Maximizing Science from Returned Samples through Valence State Measurements of Minerals using X-Ray Absorption Spectroscopy

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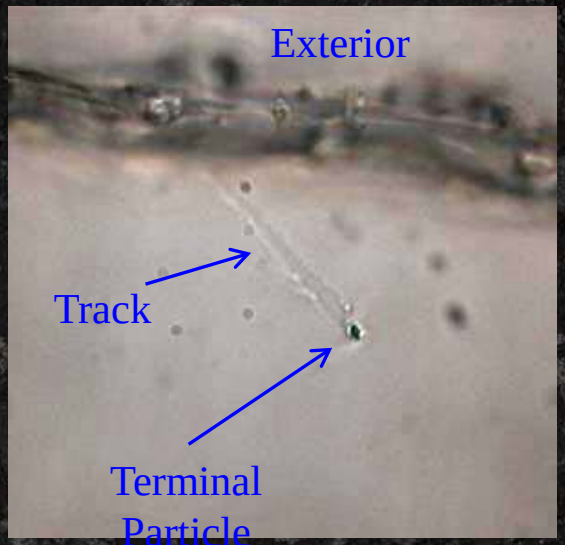
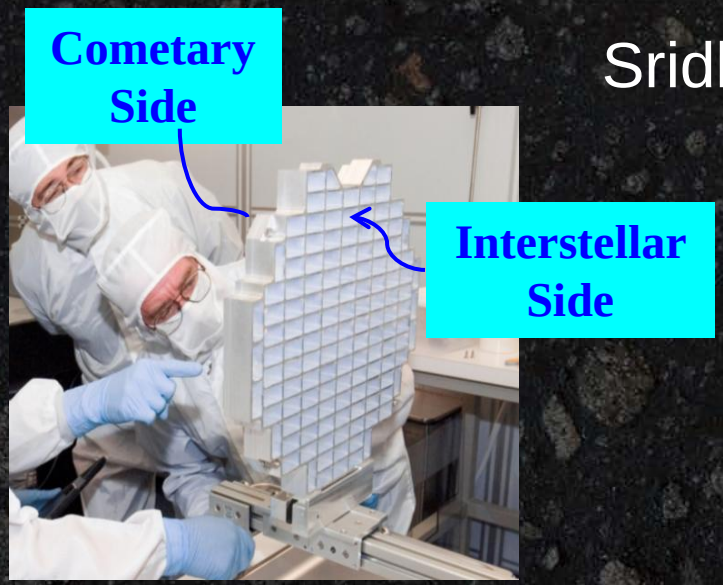




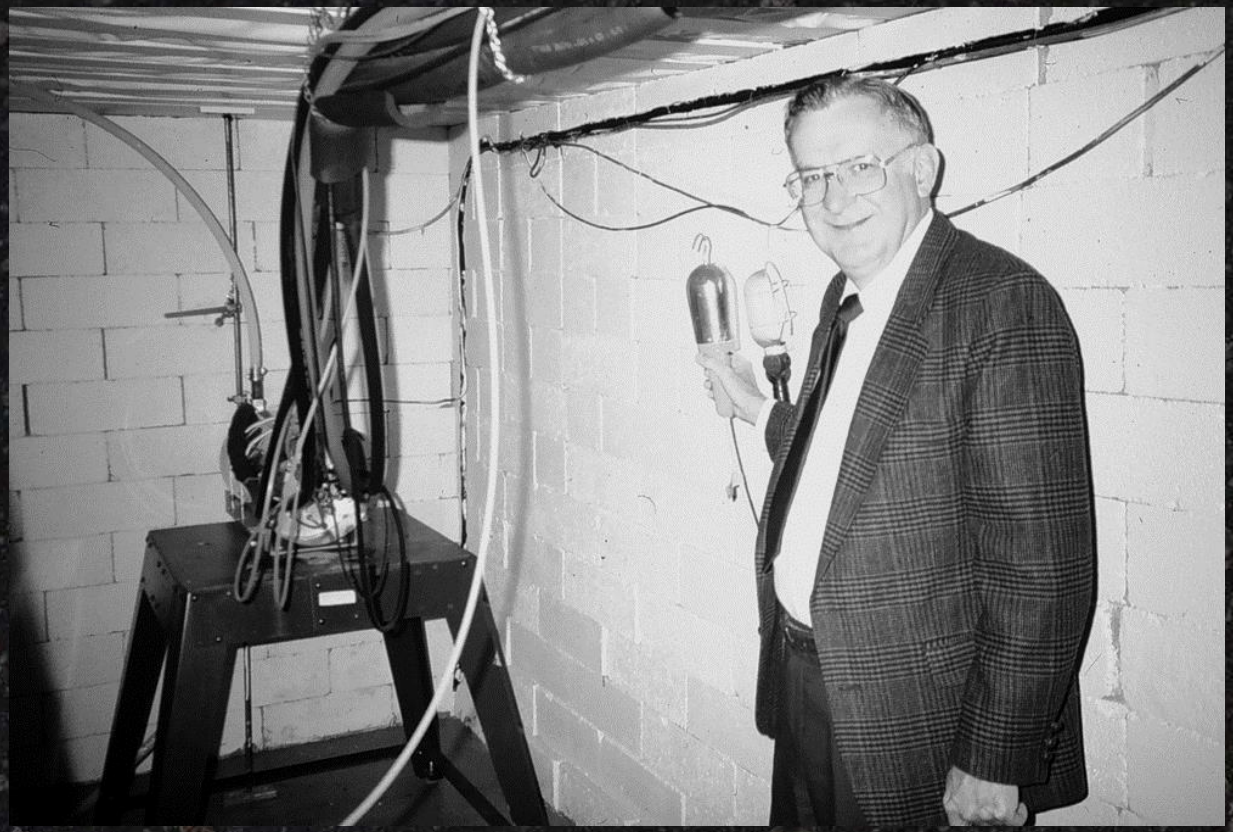
RISE4
REMOTE IN SITU AND SYNCHROTRON STUDIES FOR SCIENCE AND EXPLORATION

The amount of oxygen on a terrestrial planet affects:

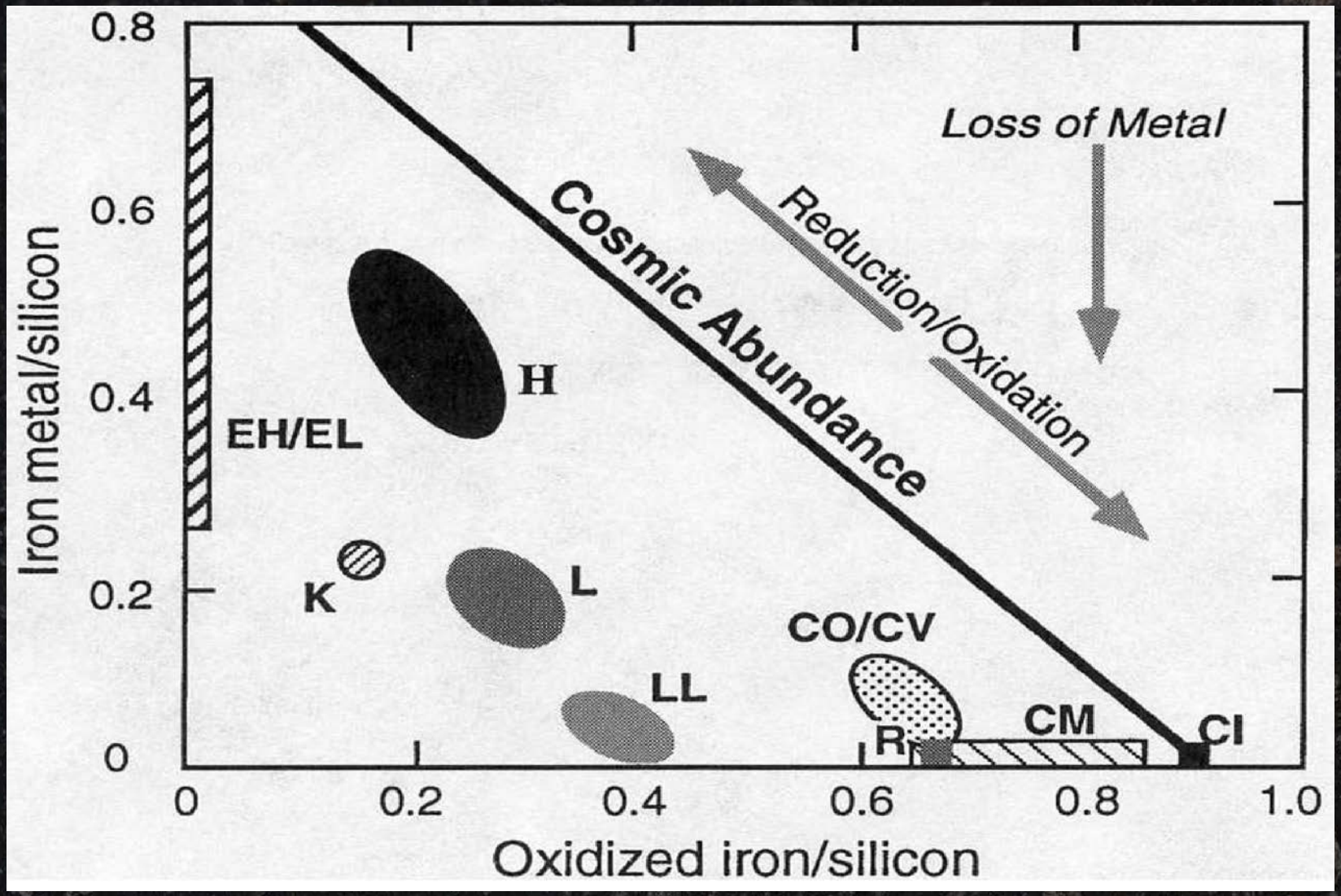
- phase equilibria
- crystallization processes of melts
- composition of the resulting phases
- partitioning of elements between the core and silicate portions of terrestrial planets during planetary differentiation
- fluid-driven metasomatism, with potential linkage to atmospheric evolution

Oxygen is *very difficult* to measure quantitatively through direct methods

Fast neutron activation analysis
Dr. Bill Ehmann
Univ. of Kentucky



- Quantified using the parameter of oxygen fugacity (f_{O2}).
- Oxygen fugacity is defined as the potential for a multivalent cation to occur in any of its valence states, either reduced, neutral, or oxidized.

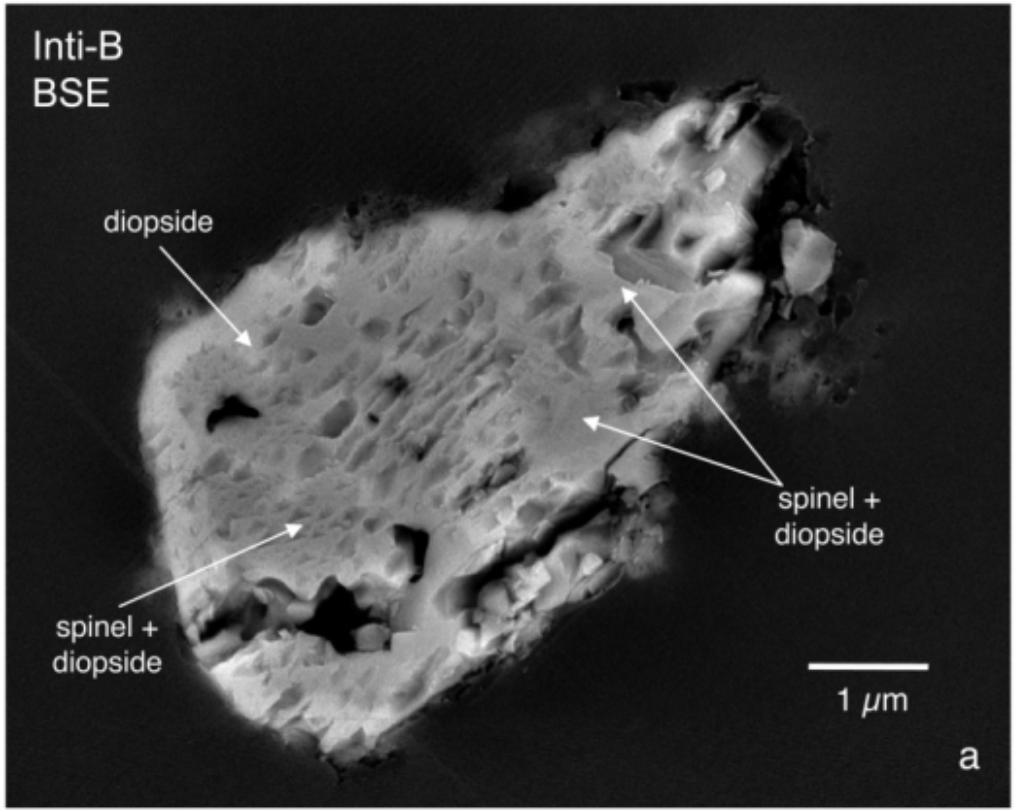


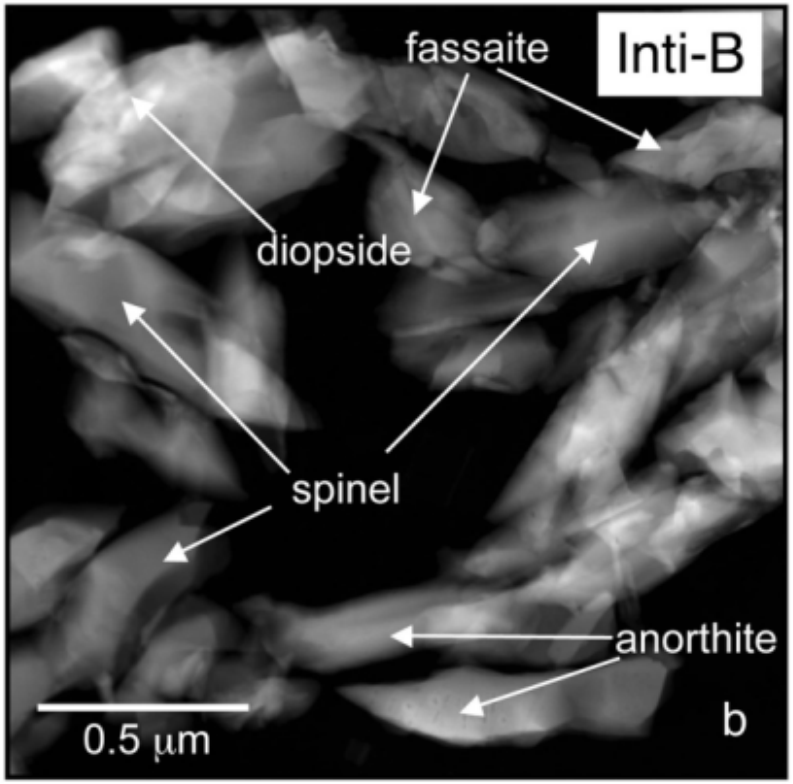
Different chondrite reservoirs showing the wide range in oxidation states. Figure from Brearley and Jones (1998).

MIMOS Mössbauer spectrometer on *Opportunity* rover

We can't measure oxygen directly,
so we study multivalent elements, which record oxygen potential, most commonly by using ratios of Fe^0, Fe^{2+}, and Fe^{3+}.

Redox ratios in tiny samples can't be measured by conventional techniques

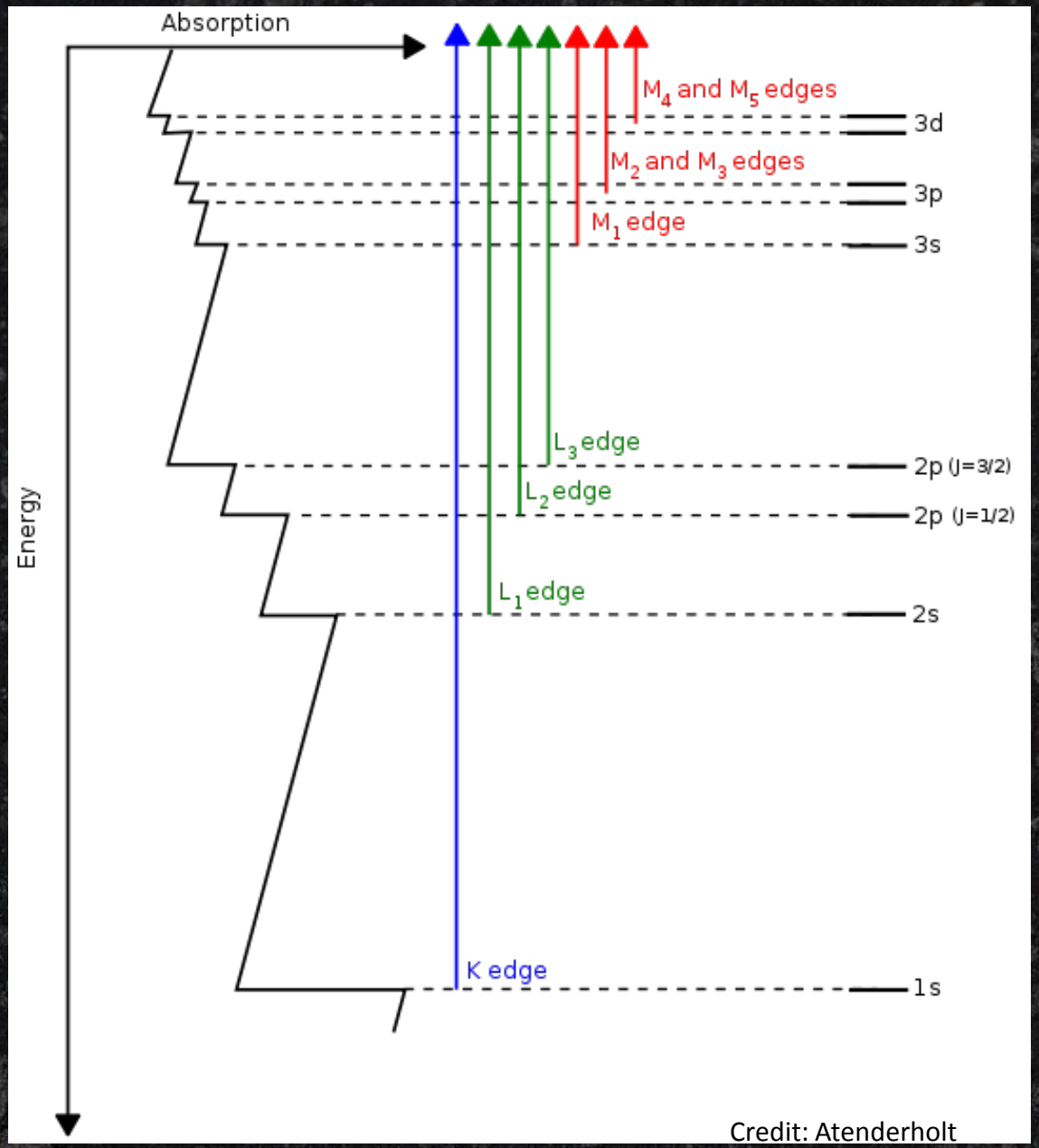




Most promising methods:

X-ray Absorption (synchrotron)

Electron energy-loss spectroscopy (TEM)

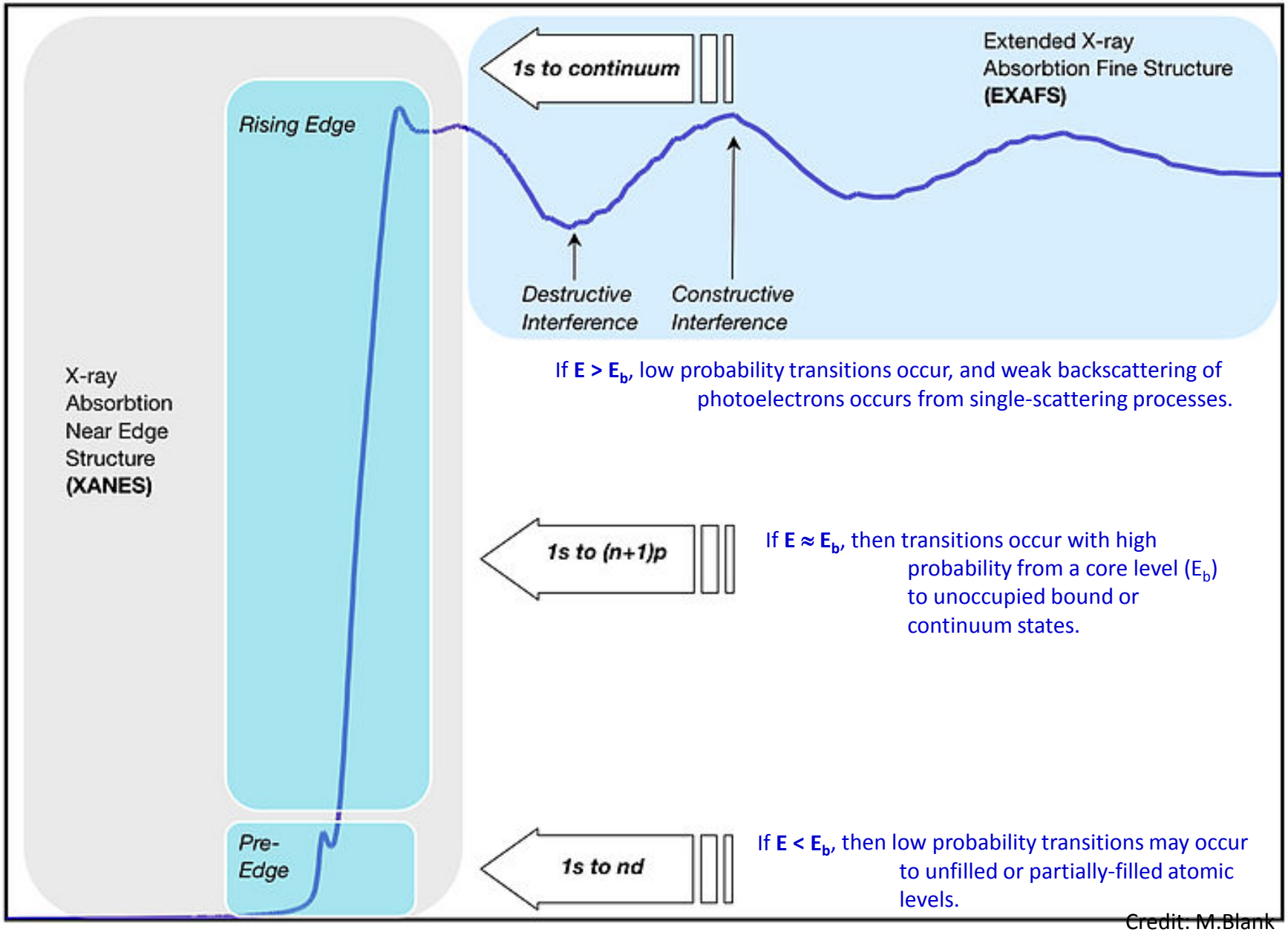


Credit: Atenderholt

X-Ray Absorption Spectroscopy (XAS)

- Excite core electrons using 0.1-100 keV photon energy from a synchrotron
- Principle quantum number determines which edge you're studying

E = incident photon energy and E_b = binding energy of core level electron in absorber



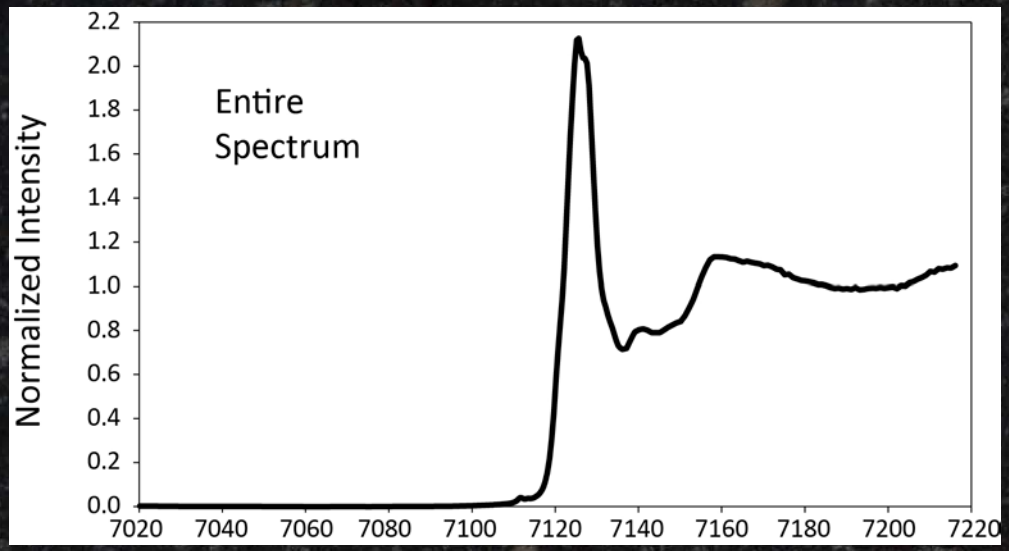
If **E > E_b**, low probability transitions occur, and weak backscattering of photoelectrons occurs from single-scattering processes.

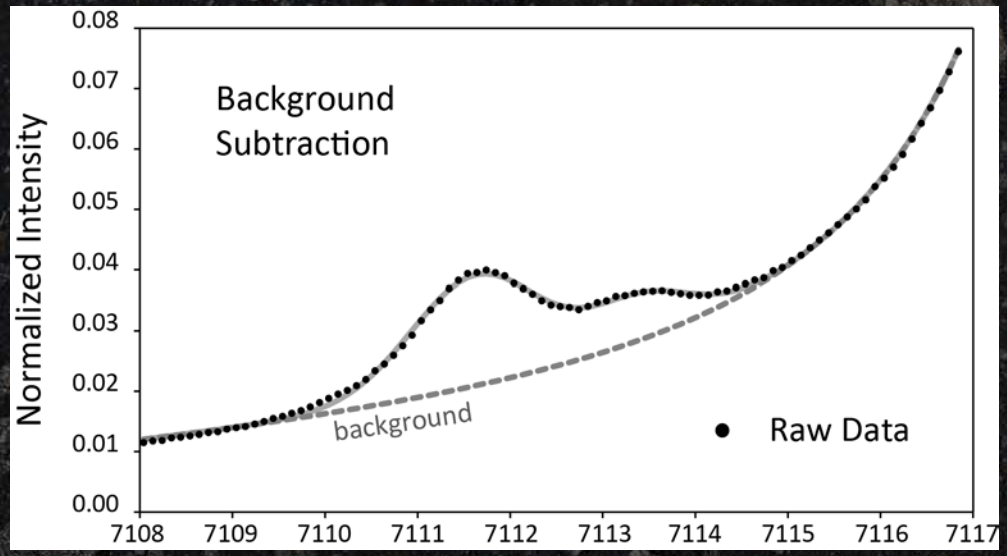
If **E ≈ E_b**, then transitions occur with high probability from a core level (E_b) to unoccupied bound or continuum states.

If **E < E_b**, then low probability transitions may occur to unfilled or partially-filled atomic levels.

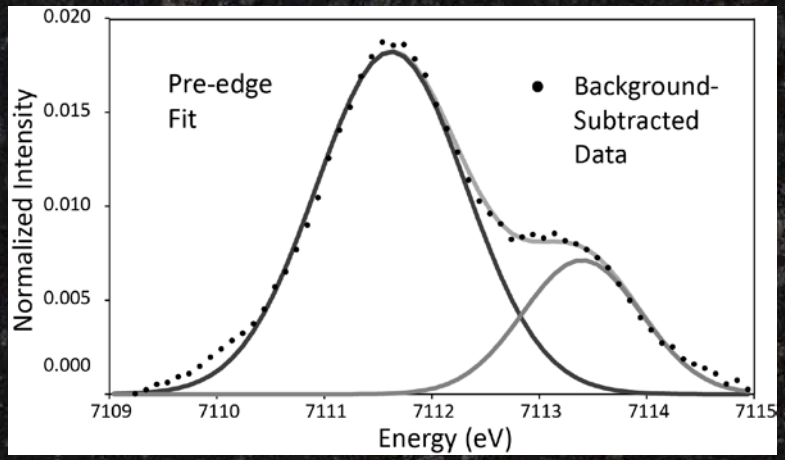
Credit: M.Blank

Important things to know about XAS

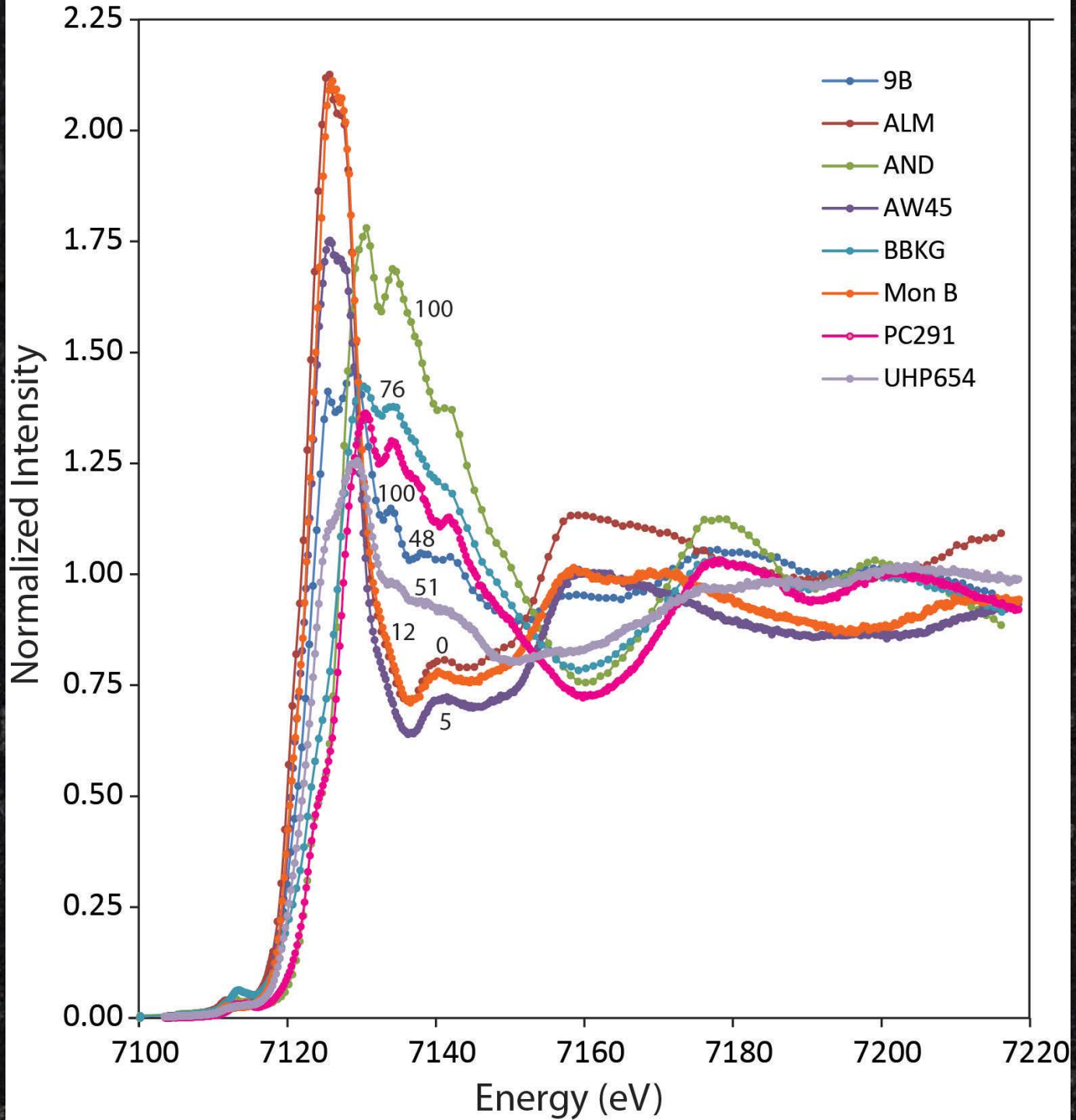




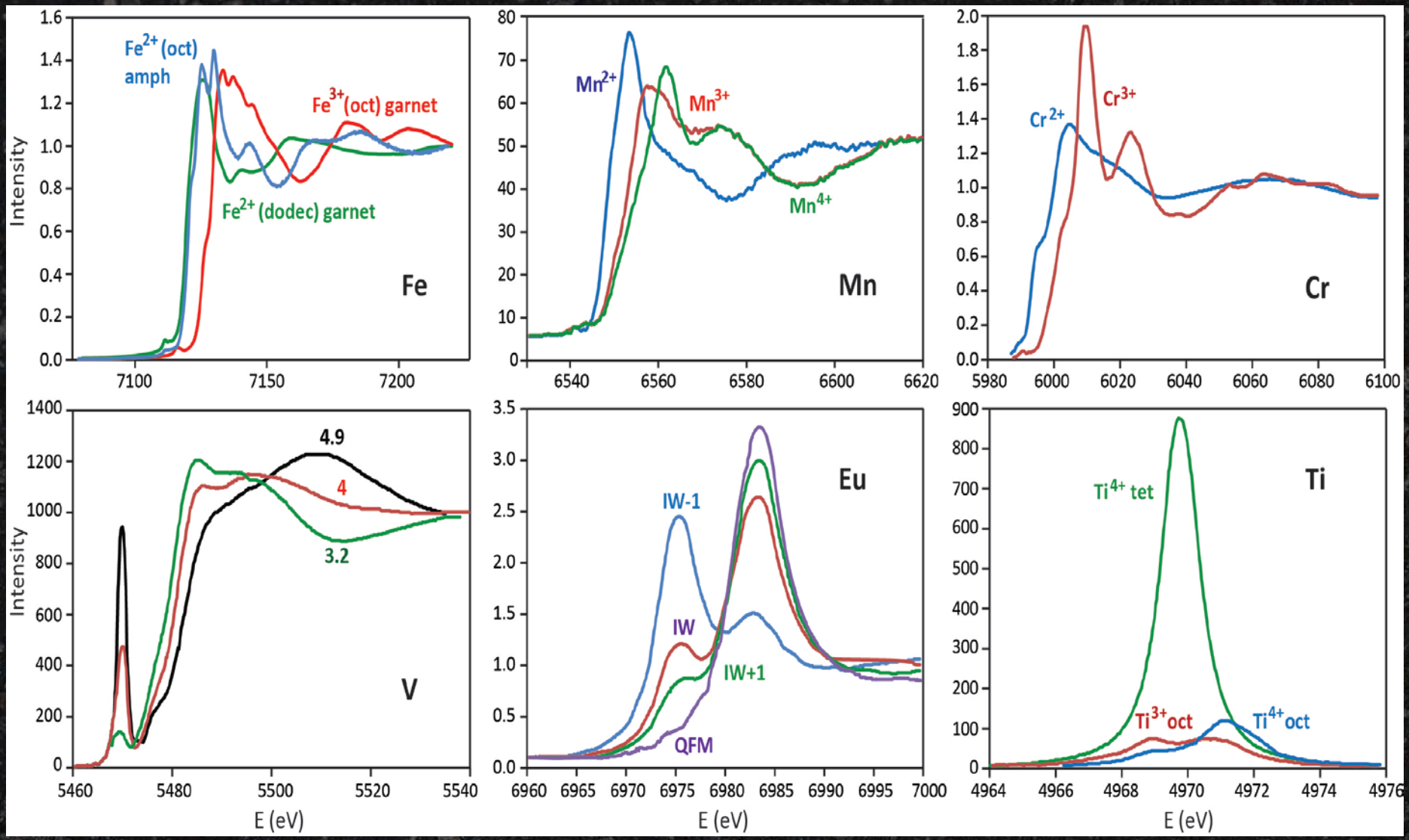
1. Traditionally, info on valence state was thought to be mostly in the pre-edge (XANES) region



BUT Pre-edge peak intensity is a function of distortion of the site; peak energy relates to valence state

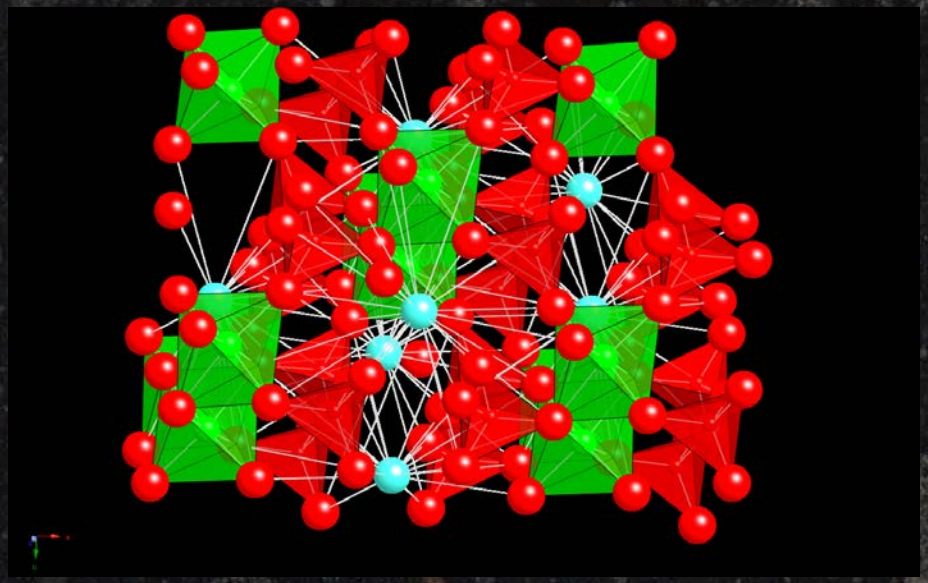

9B
ALM
AND
AW45
BBKG
Mon B
PC291
UHP654
100
76
100
48
51
12
0
5
Normalized Intensity
Energy (eV)
2.25
2.00
1.75
1.50
1.25
1.00
0.75
0.50
0.25
0.00
7100
7120
7140
7160
7180
7200
7220

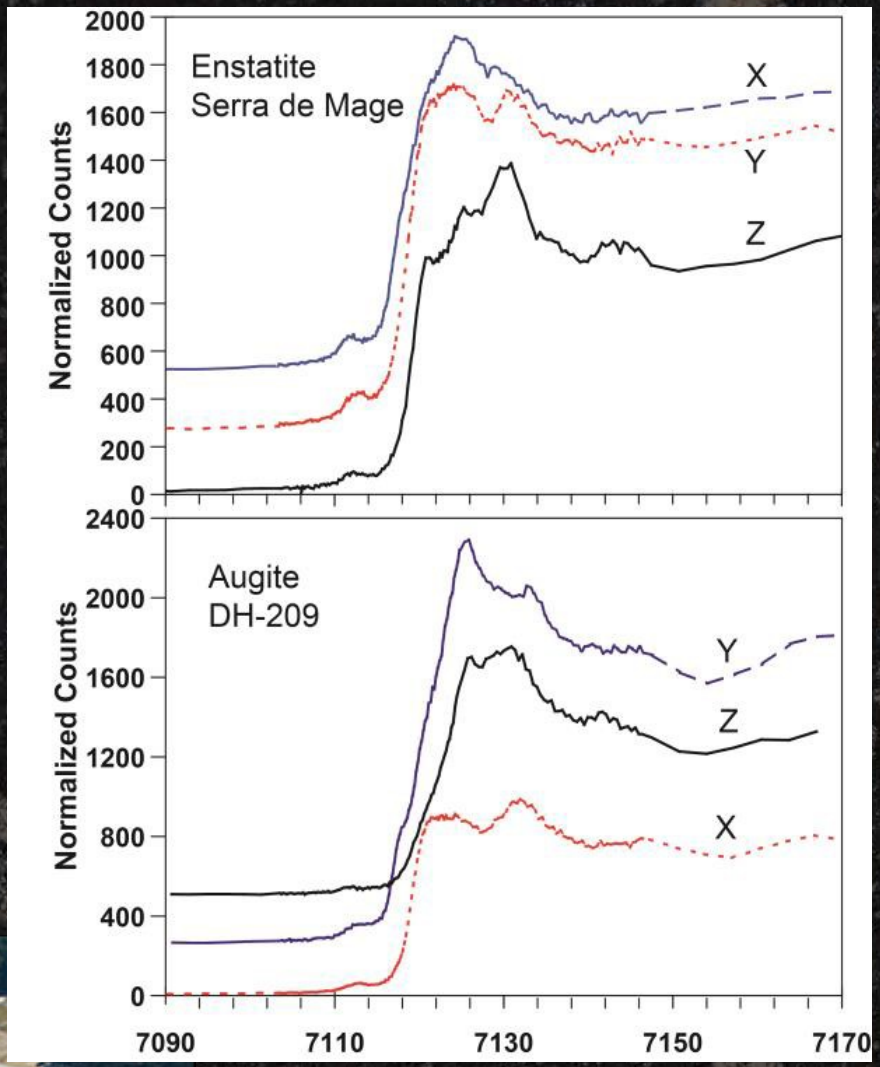
2. Several different elements occur in multiple valence states



BUT no direct method to predict peak intensities – must be done empirically

3. Synchrotron radiation is plane-polarized so many minerals show x-ray pleochroism



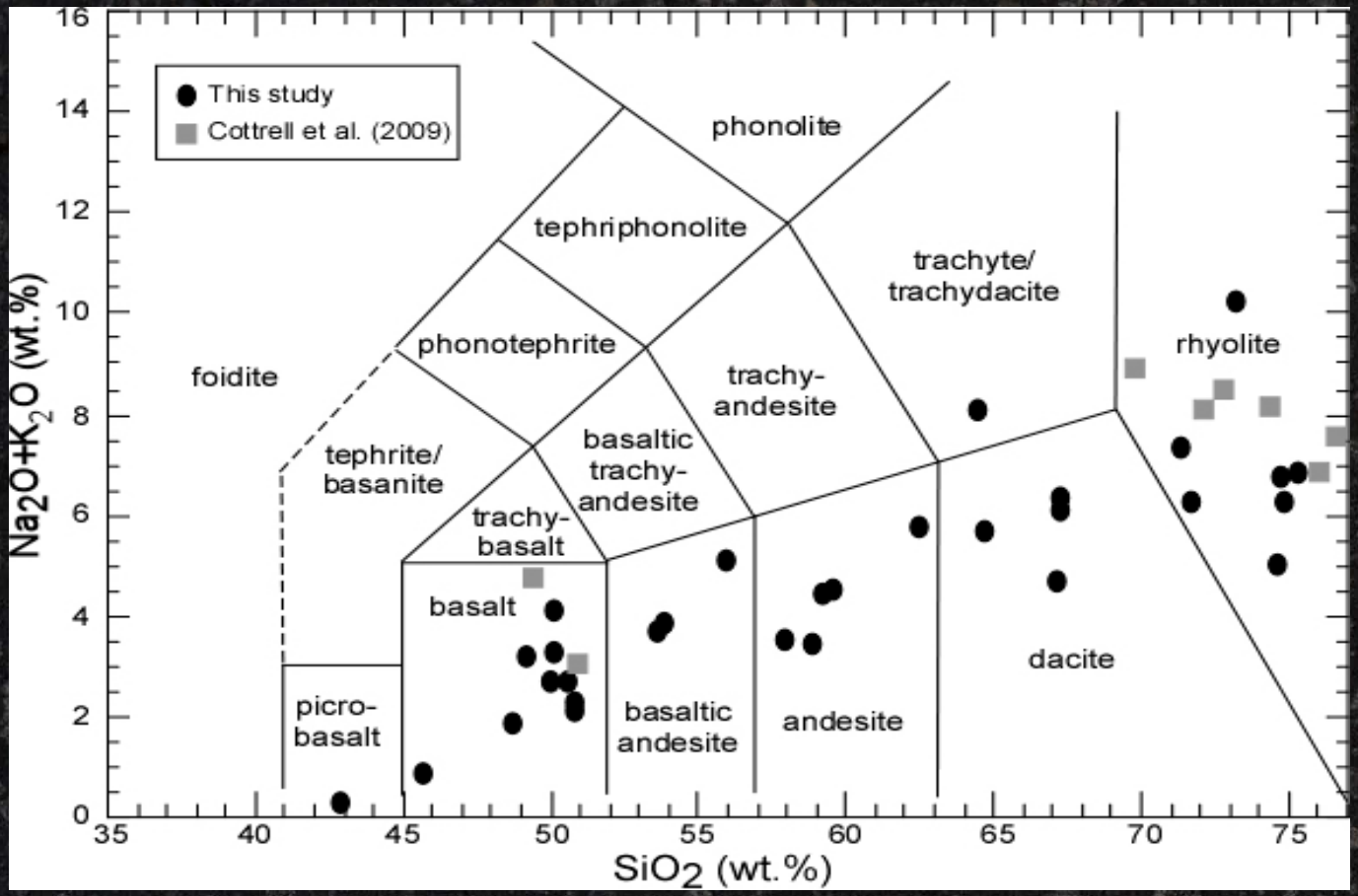


BUT with tiny samples, we can't analyze powders – must deal with single crystals

Technique development needed to realize potential of XAS

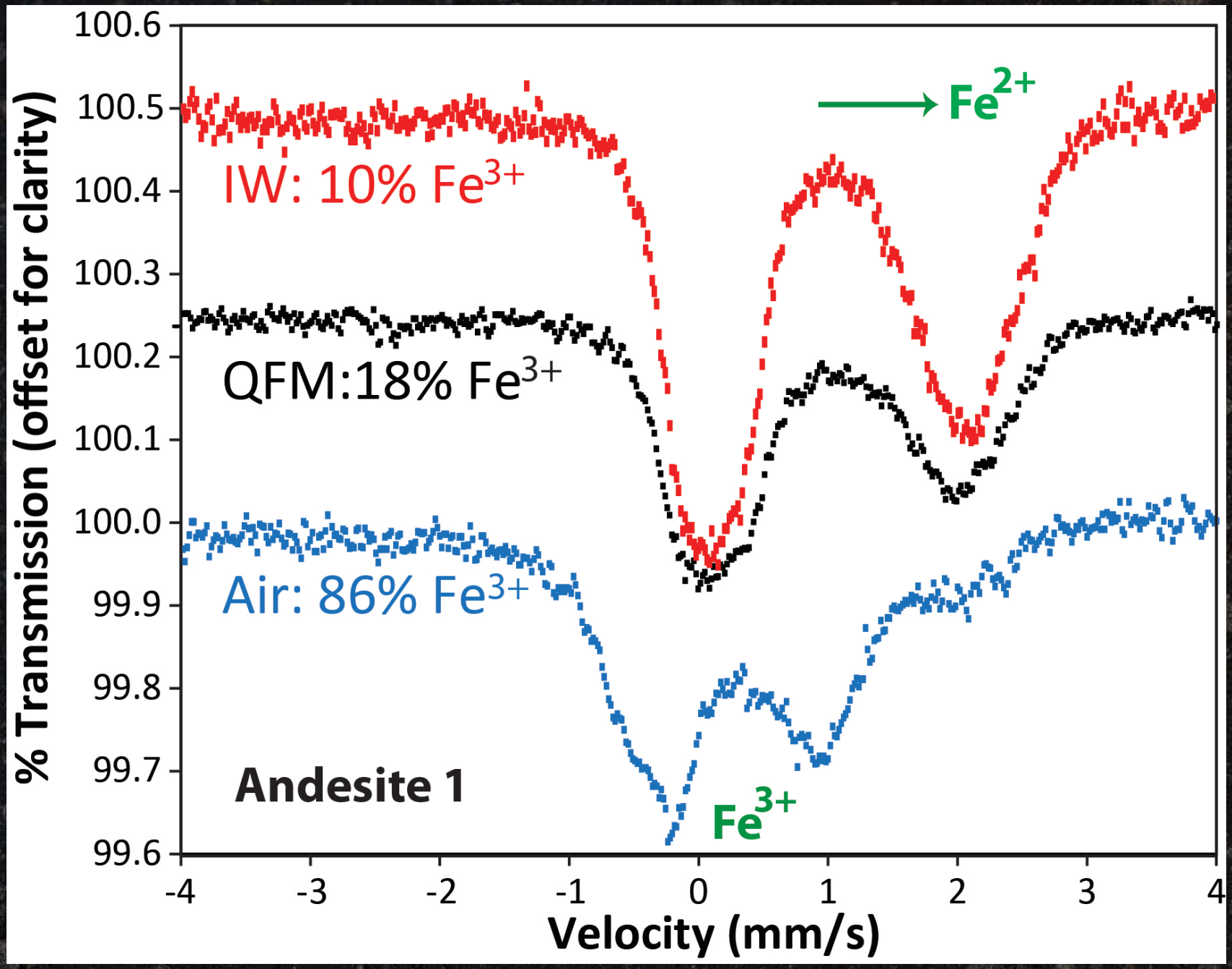
- Develop and characterize standards with known redox ratios for analysis of planetary materials
- Acquire spectra of those standards at necessary optical orientations if needed
- Use machine learning for quantification of valence states with known errors

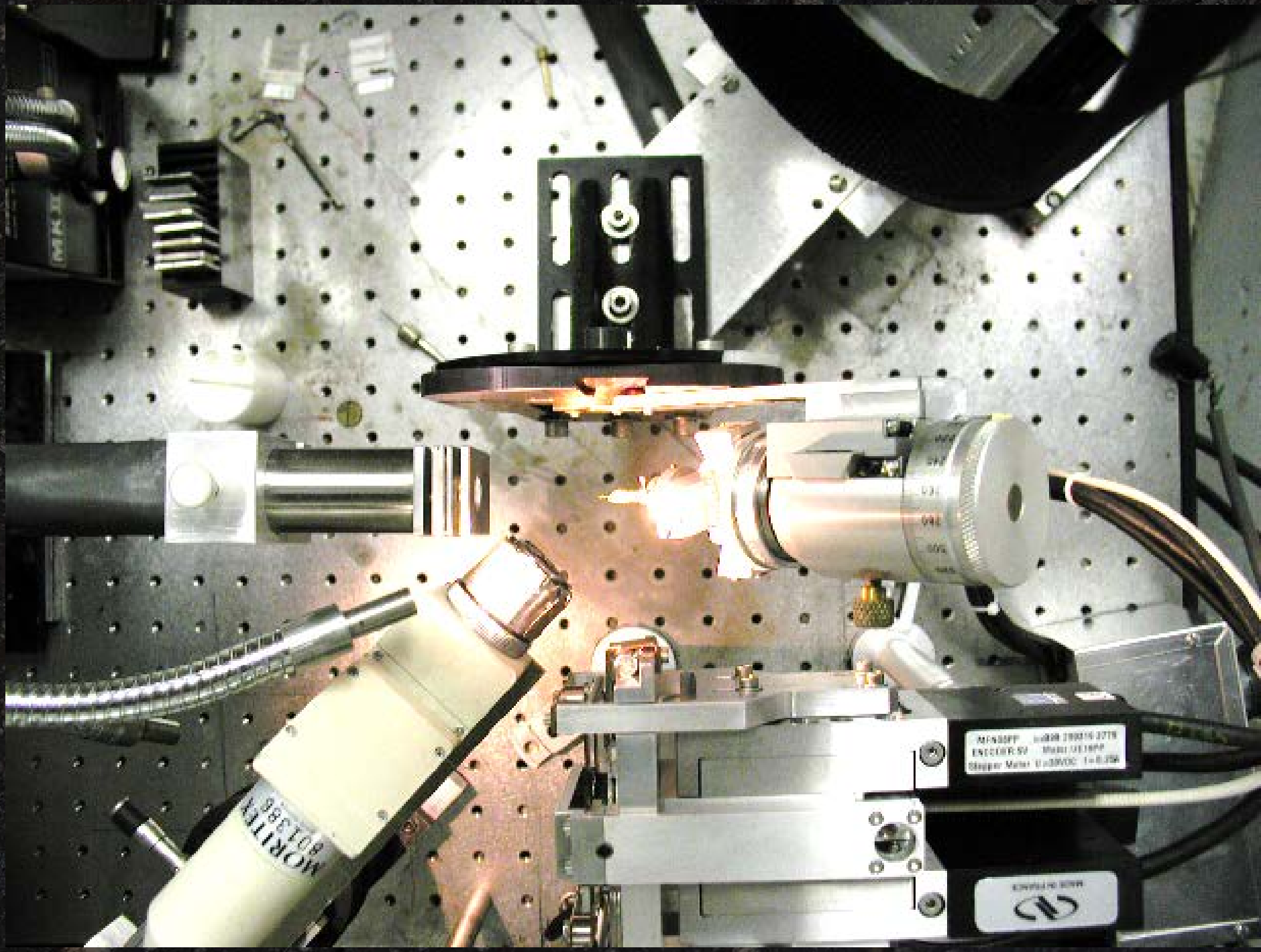
Glass Standards for Valence States

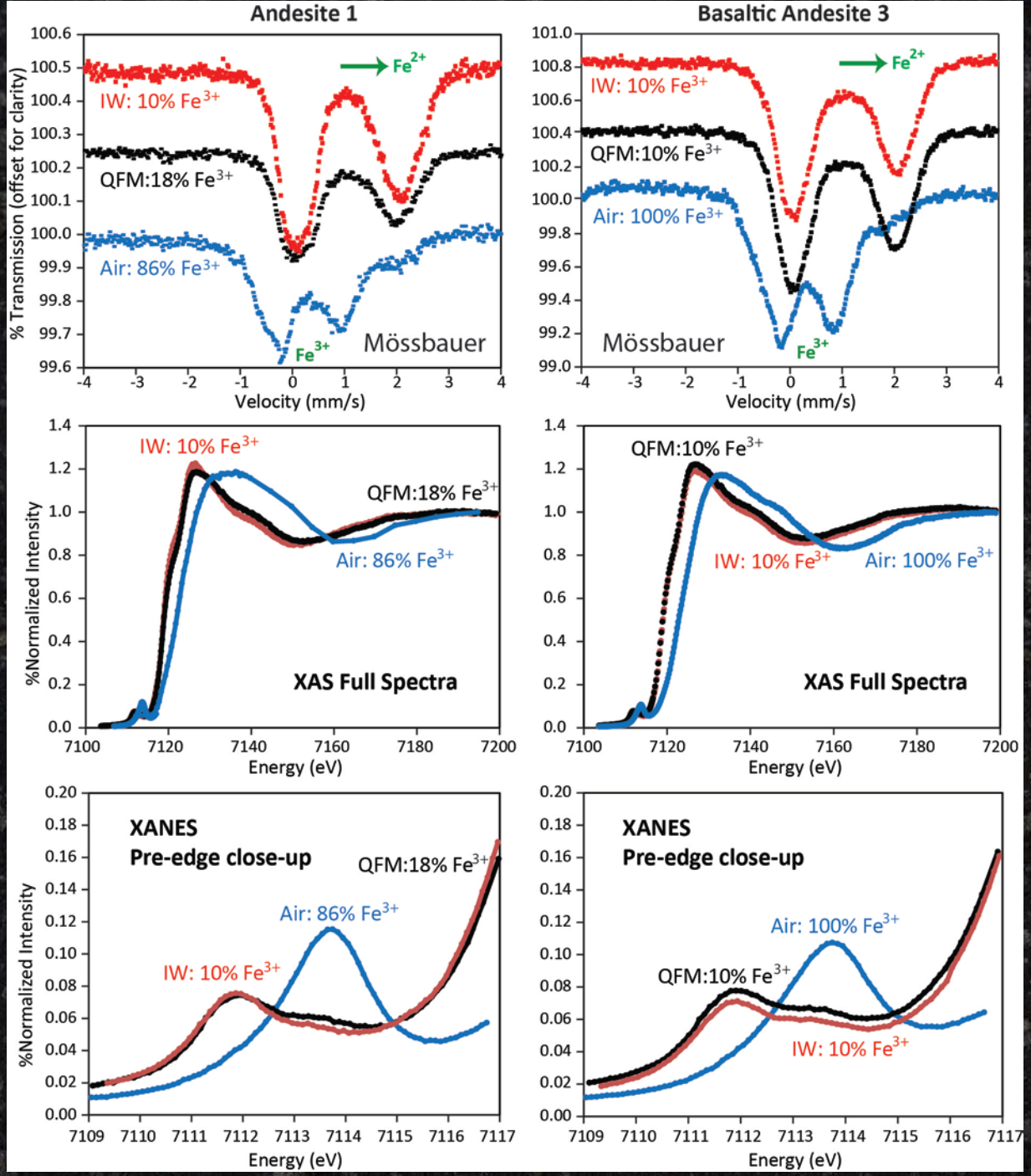


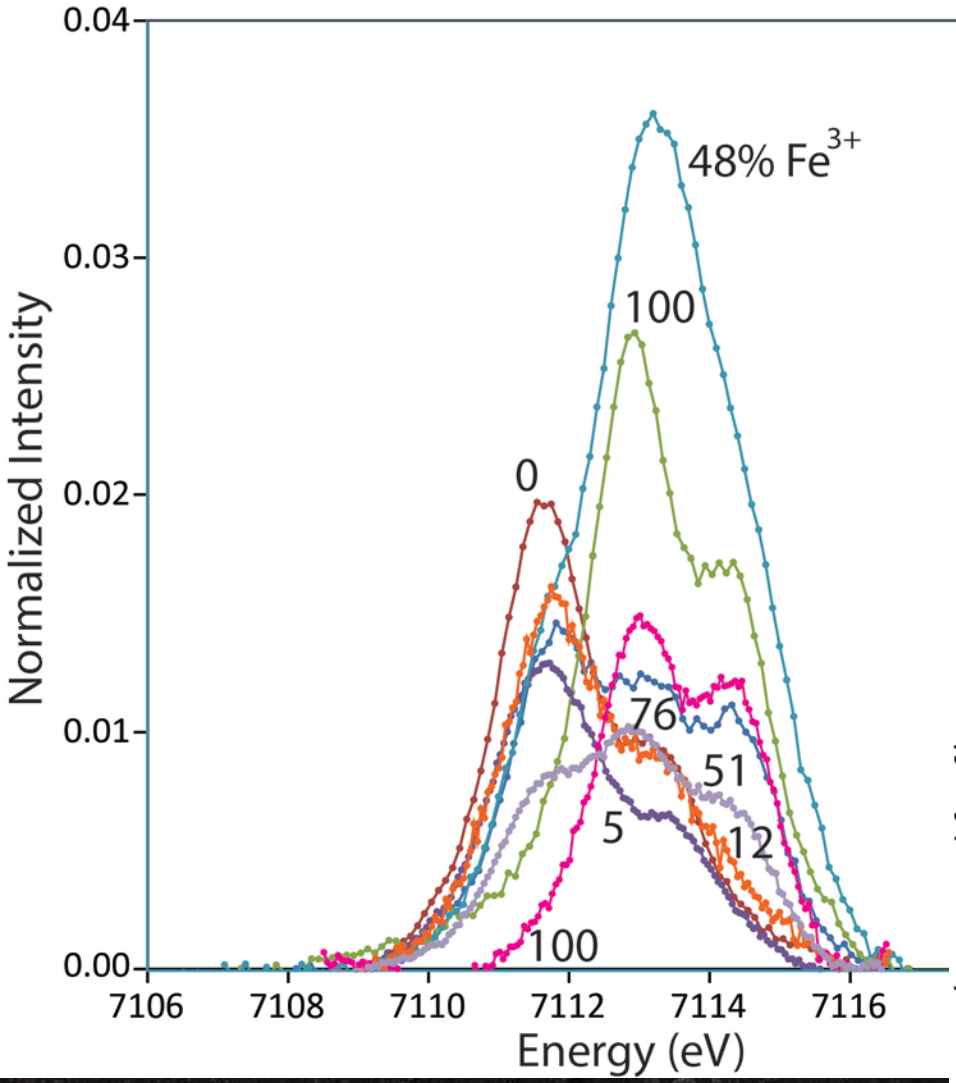
Each composition at 4 different fO_2s

Compositions chosen from natural whole rock data

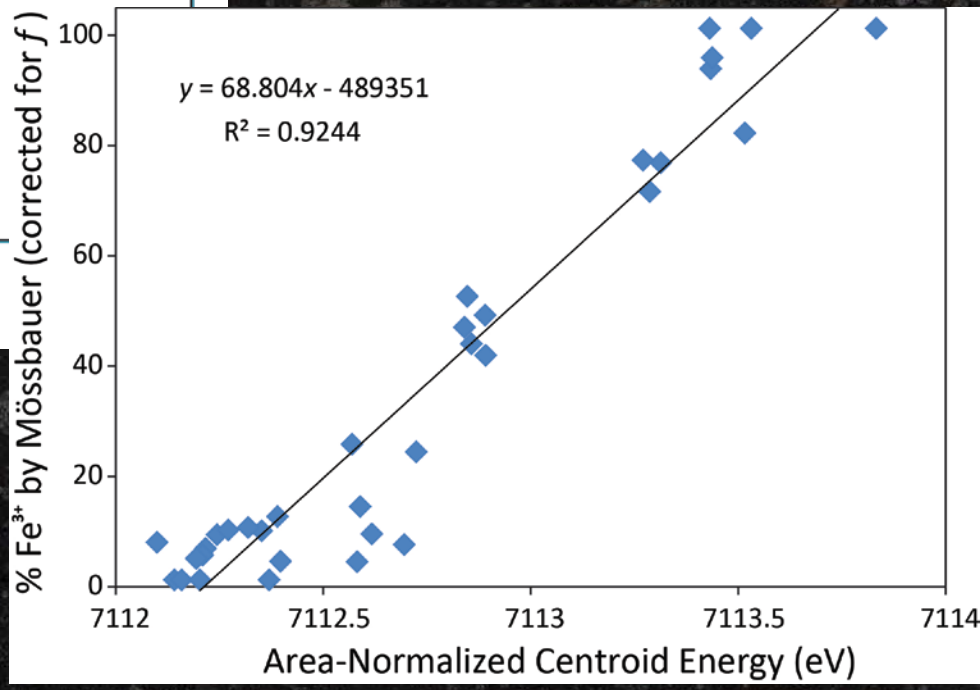

% Transmission (offset for clarity)
100.6
100.5
100.4
100.3
100.2
100.1
100.0
99.9
99.8
99.7
99.6
-4
-3
-2
-1
0
1
2
3
4
Velocity (mm/s)
IW: 10% Fe3+
QFM:18% Fe3+
Air: 86% Fe3+
Fe2+
Fe3+
Andesite 1


MIRROR
ROTOR

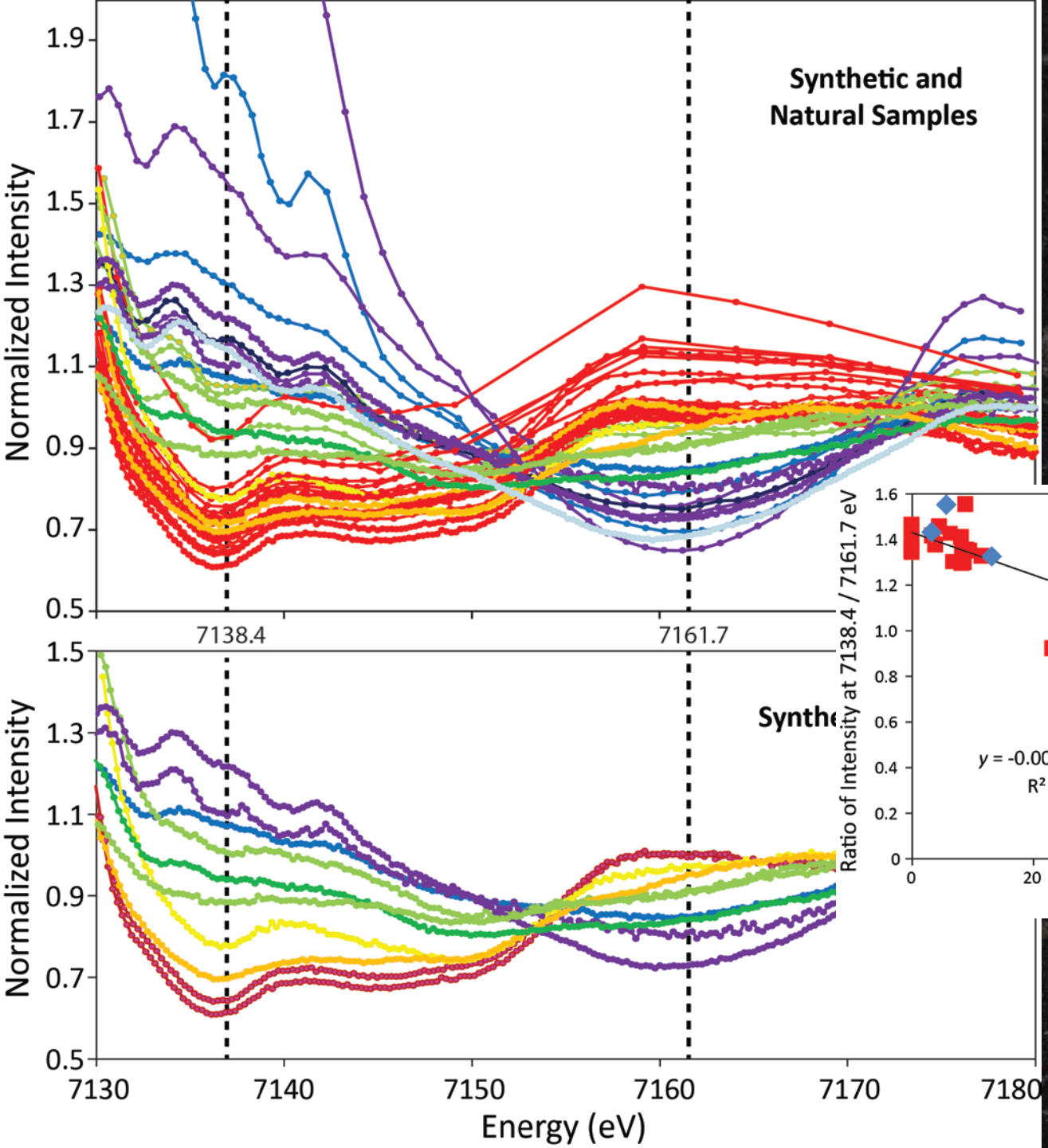

Andesite 1
Basaltic Andesite 3
% Transmission (offset for clarity)
IW: 10% Fe3+
QFM:18% Fe3+
Air: 86% Fe3+
Fe2+
Fe3+
Mössbauer
QFM:10% Fe3+
Air: 100% Fe3+
Velocity (mm/s)
%Normalized Intensity
XAS Full Spectra
Energy (eV)
XANES
Pre-edge close-up

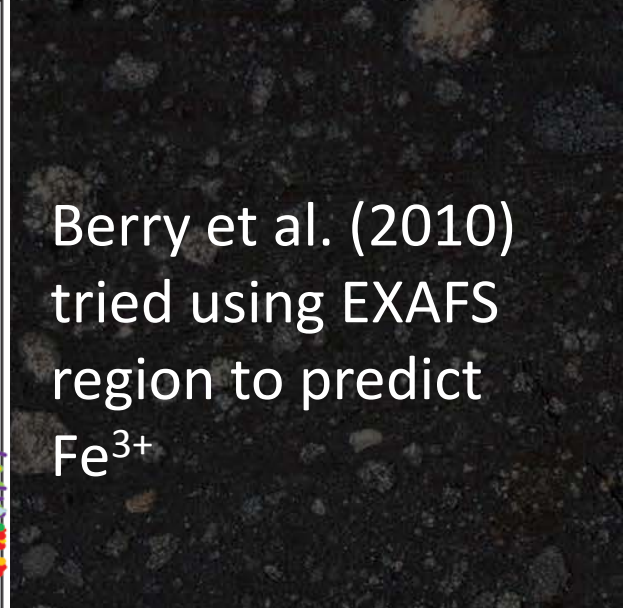


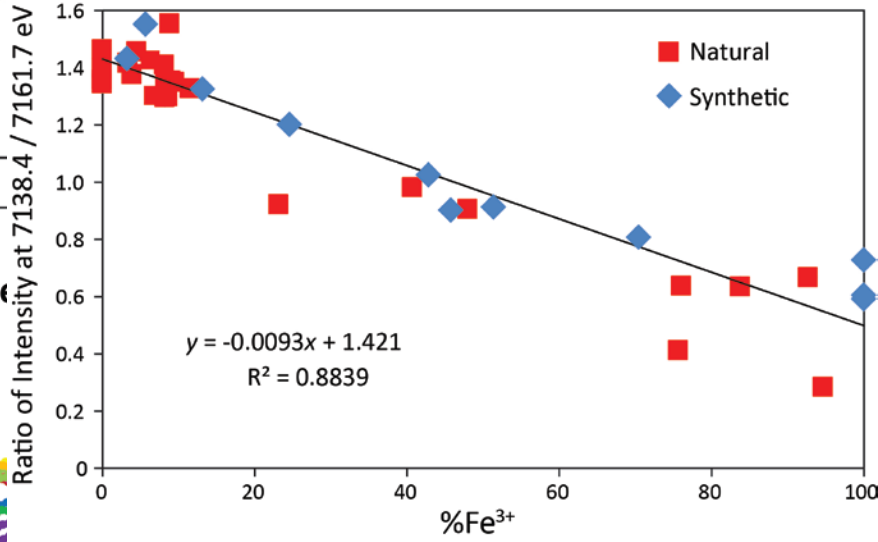
Garnet data from Dyar et al. (2012)



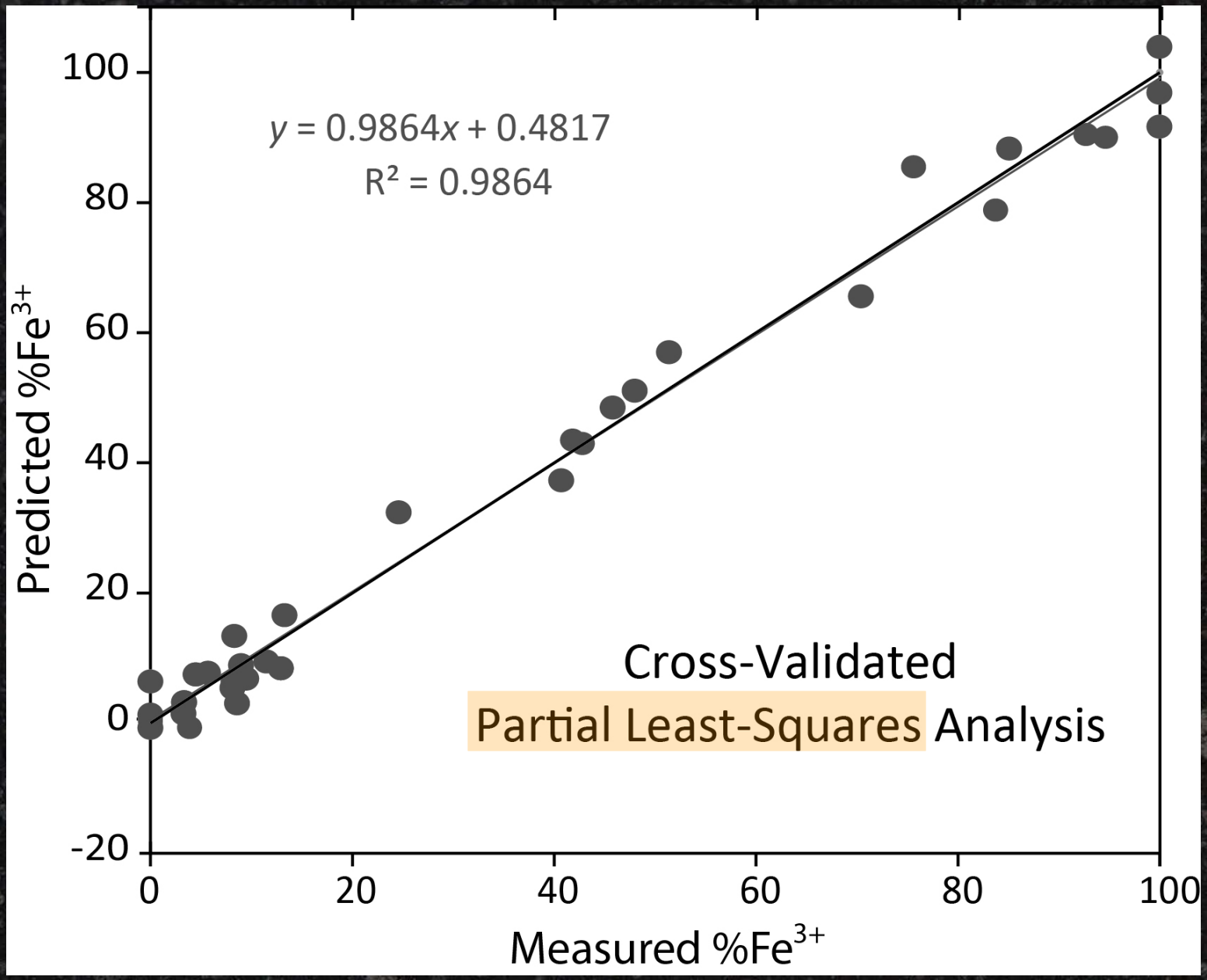
Pre-edge energy is *not* a great predictor of redox state, even in isotropic materials

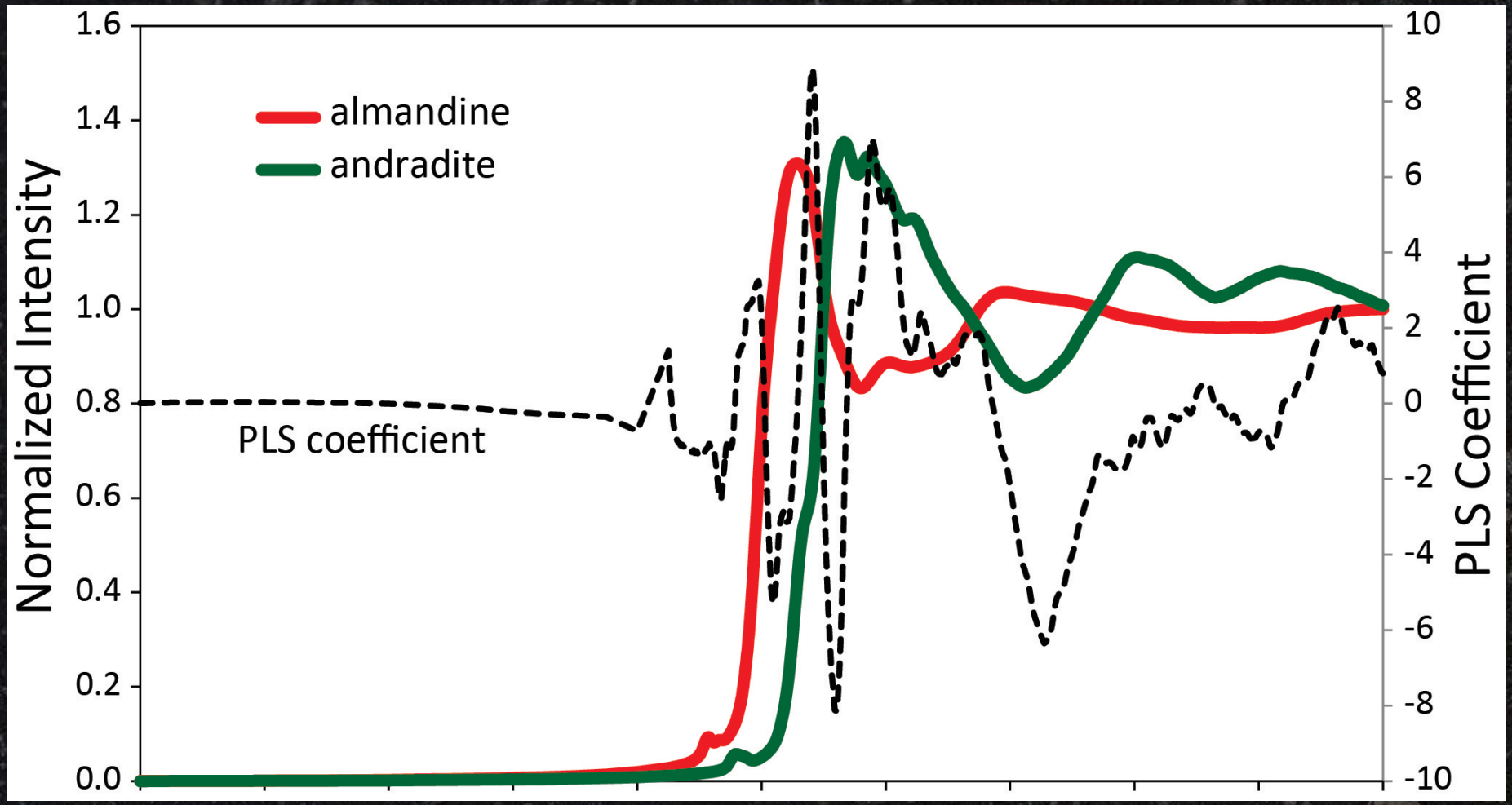

Synthetic and
Natural Samples
Normalized Intensity
1.9
1.7
1.5
1.3
1.1
0.9
0.7
0.5
7138.4
7161.7
Synthe
Normalized Intensity
1.5
1.3
1.1
0.9
0.7
0.5
7130
7140
7150
7160
7170
7180
Energy (eV)


Berry et al. (2010)
tried using EXAFS
region to predict
Fe3+


Ratio of Intensity at 7138.4 / 7161.7 eV
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
Natural
Synthetic
y = -0.0093x + 1.421
R² = 0.8839
0
20
40
60
80
100
%Fe3+

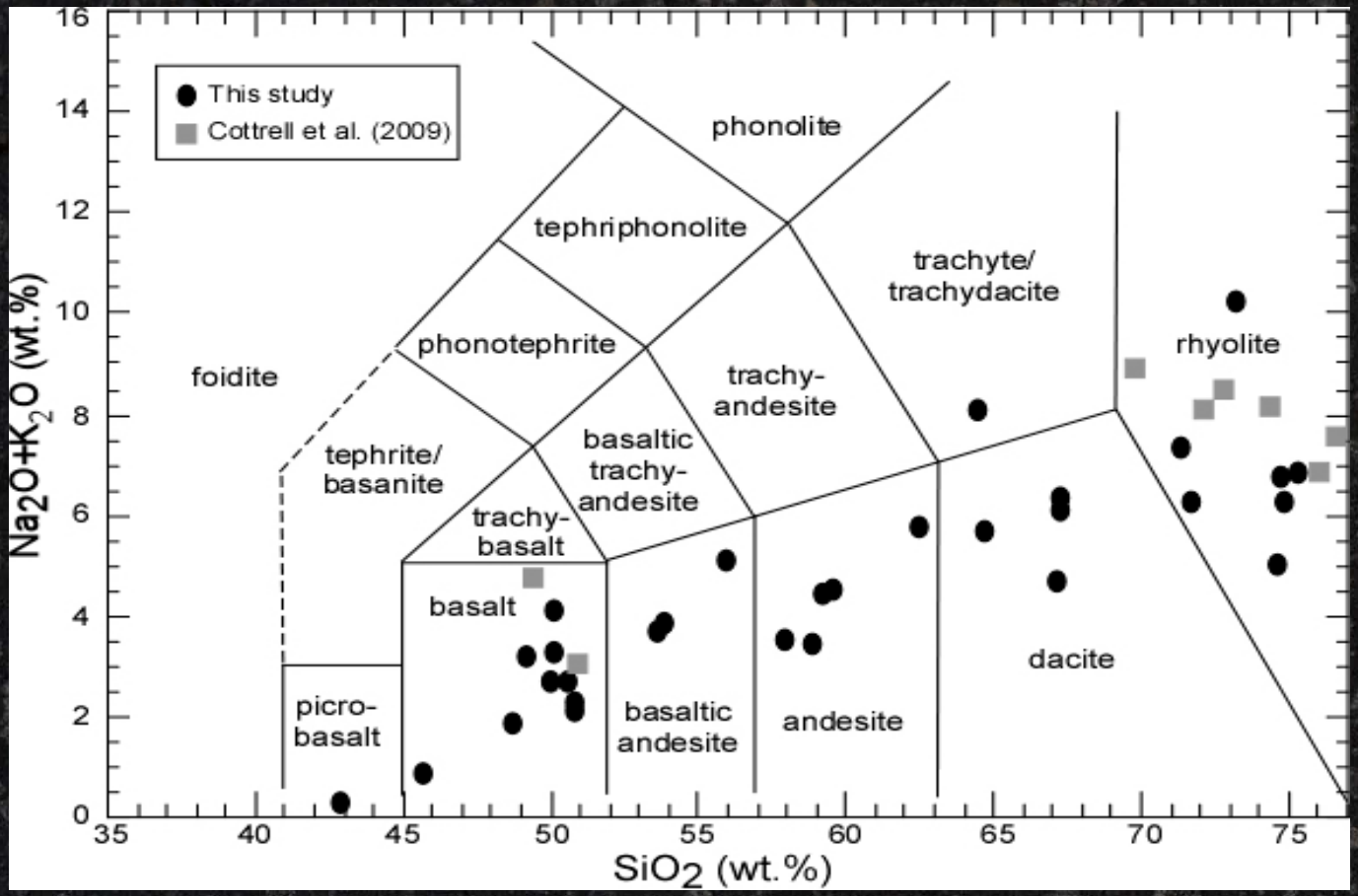
Multivariate analysis to the rescue



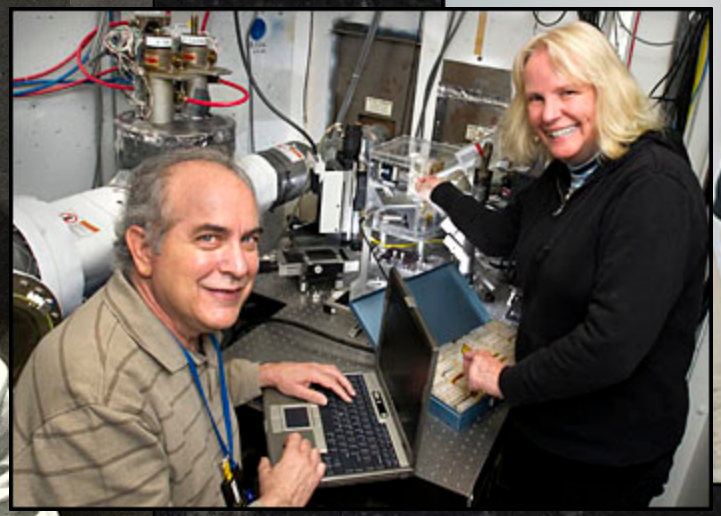


Multivariate methods (1) use all channels in the spectrum, (2) give information about channels with largest coefficients, and (3) allow for interactions of species/features

Glass Standards for Valence States



By 2016, we expect our software package to be available and in use at synchrotrons around the world



- Technique development has an important role to play in enabling solar system exploration.
- Capability of analyzing redox states in planetary materials is critical for understanding solar system evolution
- Calibration for silicate glasses to be in place worldwide by 2016
- Broader impact on materials science and geoscience communities interested in valence state measurements