Interpreting EXAFS Spectra: Toward Ramp-Compression Studies of Iron Oxide (FeO)

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Extended x-ray absorption fine structure (EXAFS) spectroscopy will be used to characterize iron oxide (FeO) ramp compressed above 500 GPa

- FeO is one of the main constituents of the Earth's lower mantle and a potential building block of the Earth's core; data on FeO material properties under these conditions are sought
- EXAFS spectroscopy provides information on local structure, density, and temperature in compressed materials
- A new high-throughput, high-resolving-power spectrometer is being designed to obtain EXAFS data at the Laboratory for Laser Energetics' Omega Laser Facility

This work provides a basis for future EXAFS experiments on OMEGA, probing FeO under core conditions of the Earth and super-Earths.

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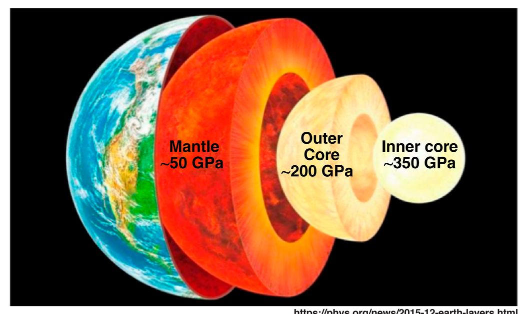
Future Experiment

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



https://phys.org/news/2015-12-earth-layers.html

- Iron is one of the most abundant elements in the Earth and, as a result of its many oxidation states, is highly reactive with oxygen; the abundance and movement of oxygen influence the evolution of the Earth's atmosphere and hydrosphere [1]
- The makeup of the Earth's core is still an open question and one potential candidate is FeO [2]

Characterizing FeO at extreme temperatures and pressures is critical in understanding the formation and evolution of the Earth and iron-rich exoplanets.

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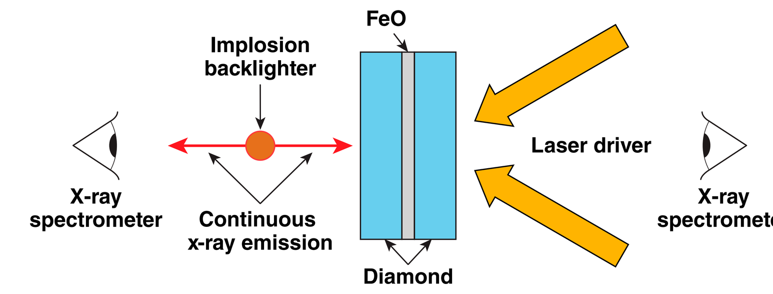
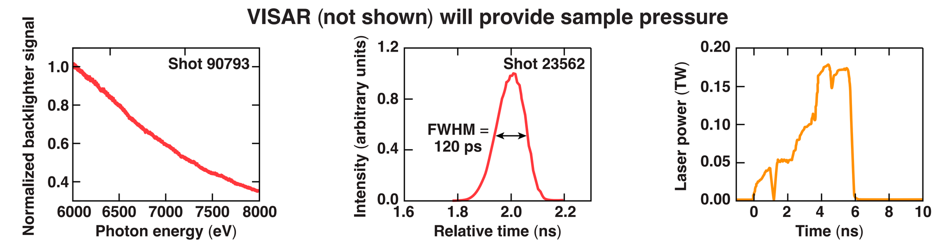
Compressed FeO will be probed using an implosion backlighter, which generates a broadband x-ray pulse [3–5]



VISAR (not shown) will provide sample pressure



Backlighter spectrum — Backlighter duration — 5-ns stitched ramp pulse

VISAR: velocity interferometer system for any reflector

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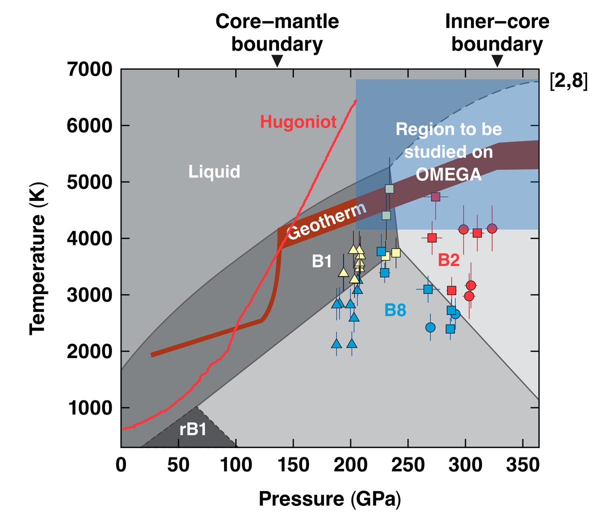
Using the ramp-compression platform, FeO will be studied at high pressures and temperatures

FeO samples will be procured in two ways:

1) FeO samples will be sintered and cut to size [6]
2) FeO samples will be layered through physical vapor deposition (PVD) onto diamond [7]



Objective: Study FeO along the geotherm (above 360 GPa) and determine the melt line.

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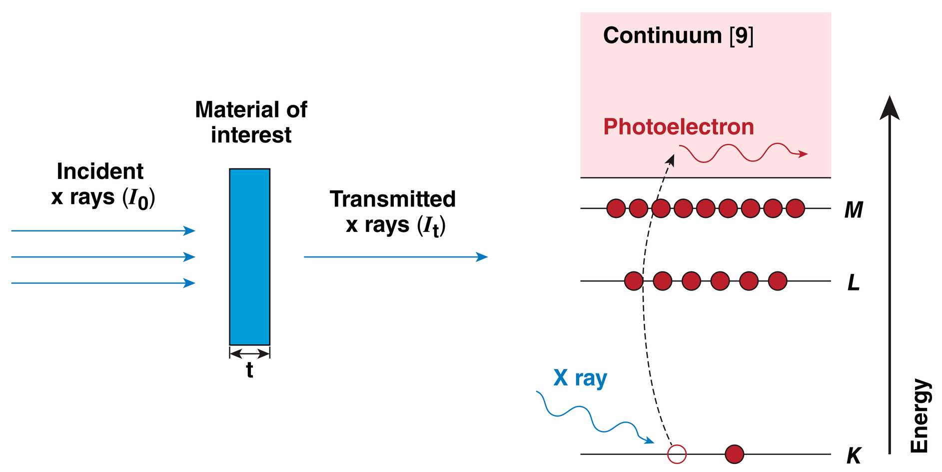
EXAFS Overview

EXAFS spectroscopy studies the modulations above an absorption edge generated by the interference of the photoelectron's wave function



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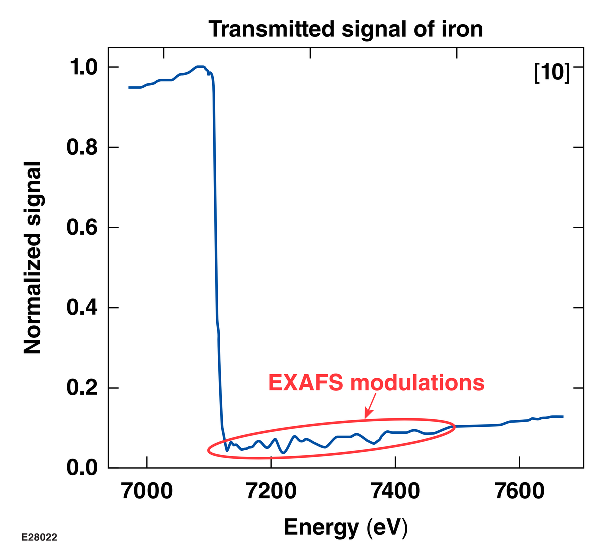
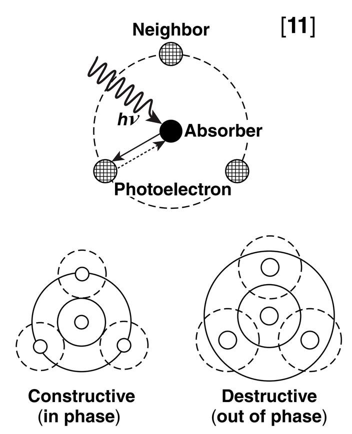
X-rays with energy greater than the binding energy of the core electrons will be absorbed.





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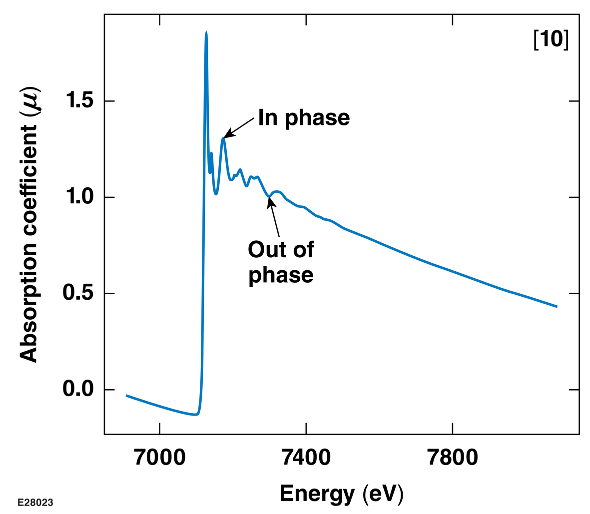
The EXAFS modulations are produced through the interface of the photoelectron's wave function reflecting off of neighboring atoms.



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The absorption coefficient (μ) is defined as $\mu(E) = -\frac{1}{t}\ln\left(\frac{I_t}{I_o}\right)$

The EXAFS modulations are fit using theoretical models, such as *FEFF*, to determine the local structure of the material

The model for the EXAFS modulations [12]

$$\chi(\kappa) = \sum_j \frac{N_j S_0^2 F_j(k)}{2kR_j^2} e^{-2k^2\sigma_j^2} e^{-2R_j/\lambda(k)} \sin[2kR_j - \Phi_j(k)]$$

Summation over all paths — Damping caused by vibrations in the lattice — Electron mean free path — Interactions between the photoelectron and absorbing and scattering atoms' potentials

N_j: Coordination number
S_0^2: Amplitude reduction
F_j: Scattering amplitude
R_j: Half-path length
ϕ_j: Phase shift
σ_j^2: Mean square variation in each path
λ: Photoelectron mean free path

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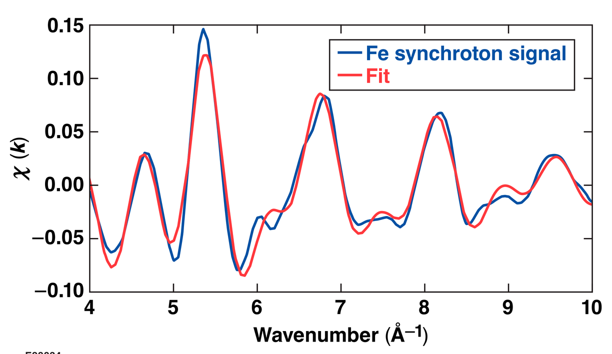

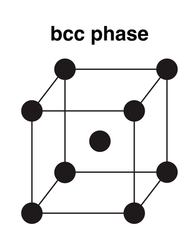

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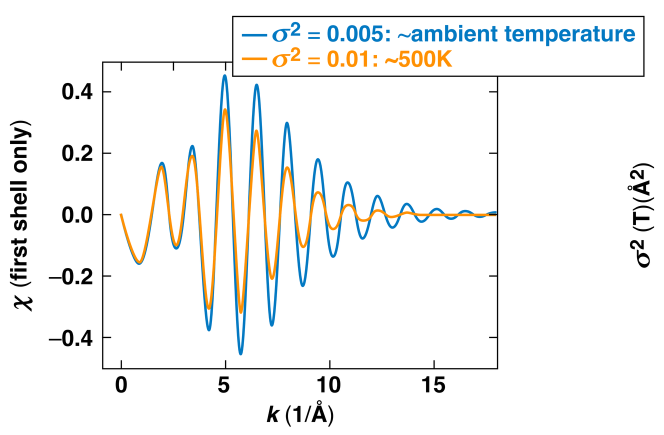
The EXAFS spectrum for iron in the body-centered cubic (bcc) phase was taken on the Advanced Photon Source (APS) synchrotron. The modulations were extracted, and χ was fit using *FEFF* [12].

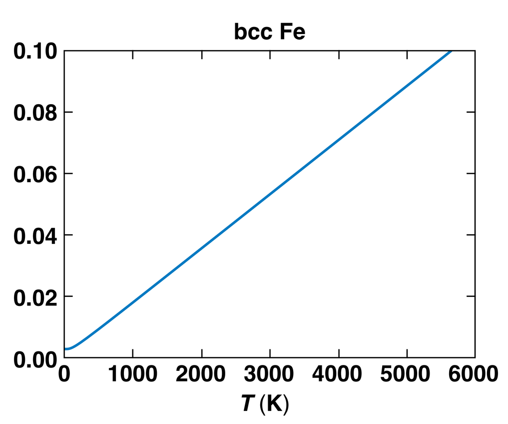
Parameter	Unit	Value	Error
R_1	Å	2.491	0.011
$\sigma^2_{R_1}$	Å^2	0.0067	0.0023
R_2	Å	2.876	0.012
$\sigma^2_{R_2}$	Å^2	0.0079	0.0029
R_3	Å	4.067	0.017
$\sigma^2_{R_3}$	Å^2	0.0095	0.0045
R_4	Å	4.779	0.021
$\sigma^2_{R_4}$	Å^2	0.0051	0.0029

The fit results for the first four shells

The Debye–Waller factor, obtained from the EXAFS fit, is used to infer the temperature of the material [12,13]



Higher temperatures cause damping in the oscillations



Assuming the correlated Debye model and harmonic potentials, a relation between the Debye–Waller factor and temperature can be estimated

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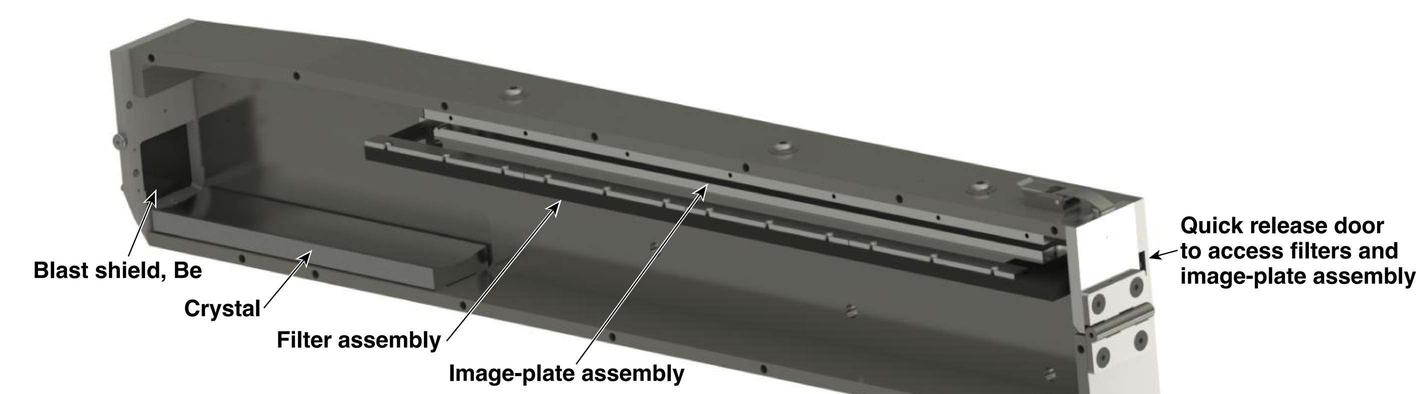
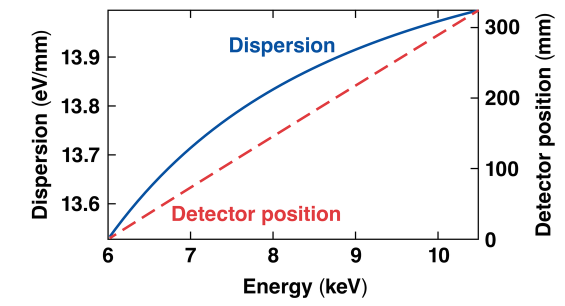
EXAFS spectroscopy provides simultaneous multi-modal state-variable measurements in low temperature high-energy-density (HED) conditions

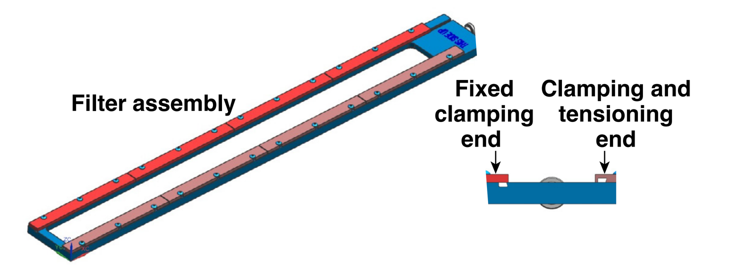
- EXAFS—the modulation of an atom's x-ray absorption probability as a result of the chemical and physical state of the atom
- As density increases, the nearest-neighbor distance becomes shorter—the EXAFS modulation period becomes longer. As temperature rises, the EXAFS signal decays faster at higher x-ray energies—the Debye–Waller Factor governs this decay
- EXAFS provides temperature measurements in the regimes of low temperature and high compression where streaked optical pyrometry (SOP) is no longer valid
- EXAFS can be coupled with VISAR and diffraction to simultaneously obtain the pressure of the material of interest along with the structure and density

EXAFS von Hamos (EvH) Spectrometer

A new high-throughput, high-resolving power von Hamos geometry spectrometer (EvH) is currently being designed and built







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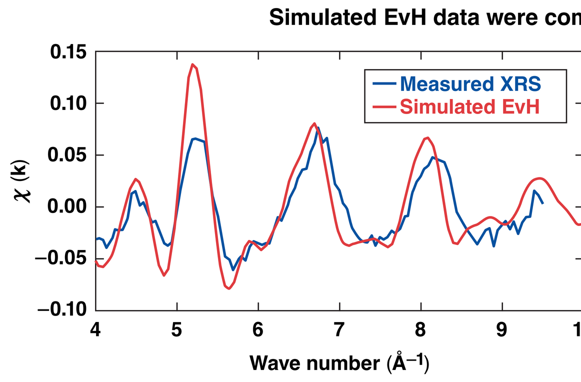
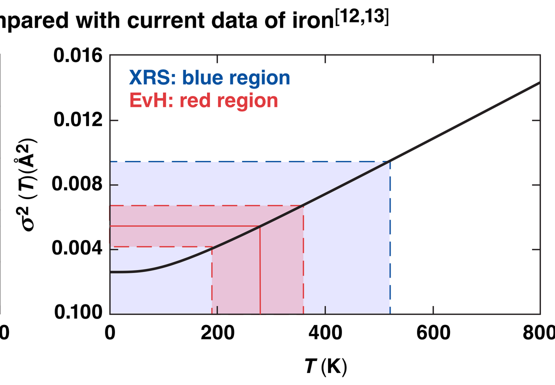
EvH will use a highly annealed pyrolytic graphite (HAPG) crystal

Parameter	Unit	EvH
Energy range	keV	6.0 to 10.5
Crystal		15-μm-thick HAPG
2*d* spacing	Å	6.708
Radius of curvature	mm	65
Angular coverage	(°)	12.0
Crystal dimensions	mm	14 × 165
Estimated spectral resolution	$E/\Delta E$	~1250

Photometric estimates predict a factor of 5 improvement in S/N

Simulated EvH data were compared with current data of iron[12,13]





Fit results for the first shell:
$\sigma^2_{XRS} = 0.00024 \pm 0.0070$ Å^2
$\sigma^2_{EvH} = 0.0054 \pm 0.0013$ Å^2

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XRS: x-ray spectrometer

References

[1] Q. Hu *et al.*, Nature 534, 241 (2016).
[2] K. Hirose, S. Labrosse, and J. Hernlund, Annu. Rev. Earth Planet. Sci. 41, 657 (2013).
[3] Y. Ping *et al.*, Phys. Rev. Lett. 111, 065501 (2013).
[4] Y. Ping *et al.*, Rev. Sci. Instrum. 84, 123105 (2013).
[5] Y. B. Yaakobi *et al.*, J. Opt. Soc. Am. B 20, 238 (2003).
[6] D. Trail and I. Szumila, University of Rochester, private communication (2018).
[7] M. Harmand, Université Pierre et Marie Curie, private communication (2018).
[8] R. Jeanloz and T. J. Ahrens, Geophys. J. Int. 62, 505 (1980).
[9] M. Newville, Rev. Mineral. Geochem. 78, 33 (2014).
[10] XAFS Spectral Library, Spectrum: Fe data, 13 June 2018, http://cars.uchicago.edu/xaslib/spectrum/611.
[11] D. C. Koningsberger *et al.*, Top. Catal. 10, 143 (2000).
[12] B. Ravel and M. Newville, J. Synchrotron Rad. 12, 537 (2005).
[13] E. Sevillano, H. Meuth, and J. J. Rehr, Phys. Rev. B 20, 4908 (1979).

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