Outline

• High pressure studies
  – Diamond anvil cell
  – Ex. Fe in the deep Earth

• What can XAS at high pressure tell us?
  – XAS in DAC
  – Ex. Fe in the deep Earth
  – Other examples enabled by NSLS-II
How do we study materials at high pressure?

- **Diamond Anvil Cell (DAC)**
  - Pressure: ambient to 500 GPa
    (1 GPa = 10,000 bar)
  - Temp: mK to 5000 K
  - Sample size: < 0.001 mm³
  - Transparent to large range of E-M radiation
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Understanding the Earth’s interior

“The interior of the Earth is a problem at once fascinating and baffling, as one may easily judge from the vast literature, and the few established facts, concerning it.”

- Francis Birch (1952)
Fe in the deep Earth

- Fe is the most abundant element by wt, most important transition element
- Complex speciation
  - Oxidation state (Fe$^{0}$, Fe$^{2+}$, Fe$^{3+}$)
  - Coordination (4, 5, 6, 8)
- Fe distribution and speciation between melt and among different crystalline phases (ol, px, wad, ringwoodite, pv, ppv, mw, etc.) throughout the mantle is a central solid-Earth question
  - controls the evolution of the Earth, core-mantle differentiation, and the geodynamics of the mantle.
  - Different P-T-x for different regions and geologic time

Ringwood, *Composition and Petrology of the Earth’s Mantle* (1975)

Fe in the deep Earth

• Our knowledge of Fe distribution relies on understanding the drastic changes in the physical and chemical properties of Fe species at extreme $P-T$ conditions:
  – Fe/Mg partitioning
  – Fe/Mg diffusion
  – Fe speciation in solid and liquid
  – Fe redox
  – Electronic spin state (high-intermediate-low)
Fe-Mg partitioning

\[ K = \frac{(Fe/Mg)_{\text{silicate}}}{(Fe/Mg)_{\text{mw}}} = \frac{(Mg,Fe)\text{SiO}_3}{(Mg,Fe)\text{O}} \]

- Measurements on \( P-T \) quenched samples
- \textit{In-situ} chemical probe

\begin{itemize}
  \item Mao \textit{et al}, \textit{Science} 1997
  \item Andrault \textit{et al}, \textit{JGR} 2001
  \item Kessen \textit{et al}, \textit{EPSL} 2002
  \item Kobayashi \textit{et al}, \textit{GRL} 2005
  \item Murakami \textit{et al}, \textit{GRL} 2005
\end{itemize}
Fe-Mg diffusion

• Very sluggish Fe-Mg interdiffusion?
  – Chemical heterogeneities could persist several cycles of mantle convection (100 Ma)

Holzapfel et al, *Science* 2005
Fe coordination in solid and liquid

- 1 bar, HT experiment on fayalite (Fe$_2$SiO$_4$)
- $\overset{VI}{\text{Fe}}^{2+}$ (solid) $\rightarrow$ $\overset{IV}{\text{Fe}}^{2+}$ (liq)

Jackson et al, Science 2005
Fe redox

- Very high Fe\(^{3+}/\Sigma\)Fe in LM?
  - 50% of Fe in pv (70 wt% of LM)
  - Inconsistent with whole-mantle convection (which would lead to similar oxygen content in UM and LM)
  - Oxygen could come from disproportionation of Fe\(^{2+}\) in LM, \(3\text{Fe}^{2+} (3\text{FeO}) \rightarrow \text{Fe}^0 + 2\text{Fe}^{3+} (\text{Fe}_2\text{O}_3)\)
  - LVP \(\sim 25\) GPa, EELS and MS of quenched run product

McCammon, Science 2005

Frost et al, Nature 2004
Electronic spin transitions

- Observations of high spin-low spin transitions in Fe using X-ray Emission Spectroscopy (XES)

FeO & Fe$_2$O$_3$

(Fe,Mg)O & (Fe,Mg)SiO$_3$ pv

Badro et al, PRL 1999
Badro et al, PRL 2002
Badro et al, Science 2003
Badro et al, Science 2004
Li et al, PNAS 2004
Lin et al, Nature 2005
Lin et al, Science 2007
RXES

$1s2p$ resonant inelastic x-ray scattering in $\alpha$-Fe$_2$O$_3$

W. A. Caliebe, C.-C. Kao, and J. B. Hastings
National Synchrotron Light Source, Brookhaven National Laboratory, Upton, New York, 11973

M. Taguchi and A. Kotani
Institute for Solid State Physics, University of Tokyo, Roppongi, Minato-ku, Tokyo 106, Japan

T. Uozumi
College of Engineering, University of Osaka Prefecture, Gakuen-cho, Sakai 593, Japan

F. M. F. de Groot
Solid State Physics Laboratory, University of Groningen, Nijenborgh 4 9747 AG Groningen, The Netherlands
(Received 18 March 1998)

- X21 of NSLS

- Similar information to $L_{2,3}$ absorption
- The pre-edge doublet due to crystal-field splitting
Fe in the deep Earth

• Our knowledge of Fe distribution relies on understanding the drastic changes in the physical and chemical properties of Fe species at extreme \( P-T \) conditions:
  – Fe/Mg partitioning
  – Fe/Mg diffusion
  – Fe speciation in solid and liquid
  – Mantle redox (ferric/ferrous)
  – Electronic spin state (high-intermediate-low)

• Progress in these areas have been dictated by advances in diagnostic high \( P-T \) probes (e.g. optical, Mössbauer, XRD, XES, and XAS)

• Extend these measurements to \textit{in-situ} mantle \( P-T \)
XAS in a DAC

- XAS has potential as a tool capable of answering all these questions, but has been hardly applied to high-$P$ Fe studies due to the x-ray absorption of diamond anvils.
- Transmission of 7.1 keV x-ray at the Fe $K$-edge through a typical pair of diamond anvils (5 mm total thickness) is only $10^{-5}$.
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C Density=3.5154 Thickness=5000. microns

![Graph showing transmission vs photon energy](image)

![Diagram of a DAC](image)
XAS in a DAC

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![Graph showing transmission vs. photon energy](image)
XAS in a DAC

This problem has been overcome by:

- Reducing the diamond thickness in the path down to 1 mm and transmission to a tolerable 0.1 by using holes in diamonds (Bassett et al., 2000; Dadashev et al., 2001)
- Supporting diamonds with holes (Silvera, 1999)
- Be gasket with inclined x-ray incident angle
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![Graph](image1)

- **X**-Density=3.5154 **T**hickness=1000. microns

![Diagram](image2)

- **A**xial 2 x 2.5 mm diamonds
- Supporting seats
XAS in a DAC

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XAS of Fe

- Pre-edge position and intensity – Fe oxidation state, coordination #, redox Fe$^{3+}/\Sigma$Fe
- Edge height: quantitative mapping of Fe
- CFSE of pre-edge 7113-7115 eV: $t_{2g}-e_g$
- XMCD: magnetism
- EXAFS: Fe coordination
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![Chemical Elements Table]

![Diagram of XAS of Fe]
Pre-edge position and intensity

- Redox and crystallographic site

Wilke et al, Amer. Min. 2001
XAS of Fe

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Chemical mapping using micro-XAS

- ED-XAS
- Maps of:
  - Fe content
  - Redox
  - Crystallographic site

ESRF ID24  Pascarelli et al, JSR 2006
XAS of Fe

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High-spin to low-spin transition in hematite

Nature of the High-Pressure Transition in Fe$_2$O$_3$ Hematite

J. Badro, G. Fiquet, V. V. Struzhkin, M. Somayazulu, H. K. Mao, G. Shen, T. LeBihan
CFSE in Fe$_2$O$_3$

PFY at $K_{\alpha 1}$

Intensity

Energy (eV)

Crystal field splitting (eV)

Pressure (GPa)

1 bar
5 GPa
1 GPa
29 GPa
45 GPa

BL12XU, SPring-8
# XAS of Fe

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X-ray magnetic circular dichroism (XMCD) at HP

- bcc → hcp transition in pure Fe
- Magnetic transition precedes (drives) structural

Mathon et al, PRL 2004
XMCD of Fe$_3$O$_4$ at HP

Y. Ding et al, PRL in press
Intermediate spin in Fe$^{2+}$

- Loss of 15% of intensity in K$_β$ peak
- Consistent with IS in Fe$^{2+}$ and 2 Fe$^{3+}$ remain HS

Y. Ding et al, PRL in press
# XAS of Fe

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- XMCD of near edge: magnetism
- **EXAFS**: Fe coordination

![Periodic Table](image-url)
Other topics to study

- Fe is just one example that shows the potential of high-pressure XAS in solving a wide range of scientific problems.
- These applications of high-pressure XAS can certainly be generalized to other elements including K-edge of TE and beyond and L-edge of REE and beyond, and have major impact in numerous other branches of high-pressure science.
- Its potential has been barely explored.
  - Absorption edge height – Quantitative mapping
  - Pre-edge and near edge features – oxidation states, electronic excitations
  - XMCD – magnetism
  - EXAFS – element specific structure of crystalline and amorphous materials
Absorption edge height

• Coupled with nanobeam capability, absorption edge height provides composition mapping and element specific tomography capability currently lacking in DAC experiments

• *In-situ* high pressure and temperature maps
Pre-edge and near edge

- Pressure has dramatic effects on charge transfer, mixed valence state, and oxidation state of $d$ and $f$ electron elements and compounds
- XAS can help to resolve various electronic states which are tuned by pressure

- HP behavior of X-ray near-edge structure at the rhenium L$_3$ edge in TlReO$_4$.
- No evidence for proposed e$^-$ transfer from Tl to Re

Ablett et al, *HPR* 2003
XMCD

- Magnetism, MR (GMR and CMR), and spin character of lanthanides, manganites, cobaltites, etc.
- Pressure can readily tune these properties and change materials among many different magnetic and electronic states, providing opportunities for discovery and study of novel materials.
Exploring magnetism within extreme magnetic fields

The feasibility of measuring X-ray magnetic circular dichroism (XMCD) within very high magnetic fields has been investigated using an energy-dispersive X-ray absorption spectrometer at the ESRF’s energy-dispersive XAS beamline ID24.

By coupling a pulsed magnetic field device developed at the ESRF (Figure 1) [1] to the fast acquisition capabilities of ID24, the Fe L₂ and L₃ XMCD signals were measured in a Ca₃Fe₃Ru₂O₉ perovskite (Figure 2) at up to 50 T and in the temperature range 10-250 K [2]. Knowledge of the field and temperature dependence of both spin and orbital magnetic moments of the under extreme magnetic fields could help answer enigmatic questions on the magnetism of these distorted double perovskites, such as why they don’t reveal saturation, whether this phenomenon is only due to anisotropy in the grain boundaries or whether it originates from the bulk.

Figure 1: Peter van der Linden setting up the pulsed magnetic field device at beamline ID24.

Considerable research effort is being made to understand properties of matter under extreme conditions. Static high pressures up to the multimegabar regime can now be reached with diamond-anvil cells, as well as temperatures from the milli-Kelvin to thousands of Kelvin using dilution refrigerators and laser heating. The exploration of ever widening P-T diagrams has lead to the discovery of a multitude of new chemical and physical phenomena - such as the discovery of the (Mg,Fe)₃SiO₄ postperovskite with significant geophysical implications for the earth mantle’s nature and dynamics - leading to a fundamental understanding as well as technological applications.
EXAFS

- Pressure induces polyamorphism in glasses and liquid-liquid transitions in high $P-T$ melts. These transitions are normally observed by XRD
- EXAFS provide element specific coordination information

Falconi et al, *PRL* 2005
Guthrie et al, *PRL* 2004
Future opportunities enabled through NSLS II

• To optimize XAS capabilities would recommend design consideration of an integral system which can accommodate multiple extreme environments
  – High-pressure cells
  – Cryostat
  – Laser heating
  – Strong magnetic field