Fe^{3+} Partitioning and Geothermometry Among Mafic Silicates in the Carthage-Colton Mylonite Zone, Adirondack Mountains, New York

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INTRODUCTION

Ferric iron (Fe^{3+}) 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 Fe^{3+} 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 Fe^{3+} partitioning among hornblende, clinopyroxene, and biotite. Variations in mineral deformation and Fe^{3+} 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 Fe^{3+} 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 $Fe^{3+}/\Sigma Fe$ 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.

Table 2. Misfit Between Calculated and Measured Unit Cell Volume

		Entire Data Set		Literature Data Set Only	
Method	a (Å)	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
Garnet Calibration†	12.0560	2.168	10.943	4.190	8.255
	12.0610	1.927	10.829	3.937	8.080
	12.1007	0.000	10.822		
	12.1382			0.000	10.215
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 $\sum$cations=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% Fe^{2+} almandine and 100% Fe^{3+} andradite standards from Dyar (1984).

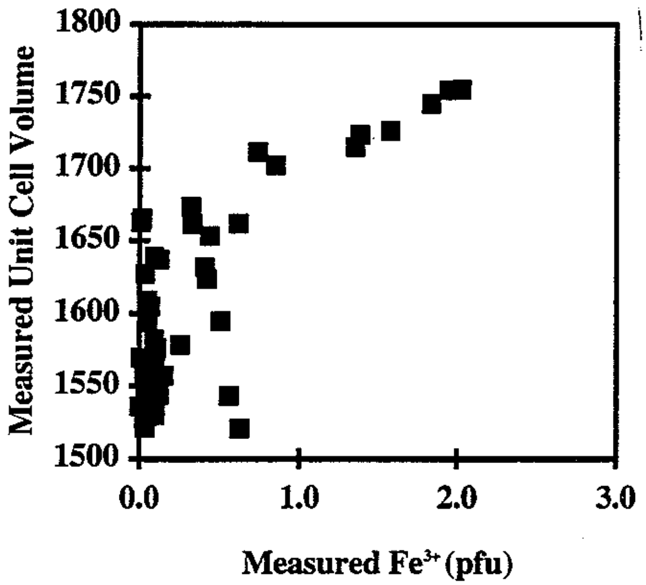

Figure 2. This plot illustrates that if only x-ray diffraction data were available, measured Fe^{3+} can be predicted only if the measured volume exceeds the unit cell volume for grossular end-member garnet. This relationship is roughly linear and can be described by the equation *y=mx+b*.

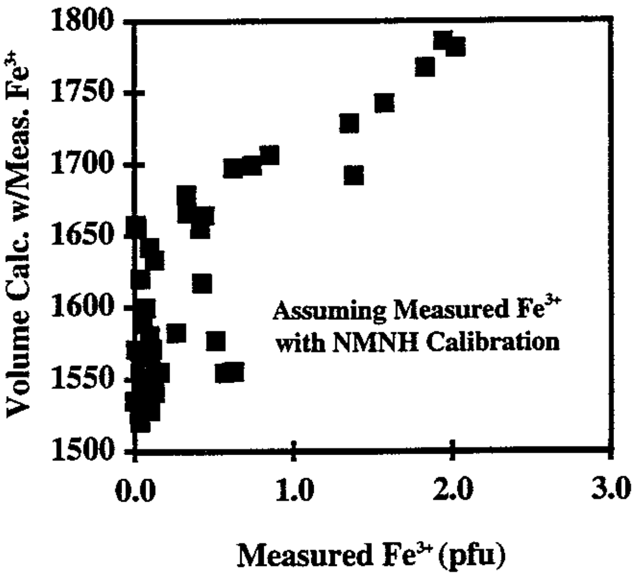

Figure 3. An alternate way of approximating Fe^{3+} content is shown here. This plot illustrates that if only SEM data were available, Fe^{3+} content can be predicted only if the calculated volume exceeds that of grossular. This relationship is roughly linear and can be described by the equation *y=mx+b*.

RESULTS AND DISCUSSION

Table 1 shows the weight percent oxide and stoichiometry of each of our analyzed points. The weight percent oxide sum is calculated by the SEM/EDS with the assumption that all Fe is Fe^{2+}. As expected, these sums are consistently lower than the weight percent oxide sum calculated with the correction factor of Fe^{3+}, obtained by the micro-XANES analyses.

The temperature range for metamorphism was determined to be 650°-750°C. This is in agreement with a prior study of the Adirondack region (Bohlen *et al.* 1985). Metamorphic pressure was assumed to be in the range of approximately 5-7 kbar. The hornblende-plagioclase thermometer yielded temperatures very tightly clustered at approximately 700°C outside of the shear zone. The two feldspar thermometer gave a broader range of approximately 500-750°C. The temperatures within the shear zone, as calculated by the two feldspar thermometer, are slightly lower, ranging from 400-700°C. In the shear zone sample, unexolved potassium feldspar yielded higher temperatures, and lower temperatures were calculated from exolved perthite.

With the values obtained from the XANES procedure, the distribution of Fe^{3+} among hornblende, clinopyroxene, and biotite was compared (Table 2). Clinopyroxene and hornblende were more oxidized outside of the shear zone than within it. This is consistent with observations of Lamb (1993) based upon coexisting illmenite and magnetite. Outside of the shear zone there was a consistent partitioning of Fe^{3+} between clinopyroxene, hornblende, and biotite, with clinopyroxene > hornblende > biotite.

In the shear zone, and thus at lower temperatures, there is more Fe^{3+} partitioning than in the area outside of the shear zone. This is in conjunction with the tendency for partitioning of elements to decrease with increasing temperature, in which minerals are "less selective."

Chemical zoning within two grains of clinopyroxene and two grains of hornblende was also calculated by the micro-XANES analyses. There was no significant Fe^{3+} zonation on three of these grains. However, one honrnblende grain from outside of the shear zone was highly Fe^{3+} zoned. The core of the hornblende grain had less Fe^{3+} than the rim.

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Table 1. Compositions

AK97#	15b-1	15b-2	15b-3	15b-4	15a-1	15a-2
Mineral	Hb center	Hb edge	Cpx center	Cpx subgrain	Hb edge	Hb center
SiO_2	50.59	50.34	51.60	53.49	45.06	44.49
Al_2O_3	1.32	1.16	1.10	0.74	8.20	8.37
TiO_2	0.14	0.17	0.32	0.10	0.92	1.09
MgO	6.39	6.39	9.73	9.95	11.49	11.39
FeO SEM/EDS	18.31	18.23	14.42	13.30	16.84	17.32
FeO	12.82	12.58	8.22	8.38	8.76	12.30
Fe_2O_3	6.11	6.28	6.89	5.47	8.98	5.58
MnO	0.38	0.31	0.90	0.86	0.61	0.64
CaO	21.11	21.32	20.76	21.14	11.13	10.88
Na_2O	1.16	0.56	1.35	1.21	2.13	2.77
K_2O	0.00	0.02	0.00	0.00	1.52	1.65
BaO	0.00	0.00	0.10	0.00	0.00	0.00
Cl	0.01	0.00	0.00	0.00	0.33	0.28
Sum SEM/EDS	99.41	98.50	100.28	100.79	98.23	98.88
Sum w/Fe^{3+}	100.02	99.13	100.97	101.34	99.13	99.44
$Fe^{3+}/\Sigma Fe$	0.30	0.31	0.43	0.37	0.48	0.29
Stoichiometry	23	23	6	6	23	23
Si	7.578	7.598	1.910	1.961	6.733	6.665
Al	0.232	0.207	0.048	0.032	1.443	1.477
Ti	0.016	0.019	0.009	0.003	0.103	0.123
Mg	1.426	1.436	0.537	0.543	2.559	2.544
Fe^{2+}	1.606	1.588	0.254	0.257	1.094	1.541
Fe^{3+}	0.688	0.713	0.192	0.151	1.010	0.629
Mn	0.048	0.040	0.028	0.026	0.076	0.081
Ca	3.389	3.448	0.823	0.830	1.781	1.747
Na	0.336	0.163	0.097	0.085	0.617	0.804
K	0.000	0.003	0.000	0.000	0.290	0.314
Ba	0.000	0.000	0.001	0.000	0.000	0.000
Cl	0.002	0.000	0.000	0.000	0.107	0.091
Sum	15.320	15.214	3.898	3.888	15.813	16.017

AK97#	15a-17	15a-21	15a-16	15a-6	15a-4	15a-3
Mineral	Cpx 17	Biotite	Cpx center	Cpx edge	Biotite A	Biotite B
SiO_2	51.27	41.79	46.39	52.24	41.10	40.97
Al_2O_3	1.43	11.16	7.42	1.18	11.14	11.12
TiO_2	0.32	2.74	1.19	0.11	3.03	2.71
MgO	9.30	18.38	10.79	9.72	16.82	17.18
FeO SEM/EDS	14.78	10.59	17.77	14.61	13.49	12.73
FeO	8.57	4.55	7.64	6.57	12.28	10.18
Fe_2O_3	6.90	6.71	11.26	8.93	1.35	2.83
MnO	0.91	0.24	0.59	0.93	0.18	0.17
CaO	21.18	0.00	12.58	21.20	0.06	0.09
Na_2O	1.43	0.36	1.90	0.56	0.40	0.52
K_2O	0.00	9.62	1.29	0.05	9.41	9.38
BaO	0.00	0.10	0.00	0.00	0.06	0.26
Cl	0.05	0.26	0.33	0.01	0.22	0.23
Sum SEM/EDS	100.67	95.24	100.25	100.61	95.91	95.36
Sum w/Fe^{3+}	101.36	95.91	101.38	101.51	96.05	95.64
$Fe^{3+}/\Sigma Fe$	0.42	0.57	0.57	0.55	0.09	0.20
Stoichiometry	6	22	6	6	22	22
Si	1.900	6.039	1.716	1.903	6.050	6.039
Al	0.063	1.901	0.324	0.051	1.932	1.932
Ti	0.009	0.297	0.033	0.003	0.335	0.300
Mg	0.514	3.960	0.595	0.528	3.690	3.775
Fe^{2+}	0.266	0.550	0.236	0.201	1.511	1.256
Fe^{3+}	0.192	0.729	0.313	0.245	0.149	0.314
Mn	0.029	0.030	0.018	0.029	0.022	0.021
Ca	0.841	0.000	0.498	0.828	0.009	0.015
Na	0.102	0.101	0.137	0.039	0.113	0.149
K	0.000	1.773	0.061	0.002	1.767	1.764
Ba	0.000	0.006	0.000	0.000	0.003	0.015
Cl	0.004	0.082	0.027	0.001	0.070	0.075
Sum	3.919	15.468	3.958	3.829	15.652	15.654

Table 2. Distribution Coefficients for Fe

SAMPLE	MINERALS COMPARED	$Fe^{3+}/\Sigma Fe$	$Fe^{3+}/Fe^{3+} + Al$	$Fe^{2+}/Fe^{2+} + Mg$
AK97-15A Outside shear zone	Hb edge/cpx 17	1.14	0.55	0.88
	Hb edge/cpx edge	0.87	0.50	1.09
	Hb edge/cpx center	0.84	0.84	1.05
	Hb edge/biotite A	5.33	5.72	1.03
	Hb edge/biotite B	2.40	2.94	1.20
	Hb center/cpx 17	0.69	0.40	1.11
	Hb cente/cpx edge	0.53	0.36	1.37
	Hb center/cpx center	0.51	0.61	1.33
	Hb center/biotite A	3.22	4.15	1.30
	Hb center/biotite B	1.45	2.14	1.51
	cpx 17/biotite A	4.67	10.47	1.17
	cpx 17/biotite B	2.10	5.39	1.36
	cpx edge/biotite A	6.11	11.51	0.95
	cpx edge/biotite B	2.75	5.92	1.10
	cpx center/biotite A	6.33	6.83	0.87
	cpx center/biotite B	2.85	3.51	1.14
AK97-15B Within shear zone	Hb center/cpx center	0.70	0.93	1.65
	Hb center/cpx subgrain	0.81	0.91	1.65
	Hb edge/cpx center	0.72	0.97	1.64
	Hb edge/cpx subgrain	0.84	0.94	1.64

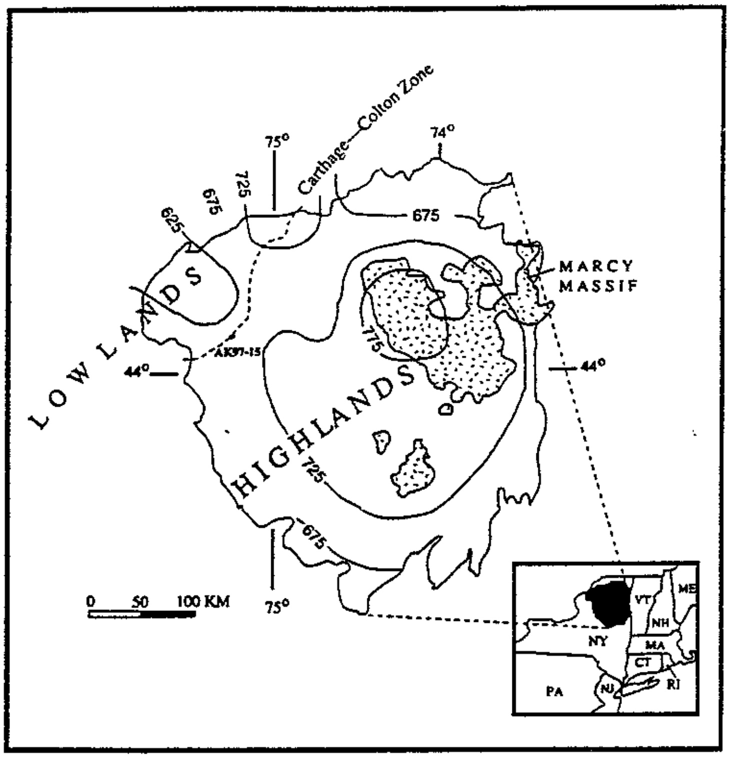

Figure 1. Adirondack Mountains, NY: Regional map with isotherms (metamorphic temperatures, °C): Samples AK97-15A and AK97-15B taken from the Carthage-Colton Mylonite Zone (CCMZ), which separates Adirondack Lowlands from Adirondack Highlands (Bohlen et al.1985).

Fe^{3+} partitioning and geothermometry of coexisting garnet and clinopyroxene pairs in Adirondack metanorthosite, northern New York

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INTRODUCTION

The partitioning of Mg^{2+} and Fe^{2+} between mafic minerals is the basis for many modern geothermometers. Although only Fe^{2+} is involved in those calculations, practical application of most geothermometers has involved the use of data for which only total Fe (i.e. Fe^{2+}+Fe^{3+}) was measured, due to the fact that conventional microprobe analysis cannot discriminate between multivalent species of iron. The oxidation state of iron, the most common multivalent element in rock-forming minerals, has previously been measured only by wet chemical and spectroscopic methods that are difficult and time-consuming. In this study, synchrotron micro-XANES (X-ray absorption near-edge structure), or SmX, has been used to measure Fe^{3+} partitioning at the micrometer scale. Our project combined mineral composition data from SEM/EDS analysis and $Fe^{3+}/\Sigma Fe$ from SmX analysis in order to give a closer look at Adirondack geothermometry and partitioning of Fe^{3+} in mafic silicates.

SAMPLE SELECTION, PREPARATION, AND ANALYSIS METHODS

This study focused on sample AK973b collected from a road cut in the anorthosite of the Marcy facies near the village of Saranac Lake, New York. The anorthosite sample thin section was mounted on 100% silica glass to ensure that there was no Fe from the thin section glass in the SmX Fe spectra.

After visually identifying the minerals in the thin section with a petrographic microscope, the SEM/EDS at Amherst College was used to determine the major element chemical composition of specific mineral grains. Petrographic microscope and SEM/EDS backscatter images allowed identification of mineral pairs in equilibrium that would be suitable for geothermometry (figures 1 and 2). Seven of these points (four mineral pairs consisting of garnet and clinopyroxene) were analyzed at the National Synchrotron Light Source at Brookhaven National Laboratory using the SmX technique to determine Fe^{3+} content (table 1). To establish established baselines, fayalite, magnetite, and hematite standards (0%, 67%, and 100% Fe^{3+}, respectively) were analyzed at the beginning and end of each 12 hour beam session. The magnetite standard was analyzed between every two unknown analyses in order to provide a calibration for Fe despite drift of the x-ray beam, using the method of Bajt et al. (1994).

Four different methods were used to generate chemical compositions that could be input in geothermometry calculations for each of the mineral pairs: (1) All Fe was assumed to be Fe^{2+}. (2) SmX Fe^{3+} data was used for both garnet and clinopyroxene. (3) Fe^{3+} in garnet was assumed to be zero, and SmX Fe^{3+} data was used for clinopyroxene. (4) Fe^{3+} in garnet was calculated using stoichiometry (Fe^{3+}=2-Al), and SmX data was used for clinopyroxene.

The garnet and clinopyroxene compositions were used to calculated metamorphic temperatures in the Saranac Lake area using the garnet-clinopyroxene geothermometers of Ellis and Green (1979) and Powell (1985).

RESULTS

The garnet SmX results gave 10%, 13%, 14%, and 21% for the $Fe^{3+}/\Sigma Fe$ of the four garnets analyzed (figure 7 and table 3). Those Fe^{3+} concentrations result in overfilling of the two 6-fold sites in the structure, such that Al + Fe^{3+} > 2. This would require that some Fe^{3+} be in 8-fold coordination, which is unlikely, indicating that our SmX calibration for garnet may not be reliable.

Four garnet and clinopyroxene pairs were used for geothermometry analysis (figures 2a-5d and table 2). Assuming that all Fe was Fe^{2+} gave metamorphic temperatures in the range of 700-750°C, but factoring in Fe^{3+} from the SmX analysis lowered the temperature to 575-600°C (figure 6). Since the garnet Fe^{3+} SmX data may not be