

# KECK GEOLOGY CONSORTIUM

## 21ST KECK RESEARCH SYMPOSIUM IN GEOLOGY SHORT CONTRIBUTIONS

April 2008

Dr Andrew P. de Wet, Editor  
Keck Director  
Franklin & Marshall College

Keck Geology Consortium  
Franklin & Marshall College  
PO Box 3003, Lancaster Pa, 17603

Dr Amy Rhodes,  
Symposium Organizer  
Smith College

### Keck Geology Consortium Member Institutions:

Amherst College Beloit College Carleton College Colgate University The College of Wooster The Colorado College  
Franklin and Marshall College Macalester College Mt. Holyoke College Oberlin College Pomona College Smith College Trinity University  
Union College Washington and Lee University Wesleyan University Whitman College Williams College

---

## 2007-2008 PROJECTS:

### Tectonic and Climatic Forcing of the Swiss Alps

John Garver (Union College), Mark Brandon (Yale University), Alison Anders (University of Illinois),  
Jeff Rahl (Washington and Lee University), Devin McPhillips (Yale University)  
Students: William Barnhart, Kat Compton, Rosalba Queirolo, Lindsay Rathnow,  
Scott Reynhout, Libby Ritz, Jessica Stanley, Michael Werner, Elizabeth Wong

### Geologic Controls on Viticulture in the Walla Walla Valley, Washington

Kevin Pogue (Whitman College) and Chris Oze (Bryn Mawr College)  
Students: Ruth Indrick, Karl Lang, Season Martin, Anna Mazzariello, John Nowinski, Anna Weber

### The Árnes central volcano, Northwestern Iceland

Brennan Jordan (University of South Dakota), Bob Wiebe (Franklin & Marshall College), Paul Olin (Washington State U.)  
Students: Michael Bernstein, Elizabeth Drewes, Kamilla Fella, Daniel Hadley, Caitlyn Perlman, Lynne Stewart

### Origin of big garnets in amphibolites during high-grade metamorphism, Adirondacks, NY

Kurt Hollocher (Union College)  
Students: Denny Alden, Erica Emerson, Kathryn Stack

### Carbonate Depositional Systems of St. Croix, US Virgin Islands

Dennis Hubbard and Karla Parsons-Hubbard (Oberlin College), Karl Wirth (Macalester College)  
Students: Monica Arienzo, Ashley Burkett, Alexander Burpee, Sarah Chamlee, Timmons Erickson  
Andrew Estep, Dana Fisco, Matthew Klinman, Caitlin Tems, Selina Tirtajana

### Sedimentary Environments and Paleoecology of Proterozoic and Cambrian "Avalonian" Strata in the United States

Mark McMenamin (Mount Holyoke College) and Jack Beuthin (U of Pittsburgh, Johnstown)  
Students: Evan Anderson, Anna Lavarreda, Ken O'Donnell, Walter Persons, Jessica Williams

### Development and Analysis of Millennial-Scale Tree Ring Records from Glacier Bay National Park and Preserve, Alaska (Glacier Bay)

Greg Wiles (The College of Wooster)  
Students: Erica Erlanger, Alex Trutko, Adam Plourde

### The Biogeochemistry and Environmental History of Bioluminescent Bays, Vieques, Puerto Rico

Tim Ku (Wesleyan University) Suzanne O'Connell (Wesleyan University), Anna Martini (Amherst College)  
Students: Erin Algeo, Jennifer Bourdeau, Justin Clark, Margaret Selzer, Ulyanna Sorokopoud, Sarah Tracy

---

Funding provided by:

Keck Geology Consortium Member Institutions and NSF (NSF-REU: 0648782)

**Keck Geology Consortium: Projects 2007-2008**  
**Short Contributions – Adirondacks**

**ORIGIN OF BIG GARNETS IN AMPHIBOLITES DURING HIGH-GRADE  
METAMORPHISM, ADIRONDACKS, NY: p129-134**

Project faculty:

KURT HOLLOCHER: Union College

**DETERMINATION OF THE DURATION OF RETROGRADE METAMORPHISM AT  
GORE MOUNTAIN AND RUBY MOUNTAIN, NY: p135-139**

ALDEN DENNY: Western Washington University

Research Advisor: David Hirsch

**ANALYSIS OF IRON OXIDATION IN GARNETS: p 140-144**

ERICA EMERSON: Mount Holyoke College

Research Advisor: Darby Dyar

**COMPARISON OF THE WARRENSBURG AND GORE MOUNTAIN BIG-GARNET  
AMPHIBOLITES, ADIRONDACK MOUNTAINS, NY: p145-150**

KATHRYN M. STACK: Williams College

Research Advisor: Reinhard A. Wobus

**Funding provided by: Keck Geology Consortium Member Institutions and NSF (NSF-REU: 0648782)**

Keck Geology Consortium  
Franklin & Marshall College  
PO Box 3003, Lancaster Pa, 17603  
Keckgeology.org

# ANALYSIS OF IRON OXIDATION IN GARNETS

---

ERICA EMERSON: Mount Holyoke College

Research Advisor: Darby Dyar

## INTRODUCTION

The oxidation state of iron indicates the amount of oxygen present when a mineral is formed. If the environment was abundant in oxygen, many of the minerals in the assemblage will contain oxidized iron,  $\text{Fe}^{3+}$ . If the environment is reducing, there is likely to be more  $\text{Fe}^{2+}$ . The amount of oxygen influences how elements interact in a magma, as well as which minerals form; this is known as oxygen fugacity ( $f_{\text{O}_2}$ ). The fundamental  $f_{\text{O}_2}$  directly describes the potential for multivalent cations to occur in one of its valence states and is therefore a direct measurement of the oxidation state. Due to their differences in both size and charge,  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ , can occupy different sites in a mineral structure. This feature makes iron one of the most common multivalent rock-forming cations.

Given that oxidation state is important, it is then important to have ways of measuring the oxidation state. In the late 1960s, Mössbauer spectroscopy was first used to determine  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ . Mössbauer, however, is a bulk technique that requires a large, homogenous sample. Thus, it would be desirable to have a method capable of measuring samples at microanalytical scale, such as XANES spectroscopy. For this study, the results of a suite of 20 garnet samples with varying amounts of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  were compared using Mössbauer spectroscopy and XANES. Many of the samples are from the former Barton Mine on Gore Mountain, New York, but due to the lack of significant  $\text{Fe}^{3+}$ , a wider range of samples was added from the collections at Mount Holyoke College.

## METHODS

### Mössbauer Spectroscopy

Each sample was handpicked under a compound light microscope to be as inclusion-free as possible. Sample amounts varied between 20-40 mg, and an occasional 100 mg sample, depending on the availability of the sample and iron content. The Mössbauer requires a minimum of ~20 mg per sample of garnet for the most accurate and visible results. Lower sample quantities may result in the gamma rays not encountering any Fe atoms, resulting in noisy data that may not produce quantitative results.

Spectra were acquired at 300K and one sample at a temperature series, consisting of 17 different temperatures from 4-295K, under low He gas pressure. A source of 100-70 mCi  $^{57}\text{Co}$  in Rh was used on a WEB Research Co. model W100 spectrometer equipped with a Janus closed-cycle He refrigerator. The time each sample ran ranged from 8-12 hours and the results were calibrated against  $\alpha$ -Fe foil. The typical count rates were between 500,000 and 900,000 non-resonant counts/hour.

The garnets were first run through Mexfieldd, a set of programs created by Eddy De Grave and Toon van Alboom (Gent, Belgium). Mexfieldd uses Lorentzian line shapes to fit doublets, and then calculates quadrupole splitting, isomer shift and peak widths in each doublet or set of doublets. The best fits are then determined by the minimizing chi-squared ( $\chi^2$ ) value. Some fits were also done using an analogous program, Disd3e\_dd, that uses velocity approximations to obtain values for isomer shift and quadrupole splitting, searching for a distribution of quadrupole splitting values rather than a single

value as in Mexdisdd (Sklute, 2006). The output values produced by each of the programs can then be used to provide information about the areas of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  doublets in the Mössbauer spectra.

## XANES

XANES is a microanalytical technique capable of analyzing  $8 \times 10 \mu\text{m}$  spots on single crystals. To allow for a selection of possible grains to analyze, multiple grains were handpicked for XANES analysis and mounted in a 1" round plexiglass holder that was then polished to expose the grains. All of the samples were analyzed using the Mössbauer spectrometer at Mount Holyoke College and x-ray ring at beamline x26a, National Synchrotron Light Source, Brookhaven National Laboratory. Due to time constraints, only two different crystals of each sample were analyzed by XANES. No attention was paid to crystallographic orientation of the grains because garnet is isometric.

The XANES spectra were collected over an energy range from -50 to 50 eV; the former to include energies below and including the pre-edge peak and the latter to include the main-edge peak spectra of the samples. Spectra on a standard magnetite sample were acquired every fifth sample in order to correct the monochromator energy for unknown samples run in between, because magnetite has a well-resolved pre-edge singlet with a known energy of 7113.25 eV. Each energy interval was counted between 5-20 seconds, depending upon the intensity of the main-edge energy, for a total acquisition time of approximately 25 minutes. After acquisition, the pre-edge peaks of each sample were determined and  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  contents calculated.

## XANES Fitting Procedures

Once spectra were collected, the data were processed using the in-house program X26A\_Data\_Plotter, where the entire spectrum was displayed for fitting. The program was used to select out the pre-edge region of interest, then fit a spline curve to the baseline beneath each pre-edge peak, so that the baseline could then be subtracted out. The output

was evaluated with the PAN: Peak Analysis program (another in-house software package). Prior to fitting, the PAN files were opened in excel and corrected to true energy (on the x axis) using the magnetite calibration data.

PAN allows a user to check to confirm that the pre-edge peak to be fit has a relatively flat baseline (from the X26A\_Data\_Plotter program). Gaussian peaks were then used to fit the pre-edge data. The number of peaks that constitute each pre-edge is unknown because theory is lacking, so the number of peaks to be fit to each pre-edge was determined by trial and error. In the end, two distinct peaks associated with  $\text{Fe}^{2+}$  and two with  $\text{Fe}^{3+}$  were identified. Each spectrum was modeled with all four of these peaks (assuming a mixture of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ ) and then the number of peaks was decreased in cases where the peak areas were zero.

## RESULTS AND DISCUSSION

### Mössbauer

Samples containing only  $\text{Fe}^{2+}$  or only  $\text{Fe}^{3+}$  were fit with one doublet. Samples with mixed  $\text{Fe}^{2+}/\text{Fe}^{3+}$  contents, such as grossular garnets and samples with impurities, were fit with a range of 2-6 separate doublets (Fig. 1).

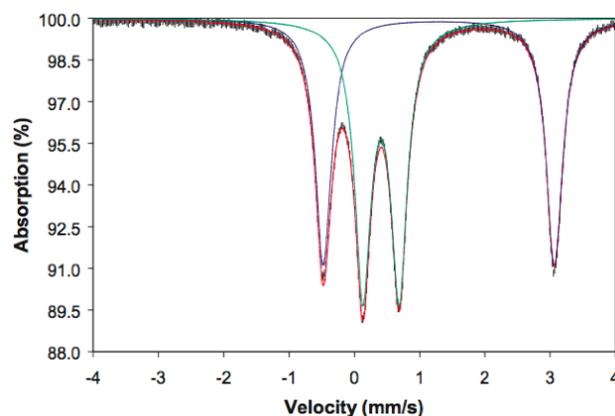


Figure 1: Example of fit Mössbauer spectra, garnet standard mix sample containing a combination of the Fort Wrangell almandine and Val Malenko andradite to model a garnet with both  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ .

The garnet standard mix is a combination of the Fort Wrangell almandine and Val Malenco andradite to model a garnet with both Fe<sup>2+</sup> and Fe<sup>3+</sup>. Spectra of this sample were acquired over a broad temperature range to allow calculation of the recoil-free fractions,  $f$ , using the change in isomer shift as a function of temperature. These values were calculated for both doublets of the garnet standard mix. The purpose of this calculation is to correct for the area ratios in a mixed mineral spectrum to provide the true percentages of Fe<sup>2+</sup> and Fe<sup>3+</sup> in a sample (Sklute, 2006) using the following equation:

$$N^{Fe^{3+}} = \frac{100 \times A^{Fe^{3+}}}{A^{Fe^{3+}} + \left( C \times \left( 100 - A^{Fe^{3+}} \right) \right)}$$

where  $C = \frac{f^{3+}}{f^{2+}}$ ,  $A$  is the doublet area of

Fe<sup>2+</sup> or Fe<sup>3+</sup>, and  $N$  is the corrected amount of each species present (Dyar et al., 2007). The corrected areas of Fe<sup>3+</sup> and Fe<sup>2+</sup> are presented in Table 1. This recoil-free fraction correction is important because it results in changes of up to 8.2% in the Fe<sup>3+</sup> concentration. Doublet areas that are corrected for  $f$  thus permit a more accurate determination of Fe<sup>3+</sup>/Fe<sup>2+</sup> ratios.

## XANES

The first samples fit were the almandine and andradite samples. These samples were fit first so that I would know where to look for the position of Fe<sup>2+</sup> and Fe<sup>3+</sup> peaks in the other samples. The almandine was fit at 7111.67 and 7113.43 eV. The andradite was fit at 7112.84 and 7114.34 eV (Fig. 2). The other samples were fit and expected to be combinations of the peaks found in almandine and andradite, which provided to be true.

The areas of the Fe<sup>3+</sup> peaks in all samples in the XANES data were then plotted against the  $f$ -corrected areas of the Fe<sup>3+</sup> doublets from the Mossbauer

Table 1: Mössbauer peak areas corrected using  $f$  values and the recoil-free fraction equation  
True Amount of Fe<sup>2+</sup> and Fe<sup>3+</sup> for Mössbauer

Sample	Sample Locality	Mössbauer % Area Fe <sup>2+</sup>	Mössbauer % Area Fe <sup>3+</sup>	Mössbauer C	Mössbauer True % Area Fe <sup>2+</sup>	Mössbauer True % Area Fe <sup>3+</sup>
alm	Fort Wrangell, AK	0	100	1.39	0.0	100.0
ak972a	Gore Mountain, NY, Pit#1	0	100	1.39	0.0	100.0
ak978a	Adirondacks, NY Keck Garnets AK97-8a	0	100	1.39	0.0	100.0
ak9729	Keck Garnets Treadway Mountain Formation, NY	0	100	1.39	0.0	100.0
hel	Keck Garnets Gore Mountain, NY	3	97	1.39	2.2	97.8
129	Jagersfontein Mine, South Africa	3.9	96.1	1.39	2.8	97.2
1251	Jagersfontein Mine, South Africa	11.1	88.8	1.39	8.2	91.8
Garnet Standard Mix	Fort Wrangell almandine and Valmalenco andradite	52.2	47.8	1.39	44.0	56.0
9b	Keck Garnets Willsboro, NY	53.9	46.1	1.39	45.7	54.3
ak9723	Keck Garnets Adirondacks, NY	6.7	93.3	1.39	4.9	95.1
2b	Keck Garnets Gore Mountain, NY, Pit#2	6.1	93	1.39	4.5	95.5
10c	Keck Garnets Woolen Mill, NY	18.3	81.7	1.39	13.9	86.1
g17	Unknown Provenance	50.7	49.3	1.39	42.5	57.5
g89	Phippsburg, ME	47.7	52.3	1.39	39.6	60.4
bbkg	Kenya, Africa	94.3	5.8	1.39	92.2	7.8
5183g	BPM 27, Anne Hofmeister	89.5	10.5	1.39	86.0	14.0
a32w	Keck Garnets Willsboro, NY	81.5	18.5	1.39	76.0	24.0
ahun	Unknown Provenance	94	6	1.39	91.9	8.1
hrm1	Keck Garnets Willsboro, NY	96.1	3.9	1.39	94.7	5.3
and	Valmalenco, Italy	100	0	1.39	100.0	0.0

spectra. It was pretty much a 1:1 line, but there were two outliers (Fig. 3). One of them was the Kenya melanite and the other was Kb-12-9. There are three possible explanations for these outliers, 1) something wrong with the spectra (i.e. a glitch in the monochromator, or somewhere in the electronics), 2) impurity of ilmenite. Samples AK-97-2b, AK-97-23 and AK-97-10c contain ilmenite, a titanium oxide impurity. The parameters for a mixed sample of Fe<sup>2+</sup> and Fe<sup>3+</sup> along with parameters for the addition of the ilmenite were used when fitting the Mössbauer data and were therefore detected early on. However, the XANES analyses of these crystals must have managed to miss seeing any of the ilmenite, and 3) zoning. Further research at BNL (such as a traverse across the grain) would be needed to conclude if this sample was in fact zoned, impure or

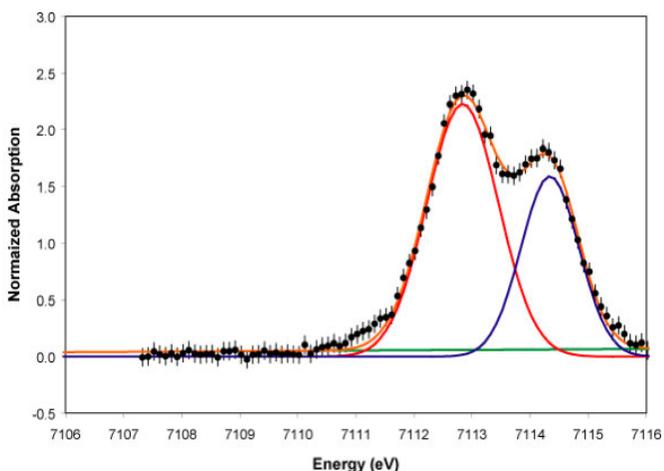
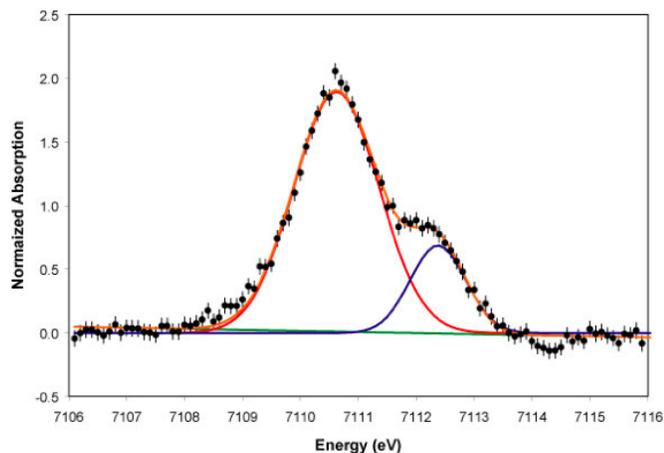


Figure 2: Example of XANES Spectra a) Fort Wrangell almandine, spectra alm.017, b) Valmalenco andradite, spectra and3.009

if the spectrum was flawed prior to being fit. SEM X-ray analyses are in progress to determine if major element composition is zoned in any way.

### CONCLUSIONS

The goal of this study was to measure the oxidation states of garnets using the Mössbauer and XANES techniques. Table 2 displays the percentages of Fe<sup>3+</sup> and Fe<sup>2+</sup> according to Mössbauer and XANES, revealing that both techniques agree well within ± 8%, with the exception of samples Kb-12-9 and the Kenyan melanite. This conclusion suggests that XANES studies of anisotropic minerals might be successful if, as in the case for this study, the optical orientation of the crystals is the same as the optical orientation of the standards.

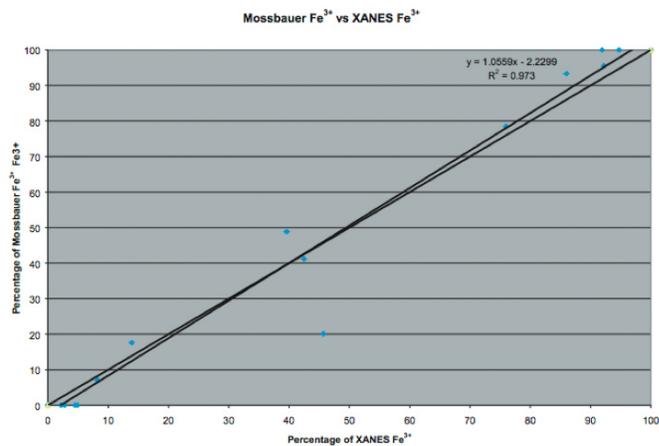


Figure 3: Percentages of Fe<sup>3+</sup> in Mössbauer and XANES

In conclusion, the Mössbauer spectroscopy and XANES results complement each other. Mössbauer and XANES data measure approximately the same percentage of Fe<sup>3+</sup> content. These two techniques are useful for determining the iron oxidation state of minerals. The combination of Mössbauer spectroscopy and XANES provides a promising outlook for microanalytical techniques in the near future.

True Amount of Fe <sup>3+</sup> and Fe <sup>2+</sup> for Mössbauer and XANES				
Samples	Mössbauer True % Area Fe <sup>3+</sup>	Mössbauer True % Area Fe <sup>2+</sup>	% Area XANES Fe <sup>3+</sup> peaks	% Area XANES Fe <sup>2+</sup> peaks
alm	0.0	100.0	0	100
ak972a	0.0	100.0	0	100
ak978a	0.0	100.0	0	100
ak9729	0.0	100.0	0	100
he1	2.2	97.8	0	100
ak9723	4.9	95.1	0	100
2b	4.5	95.5	0	100
10c	13.9	86.1	17.6	82.4
129	2.8	97.2	11	89
1251	8.2	91.8	7.1	92.9
9b	45.7	54.3	10.45	89.55
g17	42.5	57.5	41.2	58.8
g89	39.6	60.4	48.85	51.15
bbkg	92.2	7.8	95.5	4.5
5183g	86.0	14.0	93.3	6.7
a32w	76.0	24.0	78.5	21.5
ahun	91.9	8.1	100	0
hrm1	94.7	5.3	100	0
and	100.0	0.0	100	0

Table 2: Percentage of Fe<sup>3+</sup> and Fe<sup>2+</sup> for Mössbauer and XANES. The percentages of Fe<sup>3+</sup> and Fe<sup>2+</sup> were calculated for each XANES spectrum and then averaged together for the table above to be compared against the Mössbauer Fe<sup>3+</sup> and Fe<sup>2+</sup> peaks.

## REFERENCES

- Bajt, S., Sutton, S.R., Delaney, J.S., 1994, X-ray microprobe analysis of iron oxidation states in silicates and oxides using X-ray absorption near edge structure (XANES): *Geochimica et Cosmochimica Acta*. 58:23, 5209-5214.
- Bianconi, A., 1980, "Surface X-ray Absorption Spectroscopy: Surface EXAFS and Surface XANES" *Appl. Surf. Sci.* Vol. 6 pag. 392-418
- Blackwell, M., 2000, Temperature Dependence of Grunerite Mössbauer. Undergraduate Thesis, Mount Holyoke College.
- Brown, Jr., G.E.; Calas, G.; Waychunas, G.A.; Petiau, J. X-ray absorption spectroscopy and its applications in mineralogy and geochemistry. *Chp.* 11, 432-512
- Calas, G., Brown, Jr., G.E., Waychunas, G.A., Petiau, J., 1987, X-ray Absorption Spectroscopic Studies of Silicate Glasses and Minerals: *Physics and Chemistry of Minerals*, 15:19-29.
- Delaney, J.S.; Dyar, M.D.; Sutton, S.R.; Bajt, S., 1998, Redox ratios with relevant resolution: Solving an old problem by using the synchrotron microXANES probe: *Geology*. 26;2, 139-142.
- Dyar, M.D.; Gunter, M.E., Delaney, J.S., Lanzarotti, A., Sutton, S.R., 2002, Systematics in the structure and XANES spectra of pyroxenes, amphiboles, and micas as derived from oriented single crystals: *The Canadian Mineralogist*, 40, 1375-1393.
- Dyar, M.D., Klima, R., Lindsley, D., Pieters, C.M., 2007, Effects of differential recoil-free fraction on ordering and site occupancies in Mössbauer spectroscopy of orthopyroxenes: *American Mineralogist*, v. 92, p. 424-428.
- Lustig, H., 1961, The Mössbauer Effect: *American*