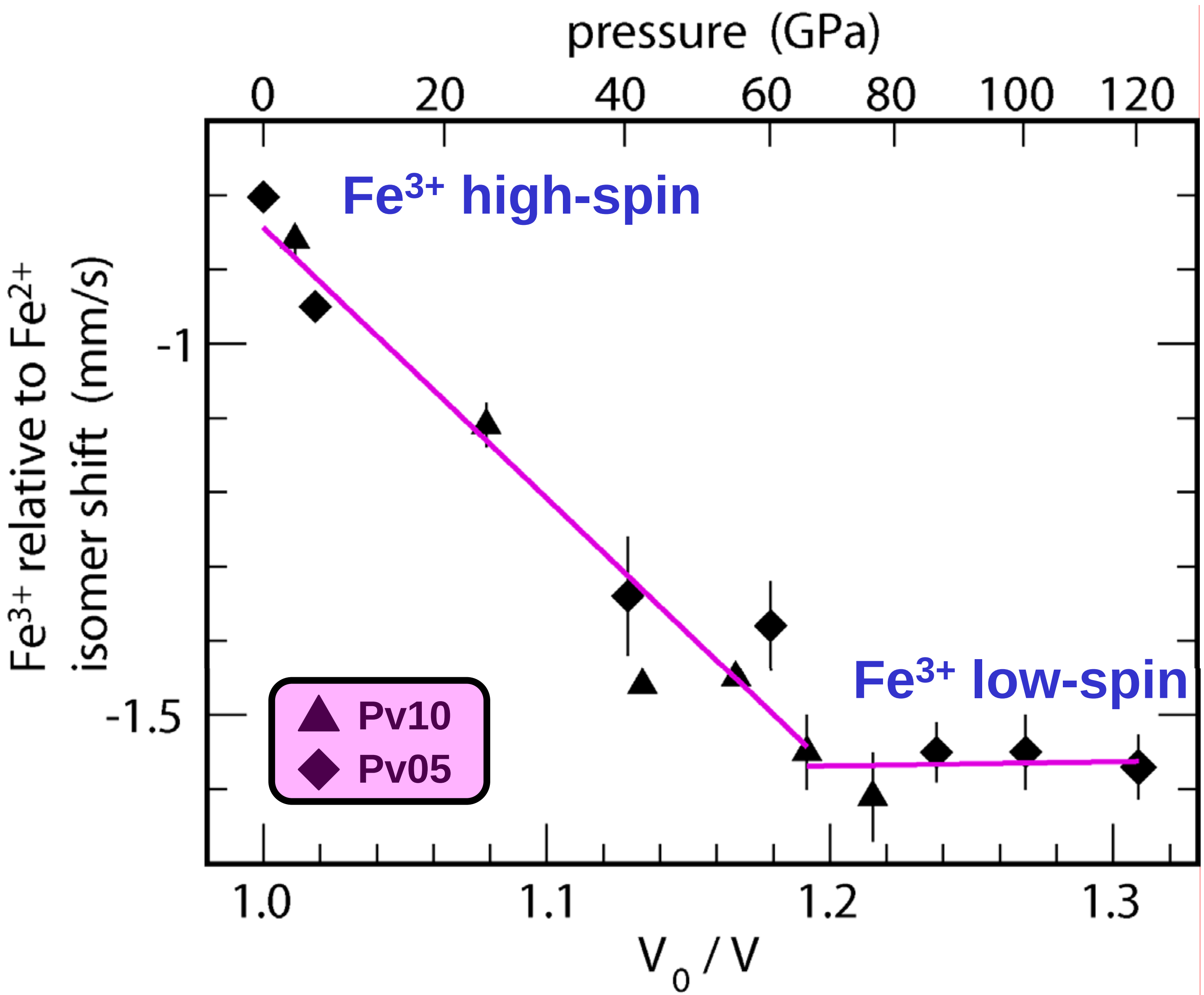
Pressure dependence on quadrupole splitting for (Mg,Fe)SiO_3 perovskite





Iron site occupancy and lattice distortion

Pressure dependence on the isomer shift and spin crossover



Comparison with recent observations of spin crossovers in perovskite under lower mantle pressures

X-ray Emission Spectroscopy (XES) results:

(Mg,Fe)SiO_3 perovskite
Pressure-induced "partial" spin-pairing transition at 70 GPa and "full" transition at 120 GPa
(Badro et al. Science, 2004)

(Mg,Fe)(Si,Al)O_3 and (Mg,Fe)SiO_3 perovskites
Spin-pairing transition is gradual to 100 GPa. Residual magnetism at 100 GPa
(Li et al. PNAS, 2004)

perovskite contains different charge states, Fe^{2+} and Fe^{3+}

Synchrotron Mössbauer Spectroscopy (SMS) results:

(Mg,Fe)SiO_3 perovskites
Pressure-induced spin-pairing crossover in Fe^{3+} component completed ~70 GPa
(this study – Jackson et al. Am Min, 2005)

Conclusions and Future Directions

- **First *in-situ* measurements of the charge states of iron-bearing $MgSiO_3$ perovskite at high-pressure**
  - **Little to no variation in Fe^{3+} content to 120 GPa**
  - **Spin crossover in Fe^{3+} is gradual and completed around 70 GPa**
- **Comparison with XES measurements**
  - **Inconsistent with sharp transition described in Badro et al. (2004)**
  - **Gradual trend is in agreement with Li et al. (2004), but discrepancies still exist in terms of behavior of individual charge states.**

Some future directions:

- **combining SMS, XES, and XRD**
- **ferropericlase, (Al,Fe)-$MgSiO_3$ perovskite, and post-perovskite at high *pressures & temperatures***
- **Electronic structure of upper mantle minerals at high P-T**
- **Very challenging!**