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 Fellah, Daniel Hadley, Caitlyn Perlman, Lynne Stewart

**Origin of big garnets in amphibolites during high-grade metamorphism, Adirondacks, NY**
Kurt Hollocher (Union College)
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**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 Paleoeconomy 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

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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, Fe$^{3+}$. If the environment is reducing, there is likely to be more 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 ($f_{O_2}$). The fundamental $f_{O_2}$ 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, Fe$^{2+}$ and 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 Fe$^{2+}$ and 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 Fe$^{2+}$ and 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 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 57Co 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 α-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 Fe$^{2+}$ and Fe$^{3+}$ doublets in the Mössbauer spectra.

**XANES**

XANES is a microanalytical technique capable of analyzing 8x10 μm 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 Fe$^{3+}$ and 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 Fe$^{2+}$ and two with Fe$^{3+}$ were identified. Each spectrum was modeled with all four of these peaks (assuming a mixture of Fe$^{2+}$ and 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 Fe$^{2+}$ or only Fe$^{3+}$ were fit with one doublet. Samples with mixed Fe$^{2+}$/ Fe$^{3+}$ contents, such as grossular garnets and samples with impurities, were fit with a range of 2-6 separate doublets (Fig. 1).
The garnet standard mix is a combination of the Fort Wrangell almandine and Val Malenko andradite to model a garnet with both Fe\(^{2+}\) and Fe\(^{3+}\). 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\(^{2+}\) and Fe\(^{3+}\) in a sample (Sklute, 2006) using the following equation:

\[
N^{Fe^{3+}} = \frac{100 \times A^{Fe^{3+}}}{A^{Fe^{3+}} + (C \times (100 - A^{Fe^{3+}}))}
\]

where \(C = \frac{f^{3+}}{f^{2+}}\), \(A\) is the doublet area of Fe\(^{2+}\) or Fe\(^{3+}\), and \(N\) is the corrected amount of each species present (Dyar et al., 2007). The corrected areas of Fe\(^{3+}\) and Fe\(^{2+}\) 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\(^{3+}\) concentration. Doublet areas that are corrected for \(f\) thus permit a more accurate determination of Fe\(^{3+}/Fe^{2+}\) 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\(^{3+}\) and Fe\(^{2+}\) 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\(^{3+}\) peaks in all samples in the XANES data were then plotted against the \(f\)-corrected areas of the Fe\(^{3+}\) doublets from the Mössbauer 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\(^{2+}\) and Fe\(^{3+}\) 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...
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$^{3+}$ and Fe$^{2+}$ 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 this study, the optical orientation of the crystals is the same as the optical orientation of the standards.

In conclusion, the Mössbauer spectroscopy and XANES results complement each other. Mössbauer and XANES data measure approximately the same percentage of Fe$^{3+}$ 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.

Table 2: Percentage of Fe$x^{3+}$ and Fe$x^{2+}$ for Mössbauer and XANES. The percentages of Fe$x^{3+}$ and Fe$x^{2+}$ were calculated for each XANES spectrum and then averaged together for the table above to be compared against the Mössbauer Fe$x^{3+}$ and Fe$x^{2+}$ peaks.
REFERENCES


