

Interrelationships Between Molar Volume and Composition in Garnet

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INTRODUCTION

The chemical composition of garnet in metamorphic rocks provides an invaluable tool to petrologists studying various conditions of metamorphism. The garnet mineral structure is a vast storehouse of many different elements, all of which have an effect on its properties. All of the major components in garnet can be easily measured, except for Fe³⁺ and Fe²⁺; only total iron can be determined by traditional microanalytical methods. Only with difficulty and/or time-consuming bulk analytical methods can Fe³⁺ be measured. As a result, the relationships between Fe³⁺ and unit cell volumes in garnet are poorly understood. The purpose of this study is to investigate the relationships between unit cell volumes of garnets and Fe³⁺ concentration, either measured or calculated.

ANALYTICAL METHODS

The Adirondack Mountains proved to be a good source in which to sample a variety of garnets and garnetiferous rocks with varying chemical compositions and physical properties. All garnets sampled were isolated from rocks collected in Adirondack Highland localities. Garnet localities at the Gore Mountain and Willsboro Wollastonite mines provided material for eight of the samples presented here, as they yielded excellent garnet crystals. All localities are shown on Figure 1.

From a collection of 13 samples, garnet was separated from the parent rock with the aid of a dissecting microscope and isolated for analysis. The garnets were pulverized, prepared by mixing with isopropyl alcohol, and placed on a microscope slide for x-ray diffraction to determine unit cell volumes. Grain mounts of the garnets were prepared by fastening the grains to a common microscope slide with epoxy glue and polished. The garnets were analyzed for major-element compositions (Table 1) using both SEM/EDS and XANES techniques. X-ray diffraction powder patterns were obtained with a Scintag XDS 2000 x-ray diffractometer with a scan time of one °/minute (total scan time of 68 minutes). Mineralogic compositions were determined with the Amherst College scanning electron microscope equipped with an EDS spectrometer, and the synchrotron X-ray microprobe to collect XANES spectra (beamline X26A, National Synchrotron Light Source, Brookhaven National Laboratory, Upton, New York).

Data collected in this study were combined with additional data from various sources contained in Deer *et al* (1961). These data were chosen on the basis of analysis for unit cell length, FeO and Fe₂O₃, SiO₂, Al₂O₃, MgO, MnO, CaO, and no other oxides >0.1 wt. %. The resultant data set contains garnets with a wide range of compositions. Calculated cell volumes were obtained by multiplying mole percent compositions of each of the five garnet end-members (andradite, almandine, grossular, pyrope, and spessartine) by the cube of the *a* axis length, assuming ideal end-member mixing. "Misfit" was defined as the difference between the calculated and measured cell volume of each sample. Distinctions were made between the entire data set and that portion taken solely from the literature (Table 2).

PREDICTION OF UNIT CELL VOLUMES FROM MAJOR-ELEMENT COMPOSITION

Four methods of calculating unit cell volume were tested (Table 2):

1. *Using Fe³⁺ measured from wet chemistry or other techniques, including XANES.* Average Misfit of the unit cell volumes was initially calculated using *a* = 12.056 Å (Deer *et al.*, 1961) -- a common value used in molar volume calculations for the andradite component. Misfit between measured and calculated molar volume was 2.194 ± 10.797 Å³. Next, Misfit was recalculated using *a* = 12.061 Å -- the value measured for the end-member andradite standard used at Brookhaven National Lab; Misfit was reduced to 1.952 ± 10.669 Å³. Finally, the value of *a* for andradite that would correspond to zero Misfit was calculated to be 12.1012 Å, suggesting that the actual unit cell length commonly reported in literature is too low and must be adjusted.

2. *Assuming all iron present is Fe²⁺.* Average misfit between measured and calculated unit cell volumes

Table 2: SEM/EDS compositional data with Fe³⁺/ΣFe determined by SmX

AK97: Mineral	19-2 fayalite	19-7 cpx	19-28 cpx	19-29 cpx	27-22* hnbnd	27-24 opx	27-35 biotit	27-41 garnet	27-43 hnbnd	27-44 hnbnd
Wt % oxide										
SiO ₂	28.79	47.09	49.31	49.40	40.41	50.87	36.09	38.65	40.52	41.55
Al ₂ O ₃	0.03	0.57	0.89	0.80	13.30	2.12	14.18	21.49	13.49	13.55
TiO ₂	0.00	0.03	0.22	0.18	3.27	0.03	4.66	0.02	3.36	3.11
MgO	0.44	0.94	1.03	1.16	9.81	19.60	12.42	6.47	9.59	10.56
FeO	64.50	25.83	24.43	23.30	12.82	21.42	14.68	23.95	12.93	13.07
Fe ₂ O ₃	3.77	2.67	4.98	6.48	2.42	3.88	2.66	3.98	2.74	2.17
MnO	1.50	0.46	0.58	0.52	0.09	0.27	0.03	1.02	0.06	0.07
CaO	0.00	19.07	19.13	19.39	10.95	0.30	0.04	4.88	10.91	10.77
Na ₂ O	0.44	0.89	1.19	0.62	2.73	0.10	0.00	0.06	2.33	2.50
K ₂ O	0.03	0.00	0.04	0.00	1.07	0.02	9.77	0.06	1.12	1.10
BaO	0.00	0.14	0.00	0.00	0.00	0.06	0.23	0.00	0.00	0.00
Cl	0.07	0.04	0.00	0.01	0.22	0.00	0.18	0.00	0.18	0.18
total	99.58	97.74	101.80	101.85	97.09	98.67	94.94	100.56	97.23	98.62
Stoichiometry	O=4	O=6	O=6	O=6	O=23	O=6	O=22	O=12	O=23	O=23
Si	0.974	1.976	1.967	1.964	6.105	1.935	5.522	2.978	6.110	6.150
Al	0.001	0.028	0.041	0.037	2.367	0.095	2.556	1.952	2.399	2.365
Ti	0.000	0.001	0.007	0.005	0.372	0.001	0.536	0.001	0.380	0.346
Mg	0.023	0.059	0.061	0.069	2.210	1.112	2.832	0.744	2.156	2.331
Fe ²⁺	1.803	0.876	0.766	0.716	1.519	0.643	1.768	1.463	1.520	1.528
Fe ³⁺	0.095	0.081	0.141	0.179	0.258	0.105	0.288	0.219	0.289	0.228
Mn	0.042	0.017	0.020	0.018	0.012	0.009	0.004	0.066	0.008	0.008
Ca	0.000	0.858	0.818	0.825	1.773	0.012	0.007	0.402	1.762	1.708
Na	0.029	0.072	0.092	0.048	0.799	0.007	0.000	0.008	0.680	0.716
K	0.001	0.000	0.002	0.000	0.206	0.001	1.908	0.006	0.216	0.208
Ba	0.000	0.002	0.000	0.000	0.000	0.001	0.014	0.000	0.000	0.000
Cl	0.006	0.004	0.000	0.001	0.073	0.000	0.060	0.000	0.059	0.057
total	2.973	3.974	3.915	3.862	15.693	3.920	15.495	7.839	15.580	15.643
Fe ³⁺ /ΣFe	0.05	0.09	0.16	0.20	0.15	0.14	0.14	0.13	0.16	0.13

Table 3: SEM/EDS compositional data for points with no available SmX data

AK97: Mineral	19-15 albite	19-17 k-spar	19-18 hnbnd	19-19 albite	19-20 albite	19-21 k-spar	27-23 plag	27-36 plag
Wt % oxide								
SiO ₂	64.94	66.74	39.31	68.10	66.55	63.89	57.72	57.93
Al ₂ O ₃	19.25	18.34	7.99	20.42	18.72	17.57	25.83	25.42
TiO ₂	0.00	0.00	2.24	0.05	0.00	0.00	0.03	0.06
MgO	0.00	0.00	0.96	0.00	0.00	0.00	0.00	0.00
FeO	0.27	0.37	33.61	0.32	0.17	0.11	0.01	0.03
MnO	0.03	0.00	0.36	0.00	0.04	0.00	0.00	0.00
CaO	1.21	0.06	9.89	1.07	0.48	0.00	8.07	7.92
Na ₂ O	10.80	1.06	1.76	11.59	11.02	0.62	6.76	7.24
K ₂ O	0.09	15.46	1.70	0.06	0.08	14.92	0.14	0.17
BaO	0.00	0.24	0.00	0.01	0.00	0.04	0.03	0.04
Cl	0.00	0.00	0.51	0.00	0.03	0.00	0.00	0.00
total	96.61	102.26	98.31	101.62	97.10	97.14	98.59	98.79
Stoichiometry	O=8	O=8	O=23	O=8	O=8	O=8	O=8	O=8
Si	2.956	3.014	6.507	2.948	3.006	3.028	2.620	2.631
Al	1.033	0.976	1.558	1.042	0.997	0.981	1.382	1.361
Ti	0.000	0.000	0.278	0.002	0.000	0.000	0.001	0.002
Mg	0.000	0.000	0.237	0.000	0.000	0.000	0.000	0.000
Fe	0.010	0.014	4.652	0.011	0.007	0.004	0.000	0.001
Mn	0.001	0.000	0.050	0.000	0.002	0.000	0.000	0.000
Ca	0.059	0.003	1.753	0.049	0.023	0.000	0.392	0.385
Na	0.953	0.092	0.566	0.973	0.966	0.057	0.595	0.638
K	0.005	0.890	0.358	0.003	0.005	0.902	0.008	0.010
Ba	0.000	0.004	0.000	0.000	0.000	0.001	0.001	0.001
Cl	0.000	0.000	0.186	0.000	0.003	0.000	0.000	0.000
total	5.017	4.993	16.145	5.028	5.009	4.973	4.999	5.029

* Percent Fe³⁺ for hornblende AK9727-22 was estimated from average of percent Fe³⁺ in AK9727-43 and AK9727-44

was calculated to be $18.889 \pm 39.365 \text{ \AA}^3$. This extraordinarily high misfit illustrates the necessity of considering the role of Fe^{3+} in any analysis. Clearly it must not be ignored.

3. *Calculating Fe^{3+} assuming all Fe^{3+} substitutes for Al in the octahedral site of the garnet structure (i.e. the $\text{Fe}^{3+}=2.0\text{-Al}$ method).* Average Misfit of the unit cell volumes was calculated to be $2.600 \pm 11.302 \text{ \AA}^3$ and $2.363 \pm 11.192 \text{ \AA}^3$, using $a=12.056$ and $a=12.061$ respectively. In order to make the average Misfit equal to zero, the unit cell length had to be increased to 12.1107 \AA .

4. *Calculations using the method of Droop (1987) method assuming the sum of all the cations equals 8.0.* Average misfit of the unit cell volumes was $-1.858 \pm 11.182 \text{ \AA}^3$ and $-2.196 \pm 11.039 \text{ \AA}^3$, again using $a=12.056 \text{ \AA}$ and $a=12.061 \text{ \AA}$, respectively. In order to make the average Misfit equal to zero, the a unit cell edge length of andradite had to be decreased to 12.0285 \AA .

INTERPRETATION

The magnitude of the Misfit value in each of the calculations just described reflects the accuracy of the predictions of unit cell volumes by the various methods. The high Misfit produced when ignoring Fe^{3+} is indicative of the importance of measuring or calculating Fe^{3+} in order to obtain an accurate analysis. Similar values of Misfit are obtained by calculating or measuring Fe^{3+} . The relatively small Misfit between calculated and measured unit cell volume in these instances suggests that molar volume of garnet can be accurately predicted without even measuring Fe^{3+} (Table 2).

PREDICTION OF Fe^{3+} CONCENTRATION FROM MEASURED UNIT CELL VOLUME

Can this reasoning be turned around to allow determination of the concentration of Fe^{3+} based only on measured unit cell volume of a sample with an unknown composition? Several plots were produced in an attempt to answer this question (Figures 2 and 3). Trends were relatively difficult to identify, which leads to the conclusion that Fe^{3+} cannot be routinely calculated based solely on measured unit cell volumes.

However, the presence of Fe^{3+} can be *confirmed* if the unit cell volume of garnet is greater than that of grossular end-member garnet. This occurs because andradite, or Fe^{3+} garnet, has the highest unit cell volume of any of the garnet end-members, and therefore any garnet sample with molar volume between that of grossular and andradite reflects changing Fe^{3+} content only. This is assuming, of course, that the sample contains no trivalent atoms other than Al^{3+} in large quantities. This relationship can be roughly described by the equation $y=mx+b$.

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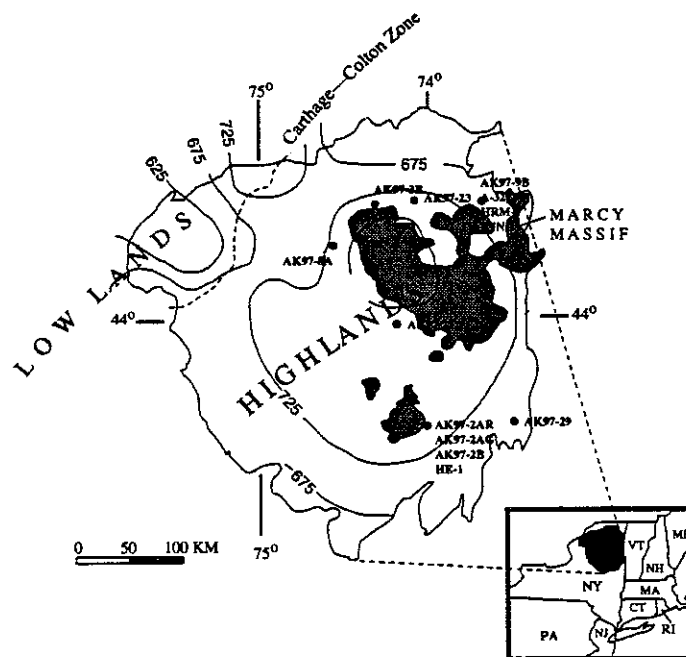


Figure 1. Approximate localities of Adirondack Highland garnets.

Table 1. Garnet compositional data.

	AK97-2AG	AK97-2AR	AK97-2B	AK97-3B	AK97-8A	AK97-9B	AK97-23
SiO ₂	39.62	40.16	39.55	38.29	39.46	38.85	38.26
Al ₂ O ₃	21.83	22.34	22.24	20.88	21.44	18.46	20.84
TiO ₂	0.00	0.00	0.00	0.00	0.00	0.46	0.00
FeO	9.71	19.26	12.11	26.44	24.05	2.71	24.26
Fe ₂ O ₃	11.32	0.66	10.15	1.71	1.71	7.37	2.67
MgO	10.67	10.96	10.16	4.38	10.23	0.57	5.19
MnO	0.38	0.32	0.29	1.00	0.75	0.66	1.06
CaO	6.62	6.76	6.60	7.72	1.85	30.96	6.76
Total	100.15	100.46	101.10	100.42	99.49	100.04	99.04
Fe ³⁺ /ΣFe*	0.51	0.03	0.43	0.06	0.06	0.71	0.09
Fe ³⁺ /ΣFe†	0.42	0.00	0.28	0.00	0.00	0.76	0.00
Cations per twelve oxygen formula unit							
Si	2.935	3.002	2.921	3.000	3.021	2.883	3.010
Al	1.906	1.968	1.936	1.928	1.935	1.614	1.933
Ti	0.000	0.000	0.000	0.000	0.000	0.026	0.000
Fe ²⁺	0.602	1.204	0.748	1.732	1.540	0.579	1.596
Fe ³⁺	0.626	0.037	0.564	0.101	0.098	0.411	0.158
Mg	1.179	1.222	1.118	0.511	1.168	0.063	0.608
Mn	0.024	0.020	0.018	0.066	0.049	0.041	0.071
Ca	0.526	0.541	0.523	0.648	0.151	2.461	0.569
	AK97-27	AK97-29	A-32-W	HE-1	HRM-1	RJN-1	
SiO ₂	38.64	37.46	39.83	38.93	38.29	39.18	
Al ₂ O ₃	21.51	21.14	18.65	21.00	9.15	14.13	
TiO ₂	0.00	0.00	0.30	0.22	0.56	0.66	
FeO	24.66	33.46	1.05	19.61	5.91	1.31	
Fe ₂ O ₃	2.06	0.00	5.71	2.16	12.19	10.70	
MgO	7.23	4.55	0.33	10.26	0.00	0.35	
MnO	0.84	1.16	0.24	0.50	0.00	0.05	
CaO	4.70	1.94	35.02	5.01	34.50	35.04	
Total	99.64	99.71	101.13	97.69	100.60	101.42	
Fe ³⁺ /ΣFe*	0.07	0.00	0.83	0.09	0.65	0.88	
Fe ³⁺ /ΣFe†	0.00	0.00	0.97	0.00	0.66	1.00	
Cations per twelve oxygen formula unit							
Si	2.996	2.994	3.014	3.009	3.078	3.021	
Al	1.965	1.991	1.663	1.913	0.867	1.284	
Ti	0.000	0.000	0.017	0.013	0.034	0.038	
Fe ²⁺	1.599	2.236	0.067	1.268	0.397	0.085	
Fe ³⁺	0.120	0.000	0.635	0.125	0.737	0.621	
Mg	0.836	0.543	0.037	1.183	0.000	0.040	
Mn	0.055	0.079	0.015	0.033	0.000	0.004	
Ca	0.391	0.166	2.838	0.415	2.971	2.895	

* by NMNH calibration (Bajt, et al., 1996). † by Dyar (1984).

Table 2. Misfit Between Calculated and Measured Unit Cell Volume

Method	a (Å)	Entire Data Set		Literature Data Set Only	
		Average	Standard Deviation	Average	Standard Deviation
using measured Fe ³⁺	12.0560	2.194	10.797	4.190	8.255
NMNH Calibration*	12.0610	1.952	10.669	3.937	8.080
	12.1012	0.000	10.564		
	12.1382			0.000	10.215
	12.0560	2.168	10.943	4.190	8.255
Garnet Calibration†	12.0610	1.927	10.829	3.937	8.080
	12.1007	0.000	10.822		
	12.1382			0.000	10.215
	n.a.	18.889	39.365	21.858	41.774
assuming no Fe ³⁺	n.a.	18.889	39.365	21.858	41.774
assuming Fe ³⁺ = 2-Al	12.0560	2.600	11.302	5.077	9.790
	12.0610	2.363	11.192	4.833	9.604
	12.1107	0.000	11.442		
	12.1593			0.000	12.275
assuming Σcations=8	12.0560	-1.858	11.182	0.364	9.395
Droop (1987) method	12.0610	-2.196	11.039	0.019	9.184
	12.0285	0.000	12.319		
	12.0613			0.000	9.173

*NMNH calibration used fayalite-magnetite-hematite method of Bajt *et al.* (1994). †Garnet calibration used 100% Fe²⁺ almandine and 100% Fe³⁺ andradite standards from Dyar (1984).

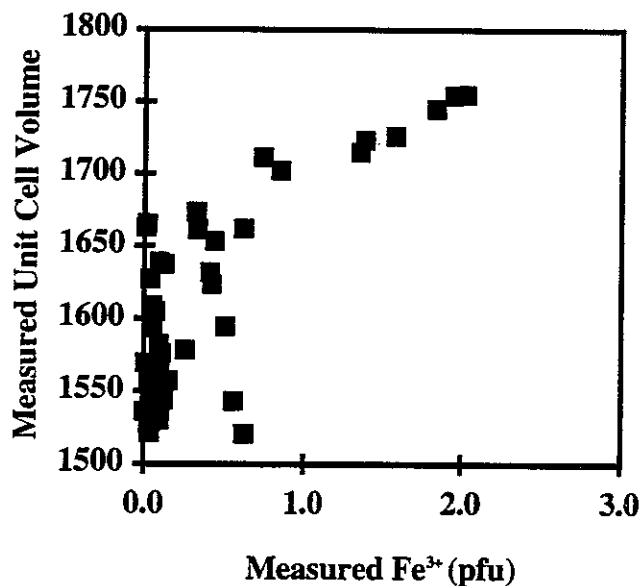


Figure 2. This plot illustrates that if only x-ray diffraction data were available, measured Fe³⁺ can be predicted only if the measured volume exceeds the unit cell volume for grossular end-member garnet. This relationship is roughly linear and can be described by the equation $y=mx+b$.

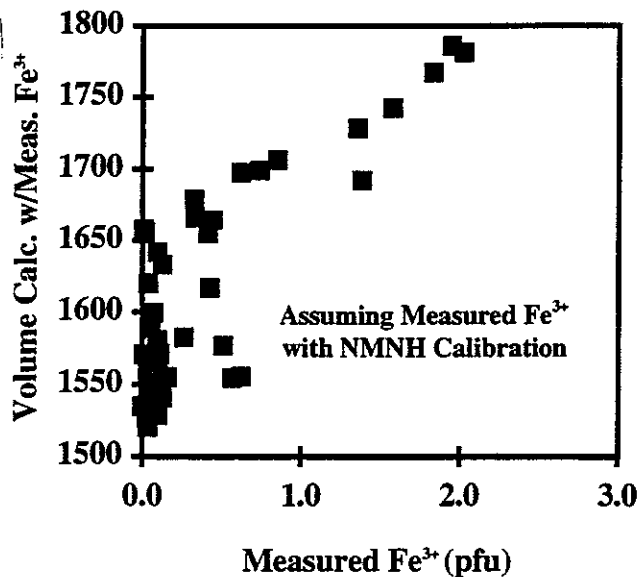


Figure 3. An alternate way of approximating Fe³⁺ content is shown here. This plot illustrates that if only SEM data were available, Fe³⁺ content can be predicted only if the calculated volume exceeds that of grossular. This relationship is roughly linear and can be described by the equation $y=mx+b$.

Fe³⁺ Partitioning and Geothermometry Among Mafic Silicates in the Carthage-Colton Mylonite Zone, Adirondack Mountains, New York

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INTRODUCTION

Ferric iron (Fe³⁺) partitioning and geothermometry calculations can reveal useful information about metamorphic conditions such as temperature and pressure. The objective of this project is to measure and understand the distribution of Fe³⁺ among coexisting minerals and the conditions that control it in a ductile shear zone environment. The Diana Complex of the Carthage-Colton Mylonite Zone (CCMZ) in the Adirondack Mountains in northern New York is the particular shear zone analyzed. Samples were taken from inside and outside of a shear zone. We determined Fe³⁺ partitioning among hornblende, clinopyroxene, and biotite. Variations in mineral deformation and Fe³⁺ partitioning were expected because of the temperature difference between the relatively cool shear zone and the area outside.

GEOLOGIC SETTING

The regional geologic history of the Adirondack Mountains can be divided into three major events: the Elzevirian Orogeny (ca. 1350-1200 Ma), the Ottawan Orogeny (ca. 1100-1000 Ma), and a period of renewed metamorphism (ca. 1000 Ma). The Elzevirian Orogeny is characterized by global-scale accretion and is also evidenced in the southwest U.S., Ireland, and Baltica. Global-scale continental collision occurred during the Ottawan Orogeny (McLelland *et al.* 1996). While both the Adirondack Lowlands and Highlands experienced peak metamorphism during the Ottawan Orogeny, granulite facies metamorphism was restricted to the Highlands as the Lowlands cooled, ca. 1000 Ma (van der Pluijm *et al.* 1994).

The Grenville Orogen is located primarily in southeastern Canada and extends south into northern New York State. The southern part of the orogen is divided into the Gneiss belt, the Metasedimentary belt, and the Granulite belt on the basis of lithologic, metamorphic, structural, and geophysical contrasts. The Metasedimentary belt, which makes up the Adirondack Lowlands, is dominated by marbles, metasedimentary rocks, and metavolcanic rocks of greenschist to granulite facies. The Granulite belt, which makes up the Adirondack Highlands, is characterized by meta-igneous rocks of upper amphibolite to granulite facies. These two belts are separated by the CCMZ, an area of normal faulting (van der Pluijm *et al.*, 1994).

MATERIALS AND METHODS

Samples were taken from an outcrop exposing the Diana Complex within the CCMZ (44°08.568' N, 75°19.991' W). One sample (AK97-15B) was taken from within a shear zone, and the second sample (AK97-15A) came from approximately 15 meters west of the shear zone (Figure 1). The outcrop was dominated by diopside, potassium feldspar, plagioclase, quartz, and hornblende. We looked closely for samples that contained biotite in addition to these other minerals, in order to characterize the distribution of Fe³⁺ among as many coexisting minerals as possible. The examination of thin sections enabled us to document deformation in individual mineral grains using a petrologic microscope. Analyses of mineral composition were conducted using a Scanning Electron Microscope with Energy Dispersive Spectrometer (SEM/EDS) at Amherst College, MA. With the aid of Dr. Jeremy Delaney, an intense X-ray beam was used to measure Fe³⁺/ΣFe ratios at Brookhaven National Lab's National Synchrotron Light Source (BNL NSLS) in Long Island, NY, using synchrotron micro-XANES (X-ray absorption near-edge structure) spectroscopy (SmX). Temperatures were calculated using hornblende-plagioclase (Holland & Bundy, 1990) and two feldspar (Haselton *et al.*, 1983) thermometers.