Ferric Iron in Rock Forming Minerals

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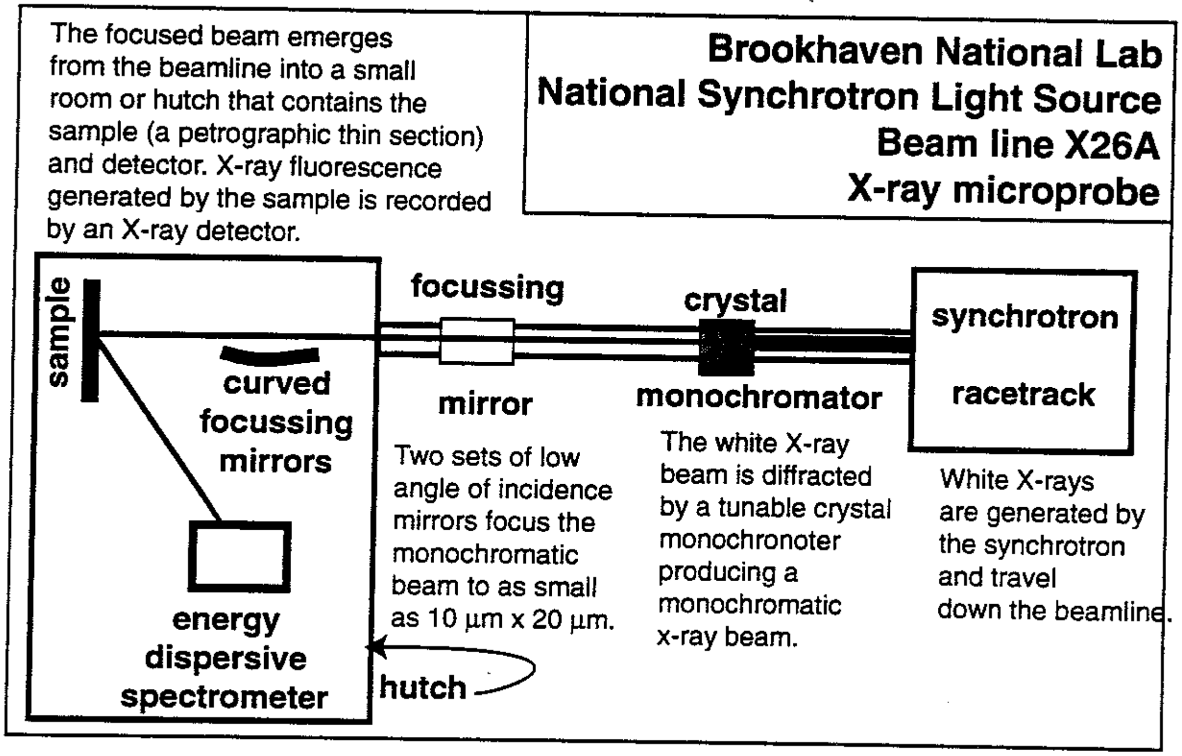
INTRODUCTION

The development or refinement of instrumentation and analytical techniques has long played an important part in geology. Advances in instrumentation and analytical techniques have commonly resulted in advances in our understanding of the earth. Isotope geochronology resulted from the development of high-resolution mass spectrometers, plate tectonics followed improvements in magnetometer design and more recently the development of seismic tomography would not have been possible without improvements in computer size and speed. Here, we describe a study that exploited recent advances in X-ray absorption spectroscopy to analyze the oxidation state of iron in rock forming minerals.

Synchrotron microXANES (SmX) analyses

X-ray absorption spectroscopy has been used since early this century to determine elemental concentration. For every element, there is a critical energy known as the absorption edge above which X-rays are strongly absorbed. Absorption of X-rays with energies greater than the absorption edge produces X-ray fluorescence whereby X-rays are emitted by the element. The energy of wavelength of both the absorption edge and the X-ray fluorescence is different for each element. The strength of the absorption or fluorescence is related to the concentration of that element. XANES (X-ray absorption near-edge structure) exploits spectroscopic features that occur near the absorption edge of a given element.



The focused beam emerges from the beamline into a small room or hutch that contains the sample (a petrographic thin section) and detector. X-ray fluorescence generated by the sample is recorded by an X-ray detector.

Two sets of low angle of incidence mirrors focus the monochromatic beam to as small as 10 µm x 20 µm.

The white X-ray beam is diffracted by a tunable crystal monochronoter producing a monochromatic x-ray beam.

White X-rays are generated by the synchrotron and travel down the beamline.

Figure 1: A specialized synchrotron beamline is needed for SmX analyses

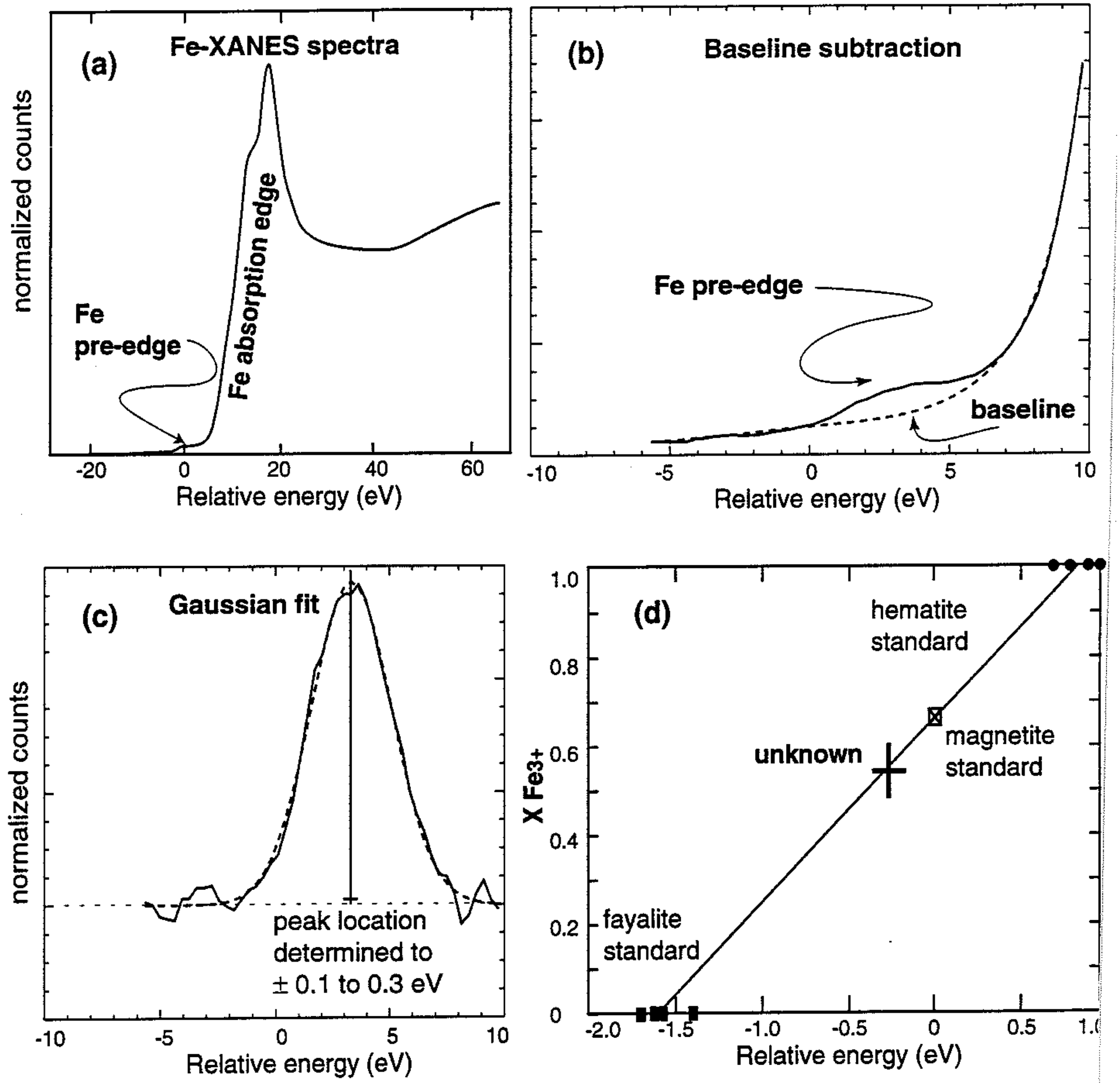


Figure 2: The Fe^{3+}/total Fe ratio is determined by the location of the pre-edge peak. Going from all Fe^{2+} to all Fe^{3+} there is an approximately 3 eV linear shift in peak position.

XANES spectroscopy uses the white or polychromatic X-rays generated by a synchrotron as its X-ray source. The synchrotron beam line used in this project is shown in Figure 1. A tunable monochromatic X-ray source is created from the white synchrotron radiation by a crystal monochromator. Using the monochromator the energy of the X-rays is varied so that it steps across the absorption edge of a given element. Downstream from the monochromator, the X-ray beam is focussed on a sample. This generates X-ray fluorescence whose intensity is recorded by a detector. Figure 2a shows a typical XANES spectrum. At the absorption edge, there is a marked increase in the fluorescence intensity. For multivalent elements such as iron, there is a small peak known as the pre-edge at an energy that is a few electron volts (eV) below the absorption edge. The location of the pre-edge varies by several electron volts depending on oxidation state of the element.

The Fe^{3+}/Fe^{2+} ratio of a mineral can be measured by Fe-XANES using the analytical method of Bajt et al. (1994). The location of the pre-edge peak is determined after the subtraction of a baseline that rises towards the absorption edge (Fig. 2b, 2c). The Fe^{3+}/Fe^{2+} ratio is directly proportional to pre-edge peak position and is determined by comparison to the peak positions of fayalite (Fe^{3+}/total Fe = 0), magnetite (Fe^{3+}/total Fe = 0.67) and hematite (Fe^{3+}/total Fe = 1) standards (Fig. 2d). The precision of these analyses is proportional to the precision in determination of the pre-edge peak location.

X-rays cannot be focused using traditional lenses. However, using a combination of apertures and flat and curved low-angle of incidence mirrors the X-ray beam used for our SmX studies can be made as small as approximately 10 x 20 µm. This is small enough to analyze Fe^{3+}/Fe^{2+} in individual mineral grains and to analyze for Fe^{3+}/Fe^{2+} zonation within mineral grains.

FERRIC IRON IN MINERALS

Iron is the only abundant element that occurs in more than one valence state. The Fe^{3+}/Fe^{2+} ratio of any given mineral should reflect the oxidation state under which that mineral formed. However, the Fe^{3+}/Fe^{2+} ratio of any single mineral is also influenced by other factors including bulk Fe concentration, temperature and pressure. The effects of these factors can be isolated by examining how Fe^{3+}/Fe^{2+} is partitioned between two coexisting minerals. This is commonly done with elemental ratios such as Mg/Fe. However, little is known about the partitioning of Fe^{3+}/Fe^{2+} between coexisting mineral pairs. Our understanding of the partitioning of Fe^{3+}/Fe^{2+} lags behind our understanding of element partitioning in part because the commonly used techniques for Fe^{3+}/Fe^{2+} determinations, wet chemistry and Mössbauer spectroscopy require bulk samples. The SmX technique used in this study allowed for micron-scale determination of Fe^{3+}/Fe^{2+} much like Mg/Fe can be measured with the electron microprobe.

The goals of this study were three-fold. First, the SmX method is still in the development stages. The effects of crystal structure and even mineral orientation on SmX results are poorly known. We wanted to compare our results with Fe^{3+}/Fe^{2+} obtained by other methods, in particular to see if there are mineral specific problems. Second, we wanted to see if there was a temperature dependence on the partitioning of Fe^{3+}/Fe^{2+} between coexisting minerals. For this reason, Fe^{3+}/Fe^{2+} of coexisting minerals was analyzed from samples that we hoped had equilibrated at very different temperatures. Finally, we wanted to evaluate the effect of ferric iron on Fe-Mg exchange geothermometry.

ADIRONDACKS

The Adirondacks of northern NY are an extension of the Grenville Province. The Adirondacks are separated by the Carthage-Colton Mylonite zone into the granulite facies metamorphosed Adirondack highlands and the amphibolite facies metamorphosed Adirondack lowlands (McLelland et al., 1996). The Adirondacks formed as a result of a several protracted periods of granitic and anorthitic magmatism between 1400 and 1000 Ma (Chiarenzelli & McLelland, 1991). Deformation and regional amphibolite to granulite facies metamorphism occurred relatively late in the evolution of the Adirondacks, during the approximately 1100-1050 Ma Ottawan orogeny. Ottawan metamorphism (Fig. 3) produced a bulls-eye pattern of metamorphic isotherms (Bohlen et al., 1985) with the highest temperature (>775 °C) granulite facies metamorphism in the central part of the highlands and successively lower temperature granulite facies metamorphism outwards. The concentric isotherm pattern has been recently questioned by Spear & Markussen (1997) who feel that the entire highlands initially equilibrated at high temperature. Metamorphic grade drops abruptly to amphibolite facies in the lowlands across the Carthage-Colton mylonite zone.

STUDENT PROJECTS

The project began with a week of field trips and sample collection in the Adirondacks. The field trips illustrated the diversity of mineralogy and rock types in the Adirondacks. Part of the time was spent collecting samples for later analysis by electron microprobe and SmX. An attempt was made to collect samples that contained several ferro-magnesian minerals (garnet, clinopyroxene, orthopyroxene, olivine, amphibole, and mica) and to create a suite of rocks that had equilibrated over the entire range of temperatures (from <650°C to >800°C) represented in the Adirondacks.

After a week in the Adirondacks, we returned to Amherst and decided upon projects that to be investigated by the students working in groups of two. The first few days back at Amherst were hectic; rocks slabs were cut and petrographic thin-sections were made. In addition, during this time, garnet mineral separates were made for X-ray diffraction and Mössbauer analysis. Once the thin-sections were made, the next week was spent identifying the minerals in them and analyzing mineral compositions with the electron microprobe. On the basis of these mineral compositions, temperatures and pressures were determined using geothermobarometry mineral equilibria. Most of these equilibria involved Fe and are affected by the Fe^{3+}/Fe^{2+} ratio. Using these results, the groups chose samples to analyze for Fe^{3+}/Fe^{2+} by SmX.

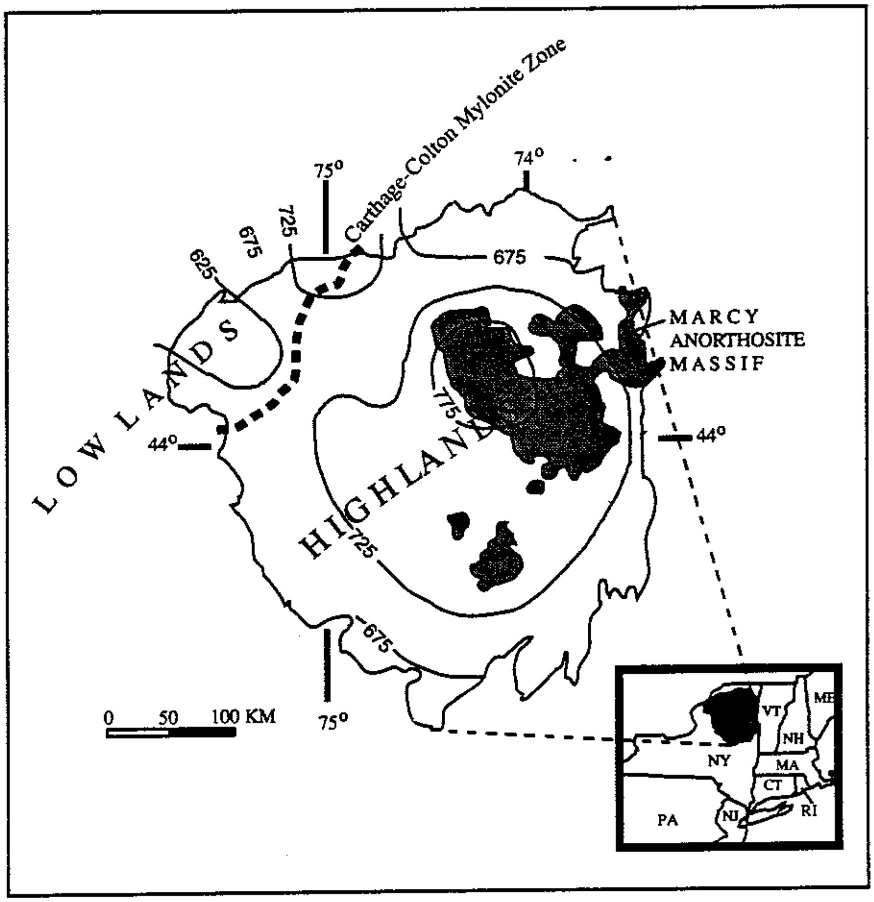


Figure 3: The Adirondack Highlands are dominated by granulite facies meta-igneous rocks whereas amphibolite facies metasedimentary rocks dominate the Adirondack lowlands The Highland-Lowland boundary is the Carthage Colton Mylonite Zone, a west-dipping normal fault .
(isotherms ater Bohlen et al., 1985)

We spent 6 days at the National Synchrotron Light Source (NSLS) at the Brookhaven National Lab (BNL) using beamline X26a to do the SmX analyses. While at Brookhaven, someone was at the beamline 24 hours/day. At 7 AM & 7 PM the synchrotron beam was "dumped" and electrons were reinjected and accelerated to recreate the synchrotron beam. Before and after beam injection the magnetite, hematite and fayalite standards had to be repeatedly analyzed. We tended to worked in 6 hour shifts, with each group responsible for analyzing the standards at either the start or end of their run. For the last 6 days of the project, we returned to Amherst and integrated the SmX results with our earlier microprobe analyses.

Halle Morrison and Zoë Brown helped with some of the ground-truthing of the SmX method. They looked at garnet with a wide range of Fe^{3+}/Fe^{2+}. The SmX results were compared with those determined by Mössbauer spectroscopy and estimated by garnet stoichiometry and garnet molar volume. Their results clearly showed that there were problems with using the Bajt et al. (1994) method with garnet and suggested revisions.

Dan Harrington and Anna Monders examined Fe^{3+} partitioning and geothermometry from a metanorthosite from presumed highest temperature part of the Adirondack highlands. Their geothermometry yields temperatures similar to those of Spear & Markussen (1997). Their results suggest a relatively small Fe^{3+}/Fe^{2+} partitioning at these high temperatures.

Mary Beth Cheversia and Becky Stamski examined Fe^{3+} partitioning and geothermometry from an olivine metagabbro and a fayalite granite from presumed lower temperature parts of the Adirondack highlands. Their geothermometry indicates a protracted thermal history that starts at temperatures greater than those suggested by the Bohlen et al. (1985) isograd pattern.

Heidi Guetschow and Ethan Gutmann examined Fe^{3+} partitioning and geothermometry in the Popple Hill gneiss formation, from the amphibolite facies Adirondack lowlands.Their geothermometry yielded lower temperatures than were found in the highlands. Furthermore, their results suggest a relatively larger Fe^{3+}/Fe^{2+} partitioning than was found at higher temperatures in the highlands.

Rachel Graham and Sue Young Jin studied the Fe^{3+} partitioning and geothermometry in the Carthage-Colton Mylonite Zone. They compared the compositions of mineral grains within a shear zone to those outside the shear zone.

REFERENCES

Bajt, S., Sutton, S.R. & Delaney, J.S. (1994) Microanalysis of iron oxidation states in silicates and oxides using x-ray absorption near-edge structure (XANES) Geochim. Cosmochim. Acta, v. 58, p. 5209-5214.

Bohlen, S.R., Valley, J.W., and Essene, E.J., (1985) Metamorphism in the Adirondacks. I. Petrology, pressure and temperature: Journal of Petrology, v. 6, p. 971-992.

Chiarenzelli, J., and McLelland, J. (1991) Age and regional relationships of granitoid rocks of the Adirondack Highlands. Journal of Geology, v. 99, p. 571-590.

Delaney, J.S., Bajt, S., Sutton, S.R. & Dyar, M.D. (1996) In situ microanalysis of $Fe^{+3}/\Sigma Fe$ in amphibole by x-ray absorption near edge structure (XANES) spectroscopy. In: Dyar, M.D. , McCammon & Schaefer, M.W. (Eds), Mineral spectroscopy: a tribute to Roger Burns. Geochemical Society. p. 165-171.

McLelland, J., J. S. Daly, and J. McLelland, (1996) The Grenville Orogenic Cycle (ca. 1350-1000 Ma): an Adirondack Perspective. Tectonophysics, v. 265-266, p. 1-28.

Spear, F.S. & Markussen, J.C. (1997) Mineral zoning, P-T-X-M phase relations and metamorphic evolution of some Adirondack granulites, New York. Journal of Petrology, v. 38, p. 757-783.

Geothermometry and Fe^{3+} Partitioning within an Olivine Metagabbro and a Fayalite Granite in the Adirondack Mountains, NY

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INTRODUCTION

This study focused on the compositions of minerals within an olivine metagabbro and a fayalite granite from the Adirondack Mountains of northern New York State. Synchrotron microscale X-ray absorption near edge structure (SmX, or XANES) spectroscopy (Delaney *et al.*, 1996) was used to analyze $Fe^{3+}/\Sigma Fe$ within the Fe-bearing silicates present in our samples. Because this type of research is in its infancy, the results provide new insight into the partitioning of Fe^{2+} and Fe^{3+} between minerals, and may be used to explain this area's metamorphic history. We compared temperatures calculated by methods that assume all iron is Fe^{2+} to temperature calculations that take into account $Fe^{3+}/\Sigma Fe$ determined by the SmX analyses. Finally, we examined how Fe^{3+} is partitioned between minerals both within our samples and within samples from the Adirondack region. The results demonstrate the importance of incorporating $Fe^{3+}/\Sigma Fe$ data into geothermometry.

GEOLOGIC SETTING AND SAMPLE SELECTION

Three major orogenic events ca. 1350-1000 Ma have been recognized within the Adirondacks, the latest of which, the Ottowan Orogeny (ca. 1090 Ma), had the most influence on the geologic record. This most recent stage involved continental collision resulting in granulite facies metamorphism (Bohlen *et al.*, 1992; McLelland *et al.*, 1996; Olson, 1992). The Ottowan event produced a bull's eye pattern of isotherms in which temperature decreases from >775°C in the Adirondack Highlands to <625°C in the Adirondack Lowlands (Figure 1). Samples of olivine metagabbro and fayalite granite were collected from areas near the 750°C and 675°C isotherms, respectively.

Sample AK97-27 was collected on the Blue Ridge Highway from a road cut exposing well-foliated, dark colored, medium- to coarse-grained olivine metagabbro. The mineral assemblage of this metagabbro includes spinel-clouded plagioclase, hornblende, orthopyroxene, garnet, biotite, and various oxides and sulfides; our sample contained no olivine. The metagabbro, dated at 1143.6+/-7 Ma using U-Pb Zircon technique (McLelland and Chiarenzelli, 1989), is contemporaneous with the anorthosite massifs. Due to the spacial and chronological proximity of the anorthosite to the metagabbro, the latter is understood to be parental to the former (Frederick *et al.*, 1994).

Sample AK97-19 is a dark grey-green fayalite granite collected from a low road cut near the town of Wanakena. The mineral assemblage includes mesoperthite, quartz, hedenbergite, fayalite, hornblende, albite, ilmenite, magnetite, and zircon. The albite occurs as rims around the mesoperthite and may represent metamorphic recrystallization (Tucker and McKinney, 1997). Unlike almost all intrusive rocks in the Adirondacks, the fayalite granite appears to be virtually undeformed and unmetamorphosed and is not foliated. It cross-cuts metamorphic fabric in the country rock. These observations suggest it was late syn- or post-tectonic. The granite has been dated at approximately 1045 Ma; this time may represent the conclusion of regional high grade metamorphism (McLelland *et al.*, 1996).

EXPERIMENTAL METHODS

One-inch round thin sections were made from sample AK97-19 and AK97-27. Each thin section was examined petrographically and selected mineral grains were analyzed using a scanning electron microscope with an energy dispersive spectrometer (SEM/EDS) at Amherst College. From this technique we obtained major element chemistry of Fe-bearing minerals. $Fe^{3+}/\Sigma Fe$ of selected mineral grains was determined by the SmX method using the intense X-ray beam supplied by the National Synchrotron Light Source (NSLS) located at the Brookhaven National Laboratory (BNL). The SmX technique is described in Delaney *et al.*, (1996) and Crowley *et al.*, (this volume). Upon our return to Amherst, we employed geothermometers based on several different mineral pairs to derive temperatures for AK97-19 and AK97-27. In all possible cases, we compared the temperatures obtained using