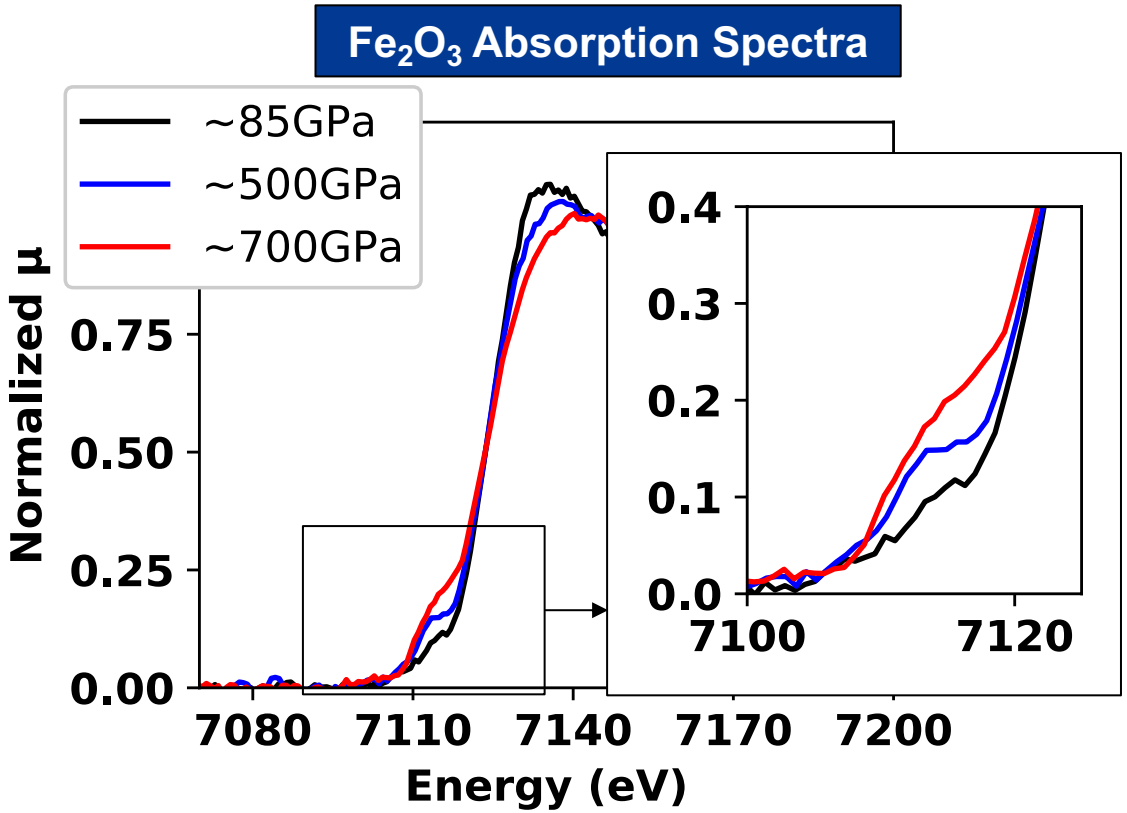
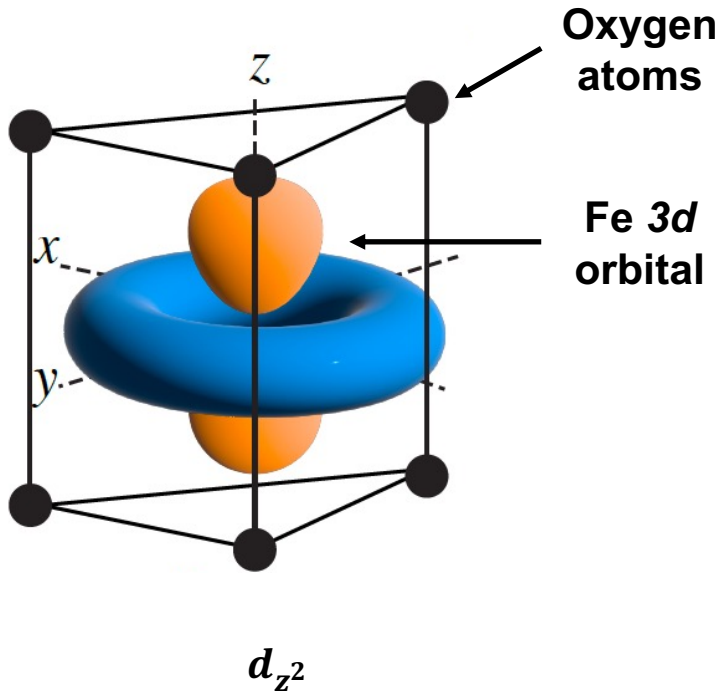
# Electronic structure of $Fe_2O_3$ above 700 GPa





D.A. Chin
University of Rochester
Laboratory for Laser Energetics


DOE NNSA SSGF
Annual Program Review
June 28th 2023

Summary

# A new x-ray spectrometer was used to measure the behavior of iron valence electrons at planetary core conditions

- XAFS is capable of characterizing both the crystal and electronic structure of matter at high-energy-density (HED) conditions
- We have measured XAFS data of compressed $Fe_2O_3$ above 700 GPa
- Analysis shows the oxygen ion potentials become skewed and the iron $d$ states broaden with increasing density

**XAFS measurements indicate the persistence of iron oxygen bonding above 400 GPa**

XAFS: X-ray absorption fine structure
XANES: X-ray absorption near edge spectroscopy
EXAFS: Extended x-ray absorption fine structure

# Collaborators

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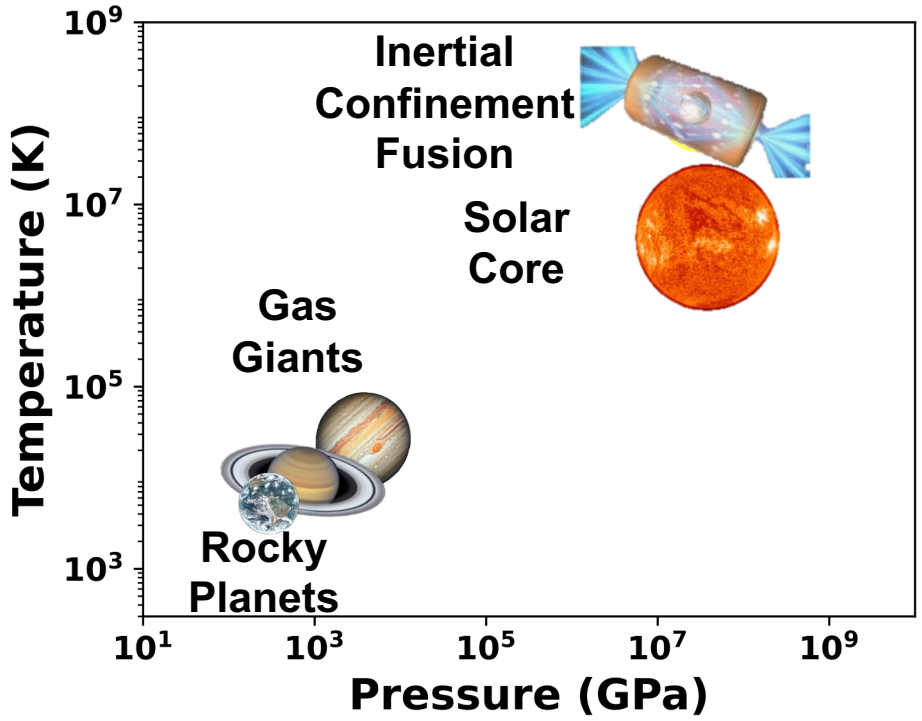
STEWARDSHIP SCIENCE GRADUATE FELLOWSHIP

This material is based upon work supported by the DOE NNSA SSGF
under cooperative agreement number DE-NA0003960

# Few experiments are capable of understanding chemical bonding and electron structure at high energy density conditions

**High Energy Density (HED) Conditions:**
- **100 GPa = 1 Mbar = $10^{11}$ Pa**
- **Atmospheric Pressure: 101,325 Pa**



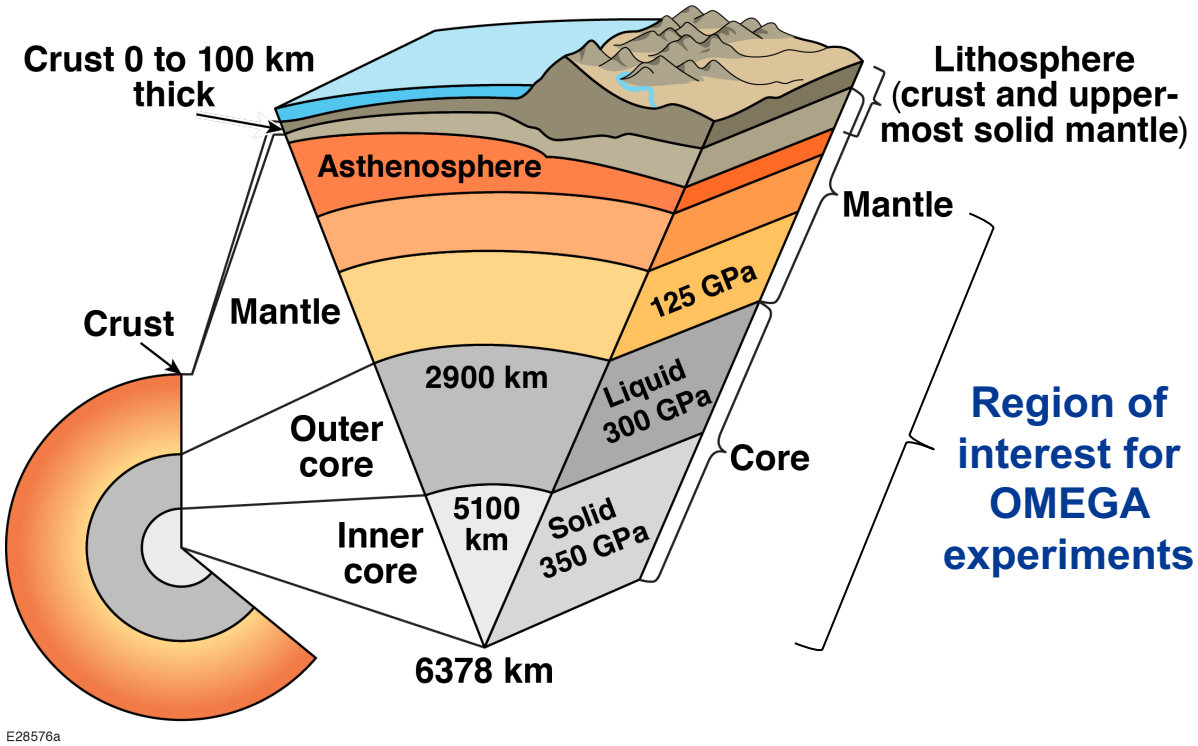

- **Reflectivity measurements show insulator-metal transitions* or electride phases** but require the material to be reflective**
- **X-ray scattering† and Raman‡ measurements diagnose electron structure information but require large photon fluxes**

**X-ray absorption fine structure spectroscopy is capable of characterizing chemical bonding and electron structure at planetary core conditions**

Images from NASA
J.J. Ruby *et al.*, Phys. Rev. Lett. 125, 215001 (2020).

*P.M. Celliers *et al.*, Science 361, 677 (2018).
**D.N. Polsin *et al.*, Nat. Commun. 13, 2534 (2022).
†S.Vinko *et al.*, Nature 482, 49 (2012).
‡N. Rohringer Phil. Trans. R. Soc. A 377 20170471 (2019)

# Iron oxides under extreme environments influence the evolution of the Earth and super-Earths



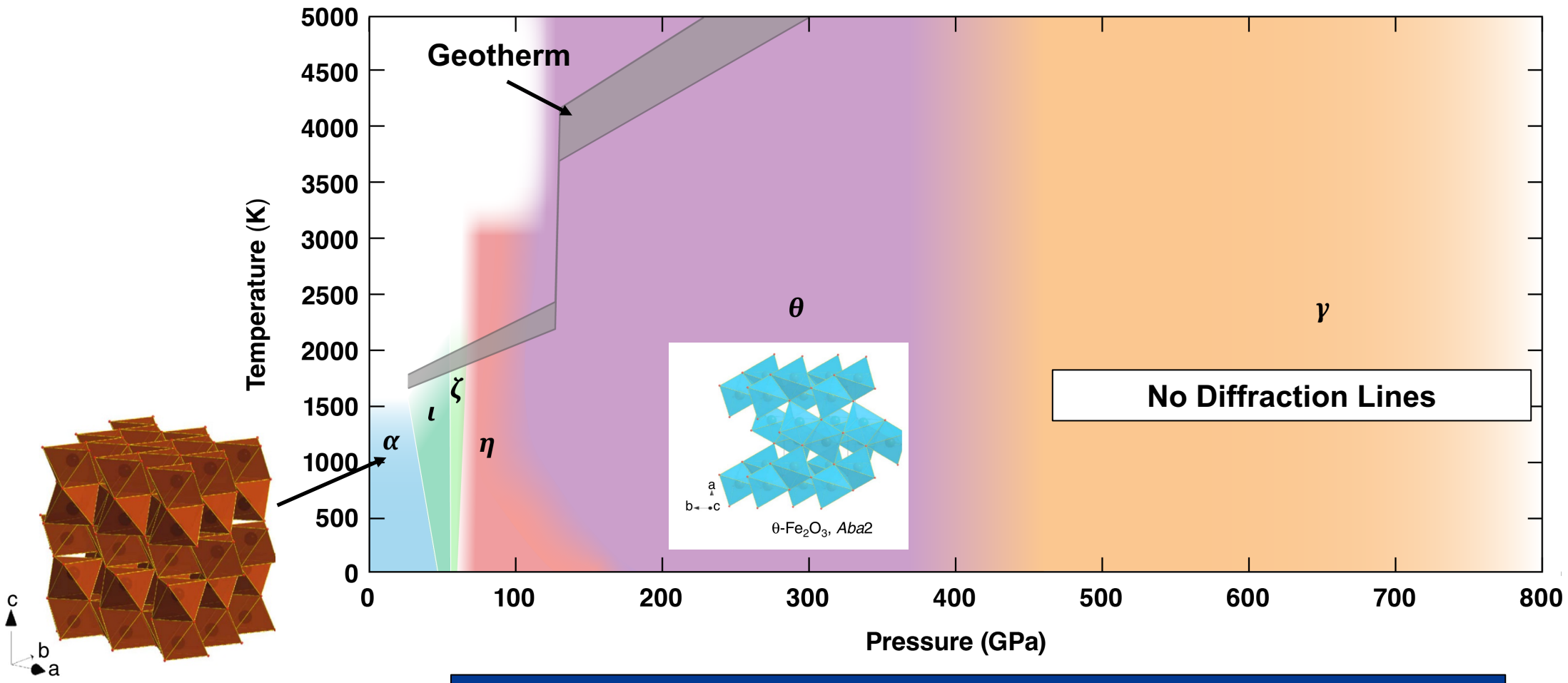

- Many different stoichiometries have been identified in iron oxygen systems up to 120 GPa*
- Iron-oxygen systems go through oxidation changes with increasing pressure**, †

**What happens to $Fe_2O_3$ when it is compressed to hundreds of GPa?**

Image: M. Williams, "What are the Earth's Layers?," Universe Today, 7 December 2015, https://phys.org/news/2015-12-earth-layers.html


Q. Hu *et al.*, Nature 534, 241 (2016).
*E. Boulard *et al.*, Geo. Res. Lett. 46, 1348 (2019).
**E. Bykova *et al.*, Nat. Comm. 7, 10661 (2016).
† E.J. Garnero *et al.*, Science 320, 5876 (2008).

# The crystal structure of $Fe_2O_3$ has been mapped out to 400 GPa




**There is an open question about the behavior of $Fe_2O_3$ above 400 GPa**




E. Bykova *et al.*, Nat. Comm. 7, 10661 (2016).
I. Ocampo *et al.*, Phys. Rev. B *In Prep*

Summary

# A new x-ray spectrometer was used to measure the behavior of iron valence electrons at planetary core conditions

- **XAFS is capable of characterizing both the crystal and electronic structure of matter at high-energy-density (HED) conditions**
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**XAFS: X-ray absorption fine structure**
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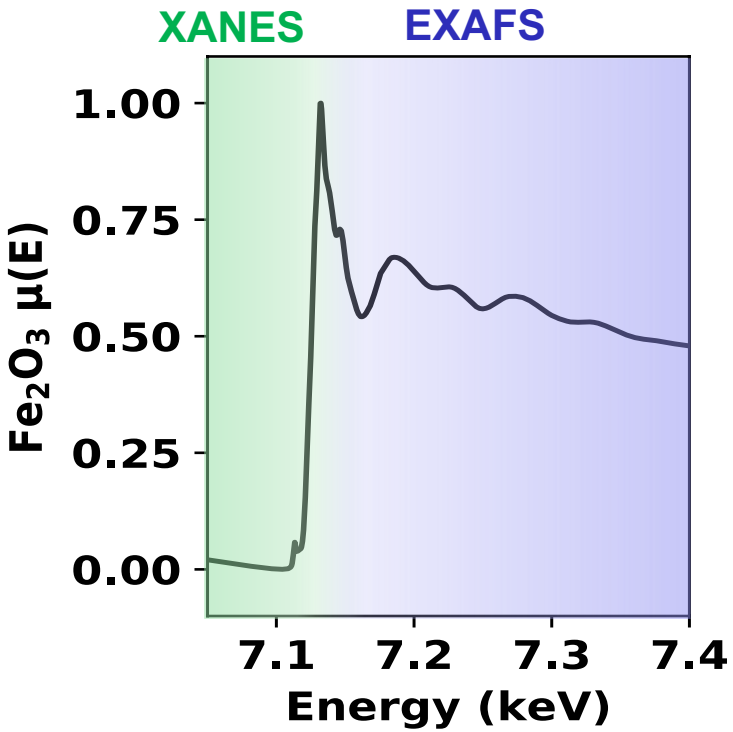
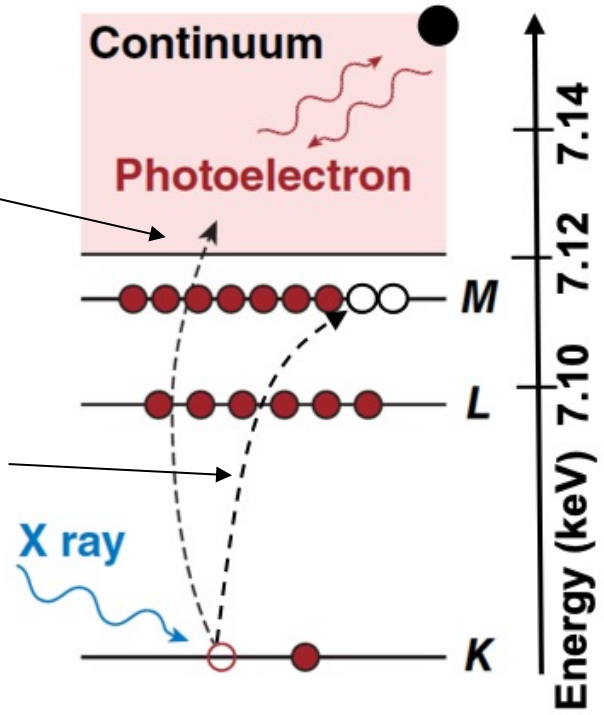
# The x-ray absorption spectrum is produced by x-ray excitations of core electrons




The photoelectron will interact with other atoms in the material

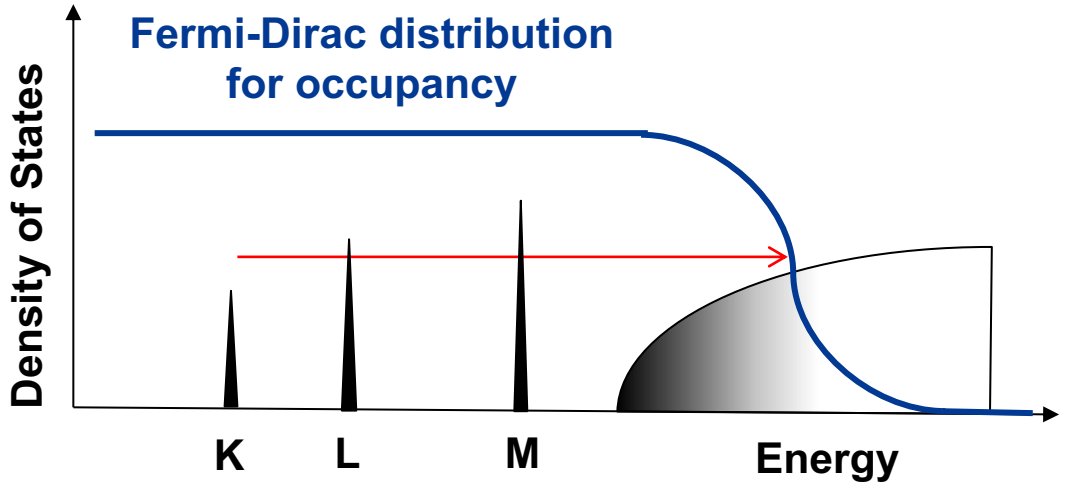
Bound-Bound transitions generating features before the absorption edge

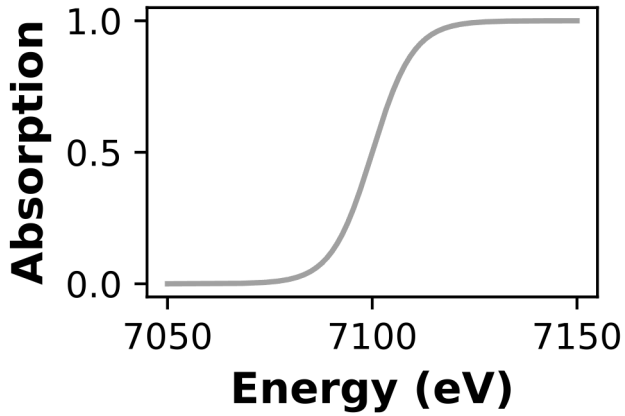


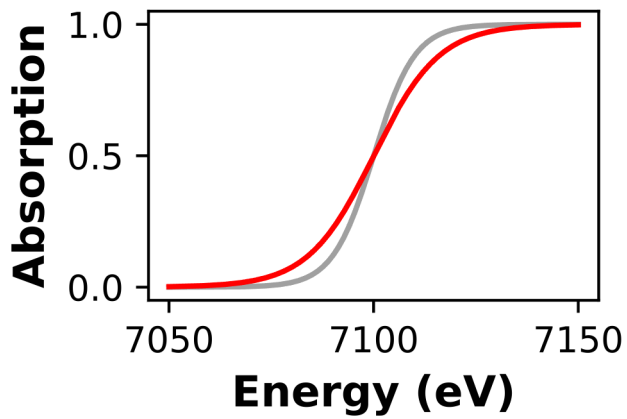

XANES: X-ray absorption near edge spectroscopy
EXAFS: Extended x-ray absorption fine structure

M. Newville, Rev. Min. Geo. 78, 33 (2014).
International X-ray Absorption Society, Fe2O3 Data, https://xaslib.xrayabsorption.org

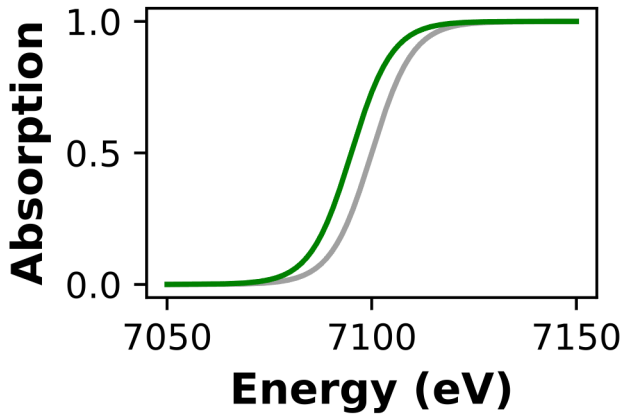
# XANES is sensitive to the electron structure around the continuum



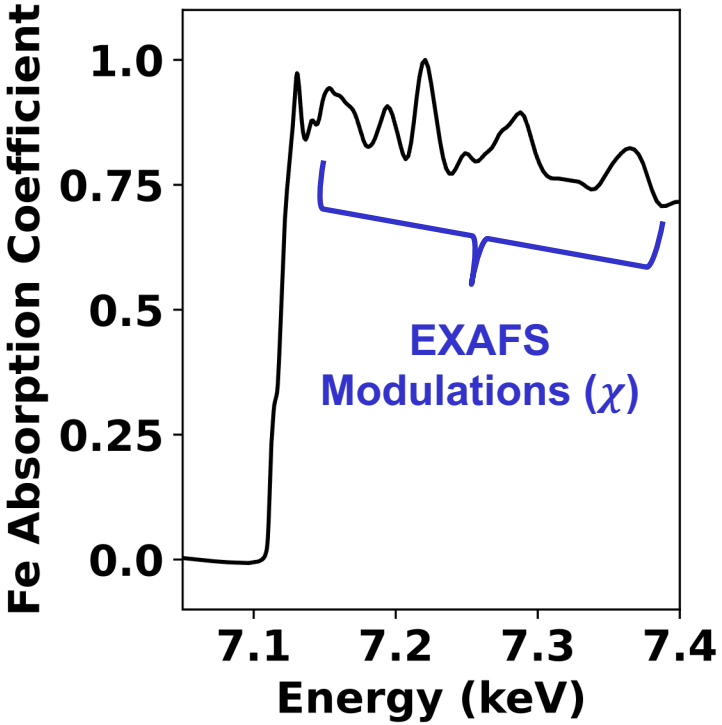

Increase in temperature can soften the slope

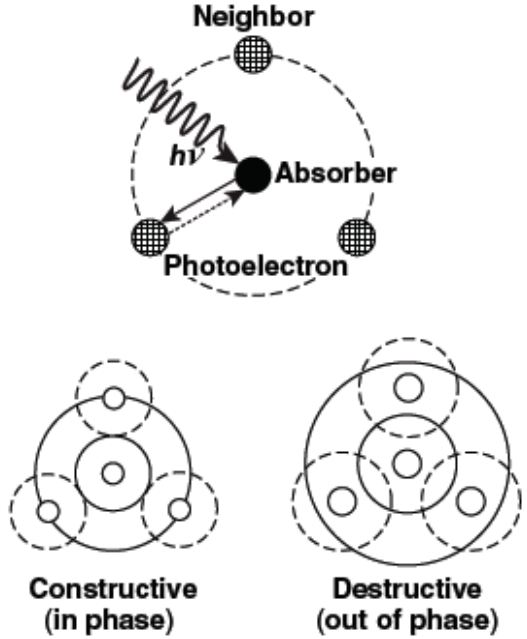



Increase in density shifts energy levels

M. Newville, Rev. Min. Geo. 78, 33 (2014).
F. Dorchies *et al.*, Phys. Rep. 657, 1-26(2016).
G. Ecker and W. Kröll, Phys. Fluids 6, 62 (1963).
J.C. Stewart and K.D. Pyatt Astro. Journ. 144, 1203 (1966).

# The EXAFS modulations are produced by scattering of the photoelectron off neighboring atoms




**The outgoing and scattered photoelectron wavefunctions interfere, impacting the absorption coefficient**

EXAFS: Extended x-ray absorption fine structure

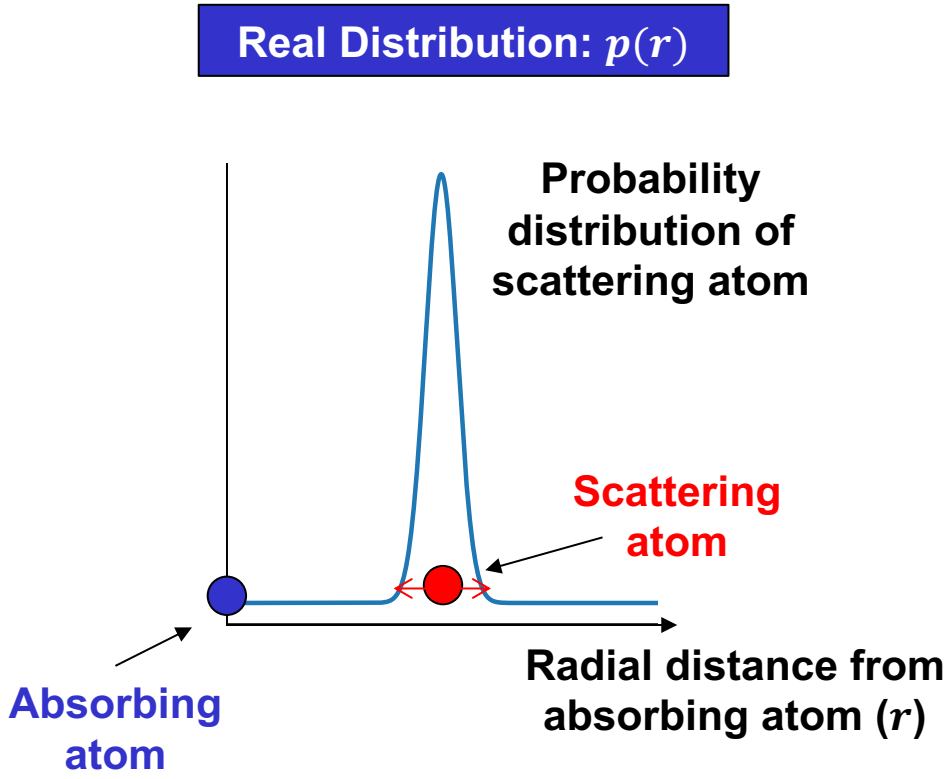
XAFS Spectral Library, Spectrum: Fe data, 13 June 2018, http://cars.uchicago.edu/xaslib/spectrum/611.
D. C. Koningsberger *et al.*, Top. Catal. 10, 143 (2000).

# The EXAFS modulations depend upon the radial distribution of atoms surrounding the absorbing atom

**The EXAFS equation for each scattering path is an integral over the real distribution ($p(r)$):**

$$\chi(k) = \int A(k,r)\,p(r)\,\sin\big(2kr + \delta(k)\big)\,dr$$

**Amplitude** — **Real Distribution** — **Phase shift**




G. Bunker *Introduction to XAFS* University Press, Cambridge, (2010).

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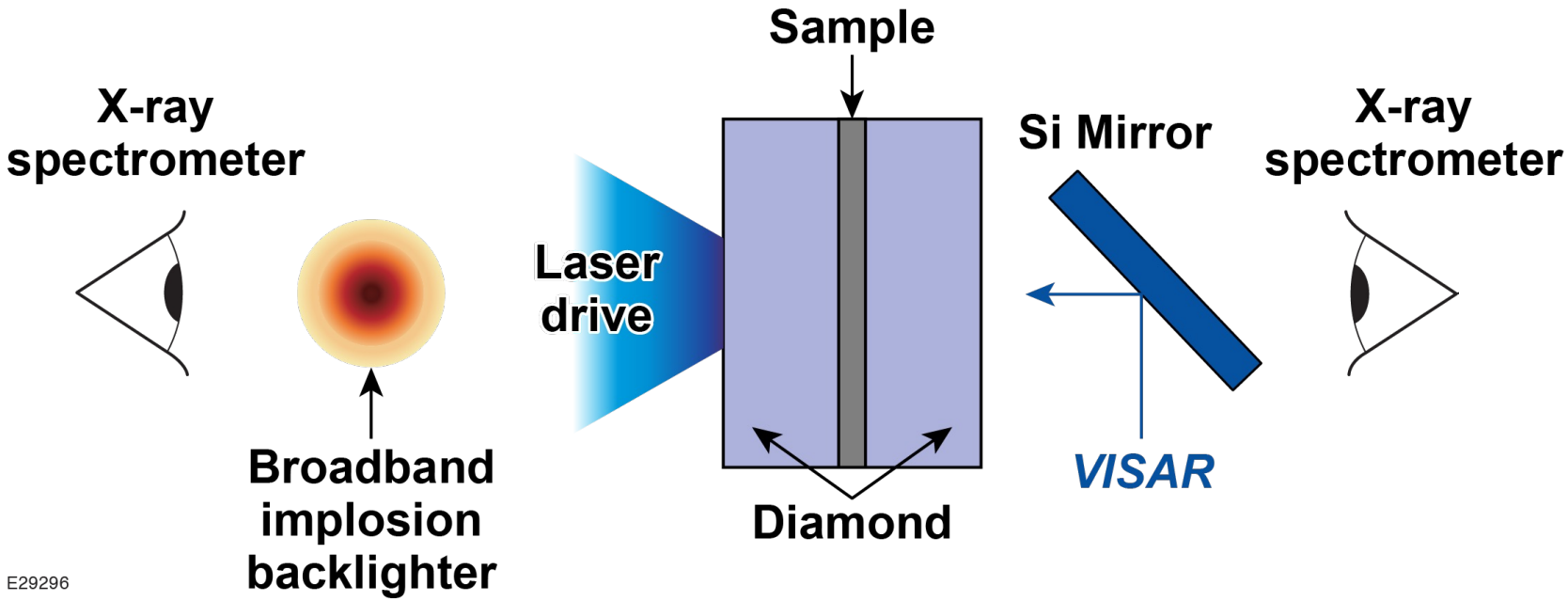
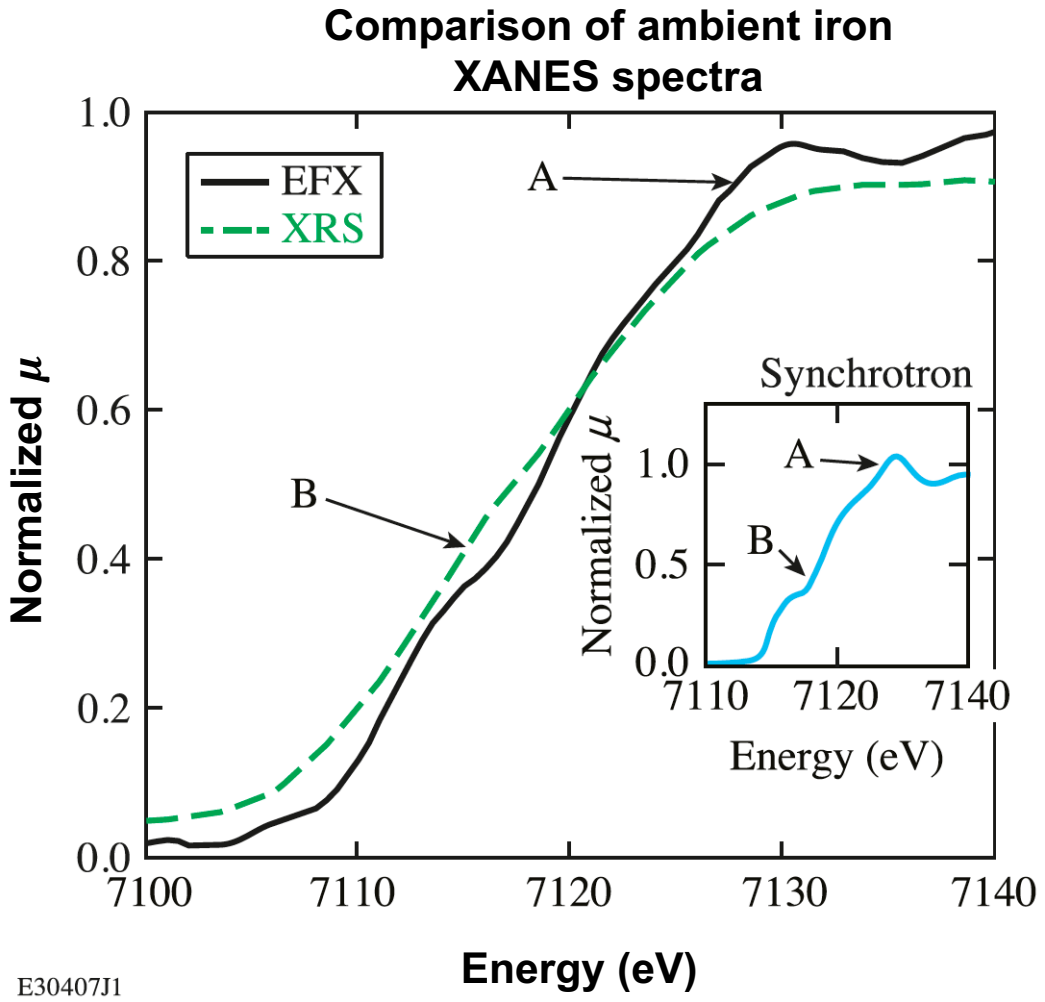
# Samples were compressed to core Earth conditions over 5 ns and probed with a broadband x-ray source for 100 ps

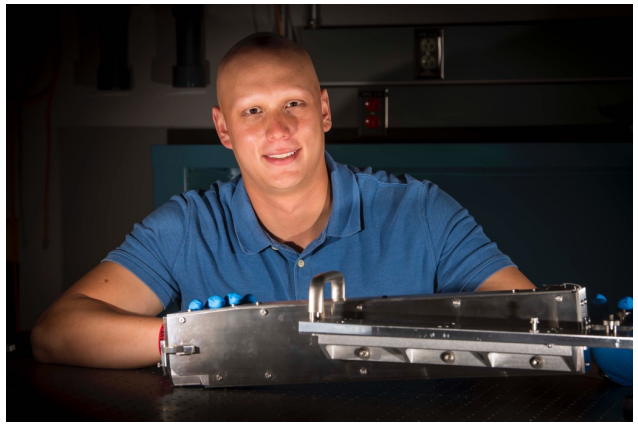



VISAR – Velocity interferometry system for any reflector

Y. Ping *et al.*, Phys. Rev. Lett. 111, 065501 (2013).
D.A. Chin *et al.*, Phys. Plasmas 29, 052702 (2022).

# We designed, built, tested and deployed a new high resolution, x-ray spectrometer (EFX) for XAFS measurements on OMEGA



**The new spectrometer allowed for XANES measurements at planetary core conditions**

XRS: Rowland Yaakobi X-ray Spectrometer (Previous XAFS OMEGA spectrometer)

D.A. Chin *et al.*, Rev. Sci. Instrum. 94, 013101 (2023).

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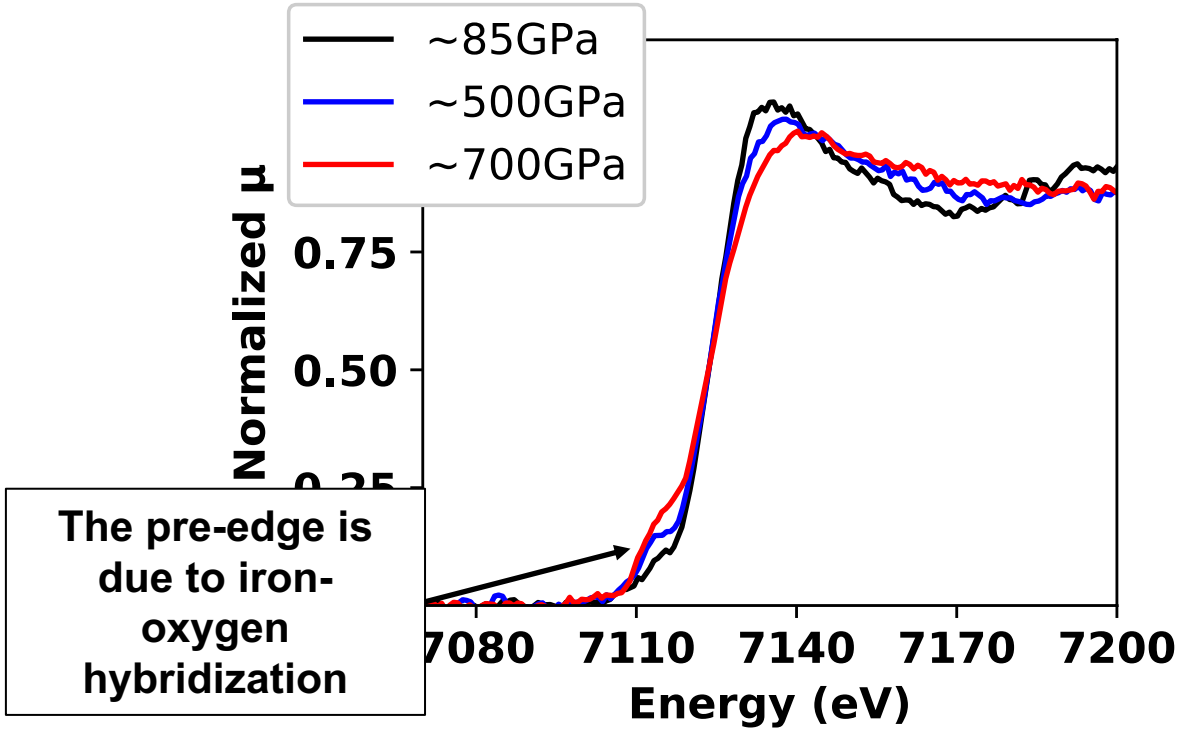
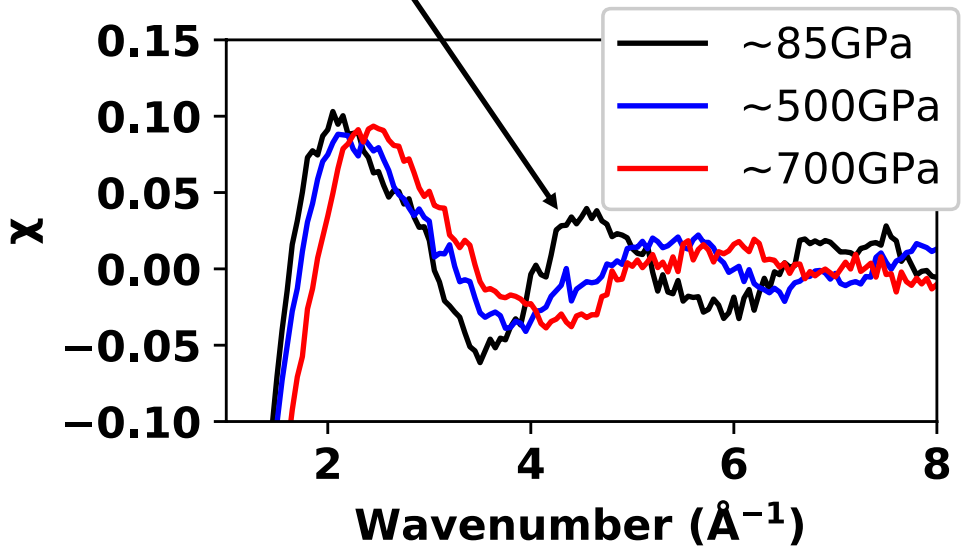
# We measured $Fe_2O_3$ XANES and EXAFS compressed above 700GPa




The pre-edge is due to iron-oxygen hybridization

XANES aligned to the edge for visibility

The EXAFS constrains local structure




B. Ravel and M. Newville, J. Sync. Rad. 12, 537-541 (2005).

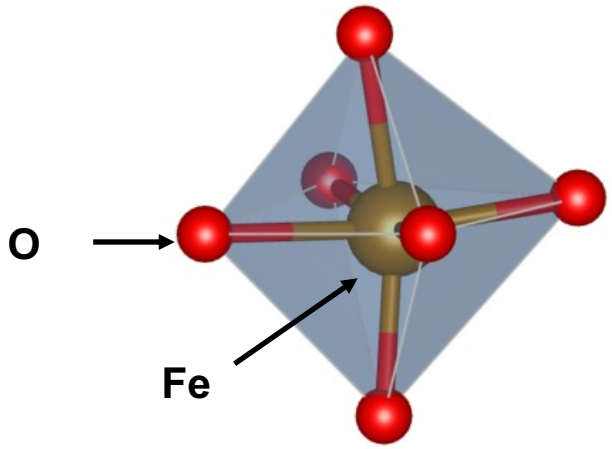
# The EXAFS spectra were analyzed assuming a ion distribution could be modeled as a skew Normal

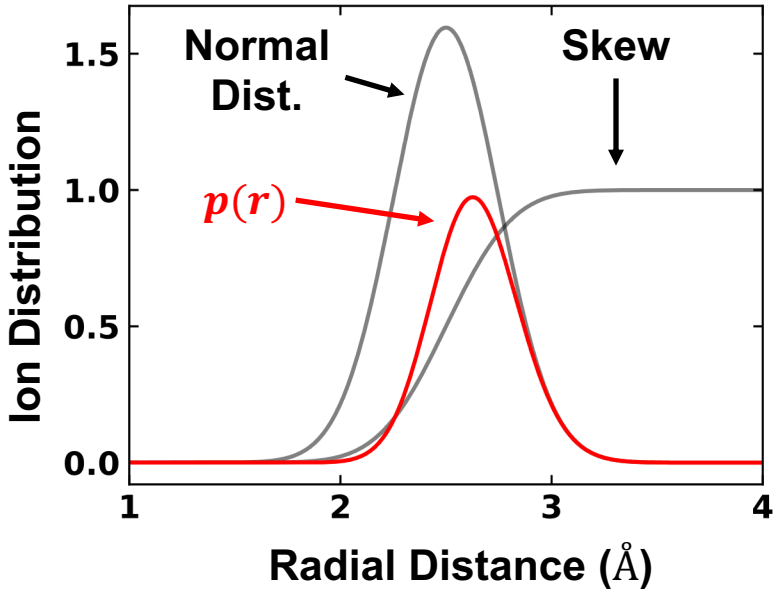
$$\chi(k) = \int A(k,r)p(r)\sin\left(2kr + \delta(k)\right)dr$$

$p(r)$ is the distribution of the oxygen relative to the iron

**Skew Normal Distribution**

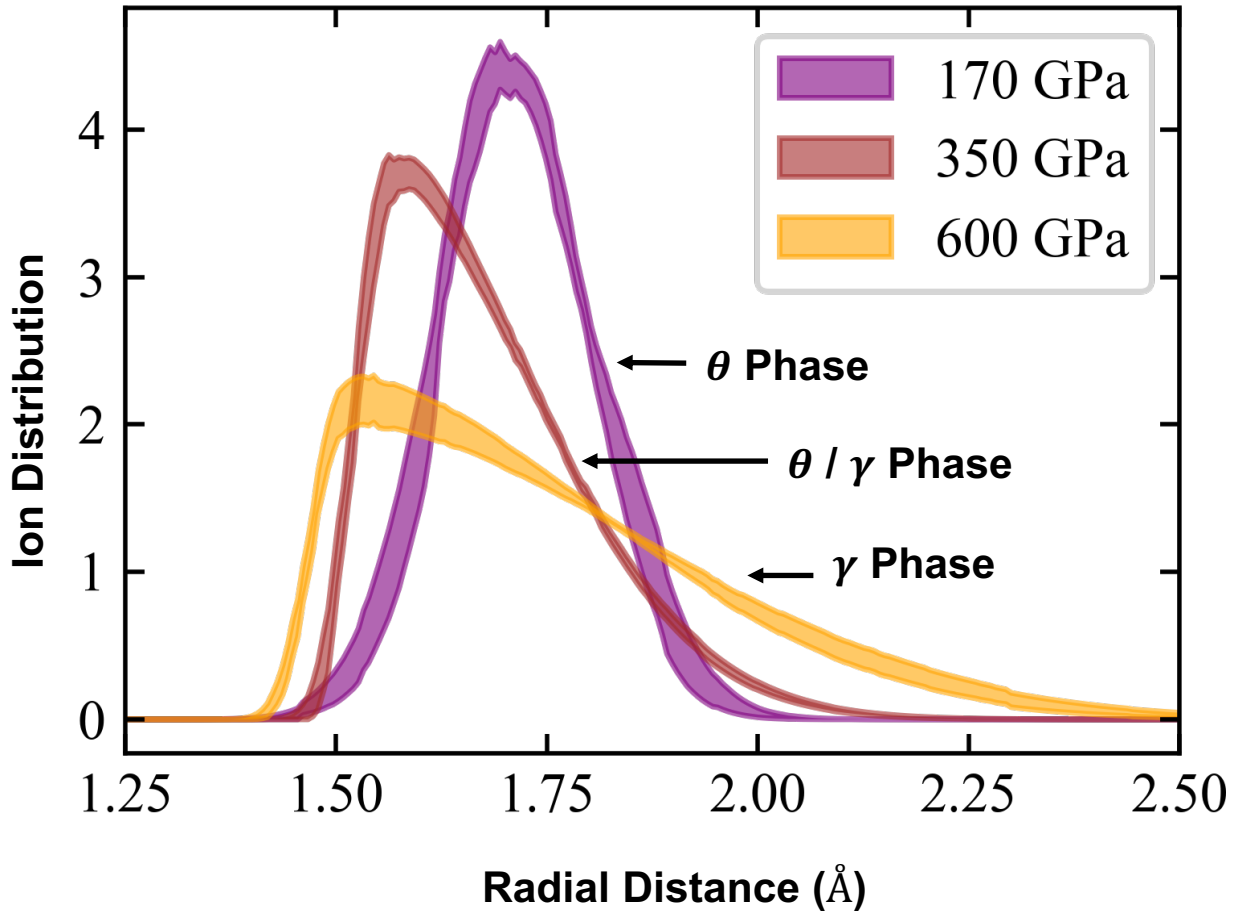
$$p(r) = \left(\frac{1}{\sqrt{2\pi}\sigma}e^{-\frac{(r-R)^2}{2\sigma^2}}\right)\left(\frac{1}{2}\left[1 + \mathrm{Erf}\left(\frac{a(r-R)}{\sqrt{2}\sigma}\right)\right]\right)$$




D.A. Chin *et al.*, Phys. Rev. B *In Prep*

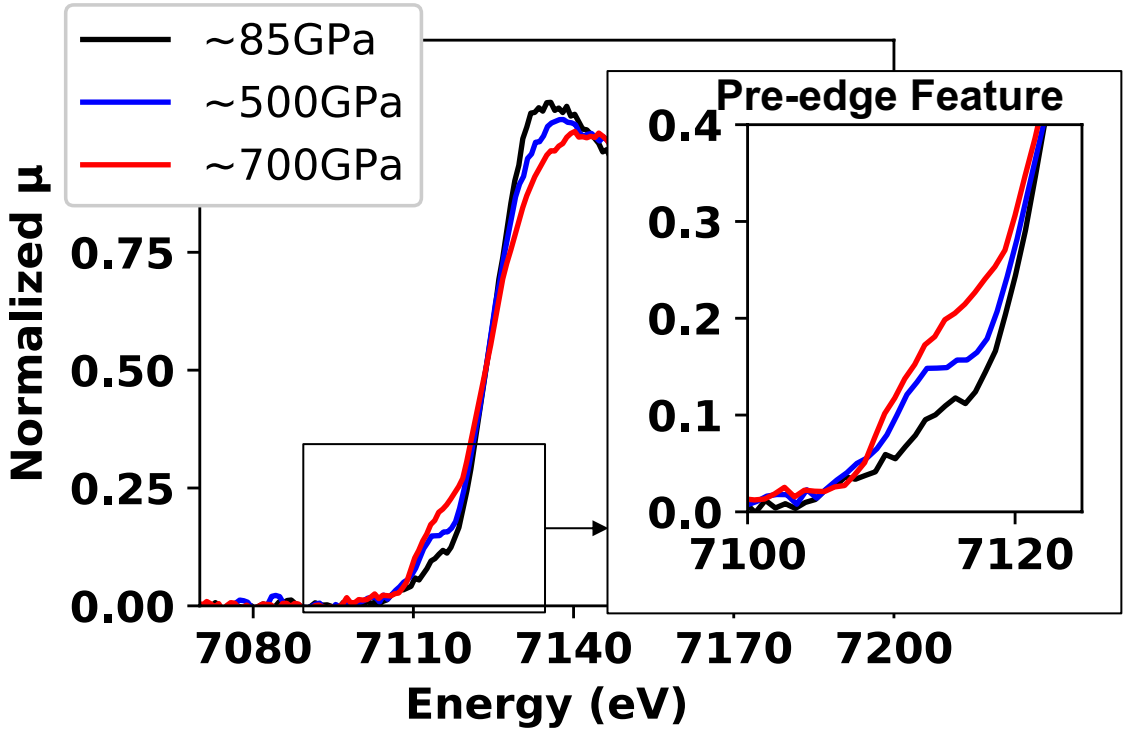
# The inference results show the distribution becomes significantly more skewed when it enters $\gamma$ phase

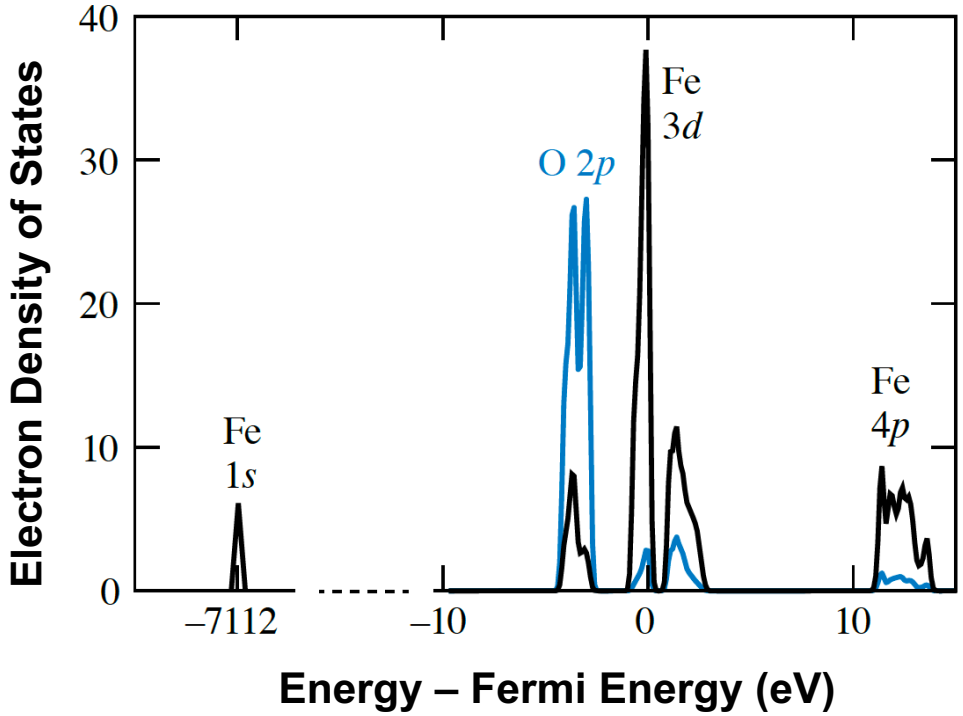



**The oxygen ion potentials become asymmetric in the $\gamma$ phase**

D.A. Chin *et al.*, Phys. Rev. B *In Prep*

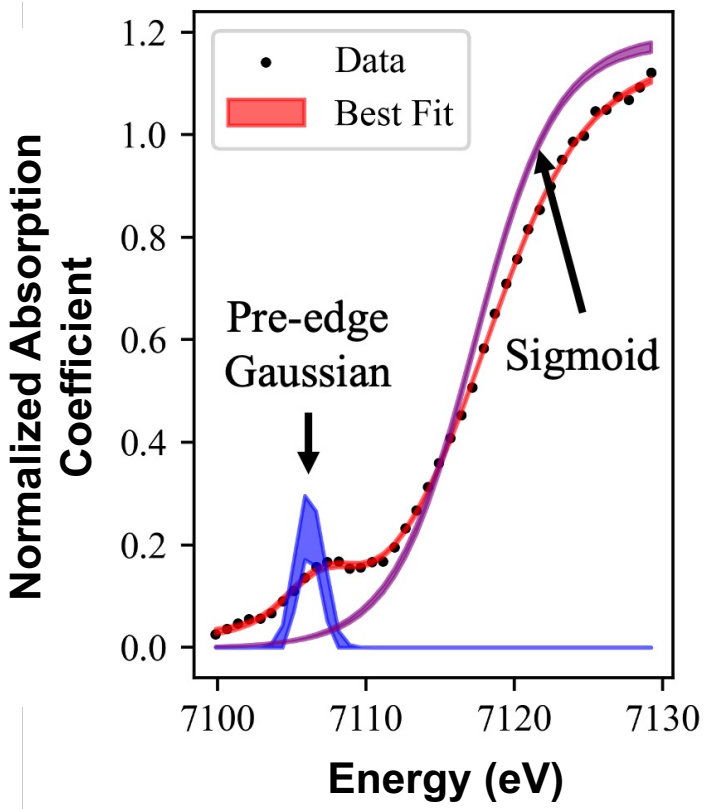
# The pre-edge feature is from a $1s$ - $3d$ transition that is allowed through hybridization with the oxygen $p$ orbital*

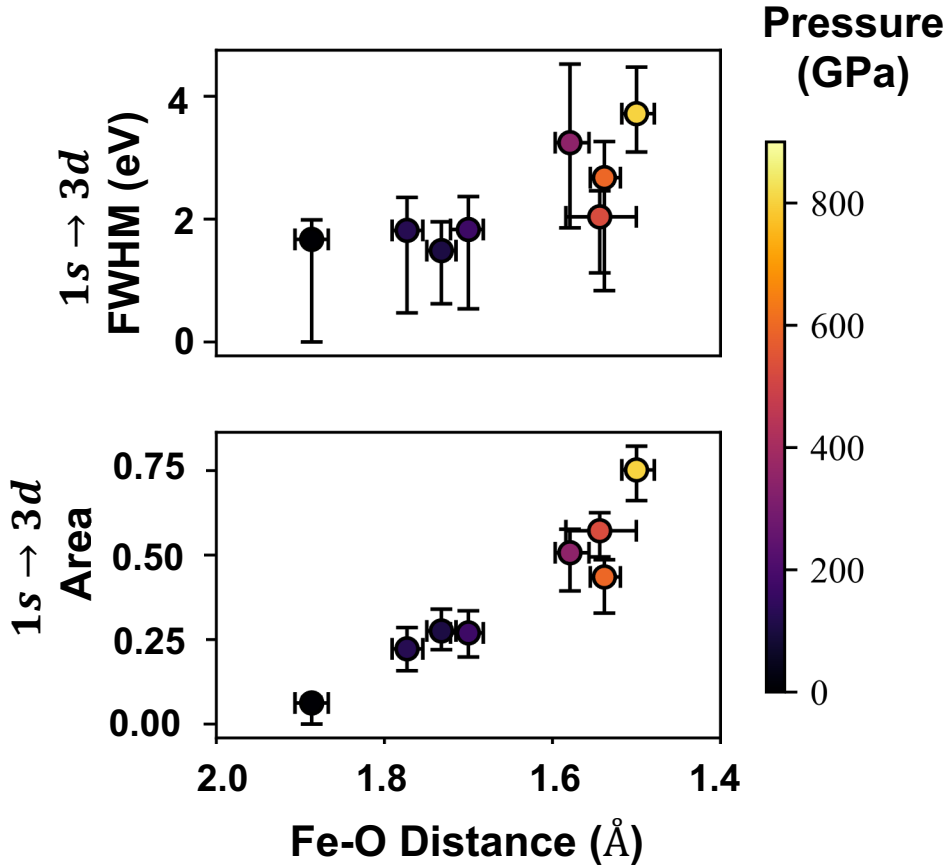



*A. Sanson *et al.*, Phys. Rev. B 94, 014112 (2016).
*D. Cabaret *et al.*, Phys. Chem. Chem. Phys. 12, 5619 (2010).
*S. Wang *et al.*, Phys. Rev. B 82, 144428 (2010).
P. Avery *et al.*, J. Phys. Chem. C 118, 1856 (2014).

# Each spectra was individually analyzed to isolate the pre-edge feature



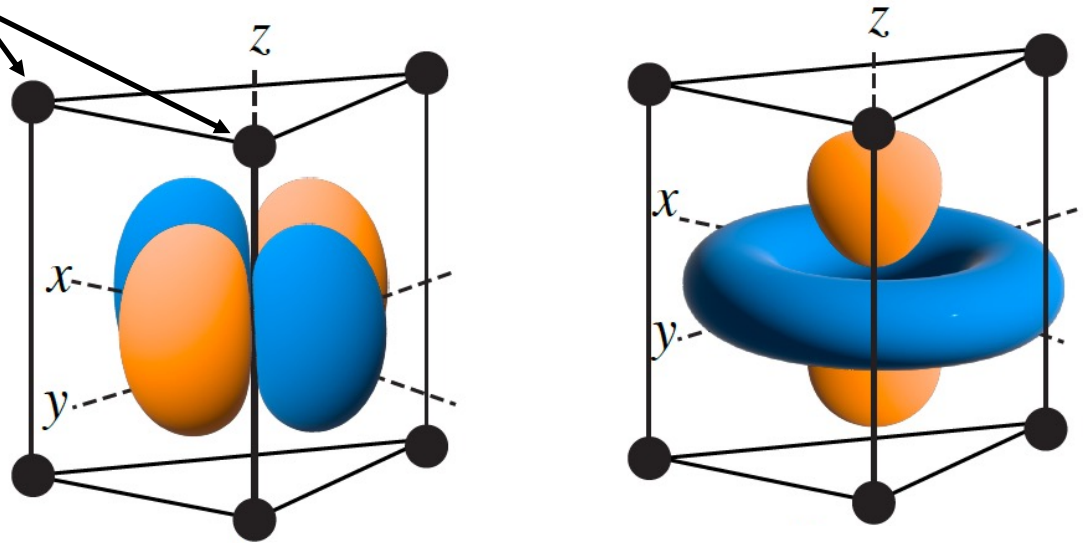

**The pre-edge Gaussian and sigmoid functions were convolved with the spectrometer spectral response and compared with the data**

*D. Phan *et al.*, arXiv preprint arXiv:1912.11554 (2019).
**E. Bingham *et al.*, J. Mach. Learn. Res. 20, 28 (2019).

# Perturbation from the neighboring oxygen atoms cause the iron d-states to broaden with increasing density

Oxygen atoms

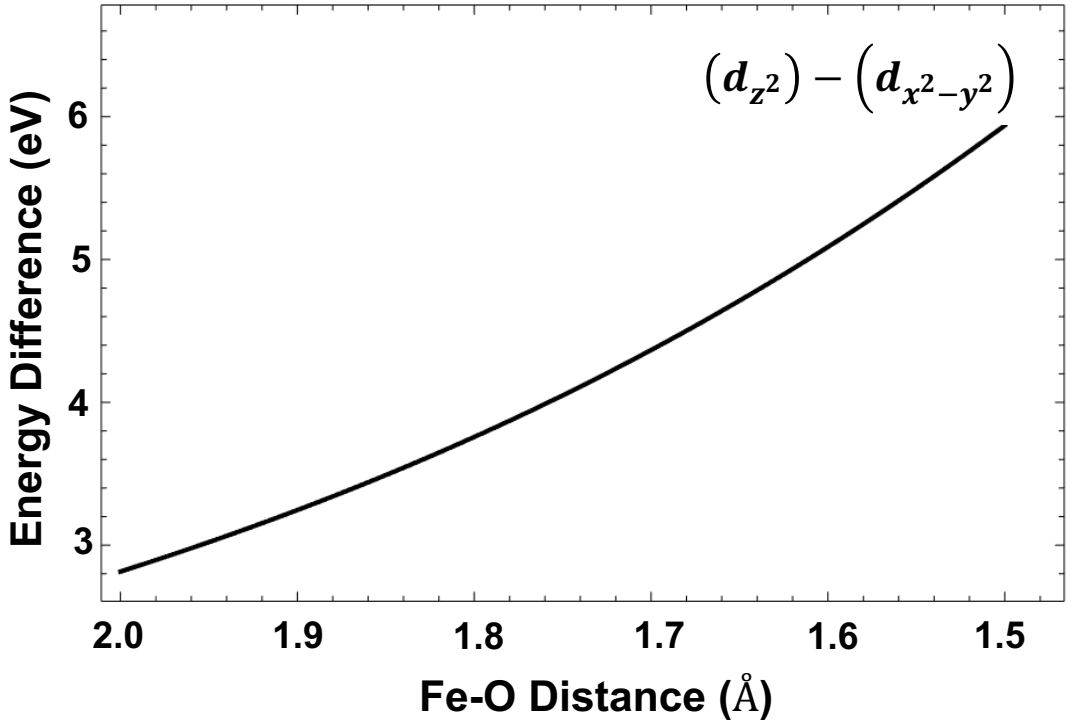
The nearest oxygen atoms break the degeneracy of the iron $3d$ electron orbitals




$d_{x^2-y^2}$
$(\mathbf{m} = \pm\mathbf{2})$

$d_{z^2}$
$(\mathbf{m} = \mathbf{0})$

Crystal Field Theory Calculation




J. Griffith *The Theory of Transition-Metal Ions* University Press, Cambridge (1964).
D.A. Chin *et al.,* Phys. Rev. Lett. *In Prep*

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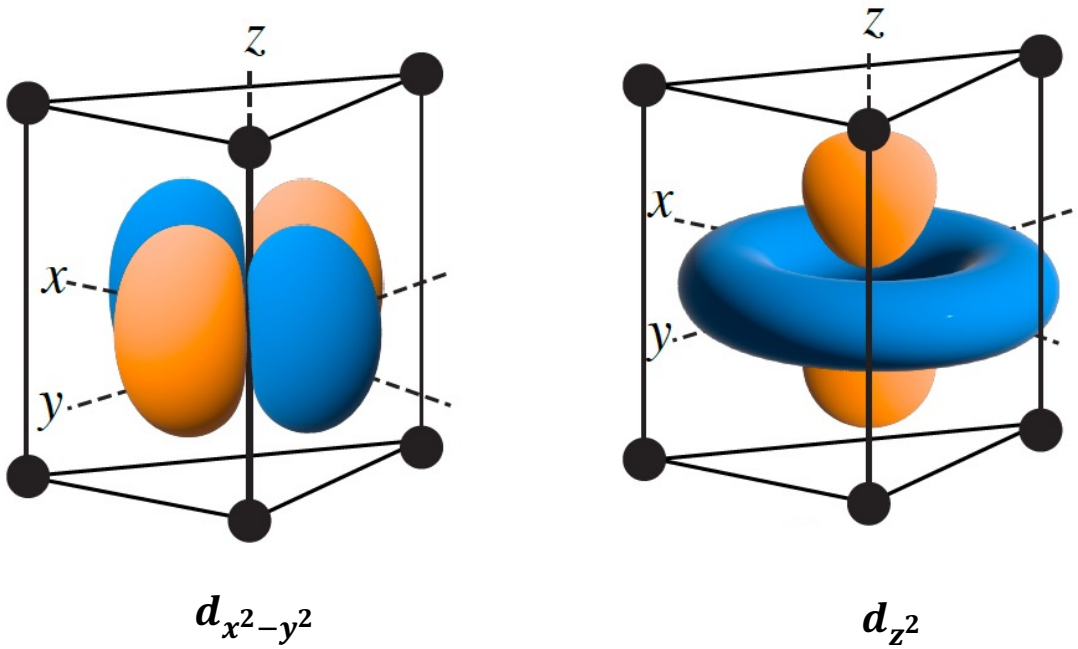
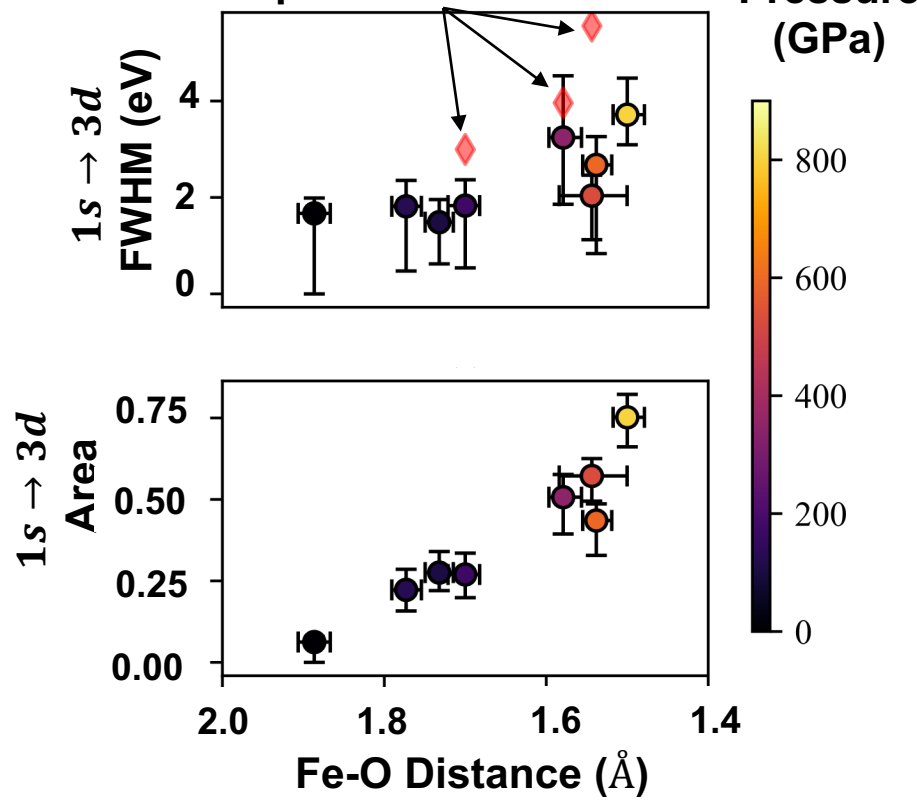


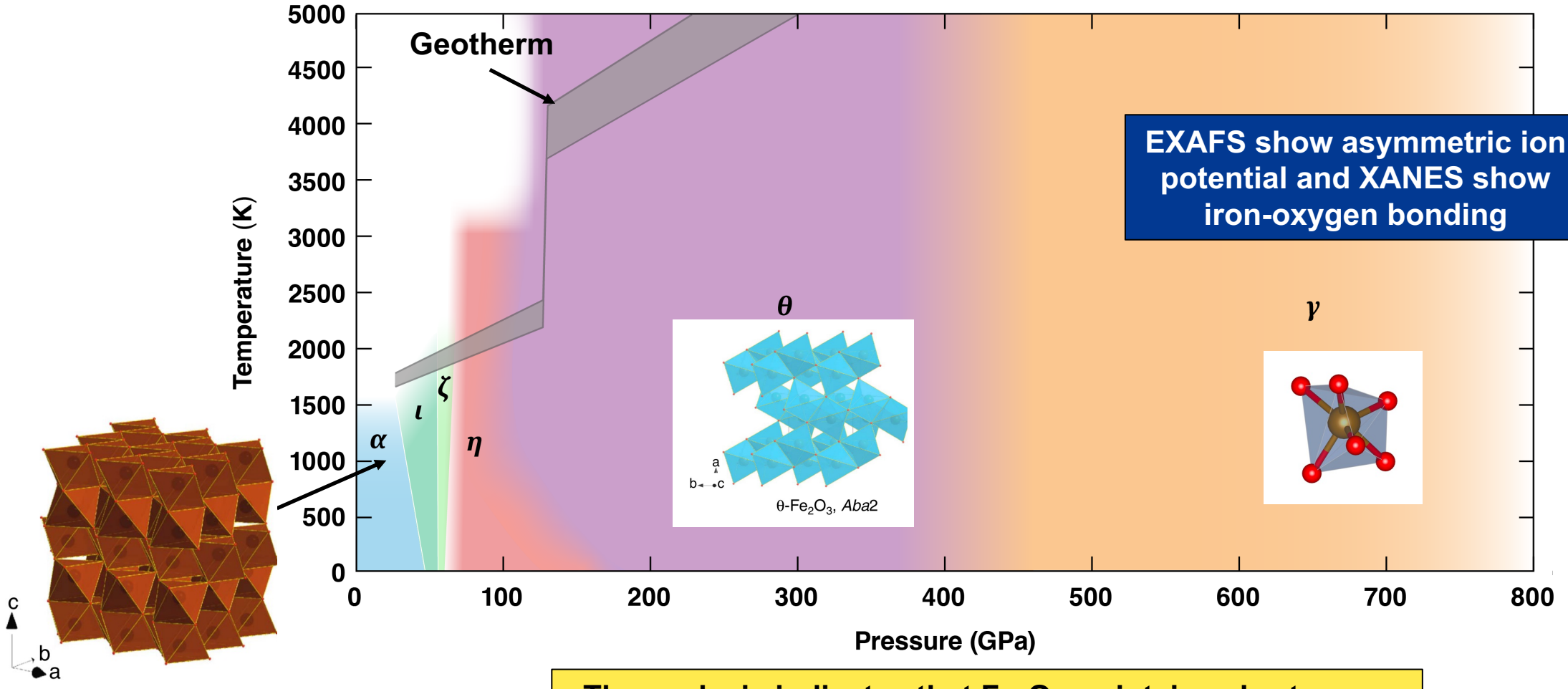

$d_{x^2-y^2}$ $d_{z^2}$

**Density Functional Theory Calculations of the width of the unoccupied $d$ state**




D.A. Chin *et al.*, Phys. Rev. Lett. *In Prep*

# The pre-edge feature is confirmation that iron and oxygen remain bonded above 400 GPa




**EXAFS show asymmetric ion potential and XANES show iron-oxygen bonding**

**The analysis indicates that $Fe_2O_3$ maintains short range order into the $\gamma$ phase**

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Thank you NNSA, SSGF and Krell for supporting this work