Volume Collapse Of Fe^{3+}-Al Perovskite At Mid-lower Mantle Pressures

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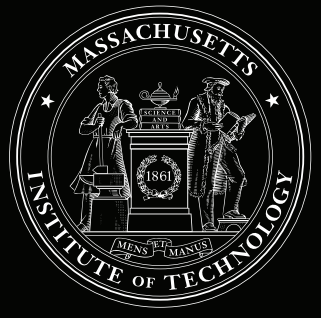

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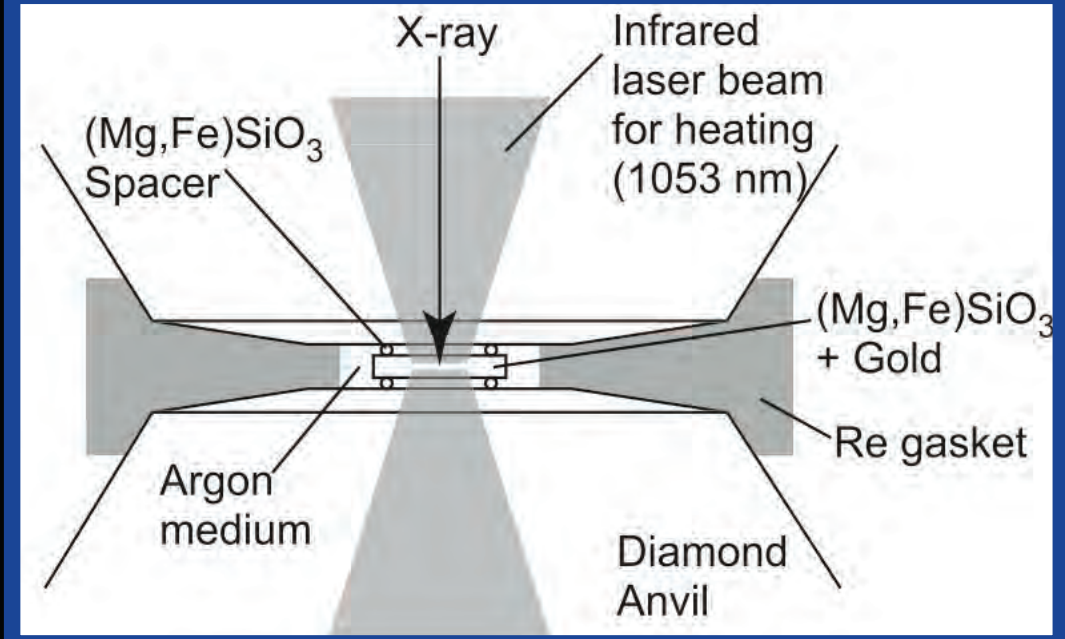
Practicum:
Lawrence Livermore National Lab

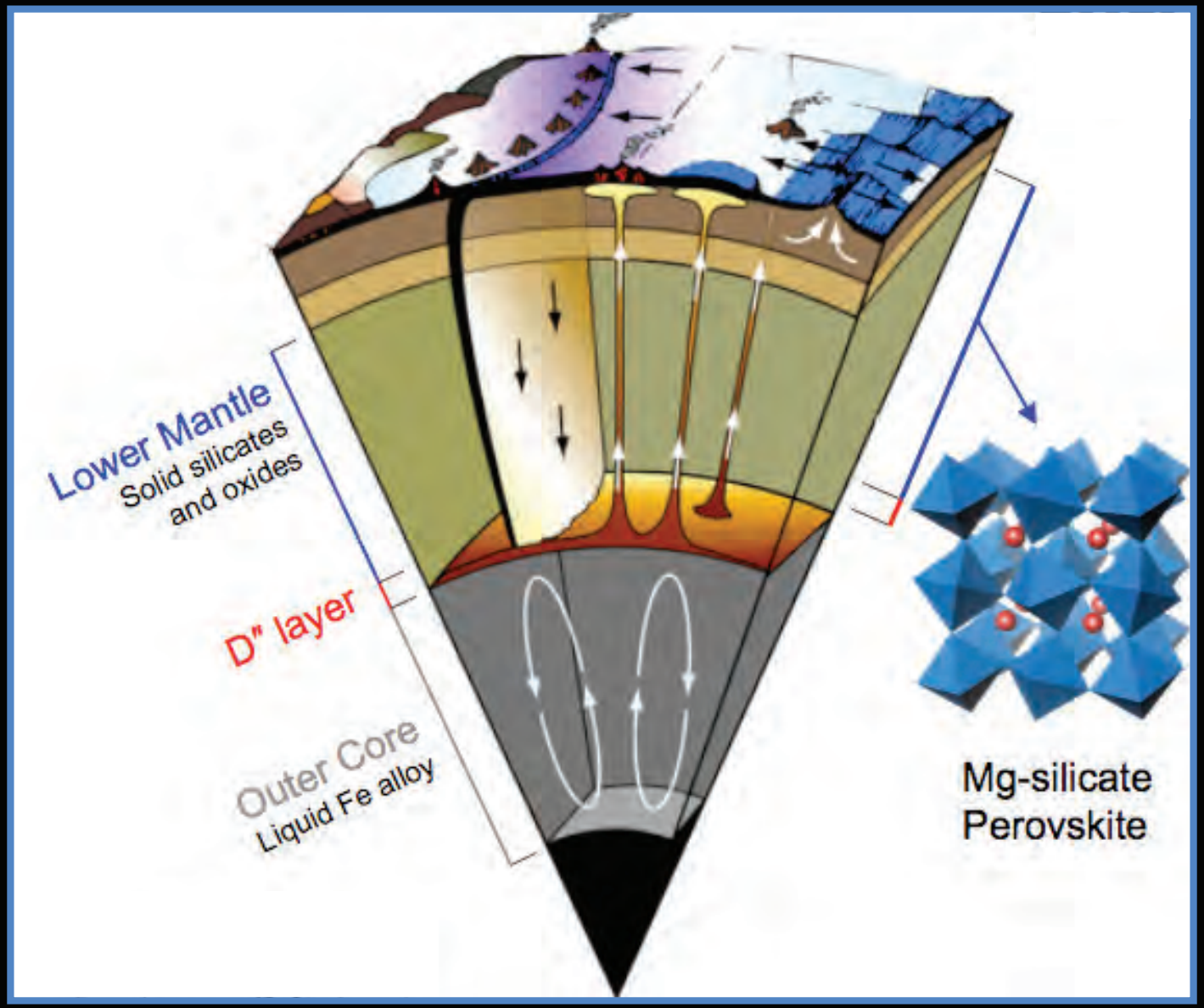
- X-ray emission spectroscopy
- Beryllium
- Beamtime - through LLNL I was allotted 9 days of beamtime at the High Pressure Collaborative Access Team beamline at APS
- Two papers currently under review

High Pressure Mineral Physics



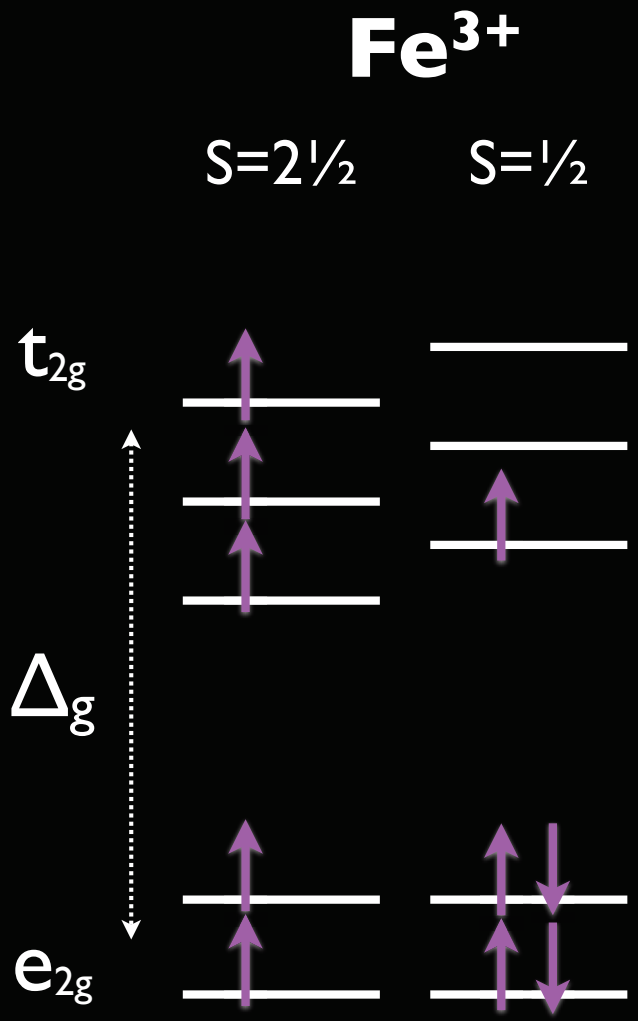
- Diamond-anvil cell
- In situ high pressure measurements
- Static pressures in excess of 135 GPa (~1.3x10^6 atm)

Earth's Mantle



- Orthorhombic $MgSiO_3$ perovskite with Fe and Al
- (Mg,Fe)O ferropericlase

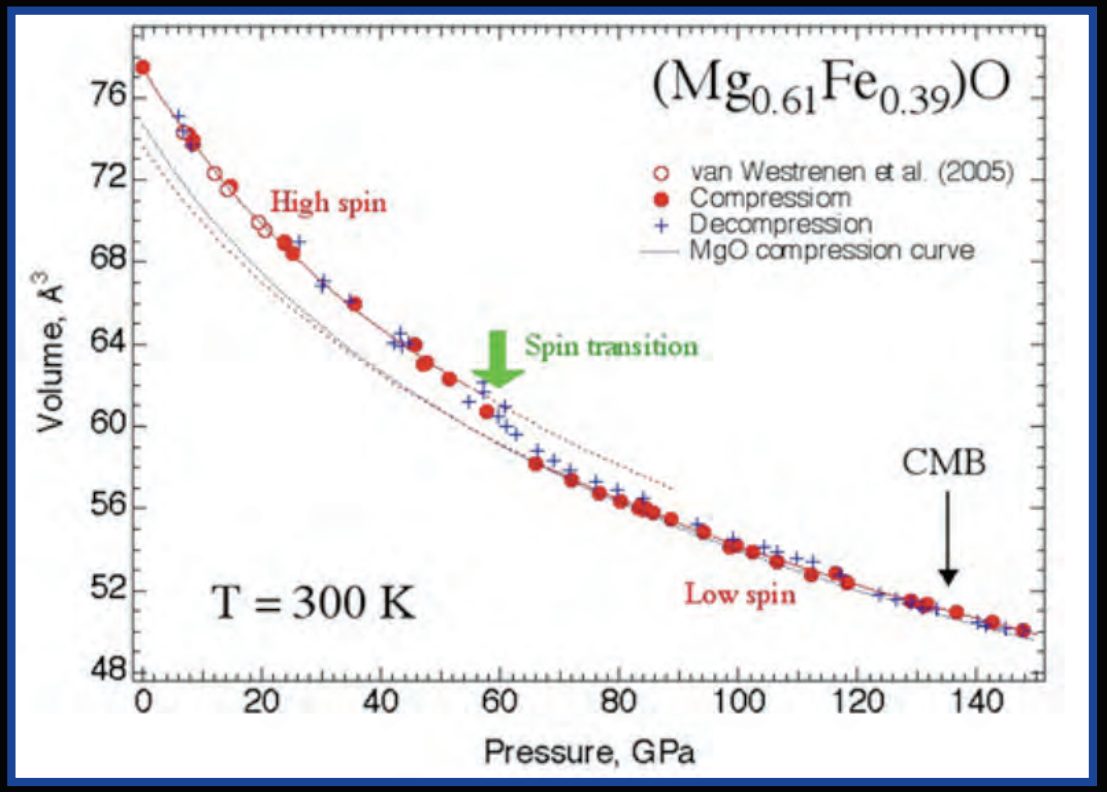
Spin-pairing Transition



As pressure is increased, the volume of the sample decreases and it becomes energetically favorable for a spin-pairing transition which allows for a reduction of the ionic radius

Volume Collapse From Spin Transitions

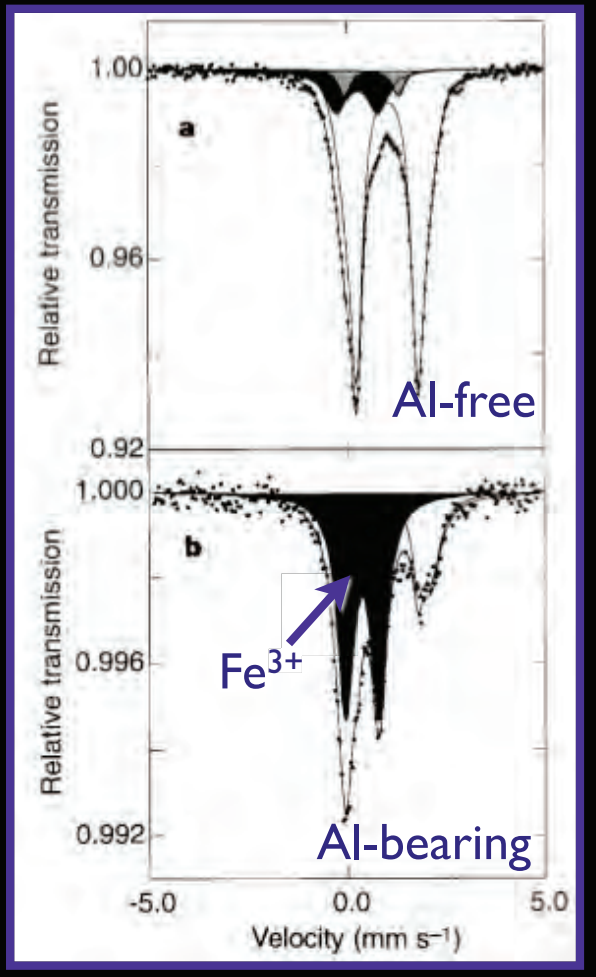
- Volume collapse of ferropericlase as a result of the spin transition in Fe^{2+}
- The same has not been observed in $(Mg,Fe^{2+})SiO_3$ perovskite (Lundin et al., 2008)



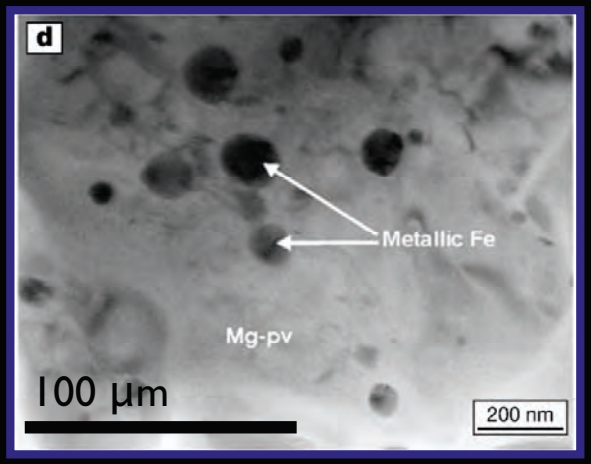
Fei et al., 2007, GRL

Fe^{3+} in Perovskite

- Fe^{3+} has been shown to be an important component of perovskite, even in samples synthesized from pure Fe^{2+} starting materials
- The inclusion of Al has been shown to further enhance the $Fe^{3+}/\Sigma Fe$



McCammon, 1997, Nature



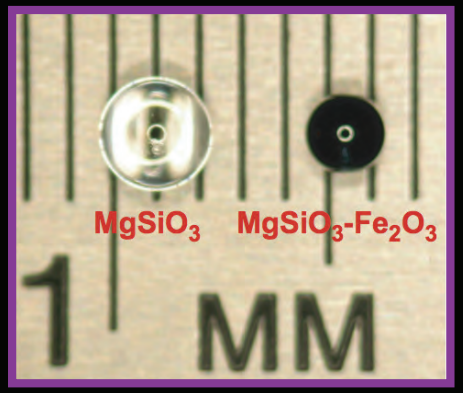
Frost et al., 2004, Nature

$$3Fe^{2+}_{silicate} \rightarrow Fe^{0}_{metal} + 2Fe^{3+}_{silicate}$$

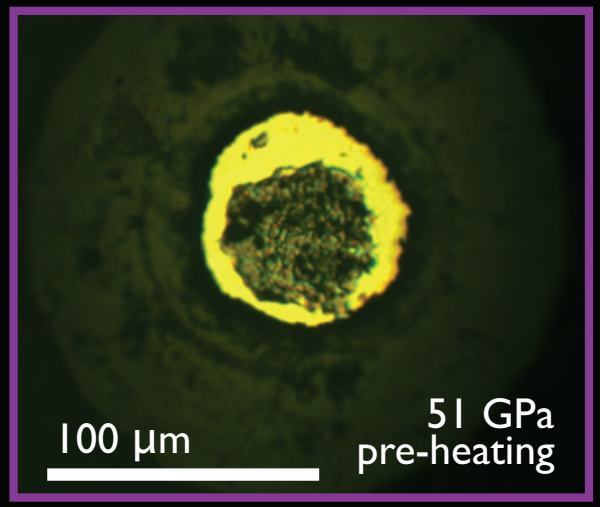
Techniques

X-ray diffraction	Volume and lattice parameters of the unit-cell and the bulk modulus
Synchrotron Mössbauer spectroscopy	Valence state, spin state, coordination
X-ray emission spectroscopy	Integrated spin moment of the sample

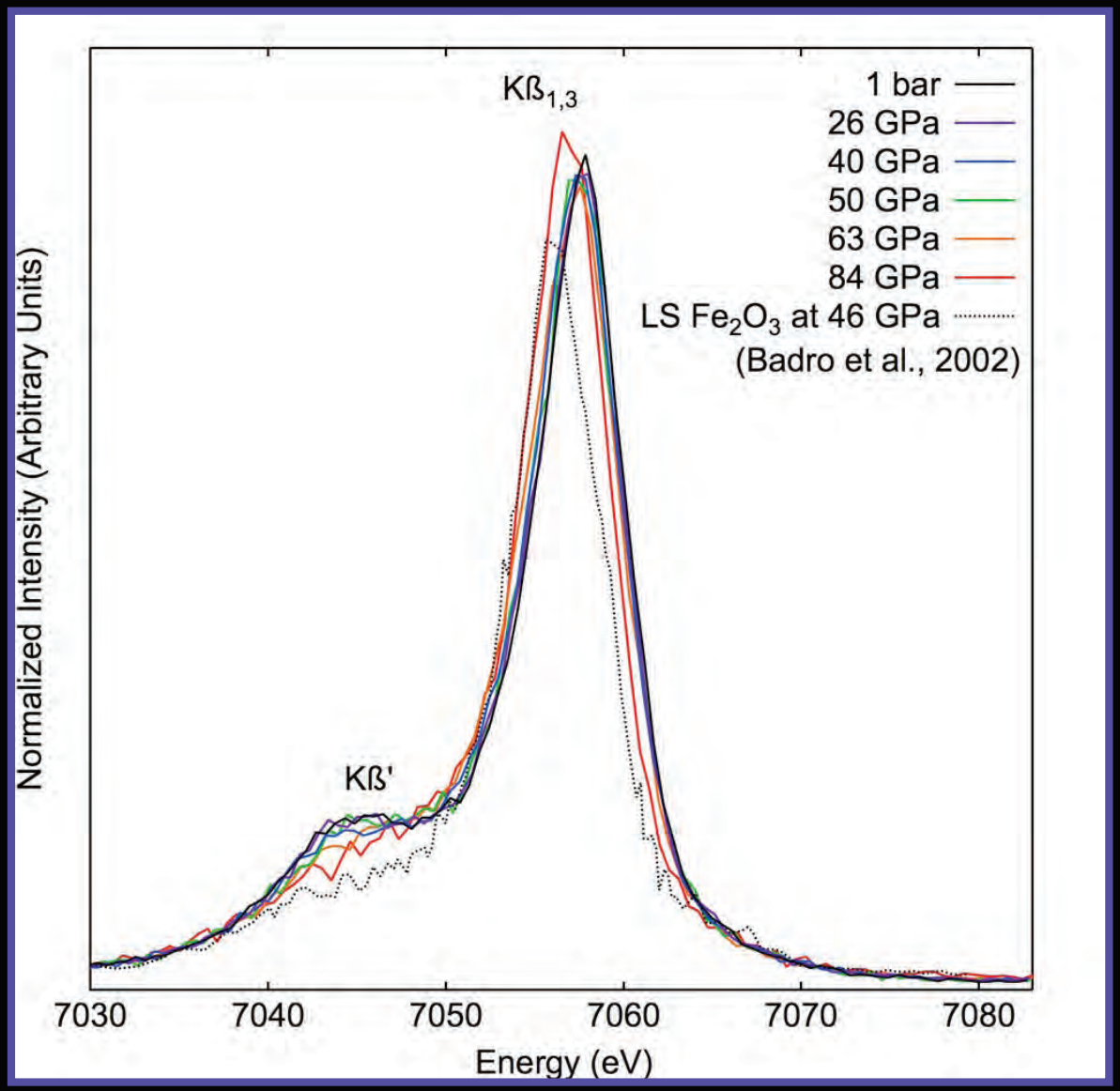
Experiments

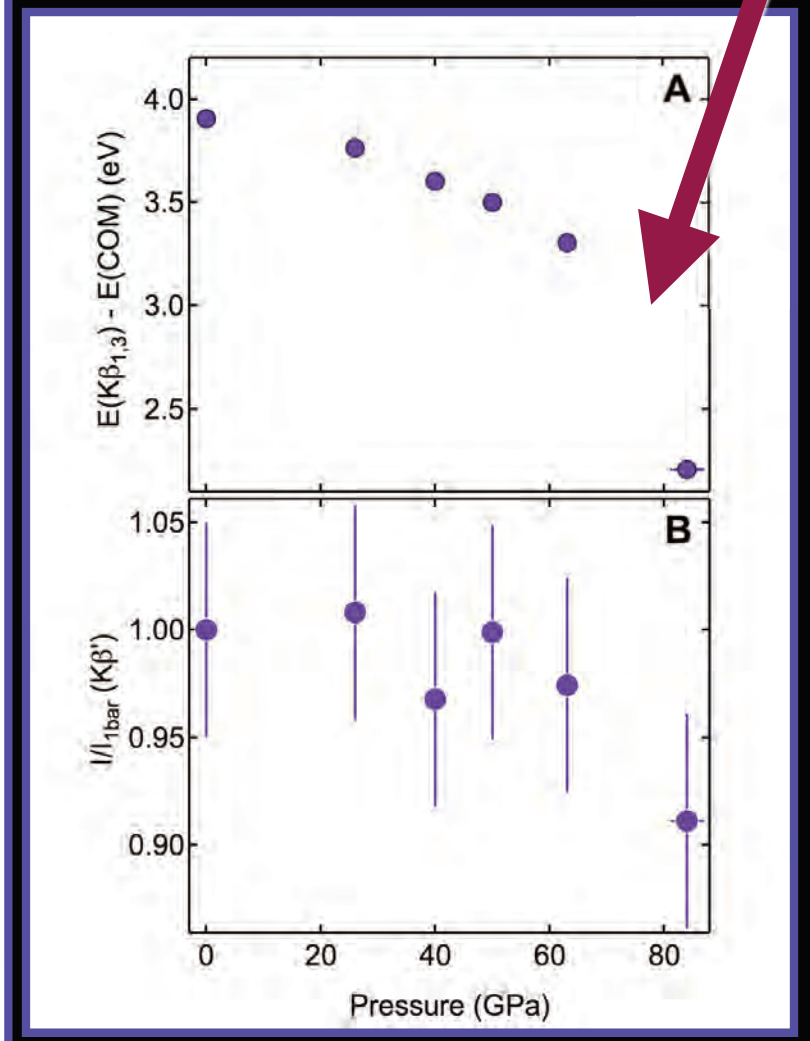


- Measurements made on $MgSiO_3$ with equal amounts of Fe^{3+} and Al (10%) synthesized using the laser levitation method
- Perovskite was synthesized in the diamond anvil cell above 50 GPa
- X-ray diffraction with Ar medium and Au standard
- Synchrotron Mössbauer spectroscopy in Ar medium with ruby pressure standard
- X-ray emission spectroscopy in NaCl medium with ruby standard
- Laser annealing at all pressures above 50 GPa

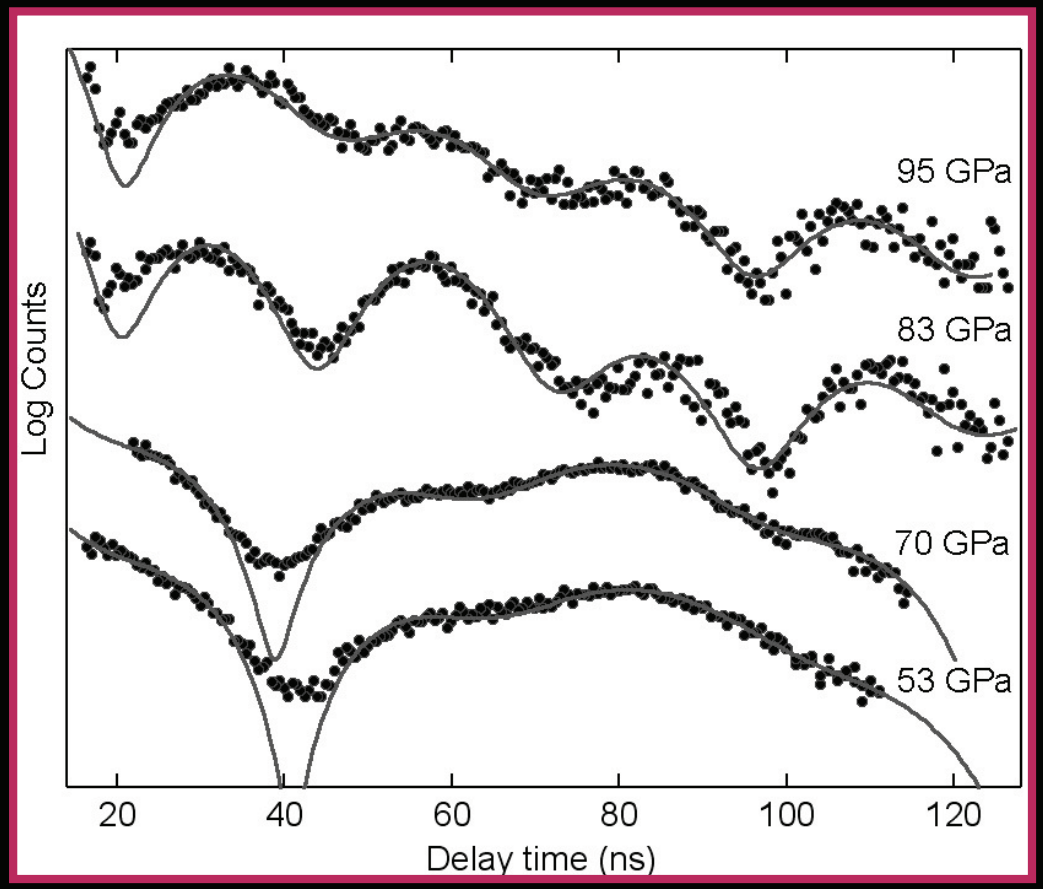


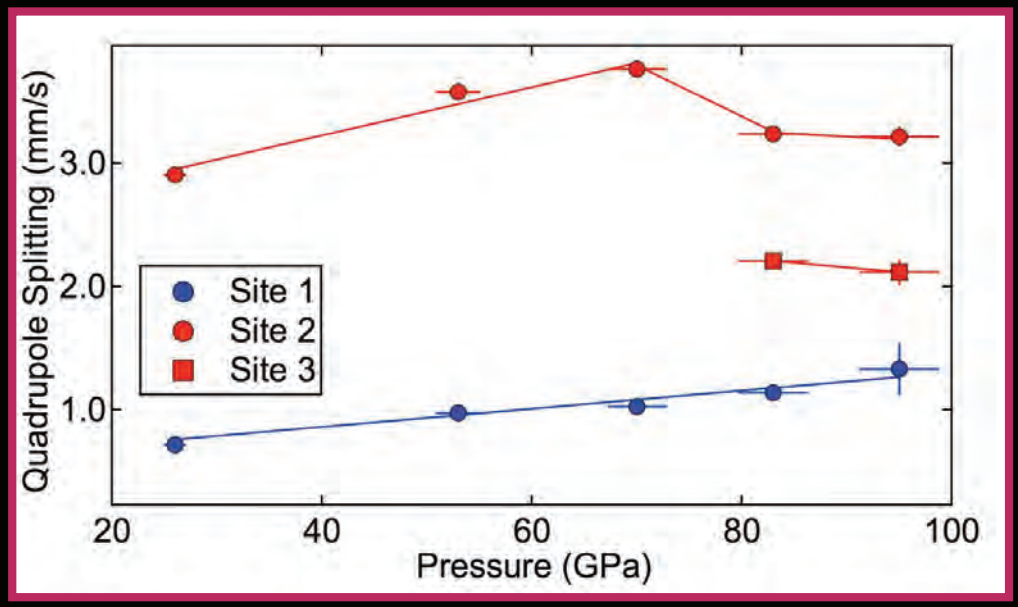
X-ray Emission Spectra

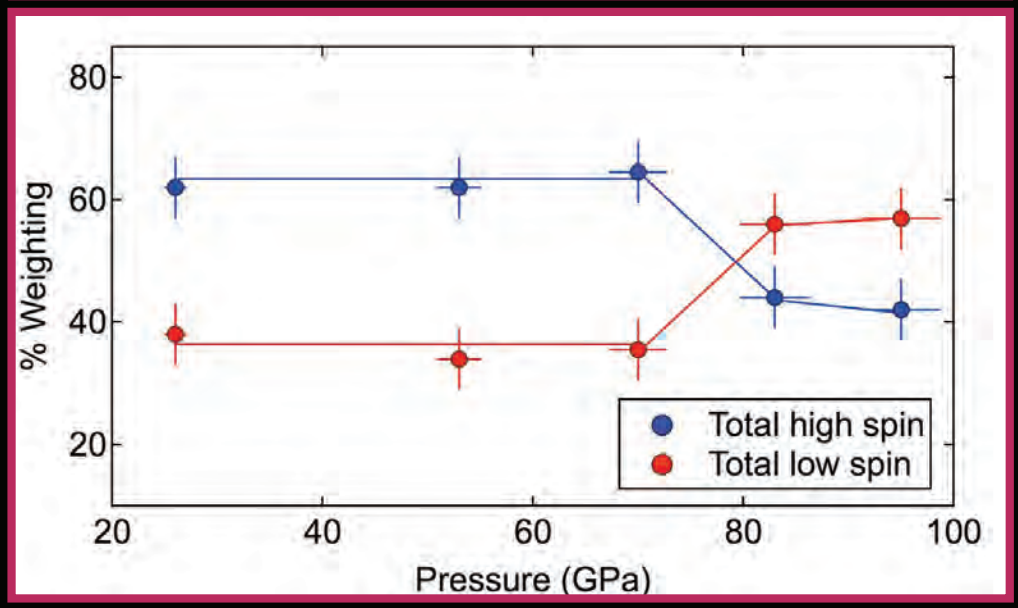




Synchrotron Mössbauer Spectroscopy

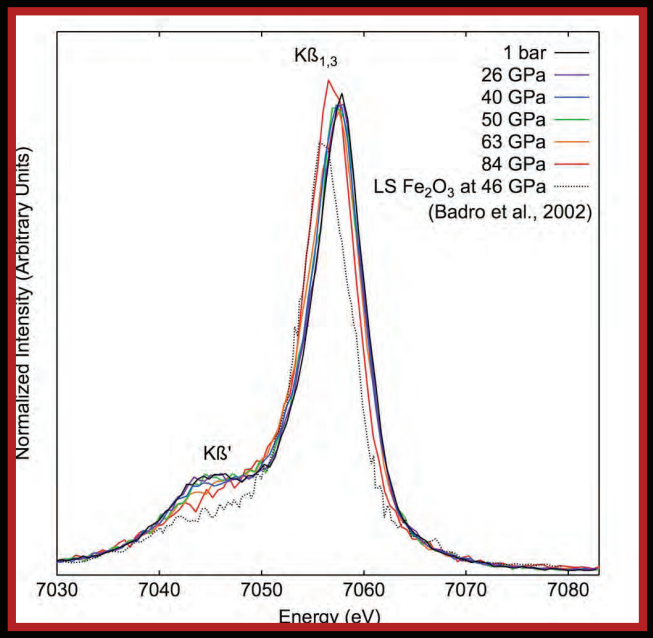


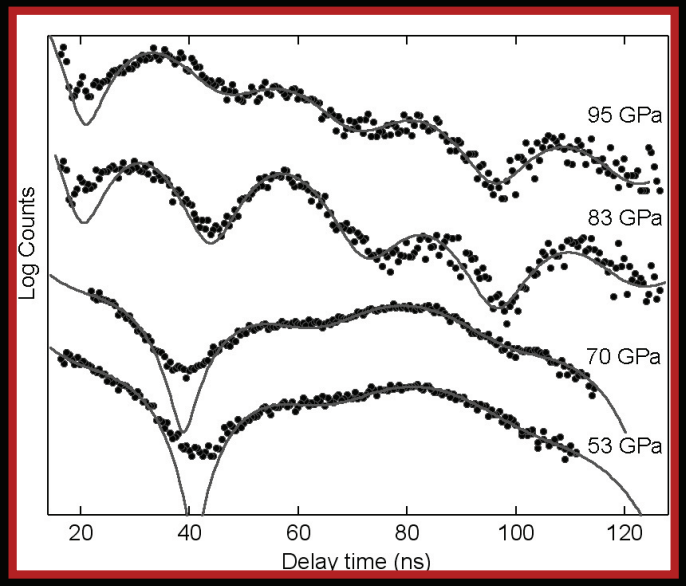




Spin State and Site Mixing

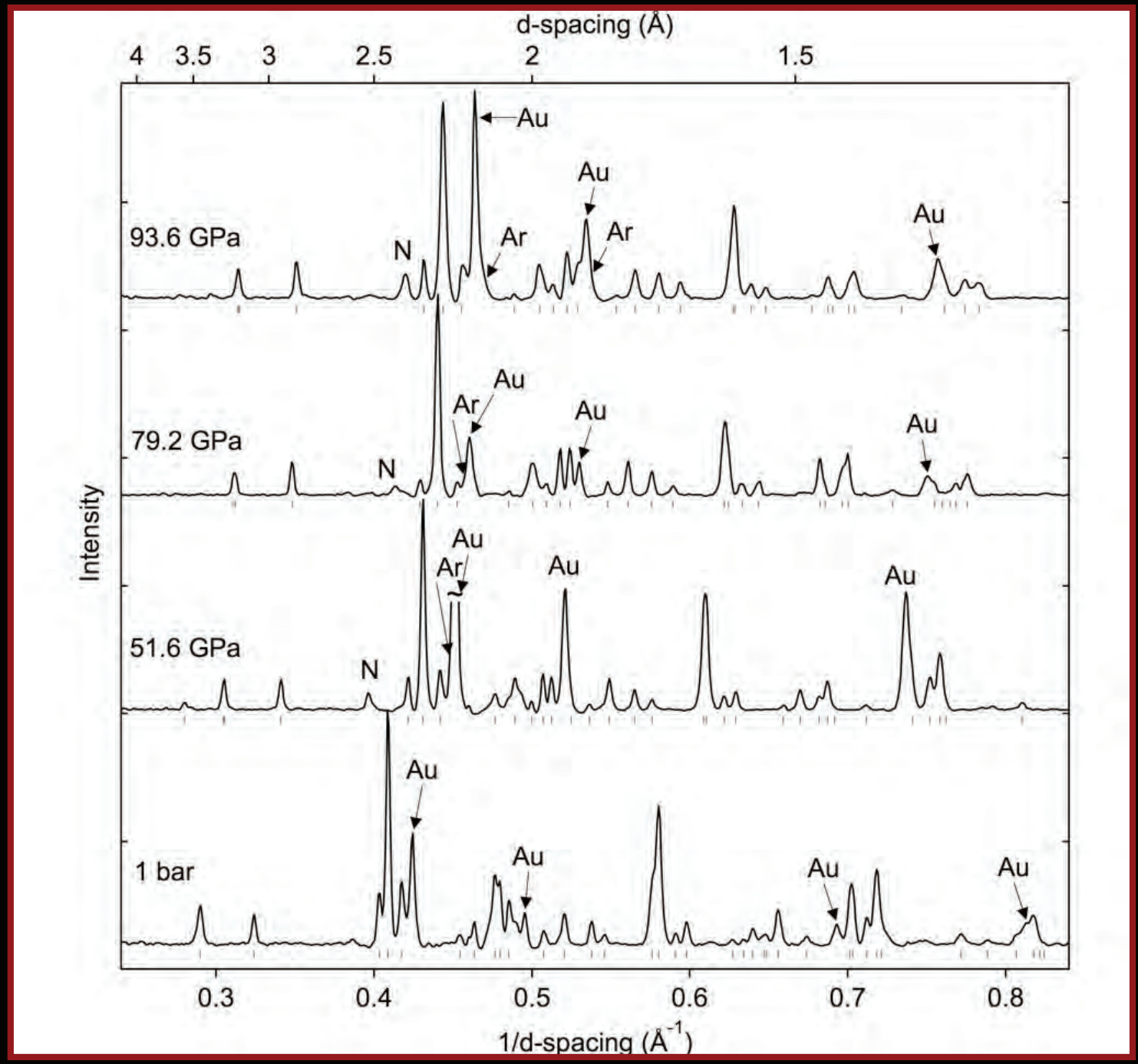
- Low spin Fe^{3+} in the octahedral site of perovskite
- Jump in the low spin component near ~70 GPa
- Increased site mixing between Al and Fe^{3+}





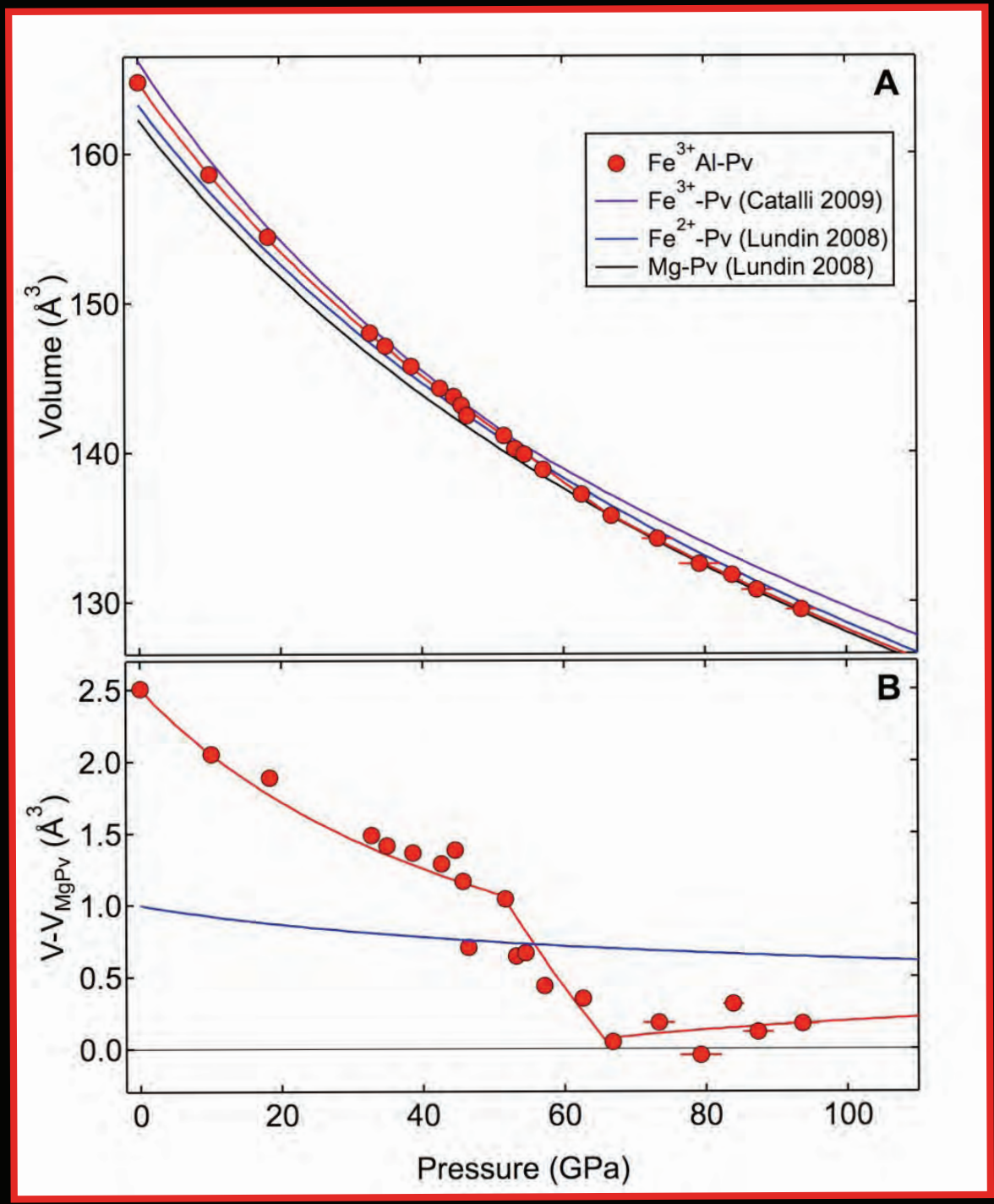
$$\cdot Mg, Fe^{3\cdot}_{HS} \cdot Al, Si \cdot O_3 \longrightarrow$$

$$\cdot Mg, Fe^{3\cdot}_{HS}, Al \cdot Fe^{3\cdot}_{LS}, Al, Si \cdot O_3$$


d-spacing (Å)
4
3.5
3
2.5
2
1.5
Intensity
93.6 GPa
79.2 GPa
51.6 GPa
1 bar
Au
Ar
N
0.3
0.4
0.5
0.6
0.7
0.8
1/d-spacing (Å^{-1})

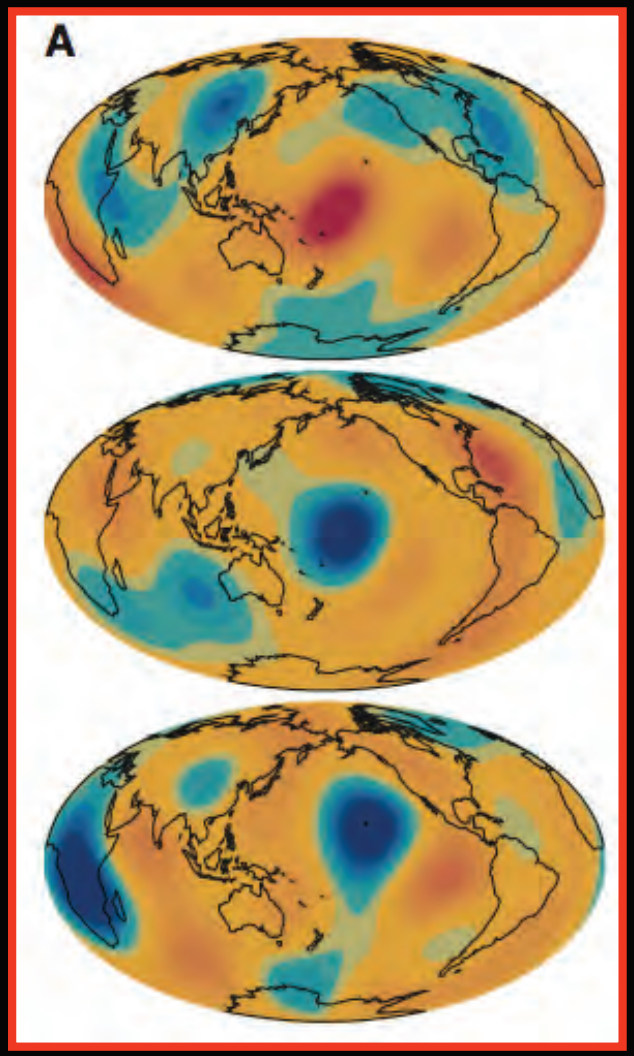
Volume Collapse

- Fe^{3+}-Al perovskite volume collapse at ~70 GPa to that of $MgSiO_3$
- Elastic softening at ~55-70 GPa
- This would likely lead to a ~0.5% increase in density in a mantle related composition



Mantle Heterogeneities

- Anticorrelation between shear velocity and density in the lowermost mantle in the Pacific
- Suggests anomalously high density that cannot be explained by a thermal anomaly



Ishii and Tromp, 1999, Science

Summary

- Low spin Fe^{3+} competes with Al for the octahedral site of perovskite with increasing pressure, pushing Al into the dodecahedral site
- The change in spin state in Fe^{3+} affects the volume and compressibility of Al-bearing perovskite, unlike Fe^{2+}
- These results may at least partially explain the density anomalies in the lowermost mantle in the Pacific and under Africa

Thank you.