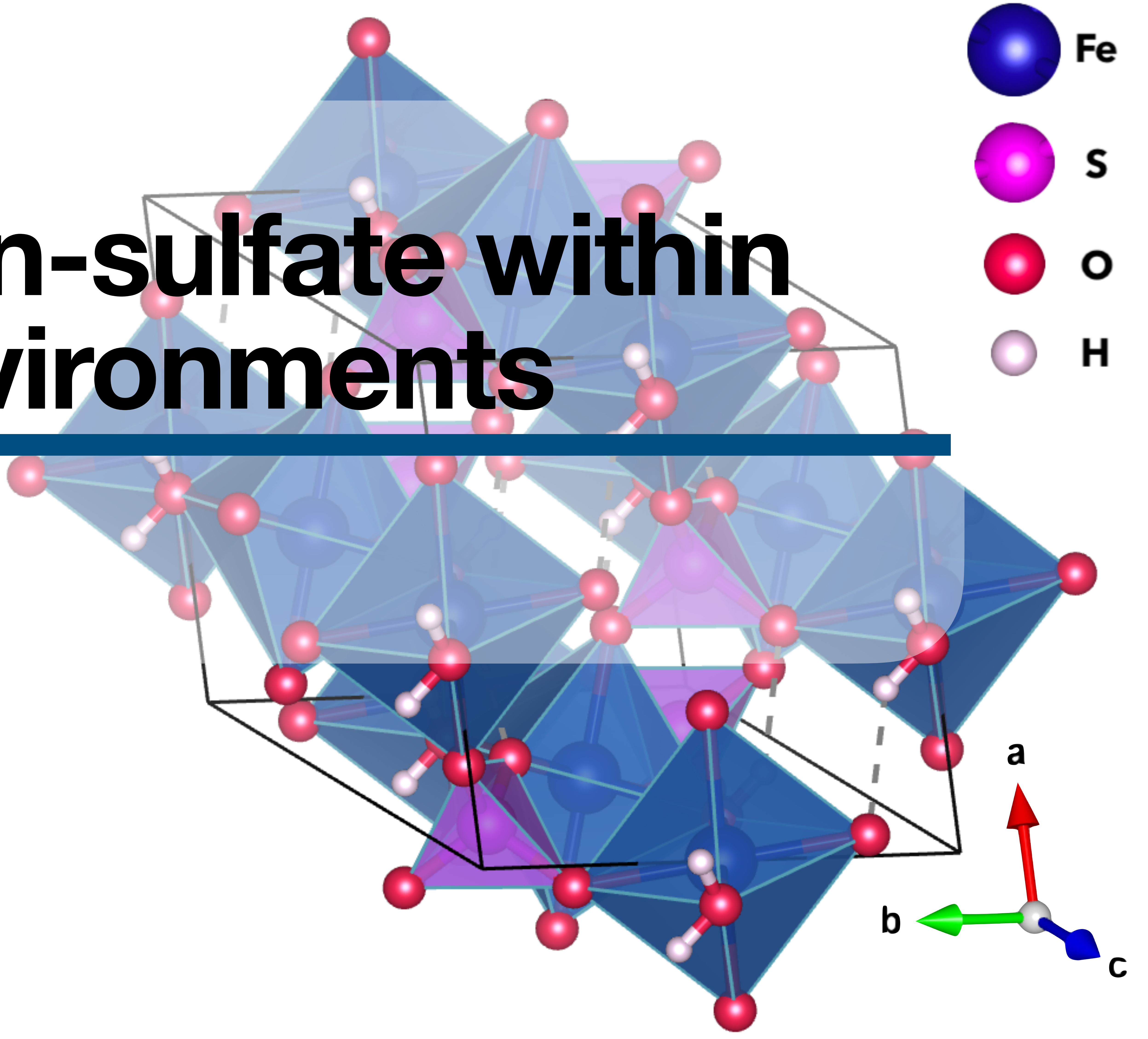
Probing a hydrous iron-sulfate within extreme planetary environments

Olivia Pardo

Vasilije V. Dobrosavljevic, Tyler Perez, Wolfgang Sturhahn, Zhenxian Liu, George R. Rossman, Jennifer M. Jackson



STEWARDSHIP SCIENCE GRADUATE FELLOWSHIP

SEISMOLOGICAL LABORATORY
California Institute of Technology

Overview

Iron sulfates in planetary environments

Measuring geophysical and geochemical properties of iron sulfates

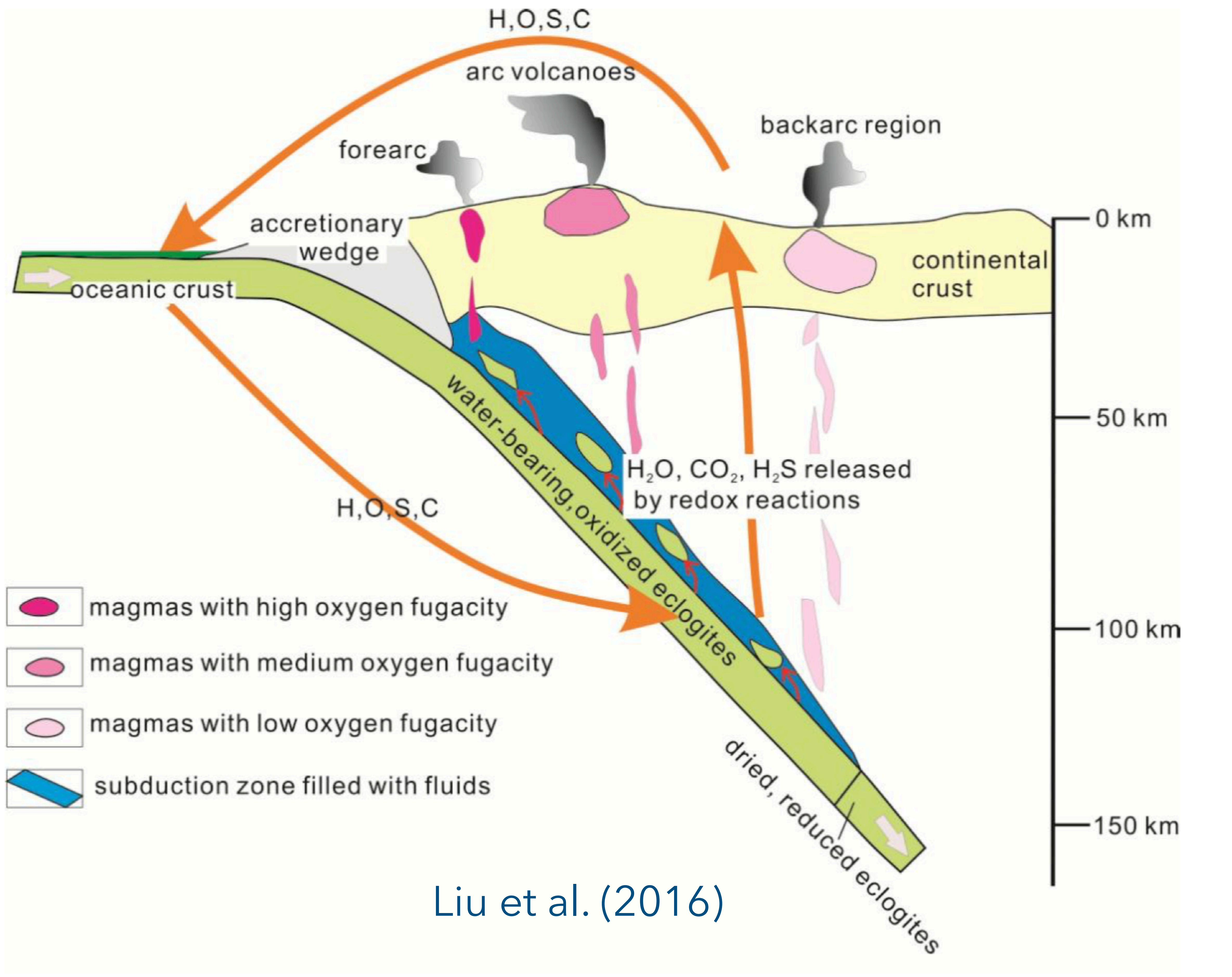
Behavior of $FeSO_4 \cdot H_2O$ under extreme pressure and cryogenic temperatures

SSGF reflection

Sulfur in planetary environments throughout the solar system

Earth —— Mars —— Icy Satellites

- Subduction zones: transport of sulfur to the deep Earth via descending slabs
- Mechanism for oxidation of the mantle
- How much sulfur is retained at depth?

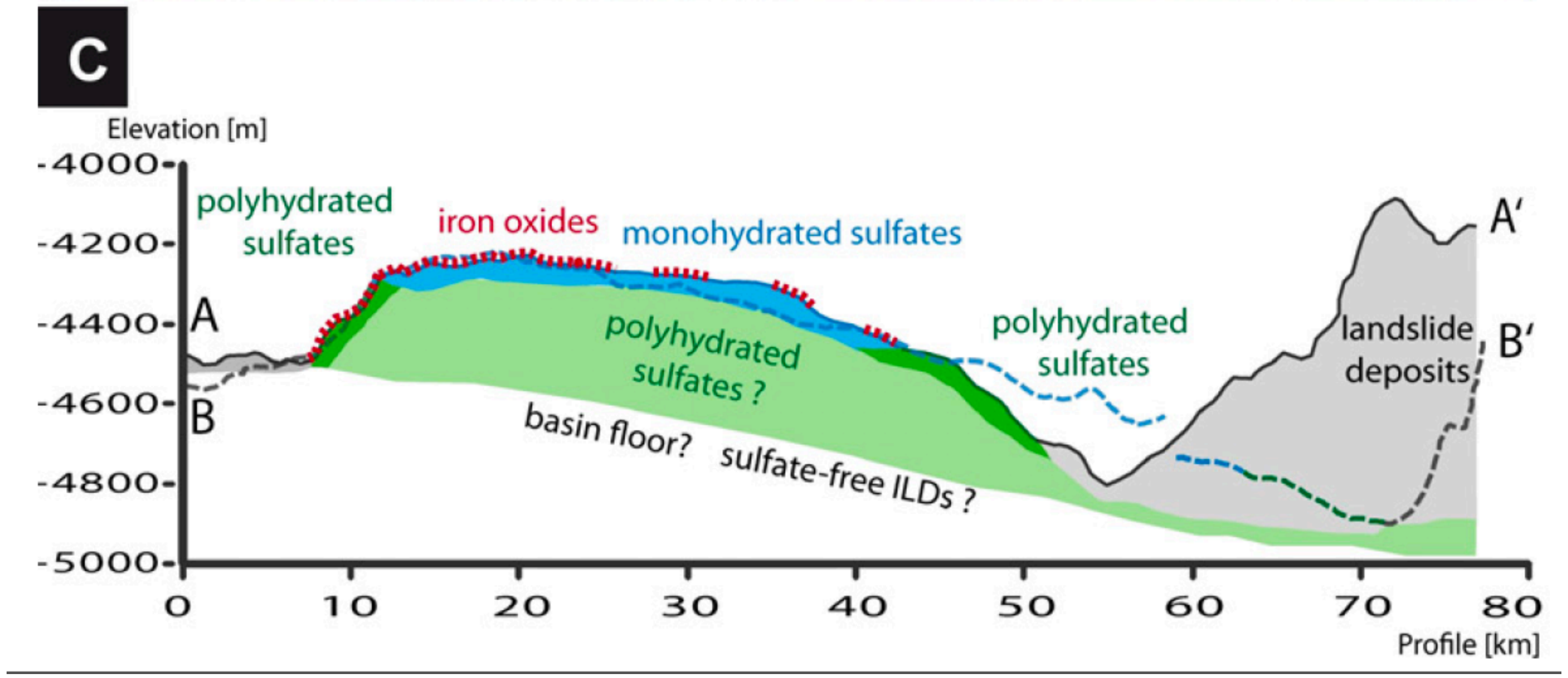


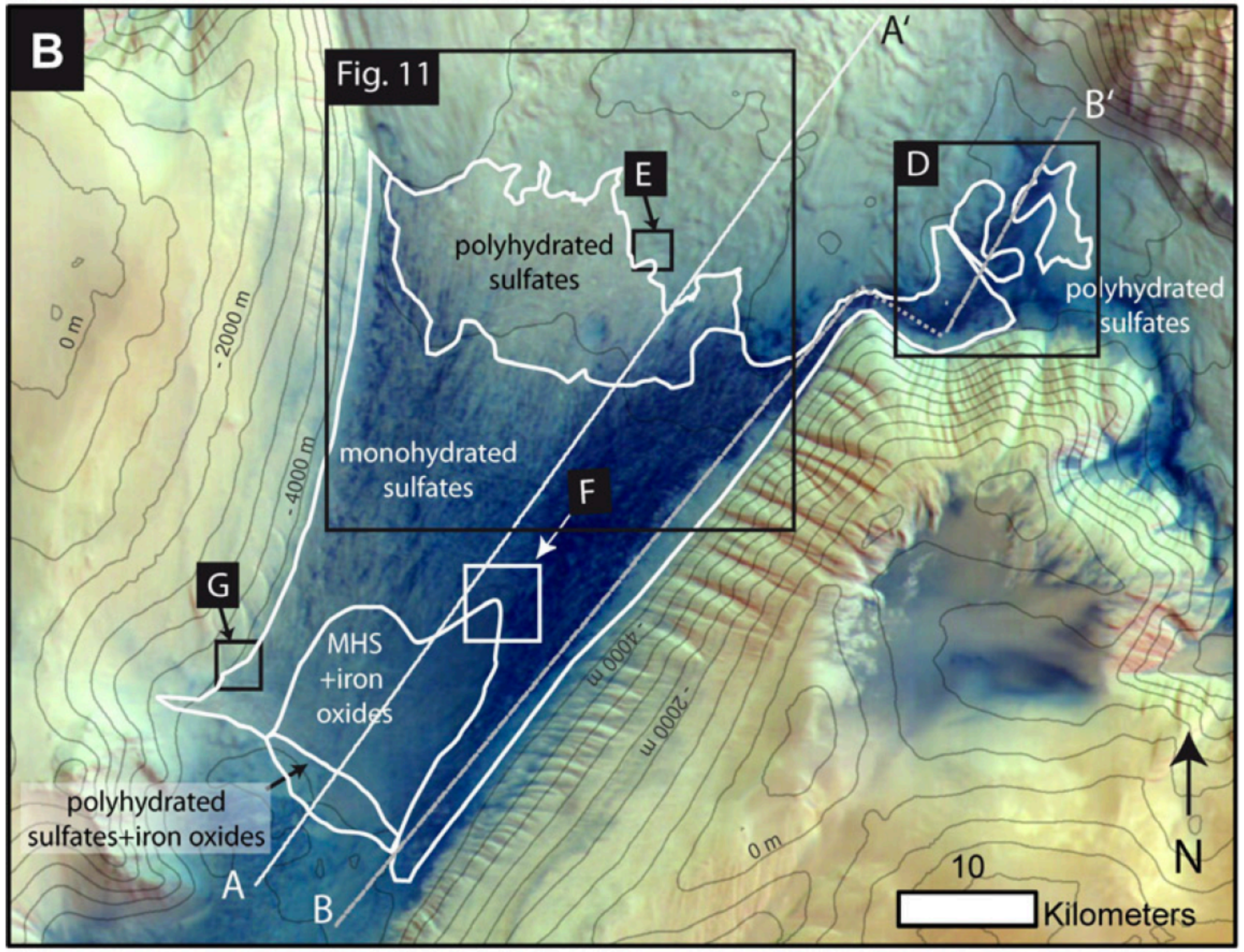
Liu et al. (2016)

Sulfur in planetary environments throughout the solar system

Earth — **Mars** — Icy Satellites

- Polyhydrated and monohydrated sulfates and iron oxides layers
- Szomolnokite $FeSO_4 \cdot H_2O$ and kieserite $MgSO_4 \cdot H_2O$ spectrally identified





Wendt et al. (2011)

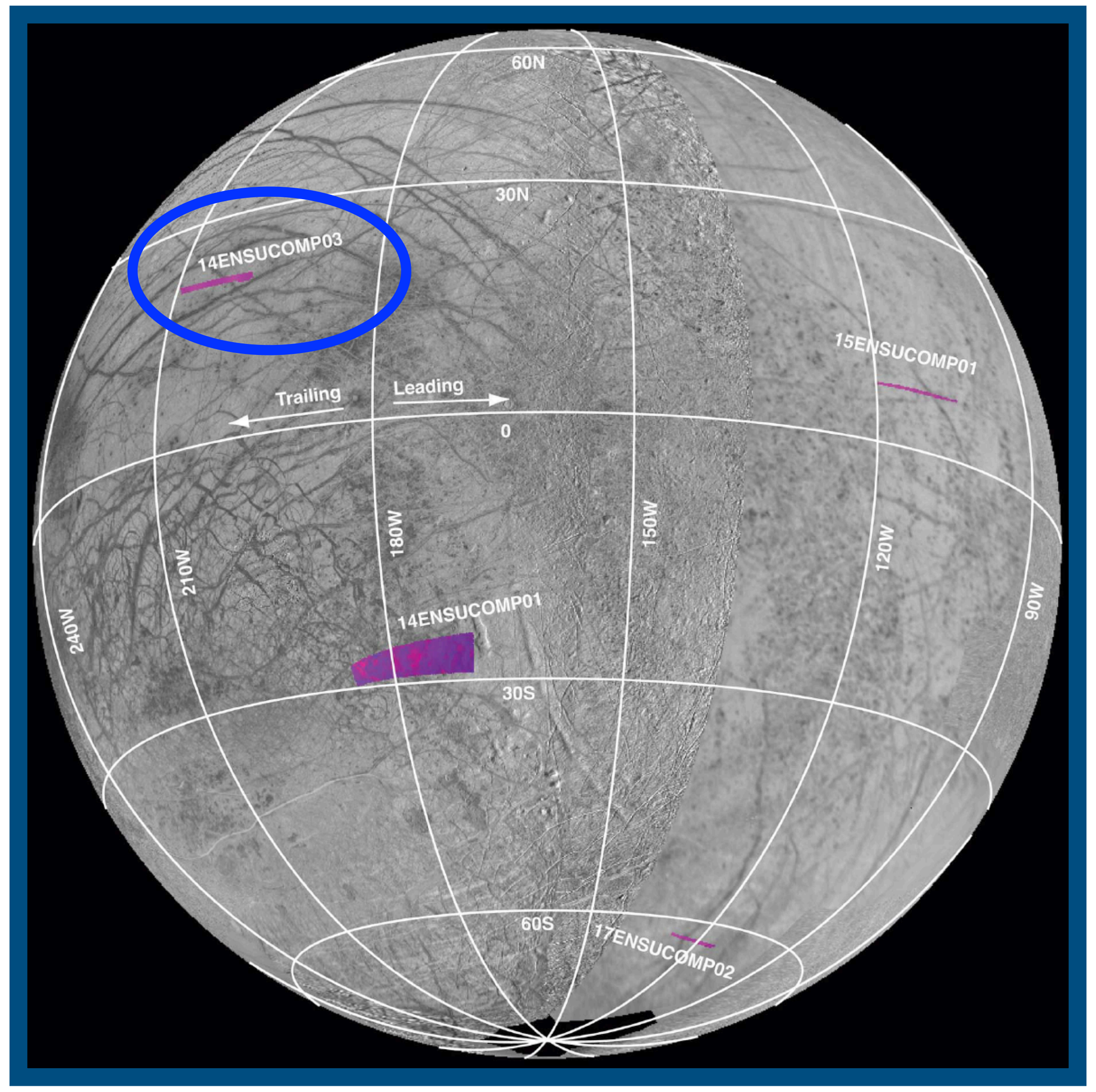
Sulfur in planetary environments throughout the solar system

Earth — Mars — Icy Satellites

- Laboratory measurements aim to identify sulfate-ice mixtures that match observations

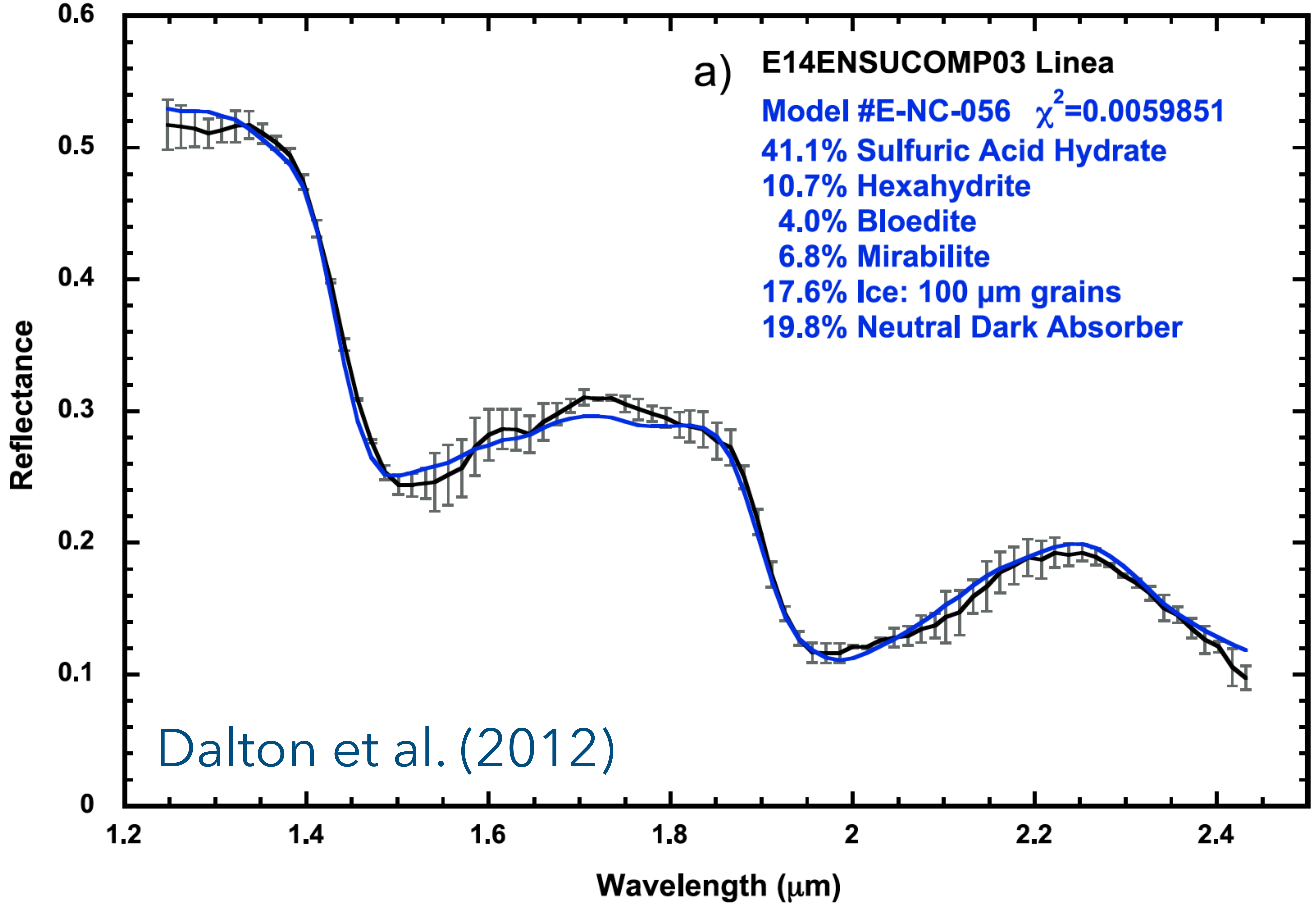
- Candidate sulfates:
  - $H_2SO_4 \cdot 8H_2O$
  - $MgSO_4 \cdot 6H_2O$
  - $Na_2Mg(SO_4)_2 \cdot 4H_2O$
  - $Na_2SO_4 \cdot 10H_2O$
  - $(Fe,Mg)SO_4 \cdot nH_2O$

Europa



- What role do sulfates play at depth?

Modeling observational data of Europa



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Measuring geophysical and geochemical properties of hydrated sulfates

1. *What role do hydrous sulfates play at depth?*
2. *What are their stabilities at non-ambient conditions, and can they retain molecular water?*
3. *How does Fe affect the properties of hydrated sulfates?* $\mathbf{FeSO_4 \cdot H_2O}$

Measuring geophysical and geochemical properties of hydrated sulfates

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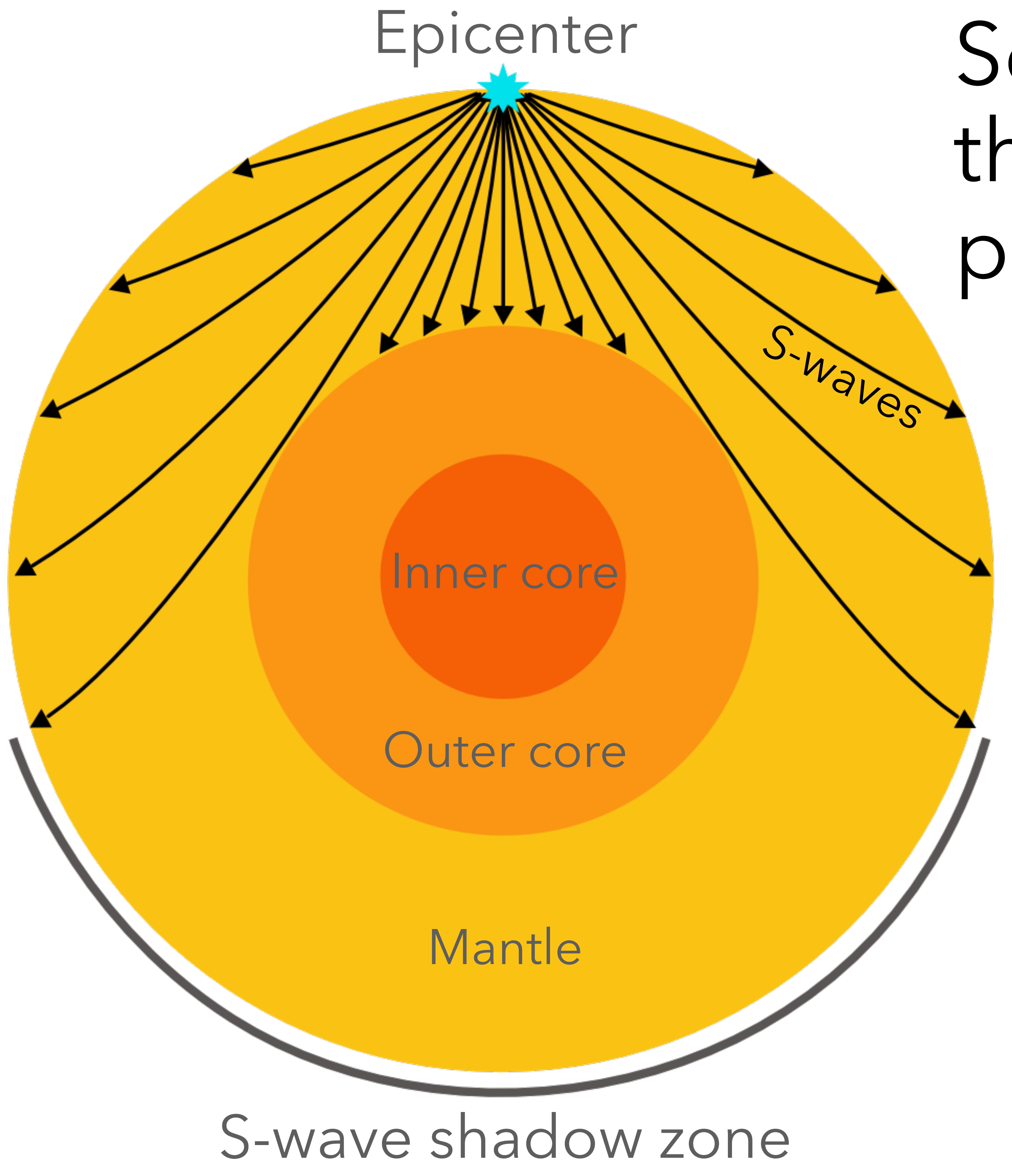
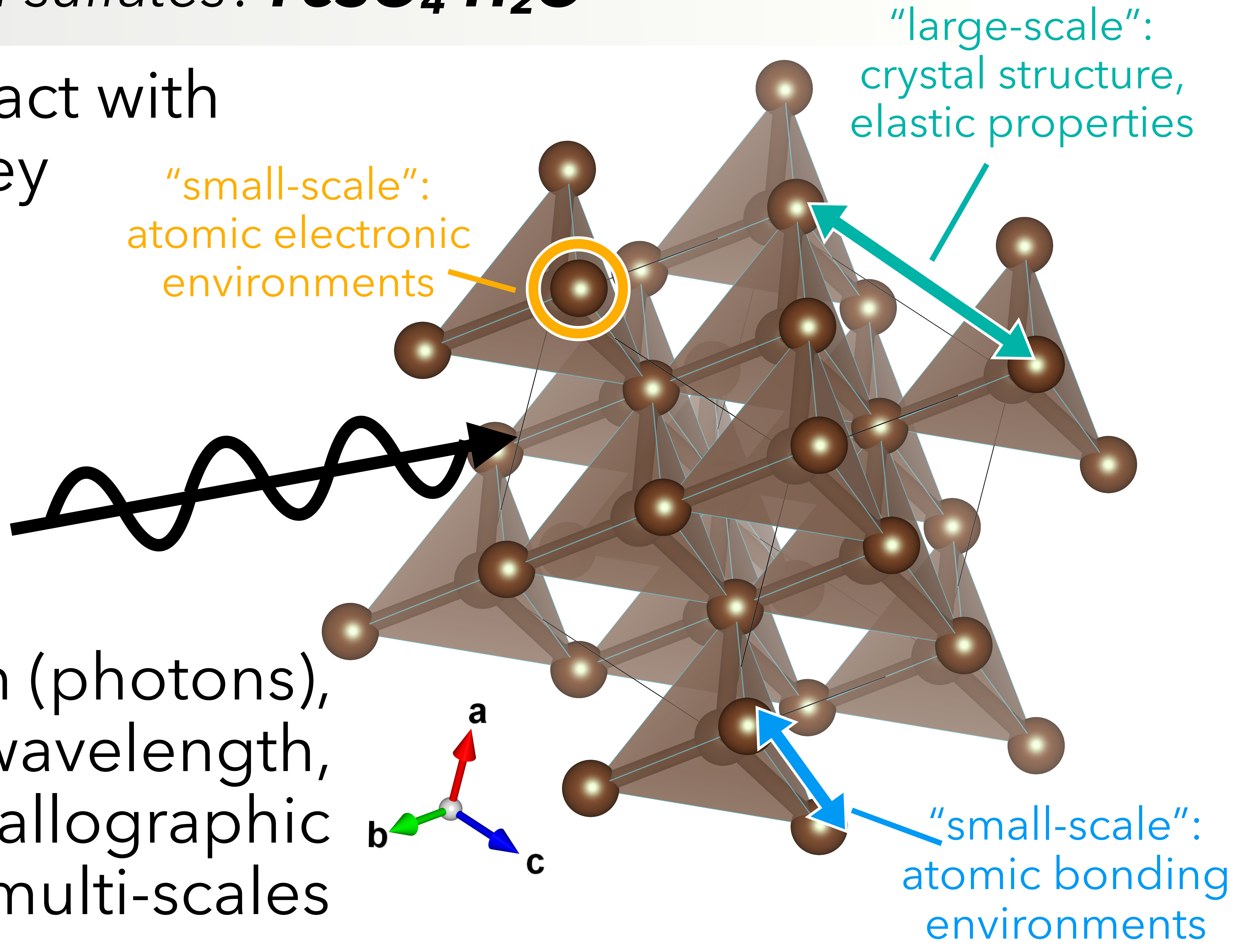


Seismic waves interact with the environment they propagate through

EM radiation (photons), dependent on wavelength, interacts with crystallographic structure at multi-scales



Measuring geophysical and geochemical properties of hydrated sulfates

1. *What role do hydrous sulfates play at depth?*
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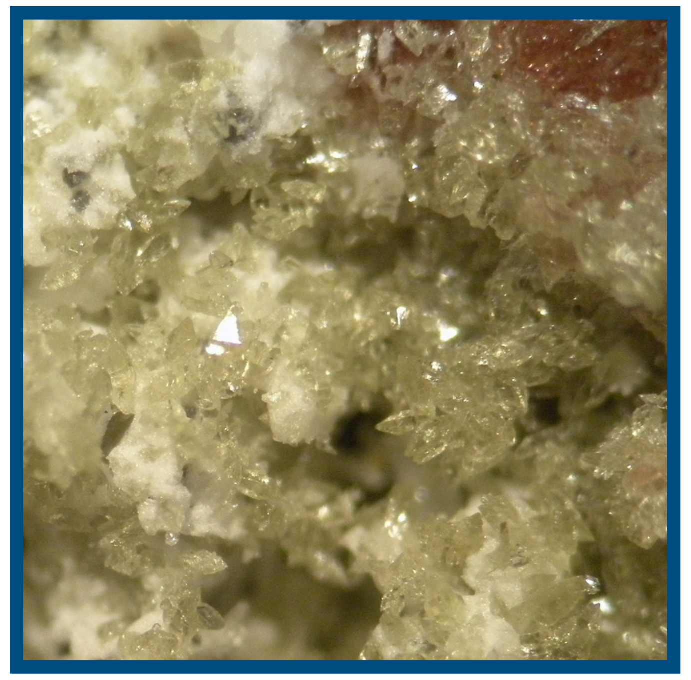
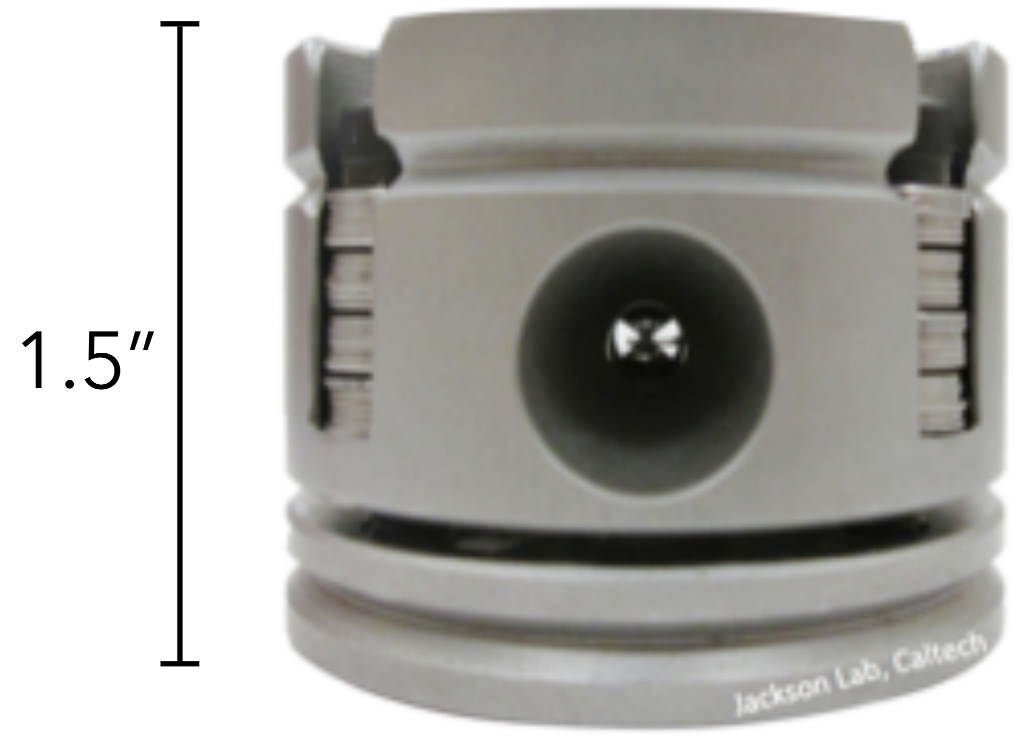


Szomolnokite $FeSO_4 \cdot H_2O$



X-ray Diffraction: crystal structure, thermodynamic parameters for modeling
e.g. equation of state, density, bulk sound velocity

Synchrotron Mössbauer Spectroscopy (SMS)/ Nuclear Resonant Inelastic X-ray Scattering (NRIXS)
e.g. spin state of ^{57}Fe, local coordination environment / sound velocities, crystal lattice softening

Infrared Spectroscopy: molecular vibrations in a material
e.g. bonding environments, thermal properties, can indicate changes in crystal structure

Olivia Pardo *opardo@caltech.edu*

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SSGF reflection

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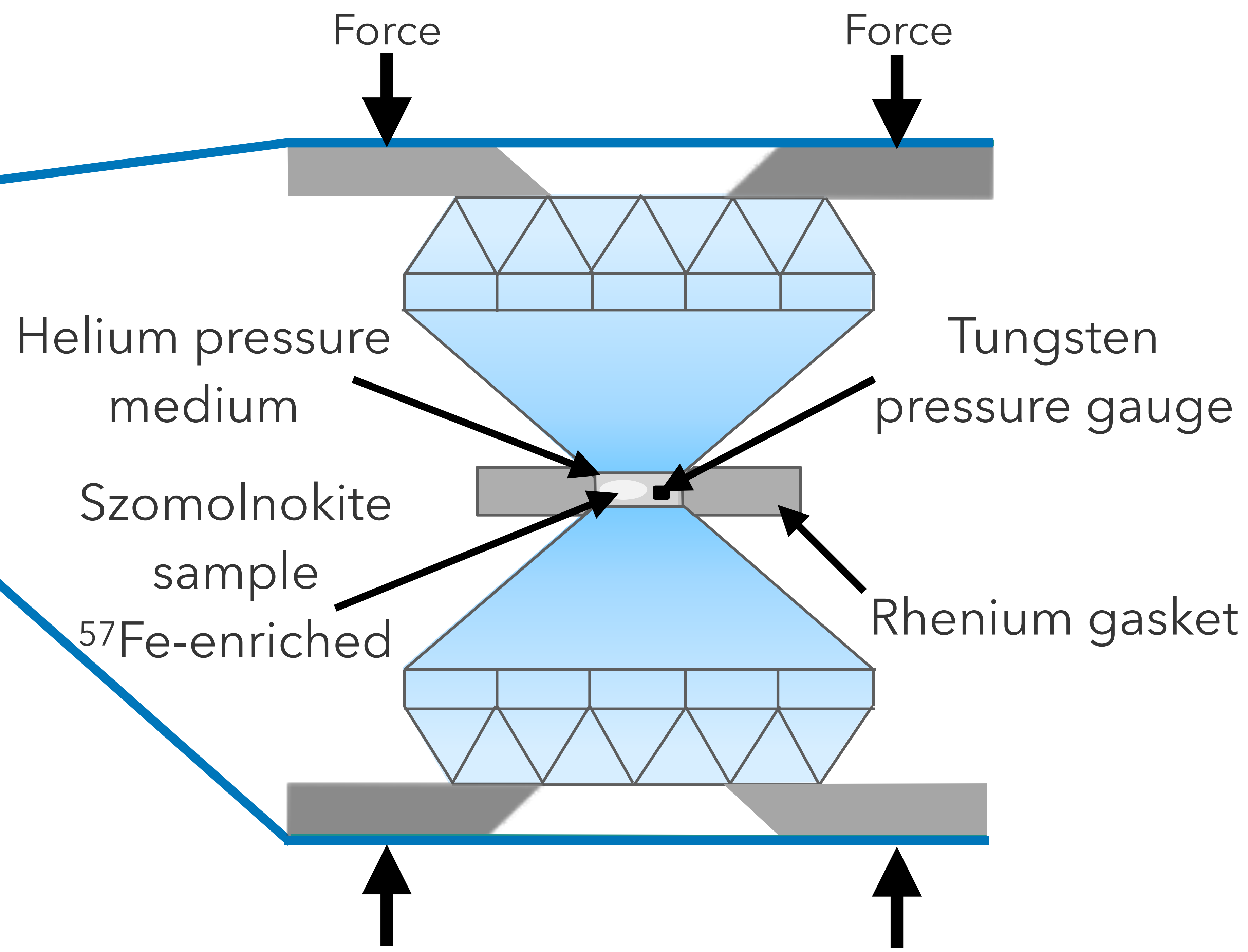
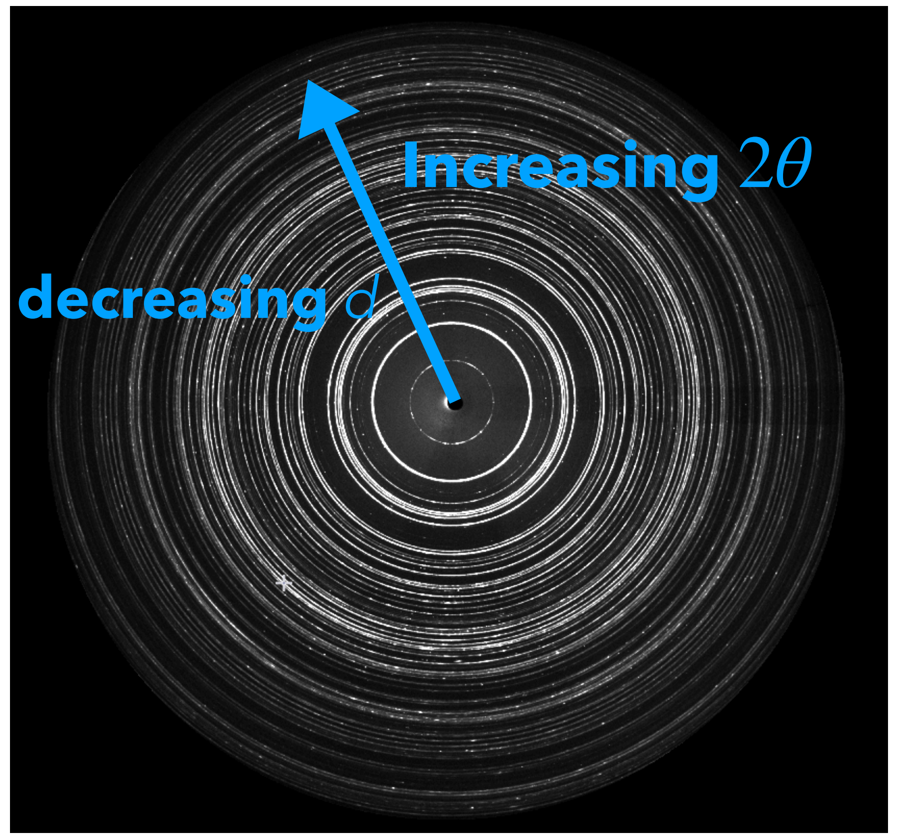
X-ray diffraction (XRD) technique

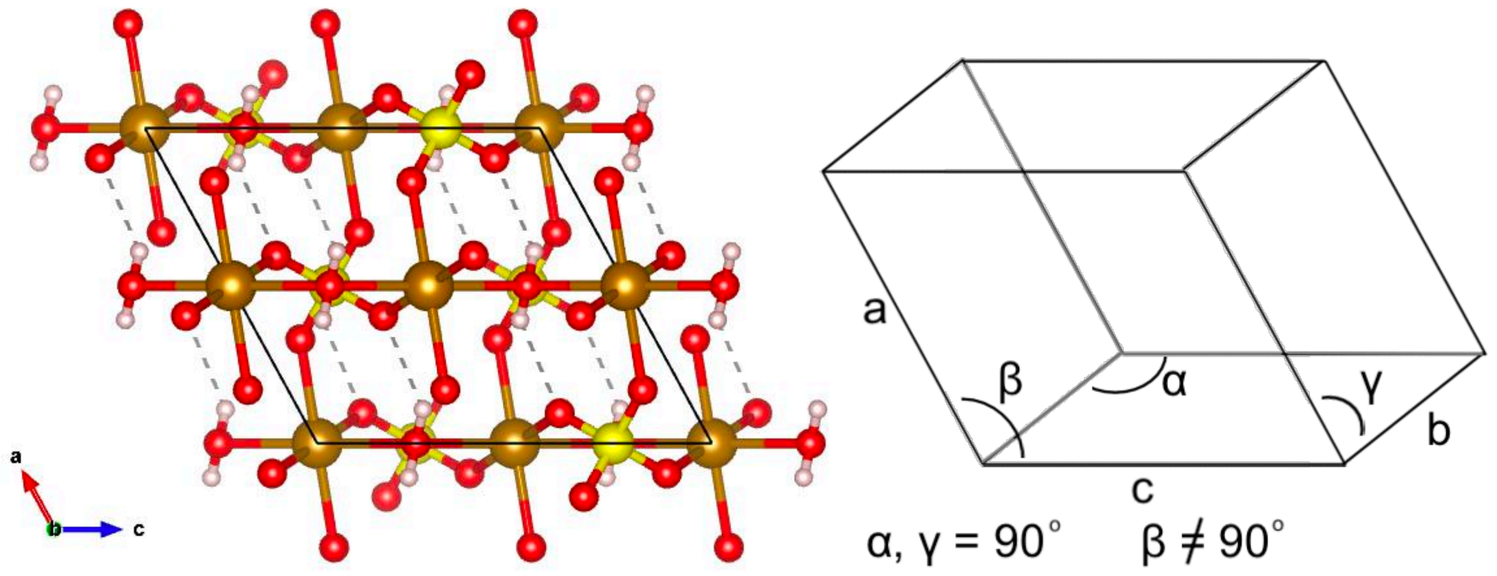
Symmetric DAC



$$n\lambda = 2d\sin\theta$$



Fit integrated XRD pattern and calculate lattice parameters



$$V = abc\sin\beta$$

X-ray source:
Advanced Light Source,
Lawrence Berkeley National Laboratory

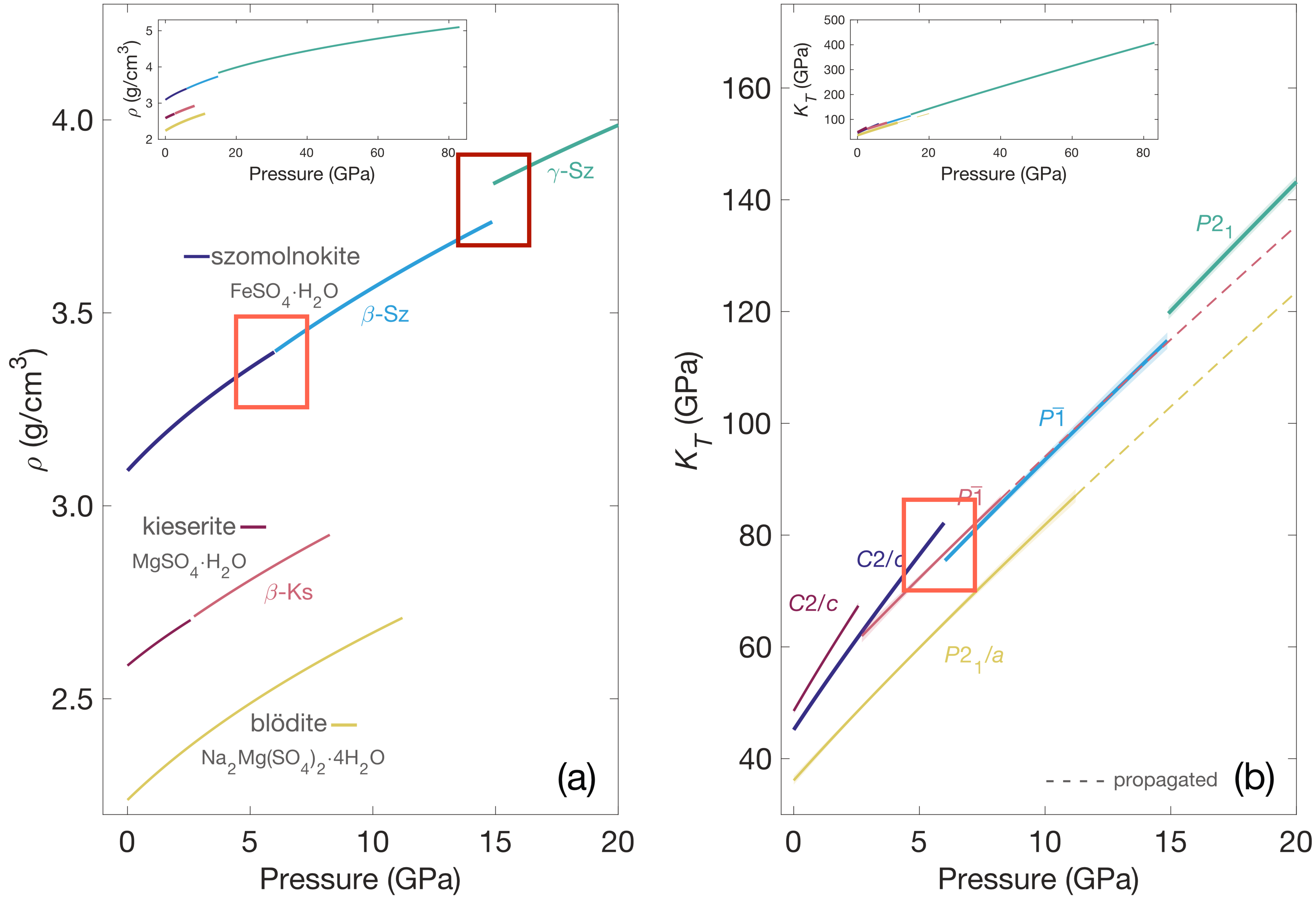
- Beamline 12.2.2
- Wavelength: 0.4972 Å
- X-ray focus full-width half-max: 20μm
- 37 compression points from 0-83 GPa

XRD reveals two structural phase transitions in $FeSO_4 \cdot H_2O$

Olivia S. Pardo, Vasilije V. Dobrosavljevic, Tyler Perez, Wolfgang Sturhahn, Zhenxian Liu, George R. Rossman, Jennifer M. Jackson, *American Mineralogist* (2022, *in press*).

Select X-ray Diffraction Patterns

XRD reveals two structural phase transitions in $FeSO_4 \cdot H_2O$



X-ray diffraction and equation of state analysis

Pardo et al., American Mineralogist (2022, *in press*)

- elastic softening, drop in K_T (α–β)
- significantly higher ρ (β–γ)

Elastic softening over a broad pressure regime?
(e.g. the SiO_2 stishovite to $CaCl_2$-type transition)

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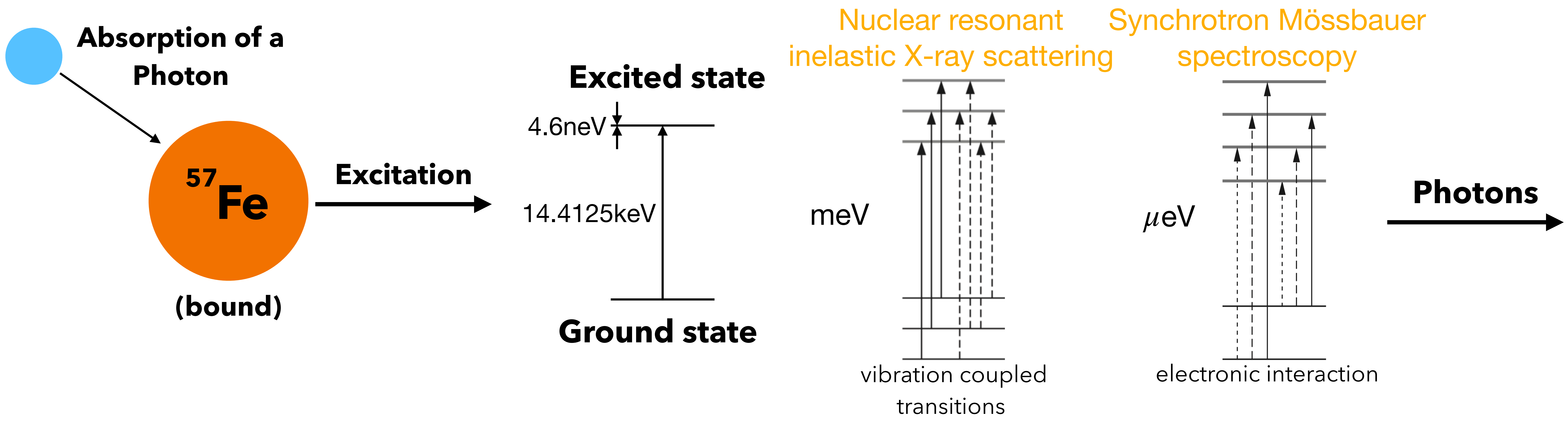
SSGF reflection

Nuclear resonant spectroscopy



Detect

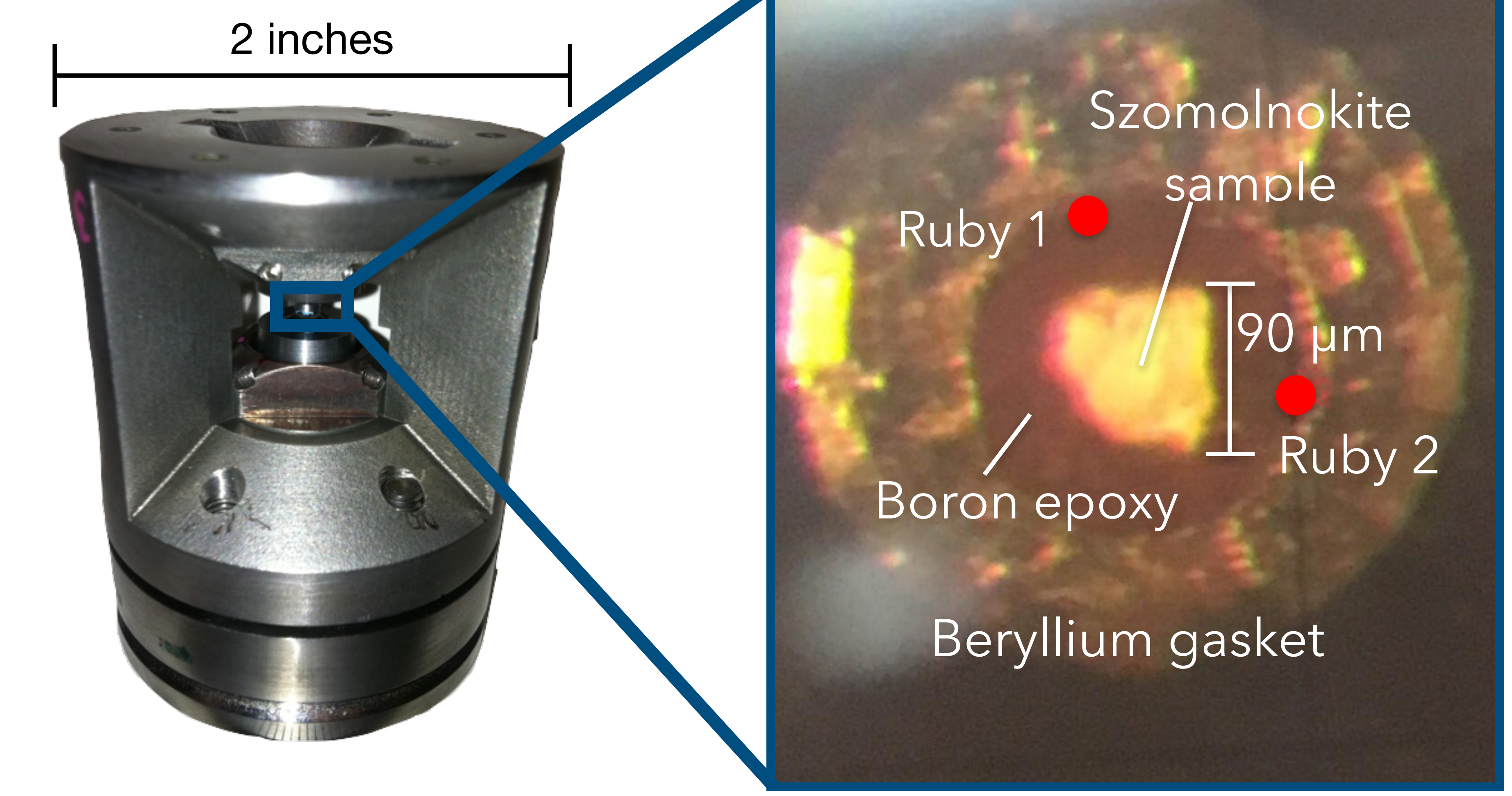
NRIXS: Intensity of emissions as a function of energy

SMS: time structure of nuclear excitation decay (hyperfine parameters)

Advanced Photon Source at Argonne National Laboratory

- Beamline 3-ID-B at the Advanced Photon Source
- Five compression points from 0 -14.4 GPa
- Operating at ^{57}Fe resonance of 14.413 keV with energy-transfer window from 0-220meV off-resonance

Panoramic diamond anvil cell



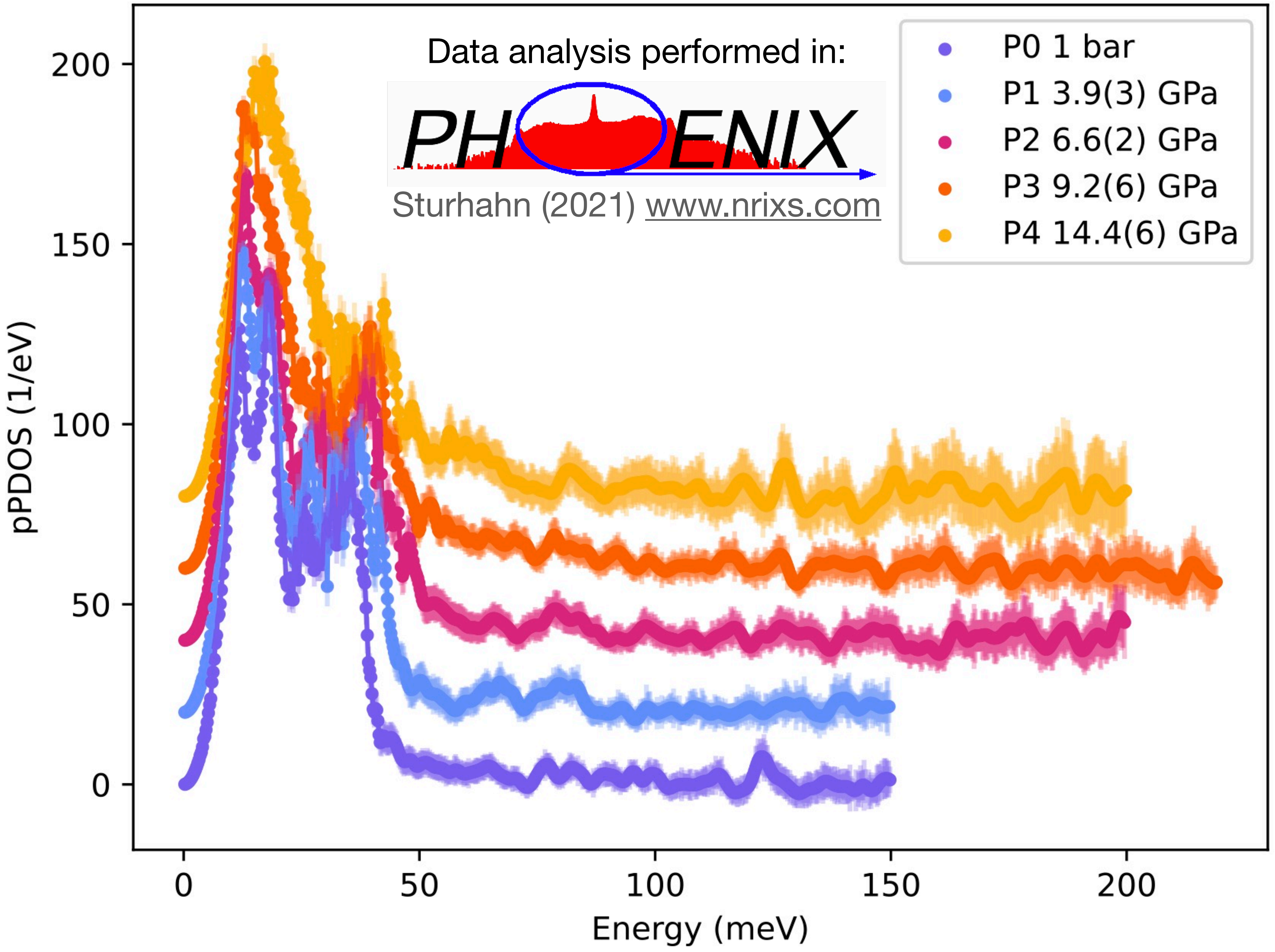
Sample Chamber

Lattice dynamics within $FeSO_4 \cdot H_2O$: high pressure

Nuclear Resonant Inelastic X-ray Scattering

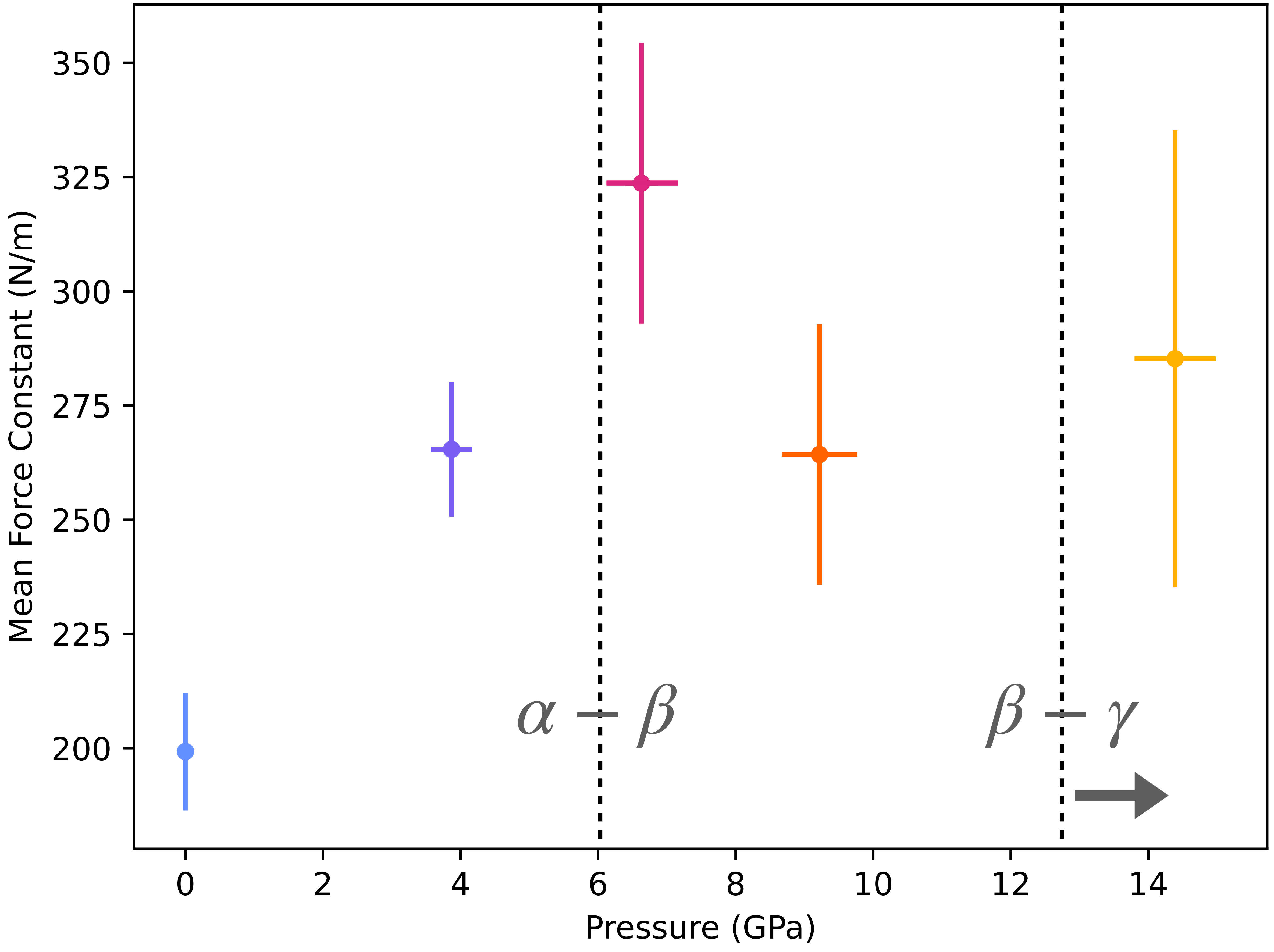
Vibrational modes per unit energy

Partial Phonon Density of States



Average force of bonds acting on the ^{57}Fe atoms

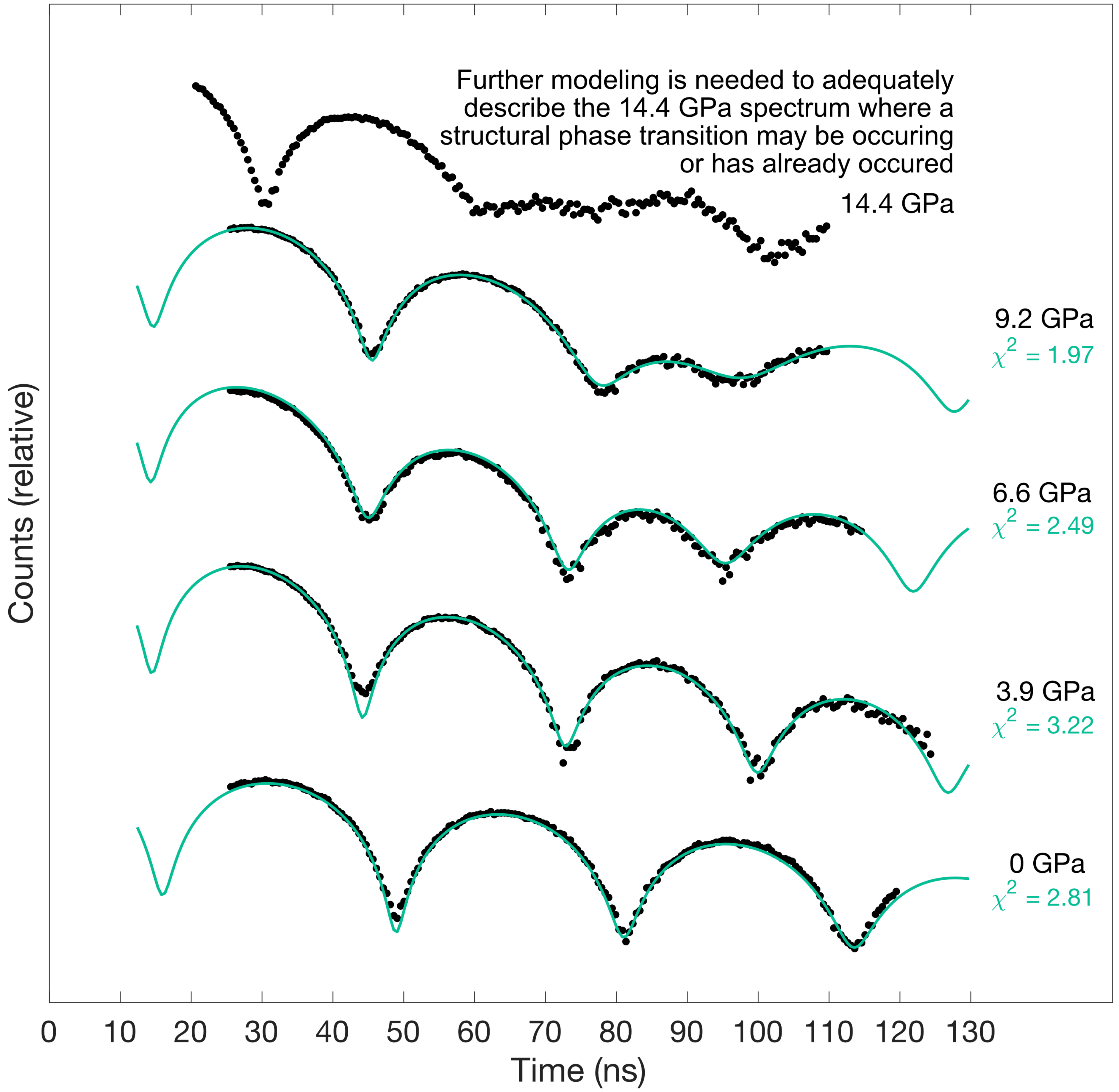
Mean Force Constant



Lattice dynamics within $FeSO_4 \cdot H_2O$: high pressure

Synchrotron Mössbauer Spectroscopy

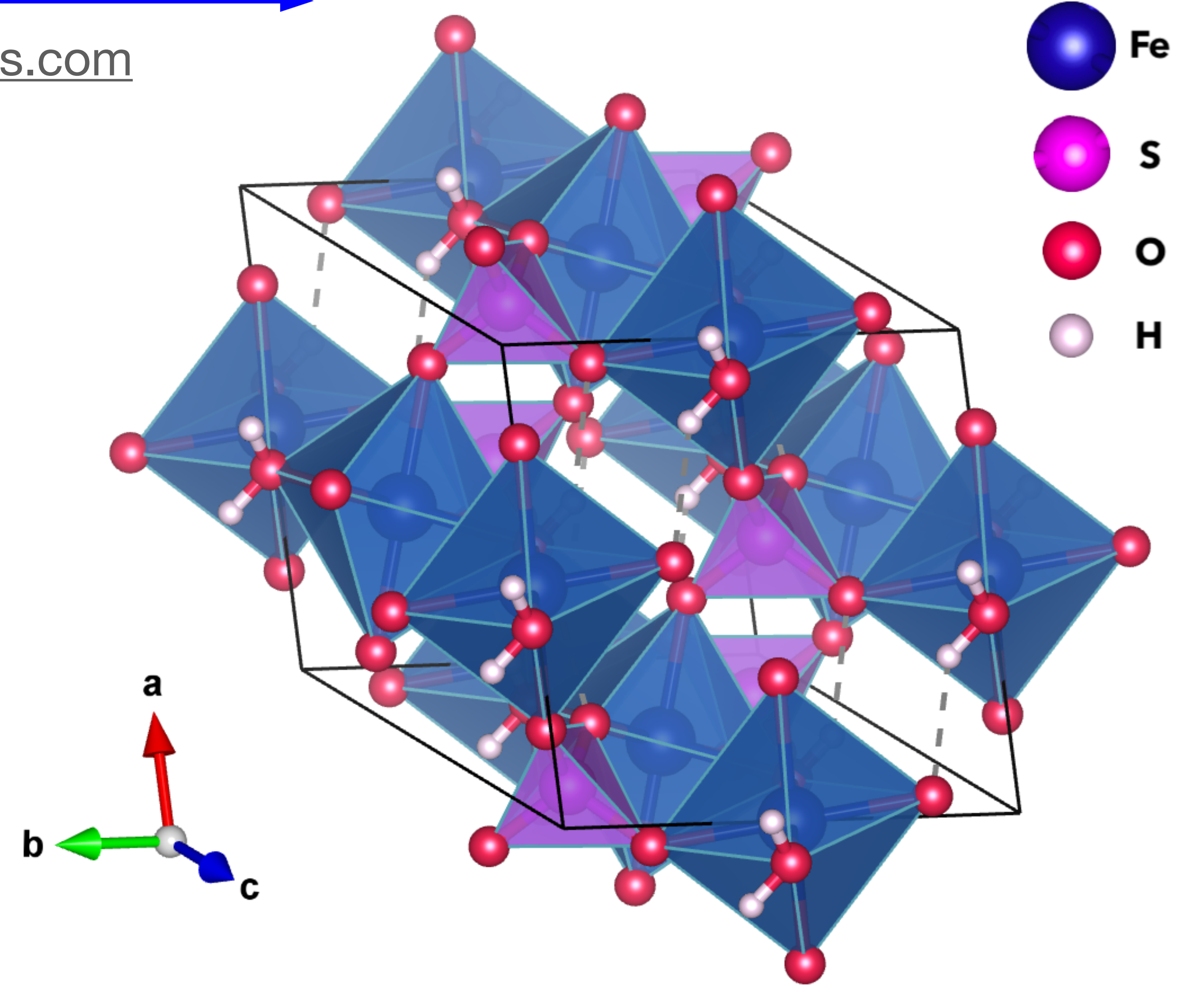
Spectra structure determined by hyperfine field parameters



Data analysis performed in:

CONUSS

Sturhahn (2020) www.nrixs.com



Lattice dynamics within $FeSO_4 \cdot H_2O$: high pressure

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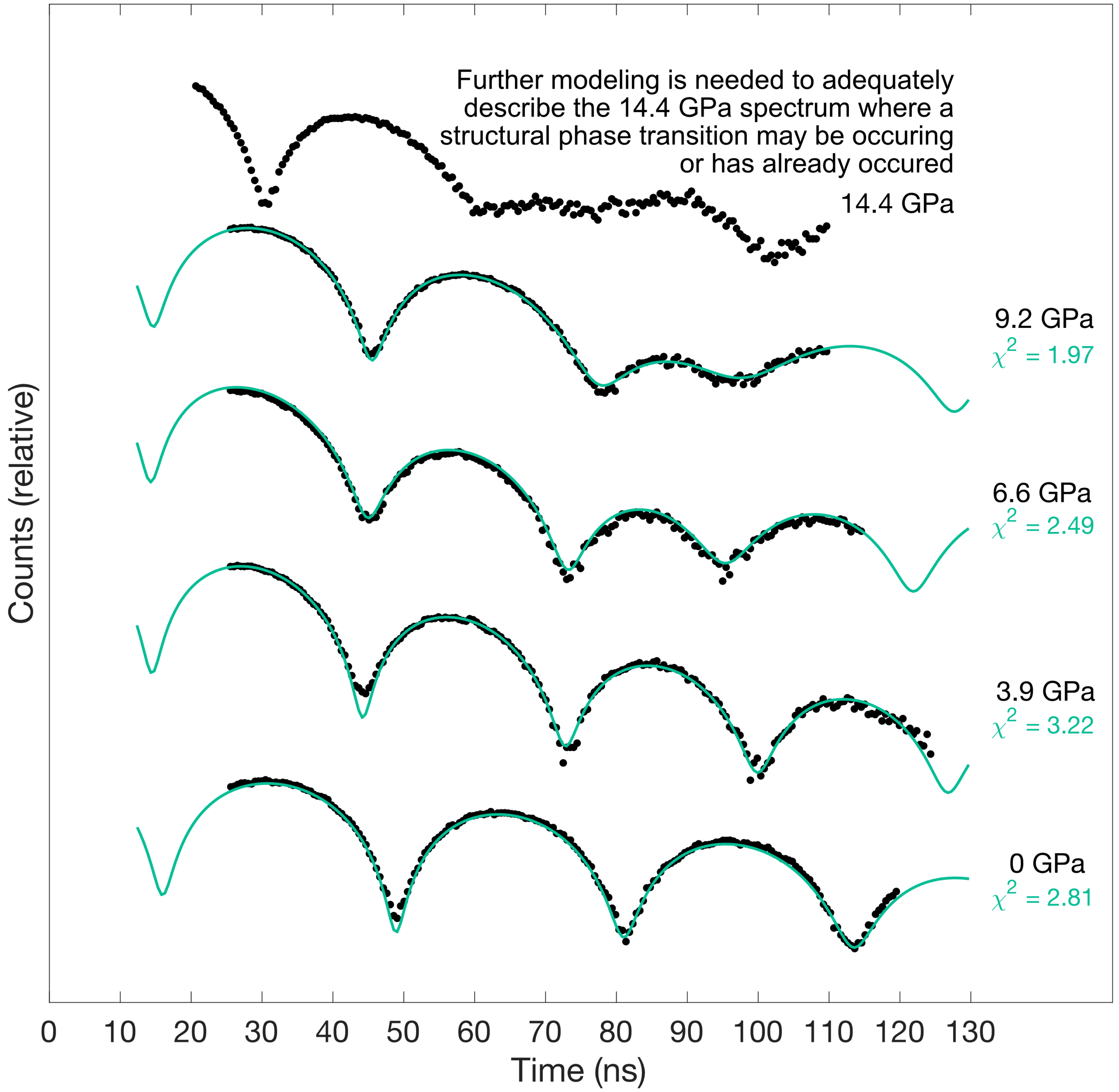
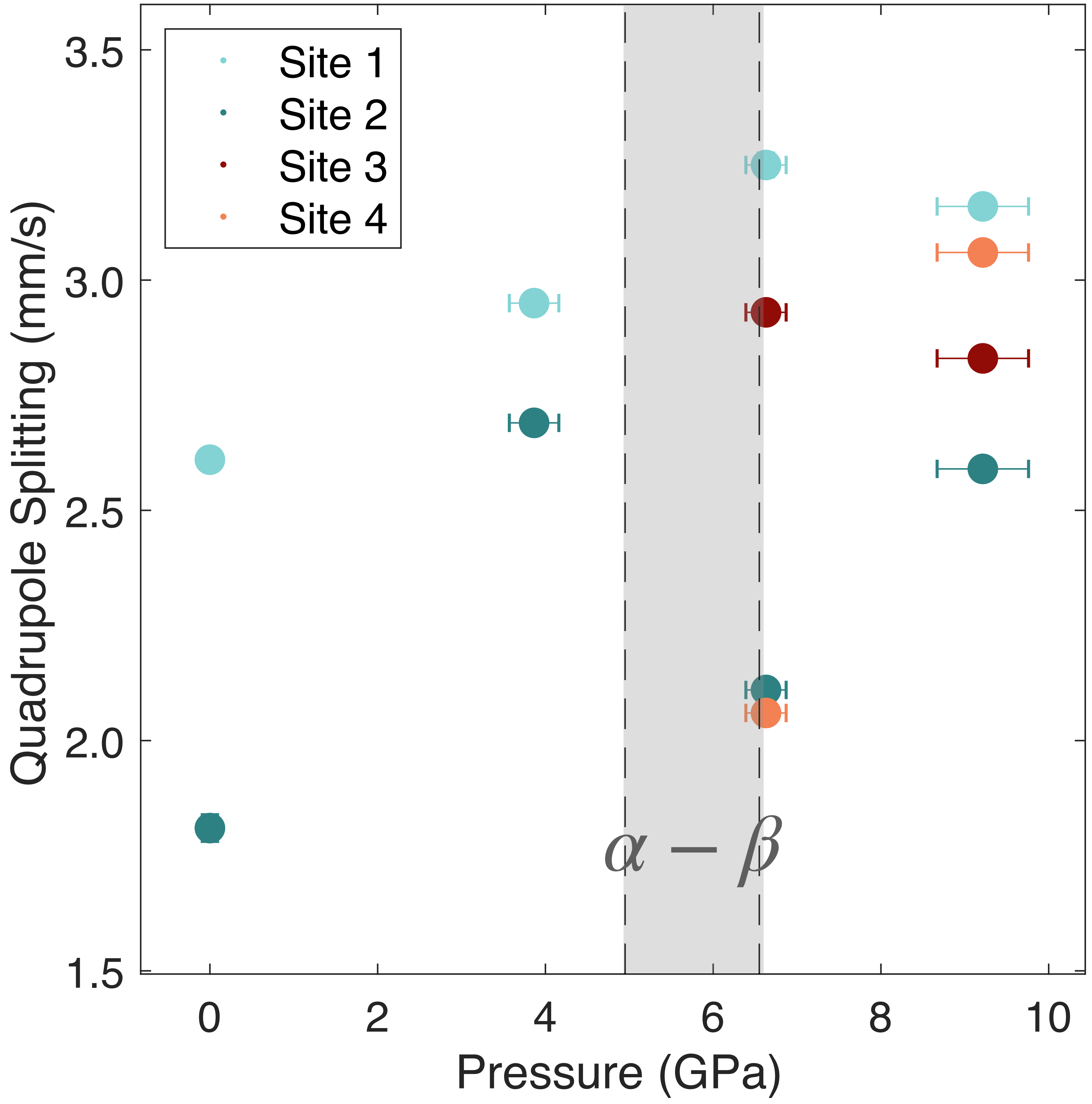


Distortion of electric field gradient around ^{57}Fe atom



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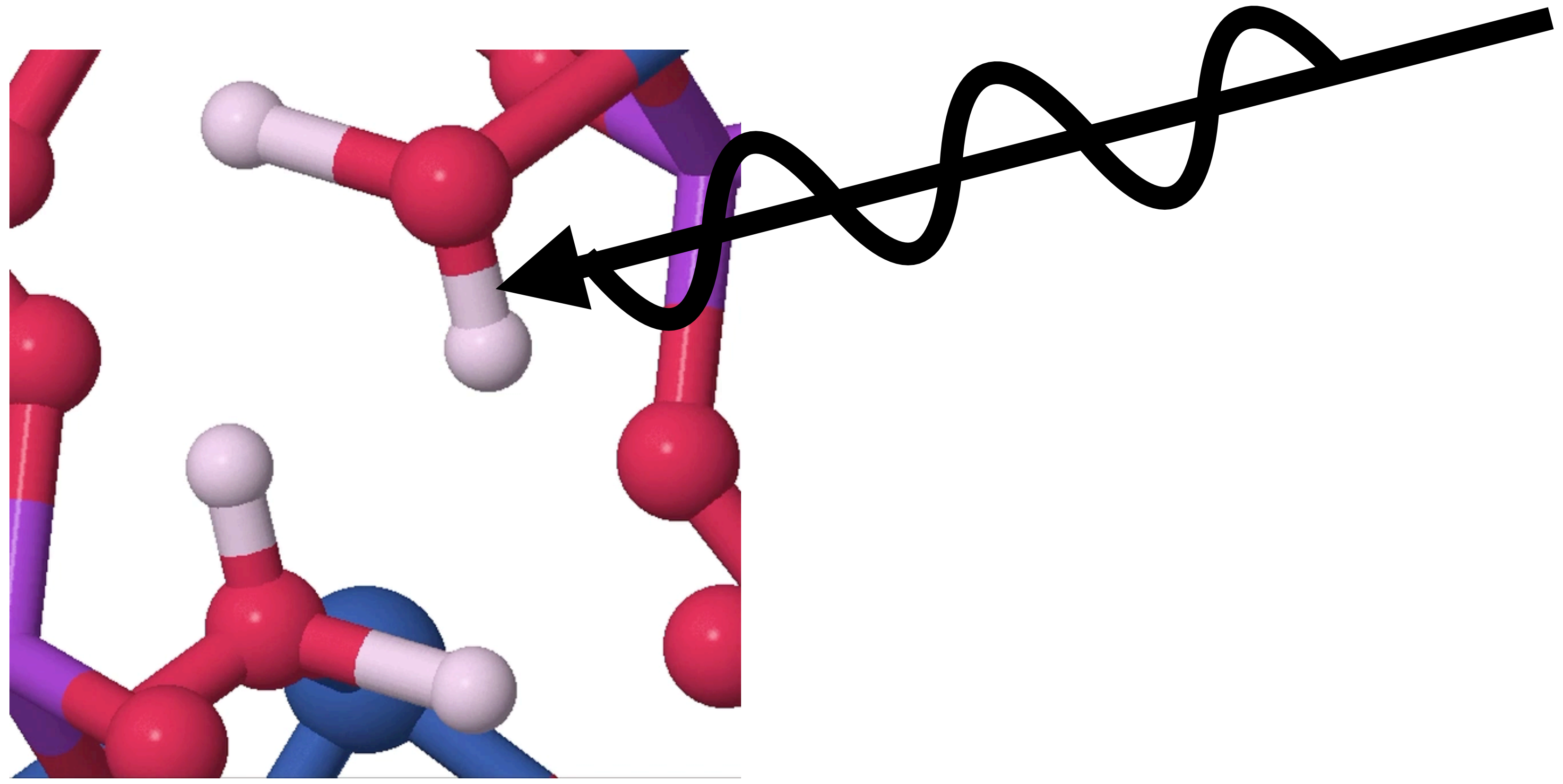
1) Structural information   2) Lattice dynamics   **3) Vibrational properties of bonds**

SSGF reflection

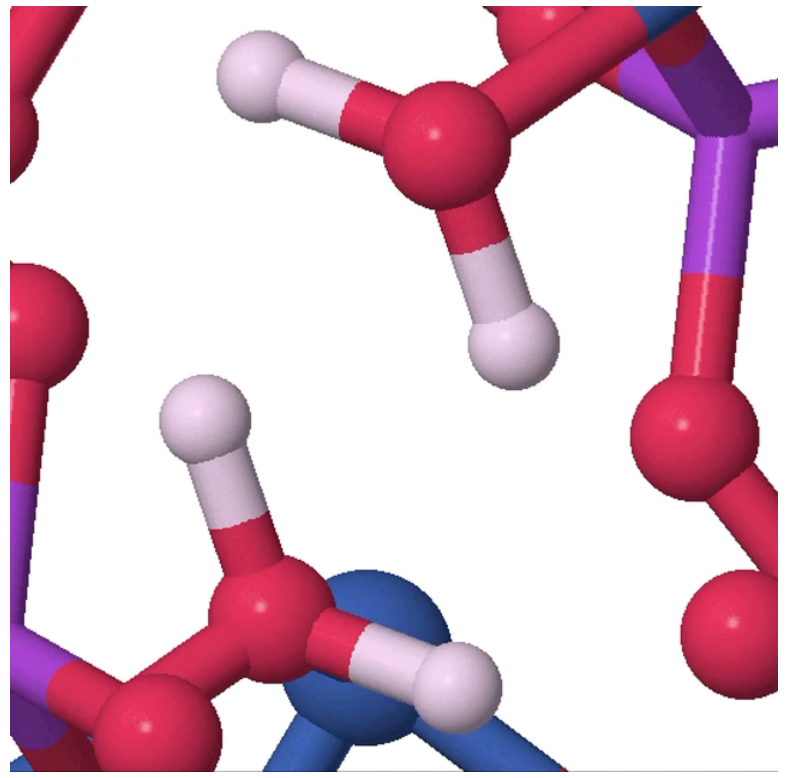
Infrared spectroscopy

Asymmetric stretching



v3: 3371 cm^{-1}

Bending



v2: 1520 cm^{-1}

- Infrared spectroscopy: infrared light is *absorbed* by a molecule when the energy of the incident light is equal to differences in *vibrational* energy levels within the molecule

Vibrational frequency: $\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$

- Vibrational motions of a molecule: bending and stretching/contracting

- Fourier transform infrared spectroscopy measurements taken at Brookhaven National Laboratory, NSLS-II
- Beamline 22-IR-1 with **Dr. Zhenxian Liu**
- Wavenumber range: 400-5000 cm^{-1}

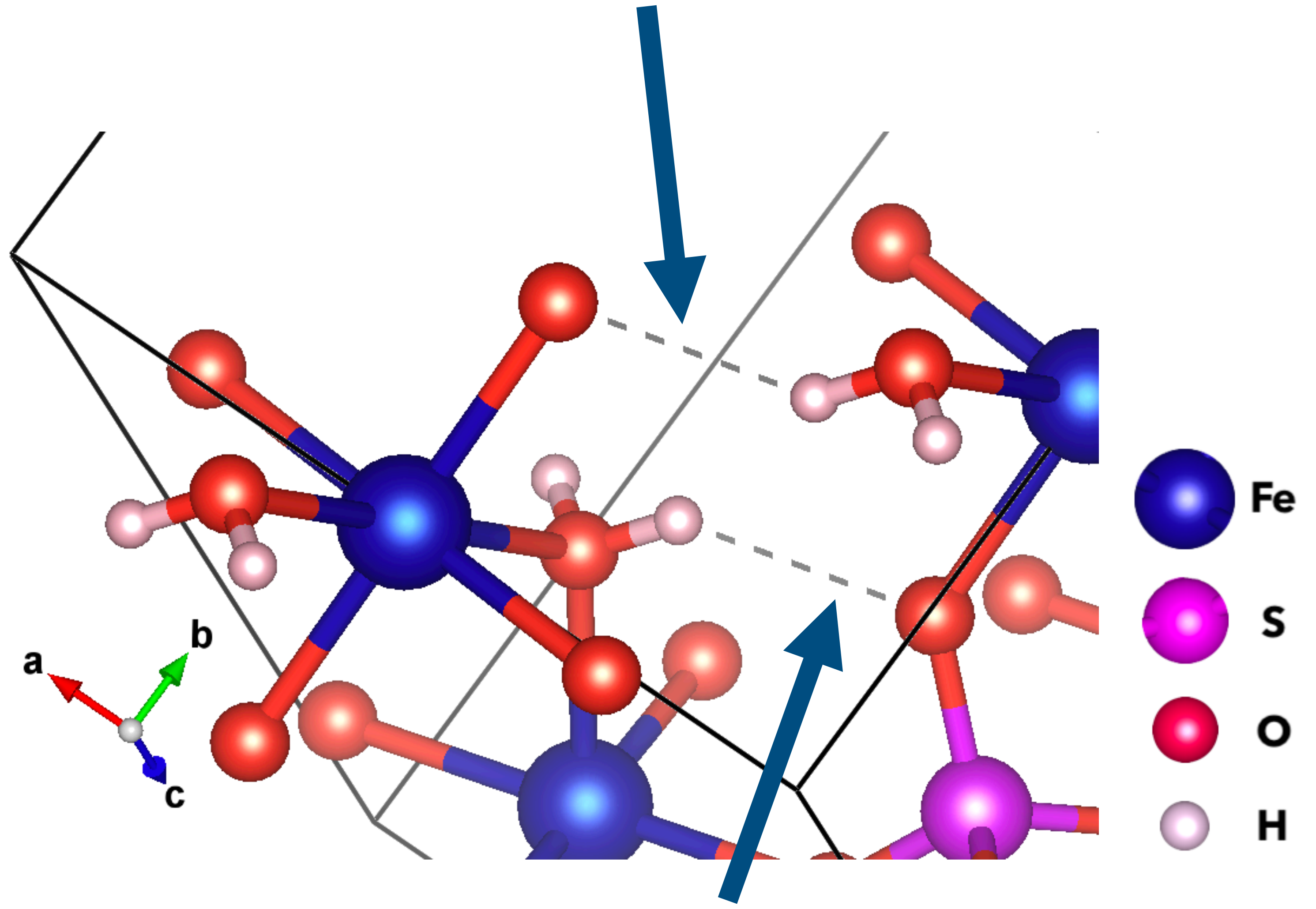
Vibrational properties of $FeSO_4 \cdot H_2O$: high pressure

Collaboration with Dr. Zhenxian Liu at Brookhaven National Laboratory

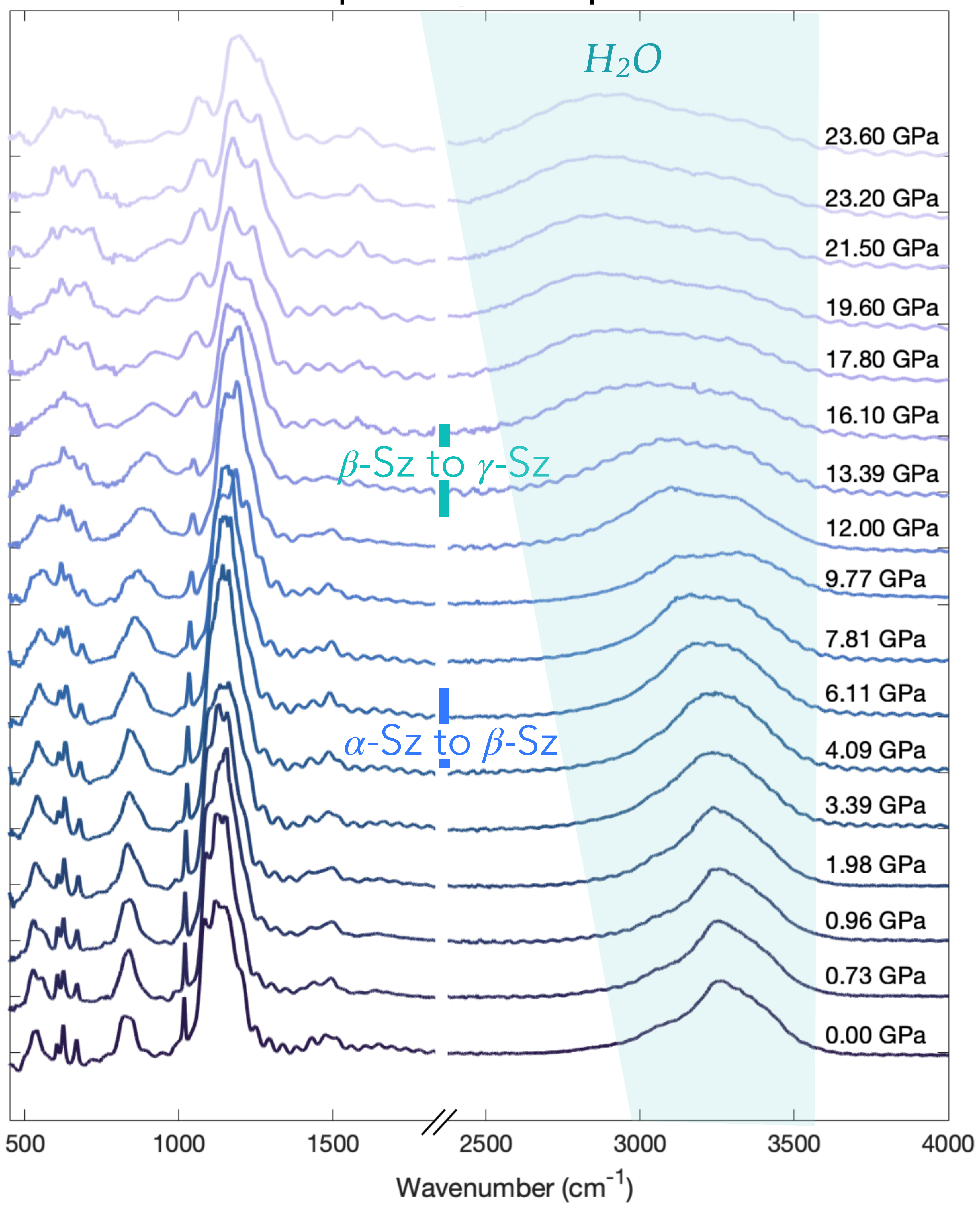
Retention of H_2O in high-pressure phases

- Indication of increased H_2O coordination within the crystal structure at pressure
- Reversible and H_2O is retained upon decompression

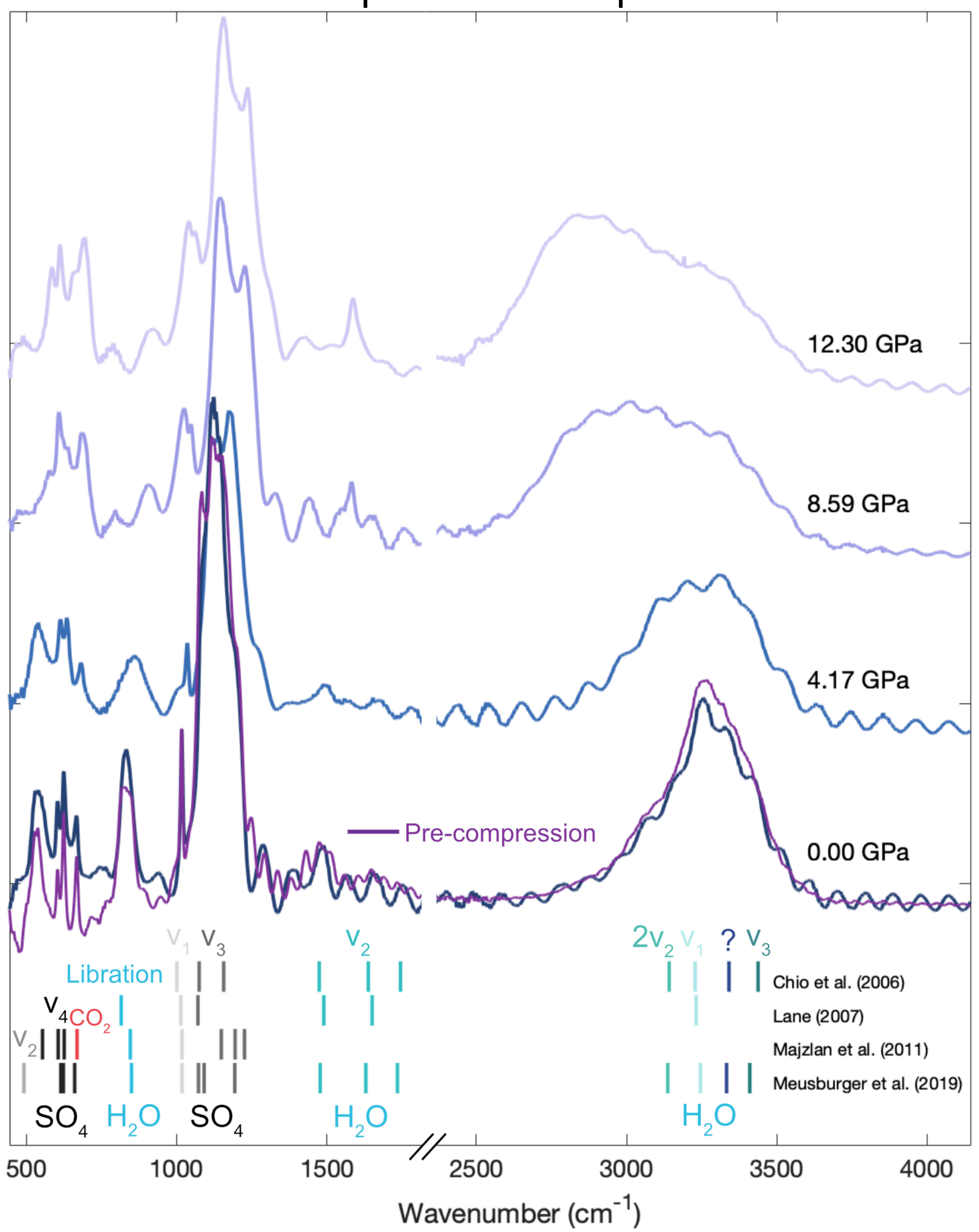
Bond strength increases



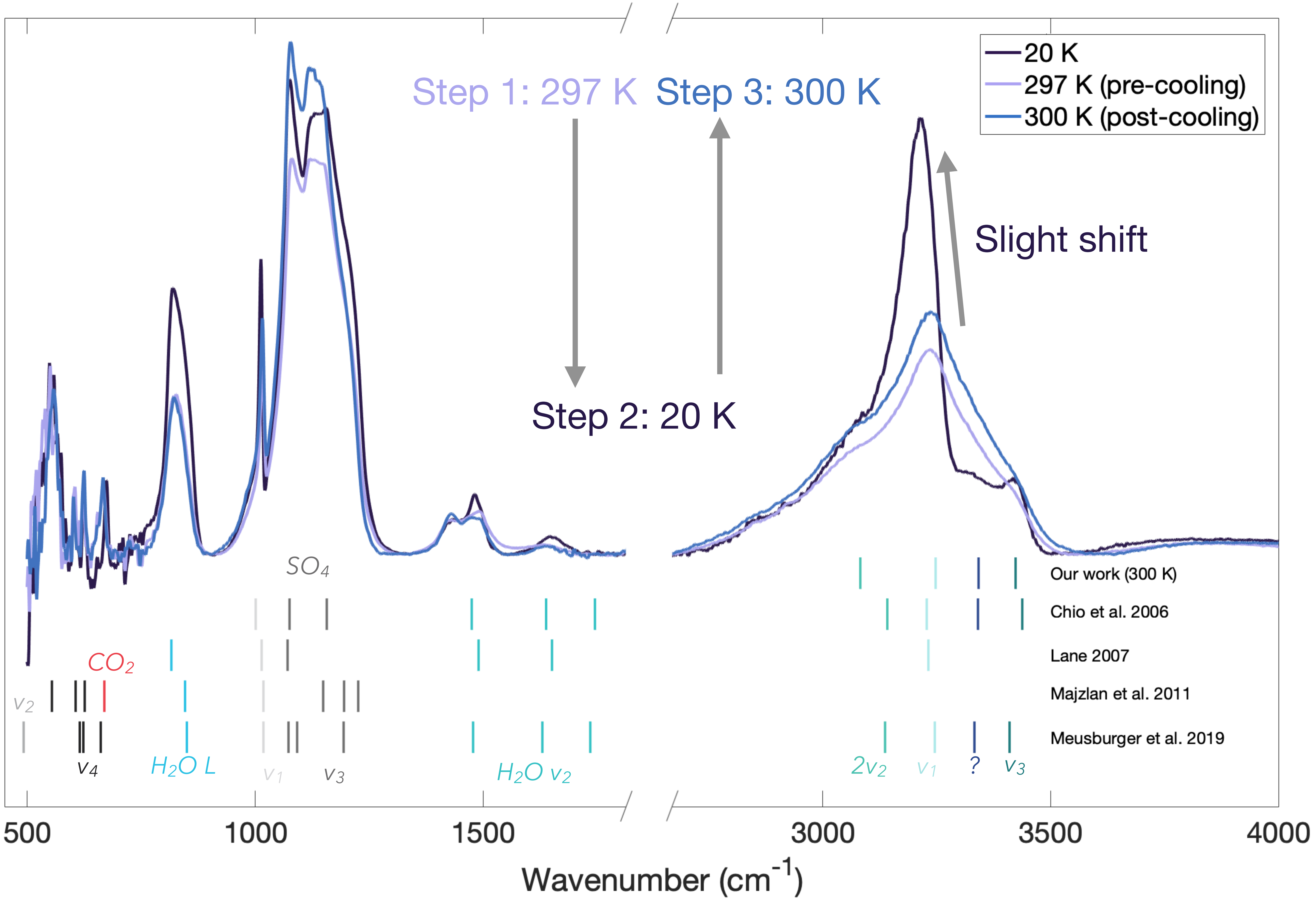
Compression Spectra



Decompression Spectra

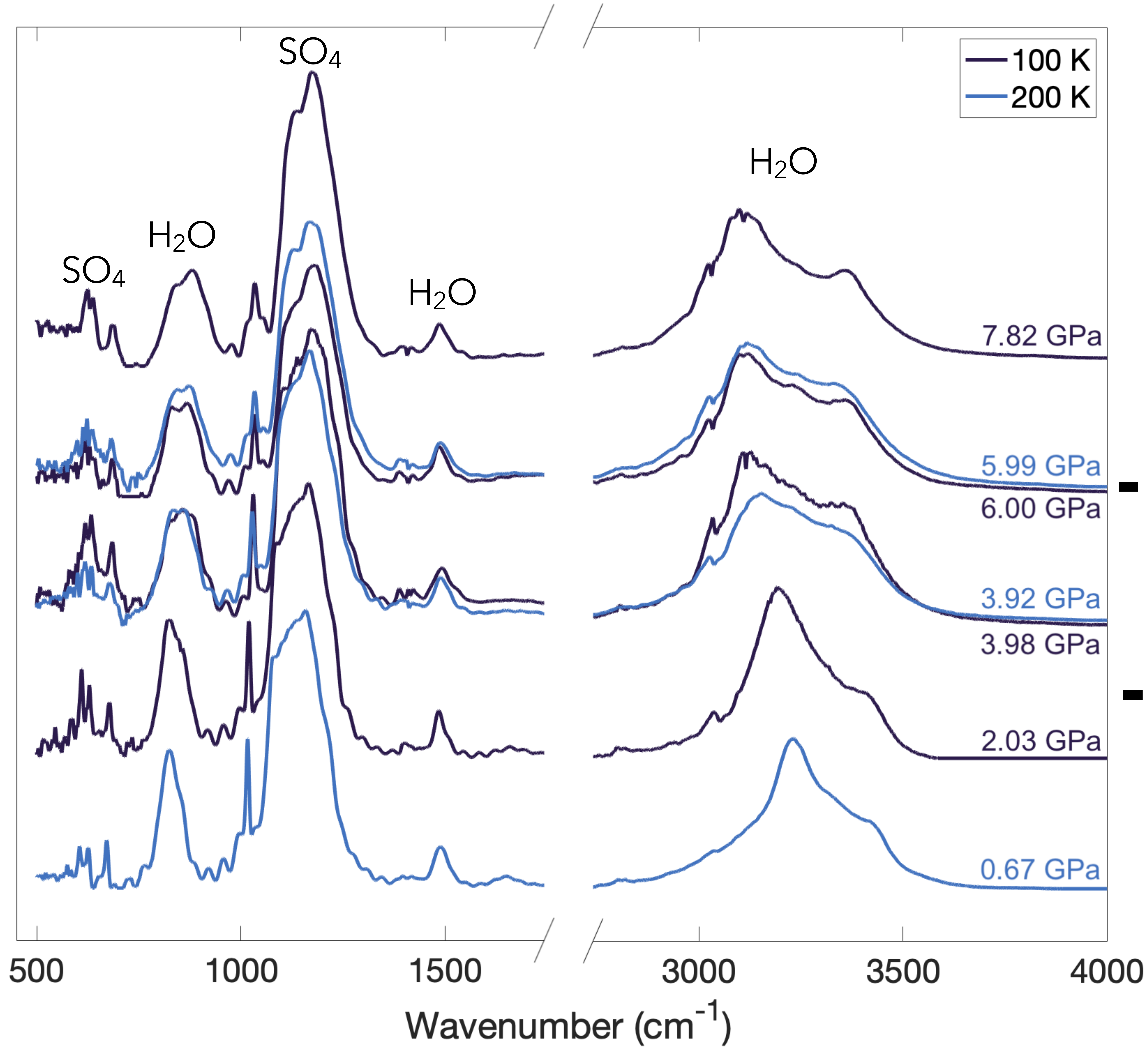


Vibrational properties of $FeSO_4 \cdot H_2O$: high pressure



Changes in the vibrational properties are **reversible** during low temperature cycling

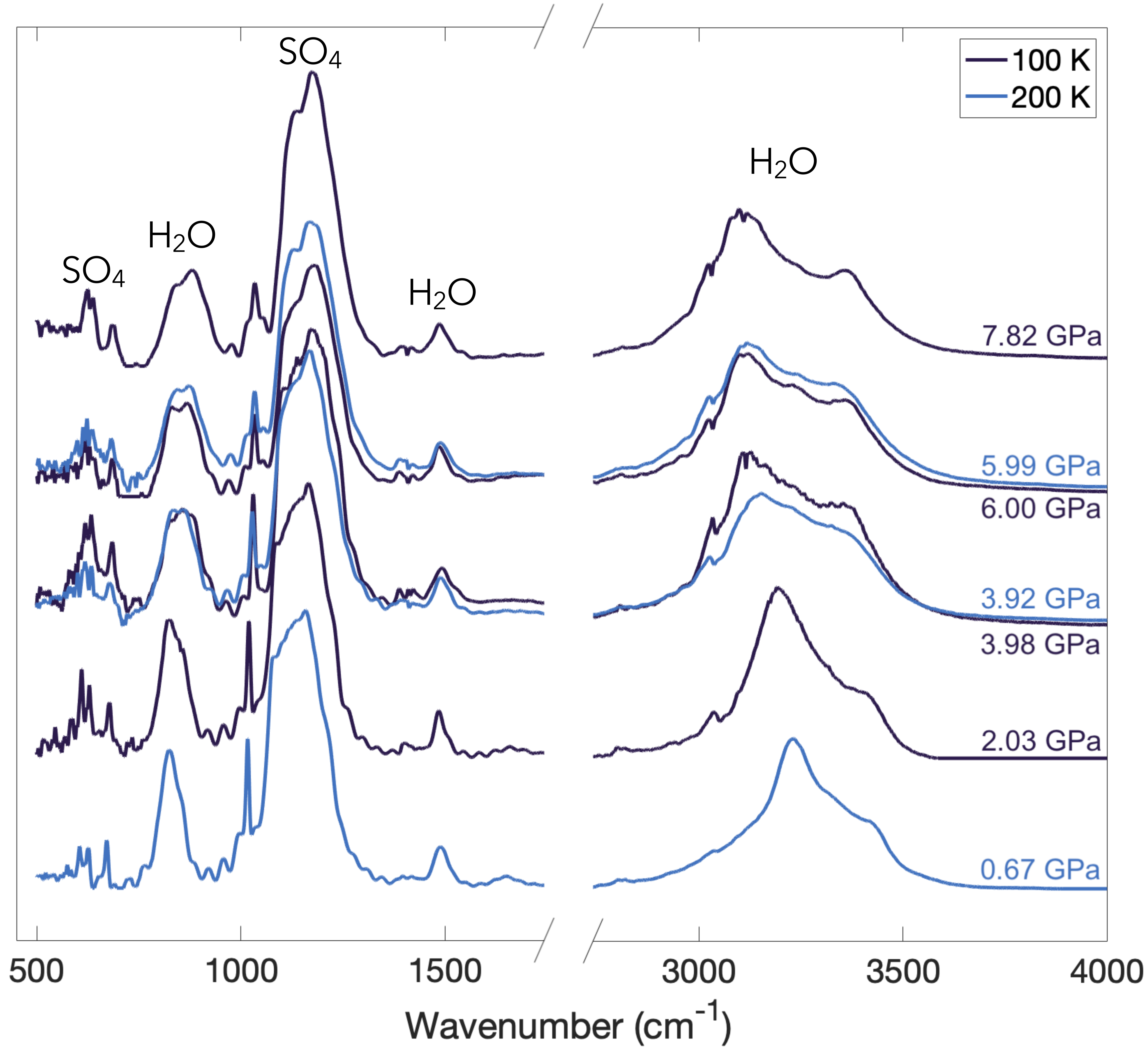
Vibrational properties of $FeSO_4 \cdot H_2O$: high pressure, low temperature



300 K structural transition

structural transition at 100 K, lower pressure?

Vibrational properties of $FeSO_4 \cdot H_2O$: high pressure, low temperature



If α-Sz to β-Sz transitions occurs at lower pressures at lower temperatures

↓

+ Clapeyron slope

At lower temperature, phase transition to *denser* β-Sz would occur at *shallower* depths, could this promote convection?

Summary of experimental results: $FeSO_4 \cdot H_2O$

X-ray Diffraction: crystal structure, thermodynamic parameters for modeling
e.g. equation of state, density, bulk sound velocity

- Discovery of a new phase transition around 14 GPa (γ-Sz)
- Elastic softening across α-Sz to β-Sz

Synchrotron Mössbauer Spectroscopy/
Nuclear Resonant Inelastic X-ray Scattering
e.g. spin state of Fe, local coordination environment /
sound velocities, crystal lattice softening

- increase in QS values and additional sites at ~7 GPa could be attributed to a decrease in symmetry in the Fe^{2+} coordination environment and structural phase transition

Infrared Spectroscopy: molecular vibrations in a material
e.g. bonding environments, thermal properties, can indicate changes in crystal structure

- Retention of molecular water in the new γ-Sz high-pressure phase
- Significant changes in spectra at low T, lower P: related to phase transition?
- Suggestions of a positive Clapeyron slope

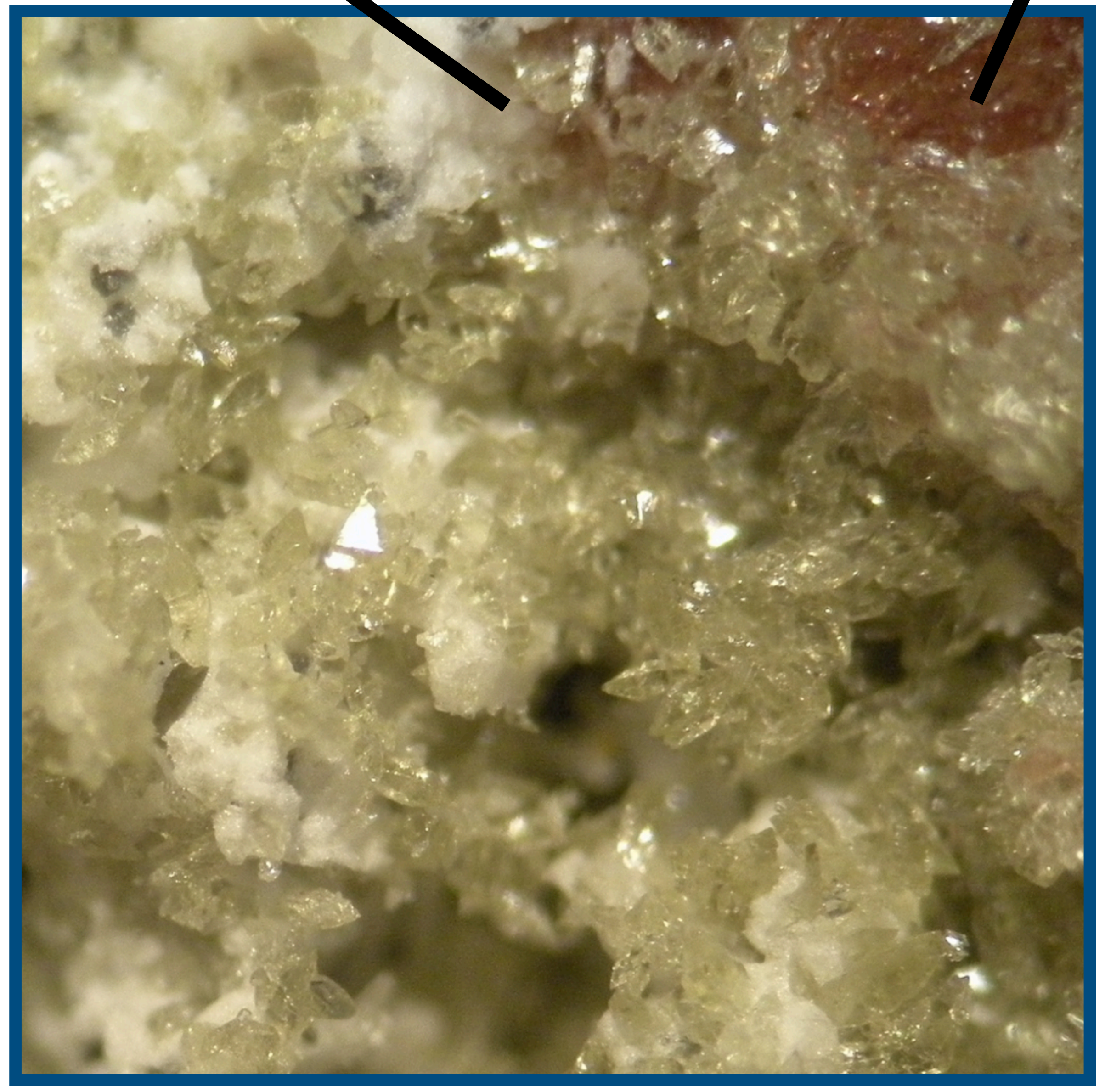
Exploring multi-valent sulfates: Römerite $Fe^{2+}Fe^{3+}_2(SO_4)_4 \cdot 14H_2O$

szomolnokite

$FeSO_4 \cdot H_2O$

… and römerite

$Fe^{2+}Fe^{3+}_2(SO_4)_4 \cdot 14H_2O$



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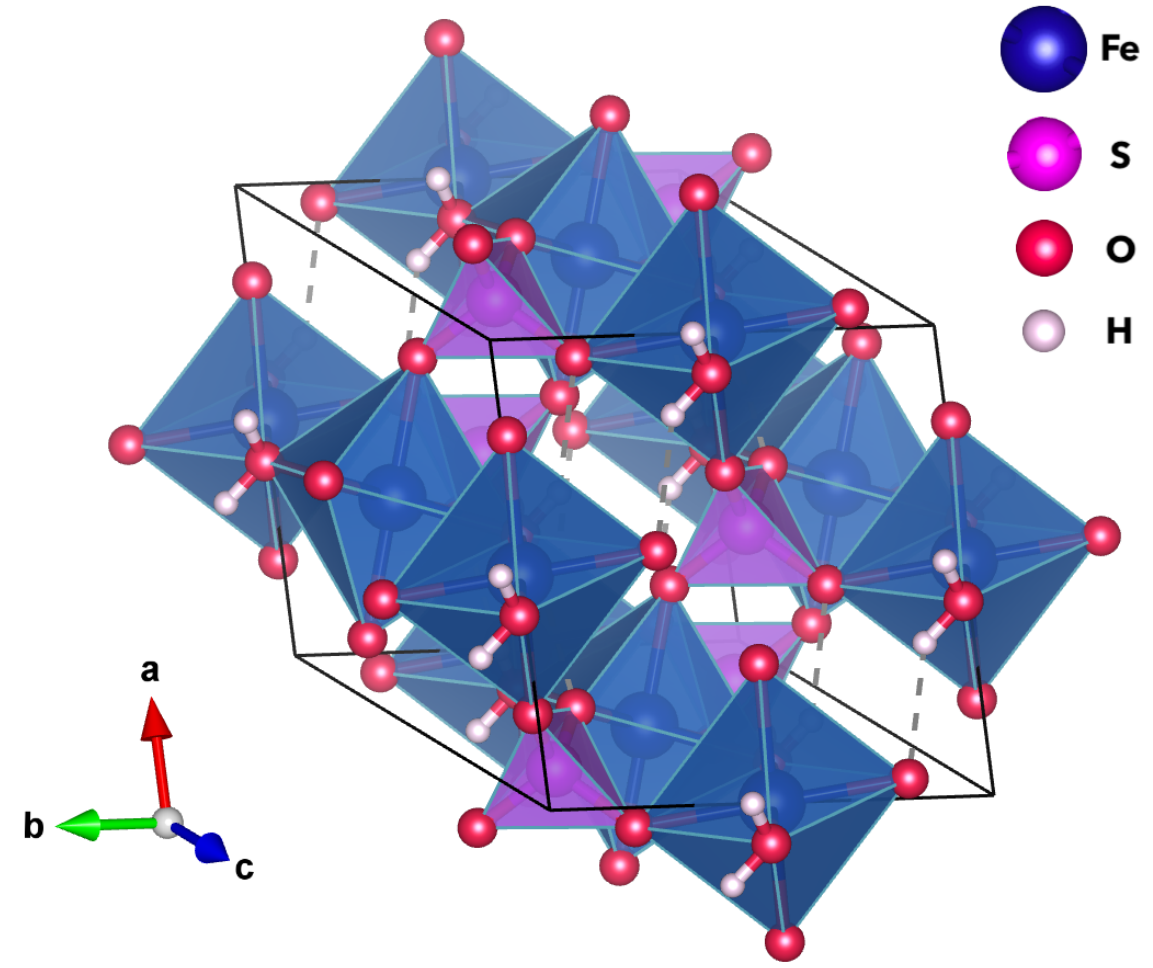
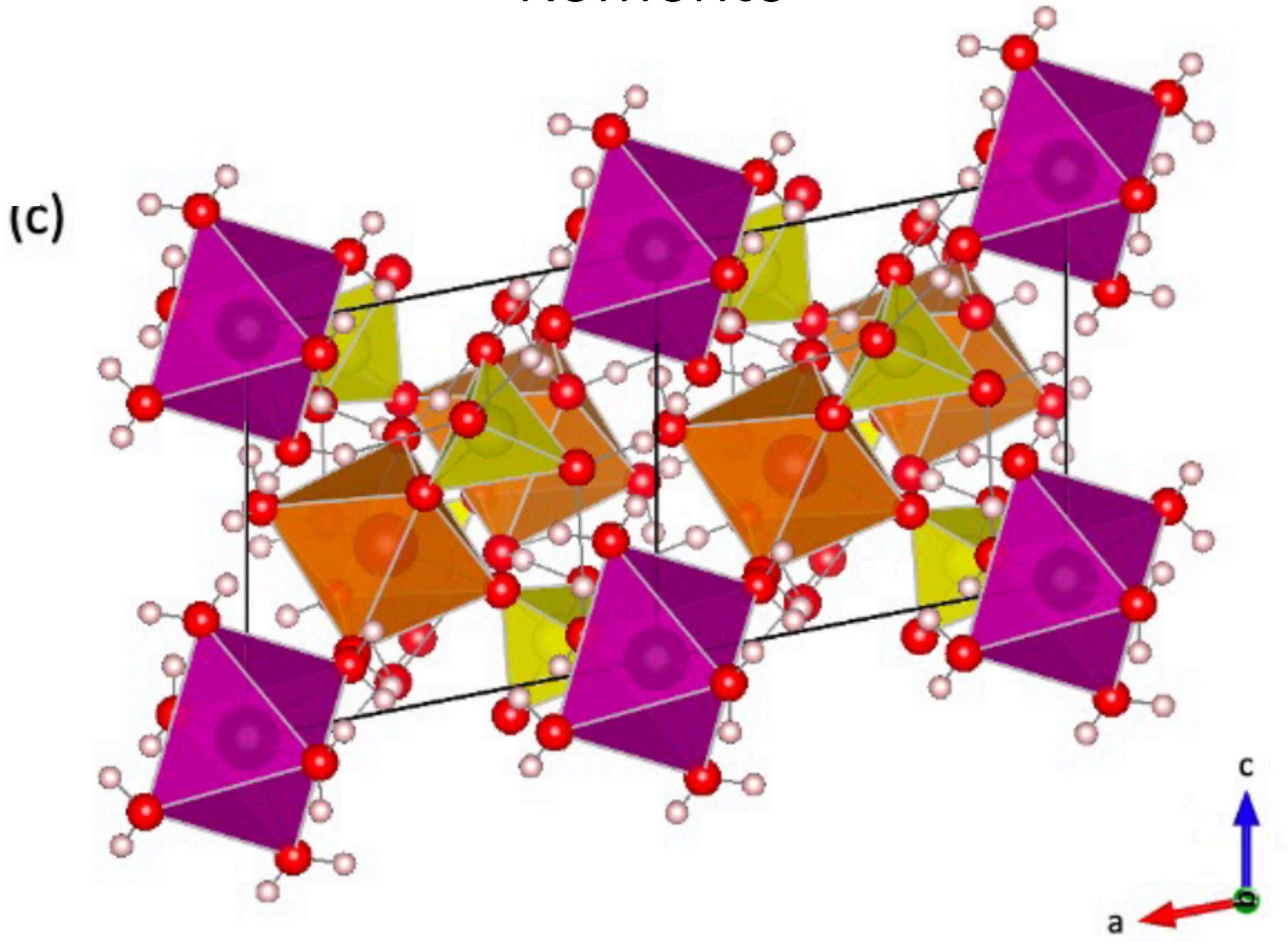
(Natural sample; Chilé)

Szomolnokite



Römerite



- Sulfate tetrahedra
- Ferrous Fe^{2+} octahedra
- Ferric Fe^{3+} octahedra
- Oxygen
- Hydrogen

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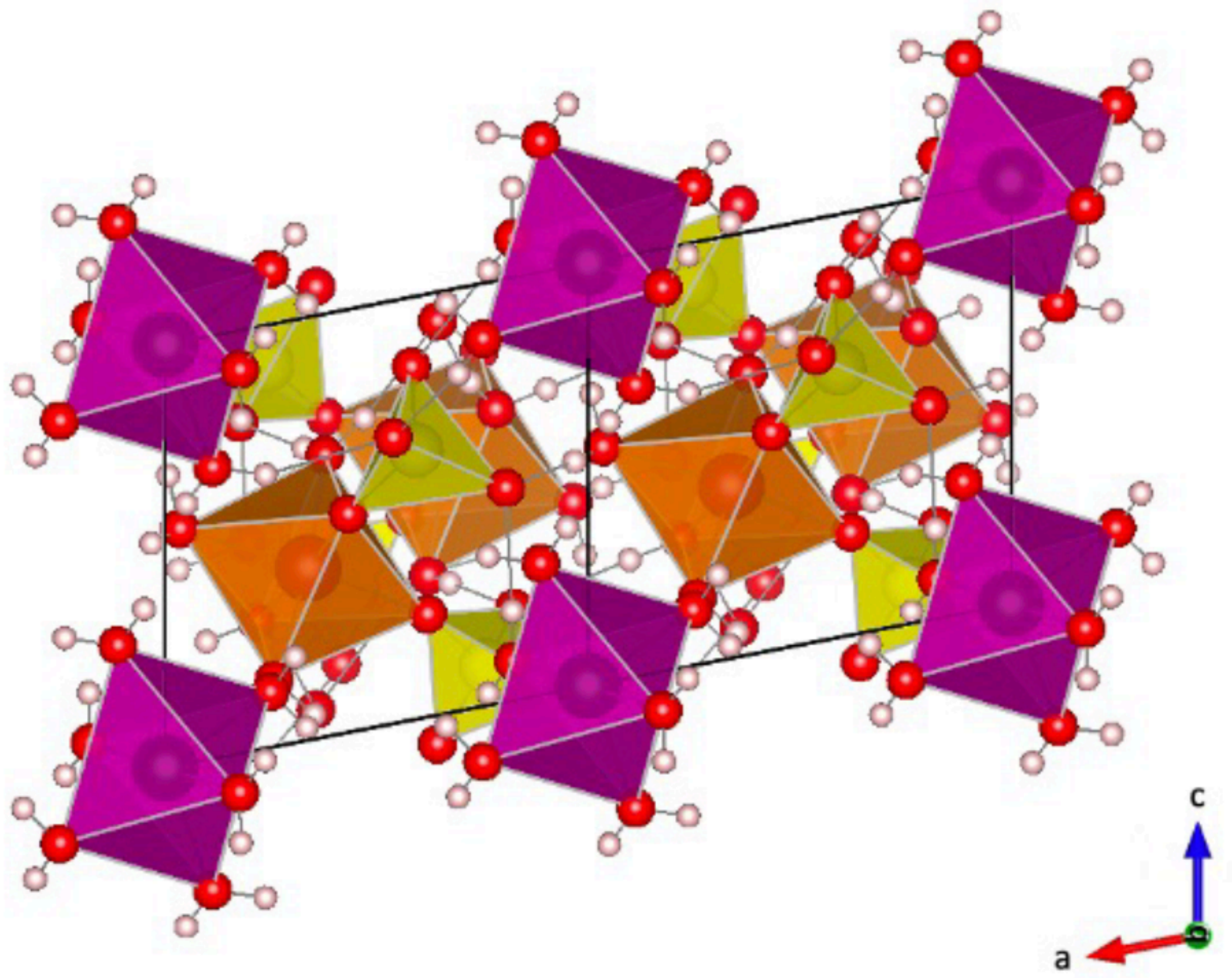
Exploring multi-valent sulfates: Römerite $Fe^{2+}Fe^{3+}_2(SO_4)_4 \cdot 14H_2O$

Work of 2021 Caltech WAVE Fellow Nina Gilkyson

- Ambient conditions, cryogenic, and high pressure synchrotron **infrared spectroscopy**
- Ambient conditions and cryogenic **single crystal-X-ray diffraction** (thermal expansion)



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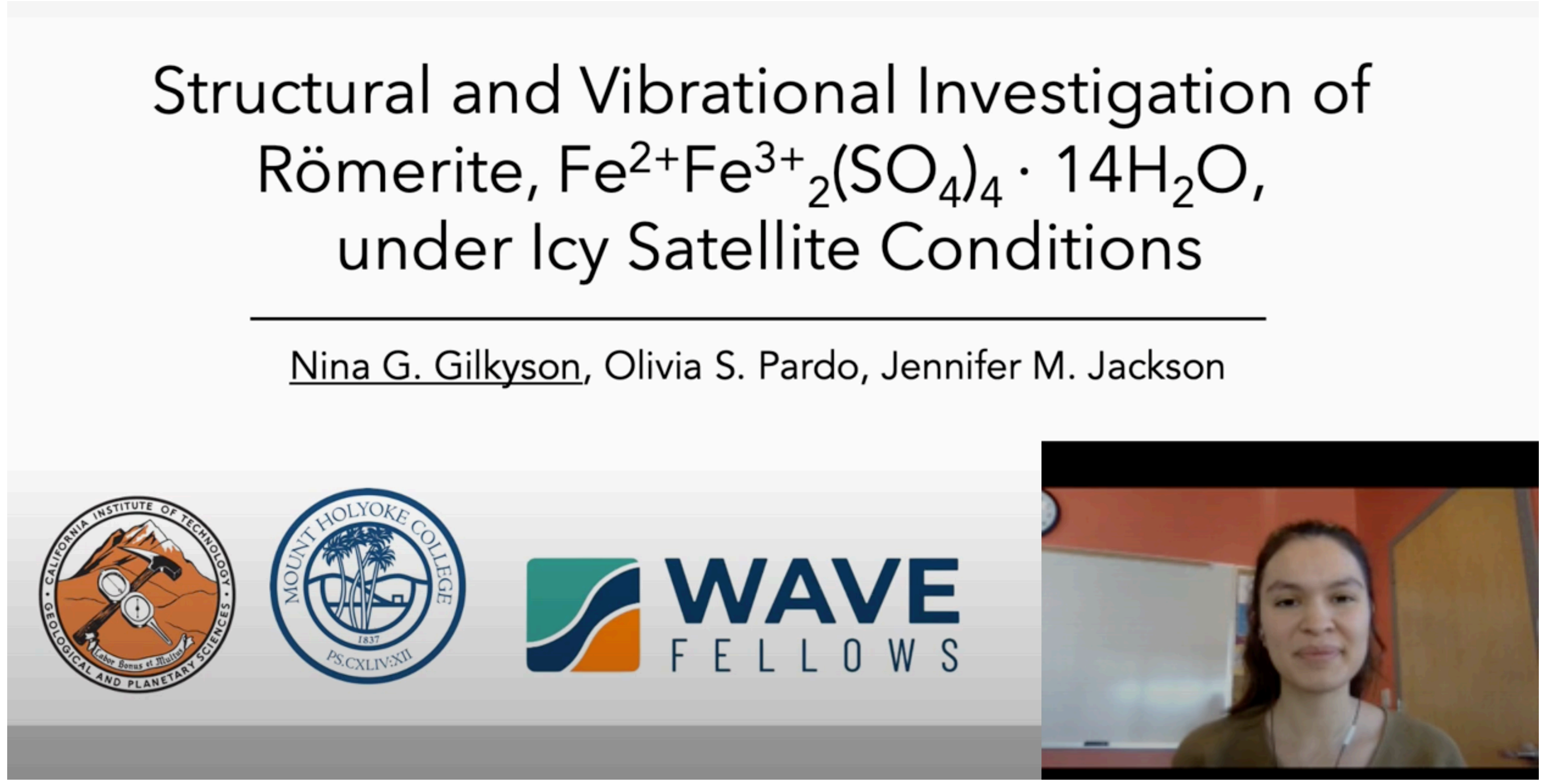
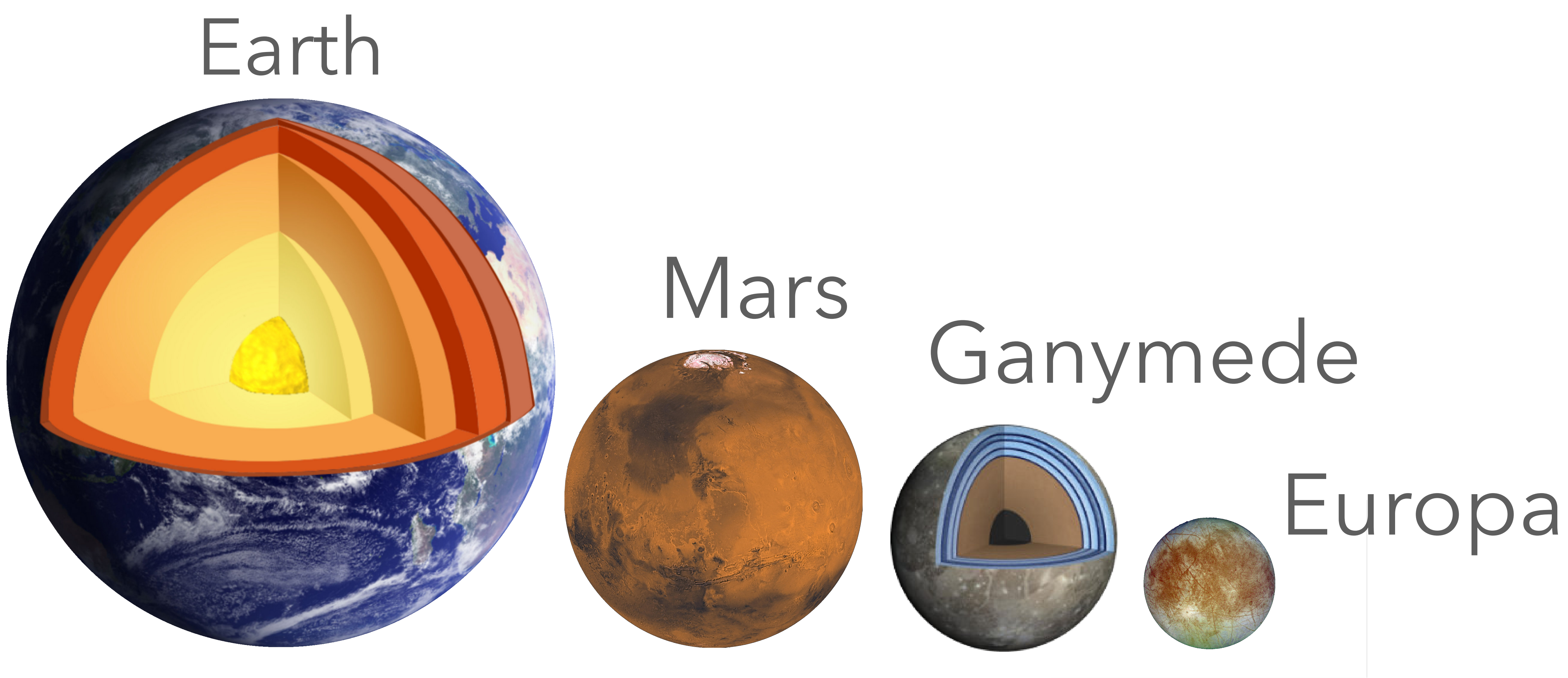


Summary and upcoming work

- As on Earth, sulfur cycling in other planetary environments requires a better understanding of the **properties of hydrated sulfates at depth**

- This work: experiments at the pressures and low-temperatures of satellite interiors like Europa and Ganymede, and extends to pressures relevant to much larger planetary bodies like Earth and Mars: **structural, vibrational, electronic properties**



Next steps:

Take a holistic approach that integrates all the macroscopic and microscopic properties to predict the elastic and transport behavior of hydrated sulfates in icy satellite interiors

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DOE NNSA SSGF Reflection

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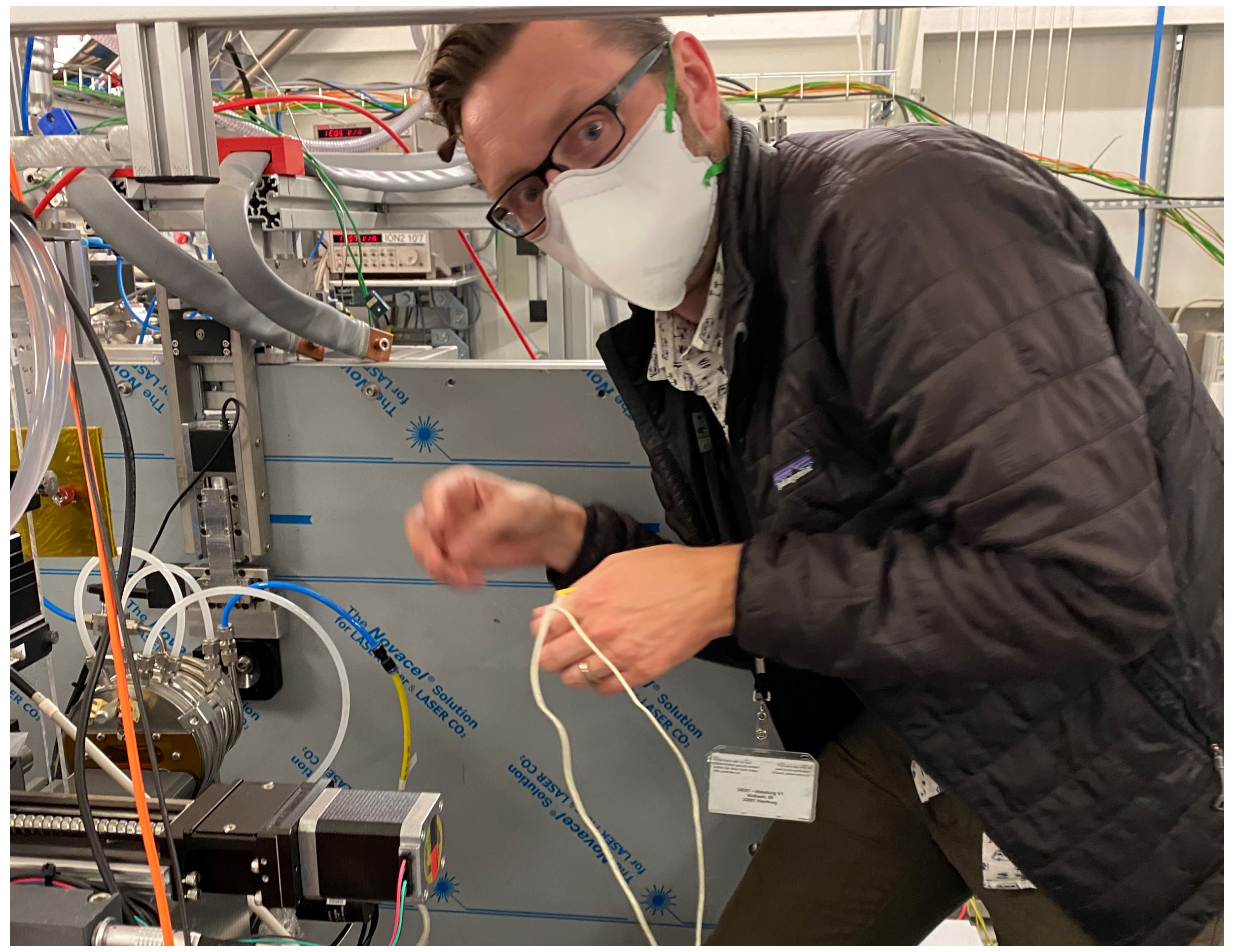
Lawrence Livermore National Laboratory Practicum 2019

Rick Kraus

LLNL Practicum Coordinator

High Pressure Physics Group

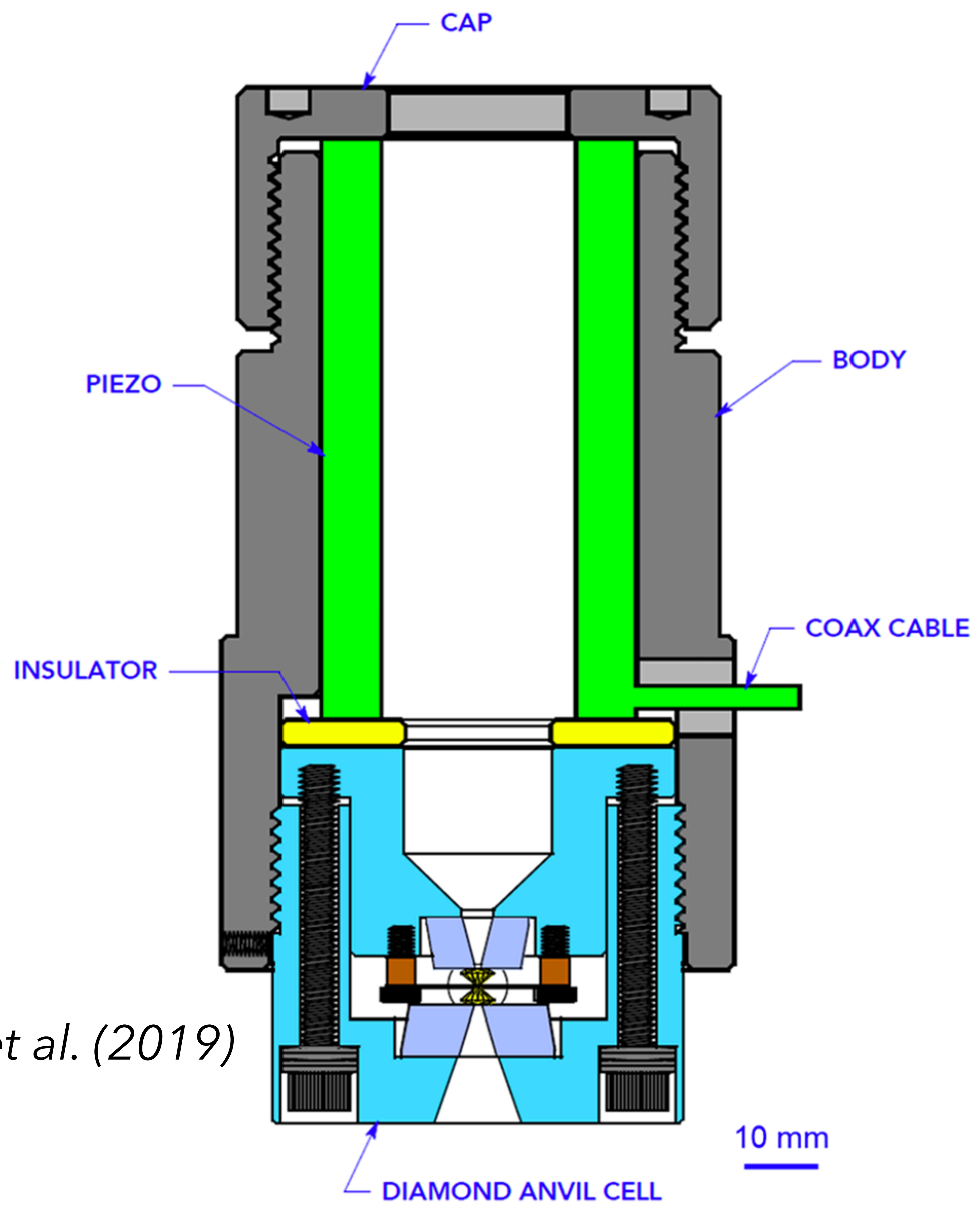


Earl O'bannon

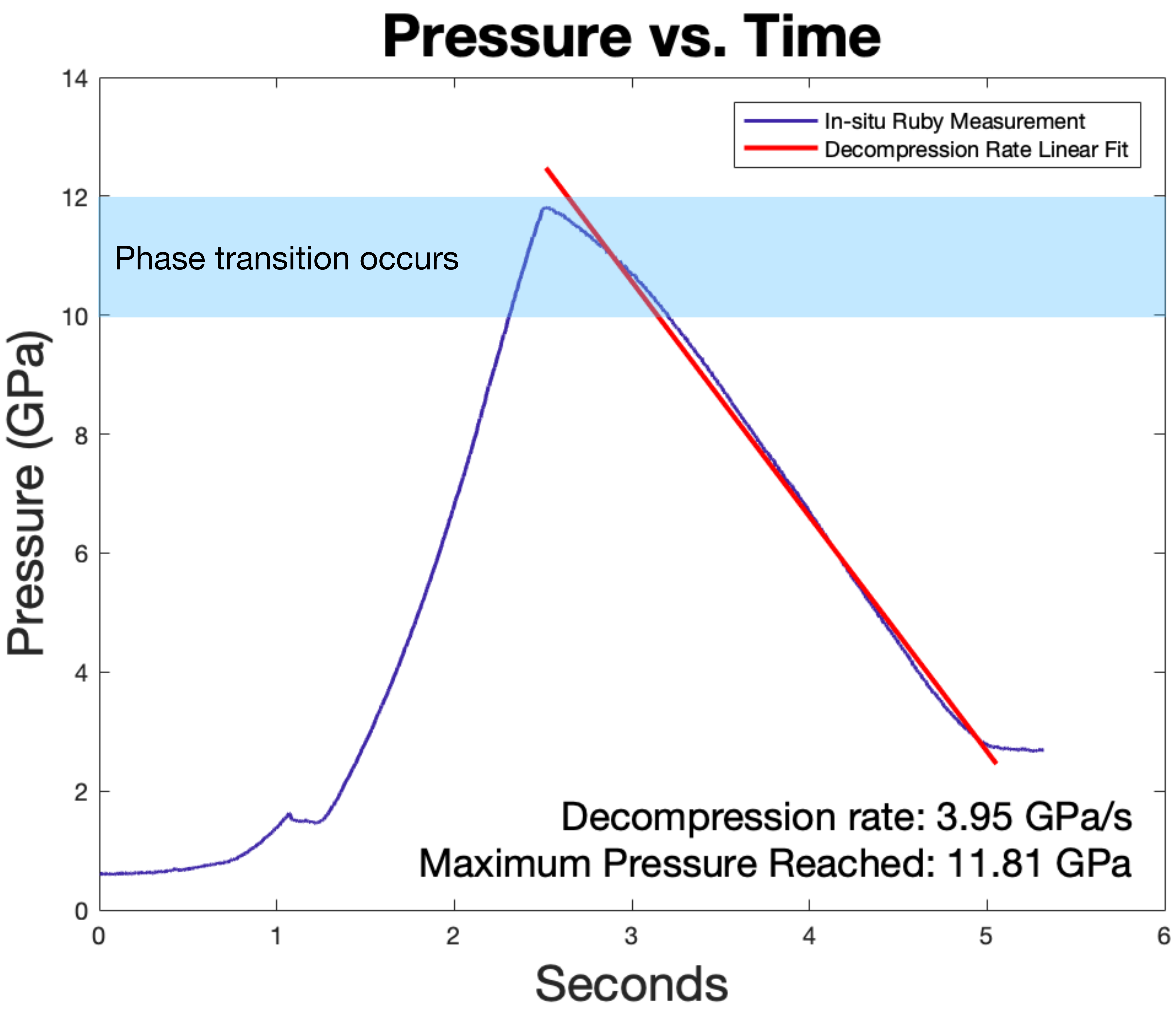
Zsolt Jenei

Will Evans

Dynamic Compression of Silicon: Behavior of Metastable Phases

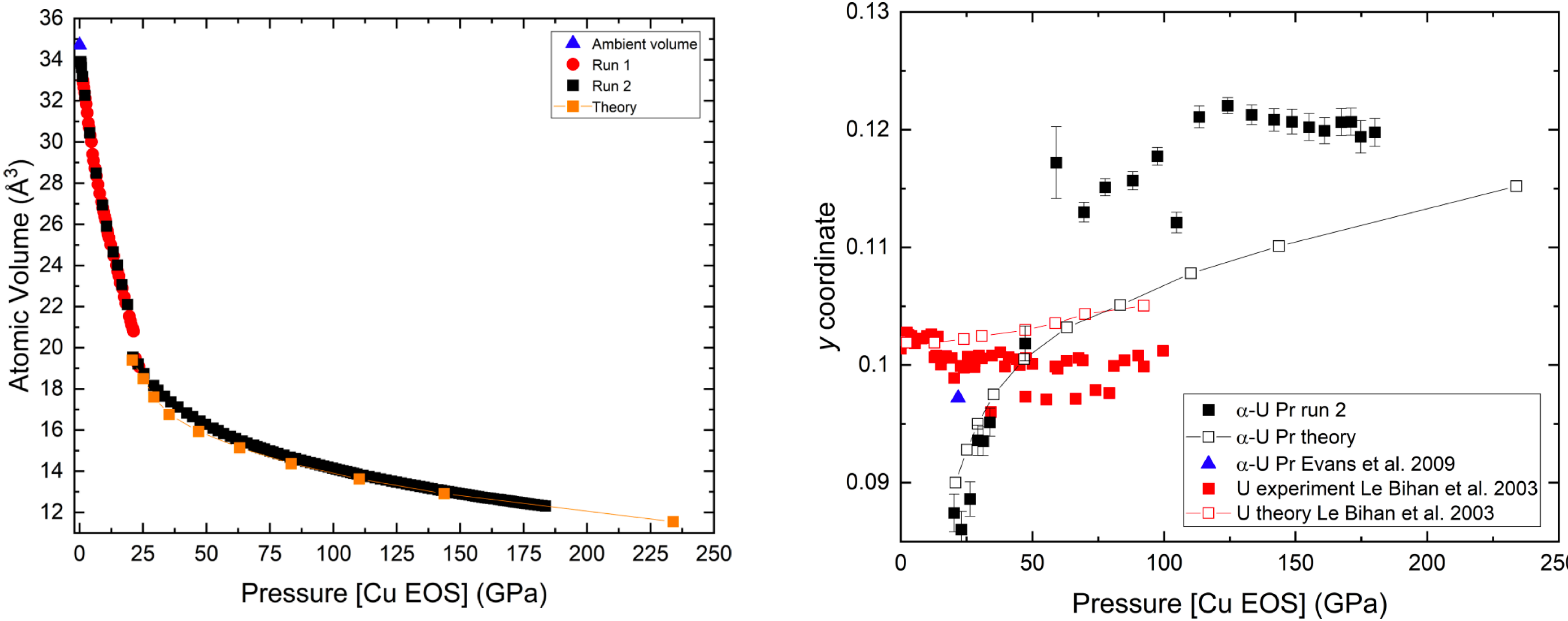


Jenei et al. (2019)



Lawrence Livermore National Laboratory ACP

Structural study in praseodymium compressed to 185 GPa



O'Bannon III, Earl & **Pardo, O.** & Söderlind, Per & Sneed, Daniel & Lipp, Magnus & Park, Changyong & Jenei, Zs. (2022). Systematic structural study in praseodymium compressed in a neon pressure medium up to 185 GPa. Physical Review B. 105.

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Questions or comments:
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