

# Fe<sup>3+</sup> partitioning and geothermometry in the Popple Hill gneiss formation, Adirondack Mountains, New York

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## INTRODUCTION

Because Fe<sup>2+</sup> and Mg<sup>2+</sup> ions have similar ionic radii and charges, they can substitute for one another in the crystal structures of common rock-forming minerals. This substitution is temperature dependent; thus the concentrations of these ions can be used to calculate the temperatures at which these minerals formed. This method has been used with other geothermometric methods to predict metamorphic temperatures in various locations in the Adirondack Mountains, New York. The application of Fe<sup>2+</sup> - Mg<sup>2+</sup> exchange thermometers is typically based on element concentrations determined by electron microprobe techniques. Because these techniques cannot distinguish between the two valence states of iron, the relative amounts of Fe<sup>2+</sup> and Fe<sup>3+</sup> must be deduced from stoichiometric constraints, which can lead to error in geothermometry calculations where only Fe<sup>3+</sup> or only Fe<sup>2+</sup> concentrations are used. This project incorporates micro-XANES (X-ray Absorption Near Edge Structure) techniques to determine Fe<sup>3+</sup> content in samples from the Popple Hill gneiss and to suggest more accurate temperature estimates for the area based on equilibria that incorporate accurate compositions for constituent minerals.

## GEOLOGIC SETTING

The current stratigraphic position and composition of the Adirondack Lowlands is understood to be the result of a series of four or five orogenic events. The juxtaposition of the lower-grade Lowland amphibolites next to the higher-grade Highland granulite facies rocks has been interpreted as evidence of a relative downward displacement of the Lowlands during the Ottowan Orogeny at ca. 1090 Ma. The Popple Hill outcrop studied here consists of a biotite-quartz-oligoclase gneiss that is distinctly banded and folded. Large boudins at the base of the outcrop may be a further indication of deformation at Popple Hill. Both light and dark layers exhibit large folds, thickening around the fold hinges, and swirled layer boundaries consistent with partial melting that exists regionally throughout the Lowlands.

## METHODS

Samples were collected during the 1997 Keck Adirondack project from the outcrop at Popple Hill (AK-97-18; Figure 1) outcrop referred to as the Popple Hill gneiss and during the 1992 IGCP-304 project (AK-95-5a), approximately one mile NW of the Popple Hill outcrop (Figure 1). Petrography and an EDS electron microprobe at Amherst College were used to examine the textures and mineral compositions of thin sections from these samples (Table 1). At Brookhaven National Laboratory we used the micro-XANES technique (Crowley *et al.*, this volume) to measure Fe<sup>3+</sup> content in biotite and garnet in the AK-95-5a sample and biotite and hornblende in the AK-97-18 sample. Biotite, hornblende, and garnet measurements used a standard magnetite calibration (Bajt *et al.*, 1994), and garnet values were also determined using an end member

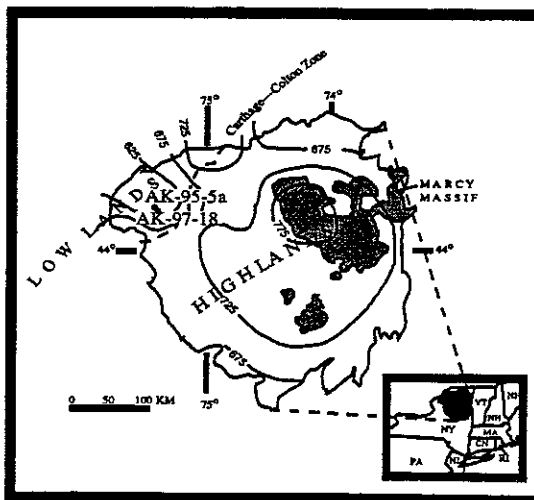


Figure 1. Area map (Bohlen *et al.*, 1985) with locations AK-97-18 and AK-95-5a.

Sample	analysis #	mineral	pair#	SiO2	Al2O3	TiO2	MgO	FeO	Fe2O3	MnO	CaO	sum
ak973bP12#7	nsls299.138	garnet	pair 1	37.427	20.319	0.072	3.990	23.505	4.253	0.753	7.437	97.756
ak973bP12#4	nsls299.62	garnet	pair 2	37.506	20.432	0.090	4.226	24.362	4.046	0.808	6.982	98.484
ak973bP12#10	nsls299.63	cpx	pair 1/2	50.910	2.819	0.267	11.159	9.362	2.602	0.087	21.240	99.161
ak973bP12#27	nsls299.65	garnet	pair 3	37.502	20.438	0.000	4.234	22.176	6.552	0.832	7.241	98.975
ak973bP12#12	nsls299.66	cpx	pair 3	51.863	2.886	0.336	11.034	10.388	1.427	0.199	21.998	100.131
ak973bP10#25	nsls299.68	garnet	pair 4	37.268	20.282	0.038	4.330	25.519	3.152	1.044	7.338	98.972
ak973bP10#20a	nsls299.69	cpx	pair 4	50.736	2.756	0.219	10.985	7.808	5.319	0.162	21.561	100.093
ak973bP12#7	nsls299.138	garnet	pair 1	2.999	1.918	0.004	0.477	1.574	0.256	0.051	0.638	7.919
ak973bP12#4	nsls299.62	garnet	pair 2	2.989	1.919	0.005	0.502	1.624	0.243	0.054	0.597	7.938
ak973bP12#10	nsls299.63	cpx	pair 1/2	1.931	0.126	0.008	0.631	0.297	0.074	0.003	0.864	3.987
ak973bP12#27	nsls299.65	garnet	pair 3	2.963	1.905	0.000	0.498	1.466	0.390	0.055	0.614	7.893
ak973bP12#12	nsls299.66	cpx	pair 3	1.947	0.128	0.010	0.618	0.326	0.040	0.006	0.885	3.961
ak973bP10#25	nsls299.68	garnet	pair 4	2.978	1.911	0.002	0.516	1.705	0.189	0.071	0.629	8.002
ak973bP10#20a	nsls299.69	cpx	pair 4	1.911	0.122	0.006	0.616	0.246	0.151	0.005	0.870	3.967

Table 1: Mineral composition data for samples (from SEM/EDS and SmX analysis)

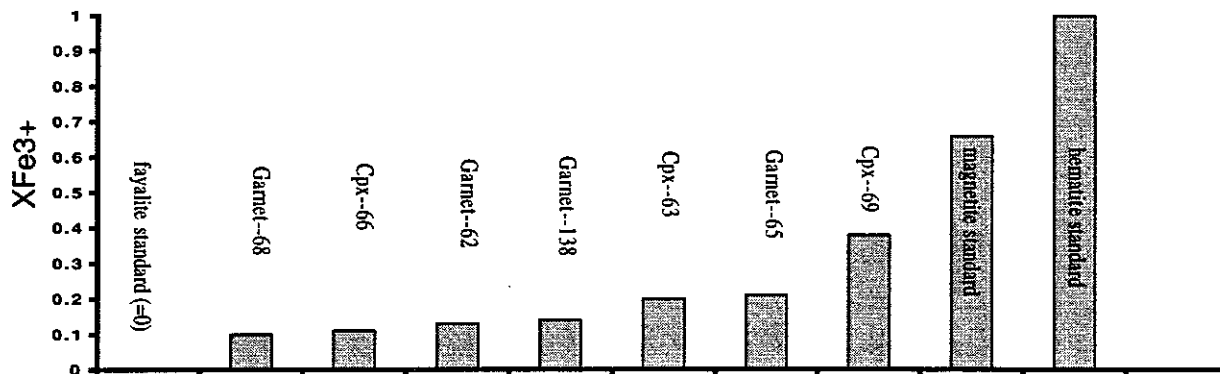
temp C @5kbar	63/138 #1	63/138 #2	62/63 #1	62/63 #2	65/66 #1	65/66 #2	68/69 #1	68/69 #2
xanes Fe <sup>3+</sup>	600	600	600	600	600	600	600	575
no Fe <sup>3+</sup>	700	700	700	700	725	700	750	725
no gt Fe <sup>3+</sup>	650	625	650	625	700	675	625	600
calc gt Fe <sup>3+</sup>	650	625	650	625	675	650	600	600

Table 2: Temperatures at 5 kbar, derived from four iron partitioning calculations and two thermometry methods (#1: Ellis and Green (1979); #2 Powell (1985))

	nsls299.138	nsls299.62	nsls299.63	nsls299.65	nsls299.66	nsls299.68	nsls299.69
Fe2+/ΣFe	0.86	0.87	0.80	0.79	0.89	0.90	0.62
Fe3+/ΣFe	0.14	0.13	0.20	0.21	0.11	0.10	0.38

Table 3: Iron partitioning in studied mineral samples

Figure 8: SmX iron partitioning for study minerals



almandine-andradite calibration.

Based on the EDS data two possible Fe<sup>3+</sup> values were calculated for the garnet from the 1995 sample based on stoichiometry:

$$\text{Fe}^{3+} = 2 - \text{Al}$$

$$\text{Fe}^{3+} = 8 - \sum \text{cations}$$

Garnet-biotite distribution coefficients for Fe<sup>3+</sup>/(Fe<sup>3+</sup> + Fe<sup>2+</sup>), Fe<sup>3+</sup>/(Al + Fe<sup>3+</sup>), and Fe<sup>2+</sup>/(Mg + Fe<sup>2+</sup>) were calculated for all six pairs. We used Spear and Kohn's 1996 Thermobarometry program to determine temperature data from the garnet-biotite pairs using five possible values for Fe<sup>3+</sup> content in garnet : two measured values from the two XANES calibrations, one value of 0% Fe<sup>3+</sup>, and two %Fe<sup>3+</sup> calculated from stoichiometry (Table 2).

Table 1. EDS measured stoichiometry with XANES Fe<sup>3+</sup> data, Bajt *et al.* calibration.

Sample Mineral	1 garnet	2 biotite	3 garnet	4 biotite	5 garnet	6 biotite	7 garnet	8 biotite	9 garnet	10 biotite
Oxide Sum	98.48	90.89	98.41	93.87	97.68	94.15	99.48	94.36	96.33	90.20
Cations per formula unit										
Si	2.84	5.43	2.81	5.44	2.90	5.38	2.96	5.36	2.89	5.32
Al	1.86	3.31	1.87	3.25	1.87	3.03	1.94	3.11	1.88	3.23
Ti	0.01	0.10	0.00	0.15	0.00	0.34	0.01	0.28	0.00	0.30
Mg	0.38	0.91	0.45	3.15	0.53	2.68	0.55	2.88	0.50	2.69
Fe <sup>2+</sup>	1.65	1.29	1.59	1.46	1.68	1.51	1.97	1.36	1.76	1.70
Fe <sup>3+</sup>	0.61	0.41	0.65	0.22	0.50	0.43	0.19	0.43	0.47	0.35
Mn	0.12	0.01	0.12	0.00	0.11	0.01	0.11	0.00	0.11	0.00
Ca	0.12	0.02	0.12	0.00	0.13	0.01	0.11	0.02	0.11	0.01
Na	0.05	0.16	0.00	0.02	0.00	0.14	0.07	0.10	0.00	0.00
K	0.00	1.63	0.01	1.76	0.00	1.76	0.00	1.76	0.00	1.65
Cation Sum	7.64	15.29	7.61	15.47	7.72	15.31	7.90	15.31	7.72	15.27
%Fe <sup>3+</sup>	27	24	29	13	23	22	9	24	21	17

Table 2. Fe<sup>3+</sup> data in garnet by five calculations.

Mineral ID #	2 - Al	8 - $\sum$ cations	Bajt calibration**	Garnet calibration*	EDS - No Fe <sup>3+</sup>
AK-95-5a-1	2.05	16.5	27	0	0
AK-95-5a-3	1.4	16.7	29	9	0
AK-95-5a-5	2.5	13	23	0	0
AK-95-5a-7	1.56	9.5	9	16	0
AK-95-5a-9	2.15	11.5	21	0	0

\*Fe<sup>3+</sup> by calibration using two end member garnets: 100% Fe<sup>2+</sup> almandine and 100% Fe<sup>3+</sup> andradite.

\*\* Fe<sup>3+</sup> by Bajt *et al.* calibration using magnetite-hematite-fayalite

## RESULTS AND DISCUSSION

The temperature estimates resulting from our analyses range from approximately 350°C to 600°C and are significantly lower than temperatures previously estimated by Bohlen *et al.* (1985). However, they are consistent within the 1997 Keck Adirondack project despite regional variations, possible back reactions, and differences in sample collection techniques. For comparative purposes we used temperatures calculated at 5 Kbars for all samples. Calculations based on EDS data alone (no Fe<sup>3+</sup>) yielded relatively higher temperatures from 396.1 - 574.8° C. Temperature calculations using Fe<sup>3+</sup> = 2 - Al for garnet yielded relatively lower temperatures from 346.9 - 516.0° C. Temperature calculations using Fe<sup>3+</sup> = 8 -  $\sum$  cations yielded mid-range temperatures ranging from 360.8 - 546.4° C.

Using a garnet calibration on the XANES garnet data yielded the lowest temperatures in all but one case, from 343.1 - 509.7°C. XANES data using the standard magnetite calibration for all minerals yielded the highest temperatures from 404.6 - 583.7° C (Figure 2). Geothermometry based on Fe<sup>2+</sup>/Mg exchange may not be accurate when  $\Sigma\text{Fe} \neq \text{Fe}^{2+}$ .

In this study, compositions of mineral pairs that included Fe<sup>3+</sup> content measured by XANES and calibrated against magnetite consistently yielded the highest calculated temperatures. However, those Fe<sup>3+</sup> values were problematic because they would require Fe<sup>3+</sup> to exist in 8-fold sites, which is unlikely due to its small ionic radius. The almandine-andradite calibration for the XANES data produces lower Fe<sup>3+</sup> measurements in the samples that would not require Fe<sup>3+</sup> to exist in 8-fold sites, making the data more reasonable. However, these sometimes yielded negative %Fe<sup>3+</sup> results outside of the standard deviation.

Temperatures were also calculated from our mineral pairs using only the EDS data and three different methods assuming 1) no Fe<sup>3+</sup> was present, 2) Fe<sup>3+</sup> = 2 - Al, and 3) Fe<sup>3+</sup> = 8 -  $\Sigma$  cations. These three methods yielded temperatures ranging from 396.1 - 574.8° C, 346.9 - 516.0° C, and 360.8 - 546.4° C, respectively.

The presence of sillimanite in the Popple Hill outcrop limits peak temperatures to approximately 500° C and greater. Many of the data we collected fall below this limit and therefore cannot represent peak metamorphism. This could be attributed to back reactions between the biotite and garnet. These retrograde reactions are suggested by the fractured nature of these garnets. Furthermore, the highest temperatures are calculated with biotite with a TiO<sub>2</sub> content greater than 2.0wt%. The lowest temperatures come from biotite with a TiO<sub>2</sub> content less than 1.0wt%.

The XANES data collected from pair 7/8 was not collected at the same resolution as the other samples. Thermometry using these data results in temperatures that are significantly lower than other mineral pair compositions based on XANES estimates using standard magnetite calibration (489.3° C). The pairs 9/10, and 5/6 yield temperatures closest to peak metamorphic conditions.

Calculated values of Fe distribution coefficients are shown in Table 3. Garnet and hornblende contain higher %Fe<sup>3+</sup> relative to biotite.

## CONCLUSIONS

Thermometry based on analyses in which Fe<sup>3+</sup> is measured by the micro-XANES technique yields temperatures 50-100° C higher than temperatures calculated using mineral compositions for which Fe<sup>3+</sup> is ignored or estimated. Although XANES measurements of Fe<sup>3+</sup> in garnet vary with calibration techniques, further characterization of partitioning behavior of Fe<sup>3+</sup> and Fe<sup>2+</sup> could produce a substantial improvement in the accuracy of geothermometry calculations.

## REFERENCES

- Bajt S., Sutton S. R. And Delaney J.S. (1994) Microanalysis of iron oxidation states in silicates and oxides using x-ray absorption near edge structure (XANES). *Geochim. Cosmochim. Acta* 58, 5209-5214.
- Bohlen, S., Valley, J., and Essene, E., 1985, Metamorphism in the Adirondacks. I. Petrology, pressure and temperature : *Journal of Petrology*, 6, 971-992.

Table 3. Iron partitioning between garnet-biotite, hornblende-biotite pairs using  $Fe^{3+}/(Fe^{3+} + Al^{3+})$  and  $Fe^{2+}/(Fe^{2+} + Mg^{2+})$ ; Garnet:biotite, hornblende:biotite distribution coefficients for  $\%Fe^{3+}_A/\%Fe^{3+}_B$ ; Ratios of partitioning between pairs.

Mineral	Sample #	$Fe^{3+}/(Fe^{3+} + Al^{3+})$		$Fe^{2+}/(Fe^{2+} + Mg^{2+})$	
		Standard*	$\Sigma Cations^{**}$	Standard*	$\Sigma Cations^{**}$
Garnet	1	0.244	0.167	0.810	0.833
Biotite	2	0.110	0.110	0.308	0.308
Garnet	3	0.254	0.167	0.777	0.807
Biotite	4	0.063	0.063	0.316	0.316
Garnet	5	0.208	0.131	0.757	0.782
Biotite	6	0.124	0.124	0.361	0.361
Garnet	7	0.091	0.096	0.781	0.780
Biotite	8	0.121	0.121	0.321	0.321
Garnet	9	0.196	0.120	0.775	0.797
Biotite	10	0.098	0.098	0.388	0.388
Hornblende	11	0.224	0.224	0.517	0.517
Biotite	12	0.021	0.021	0.479	0.479

Mineral Pair	$Fe^{3+}/(Fe^{3+} + Al^{3+})$	$Fe^{2+}/(Fe^{2+} + Mg^{2+})$	$Fe^{3+}/(Fe^{2+} + Fe^{3+})$		
			$\Sigma Cations^{**}$	Mag Standard*	Gar Standard***
Garnet:Biotite					
Garnet:Hornblende					
1:2	2.218	2.630	0.688	1.125	0.000
3:4	4.032	2.459	1.285	2.231	0.692
5:6	1.677	2.067	0.591	1.045	0.000
7:8	0.752	2.433	0.396	0.375	0.000
9:10	2.00	1.997	0.676	1.235	0.000
11:12	10.667	1.079	n/a	0.089	n/a

\* $Fe^{3+}$  by Bajt *et al.* calibration using magnetite-hematite-fayalite. \*\* $Fe^{3+} = 8 - \Sigma Cations$ . \*\*\* Crowley, 1984

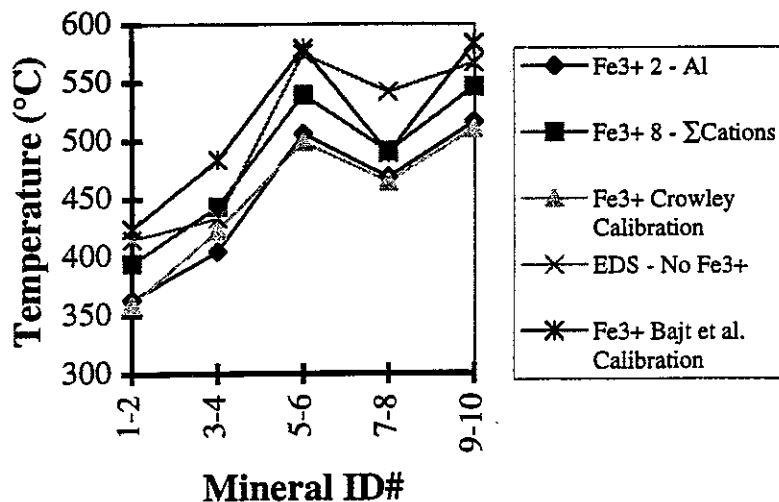


Figure 2. Temperature vs. pair for five thermometry techniques. The lower temperatures in samples 1-2 and 3-4 are due to biotite-garnet back reactions. The temperatures for samples 5-6 and 9-10 represent our best data and most accurate temperatures. Samples 7-8 are inaccurate due to an inconsistent garnet data collection technique. The XANES Bajt *et al.* calibration and two stoichiometric calculations have the same slope for all pairs except 7-8, implying consistency between the results. The XANES Crowley calibration follows the same general trend, with the slight variations illustrating the inaccuracy of the calibration technique. The EDS data differ dramatically from both the XANES and stoichiometric calculations, suggesting the need to account for  $Fe^{3+}$  in thermometry calculation.

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