

# Fe<sup>3+</sup> partitioning and geothermometry of coexisting garnet and clinopyroxene pairs in Adirondack metanorthosite, northern New York

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## INTRODUCTION

The partitioning of Mg<sup>2+</sup> and Fe<sup>2+</sup> between mafic minerals is the basis for many modern geothermometers. Although only Fe<sup>2+</sup> is involved in those calculations, practical application of most geothermometers has involved the use of data for which only total Fe (i.e. Fe<sup>2+</sup>+Fe<sup>3+</sup>) 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<sup>3+</sup> partitioning at the micrometer scale. Our project combined mineral composition data from SEM/EDS analysis and Fe<sup>3+</sup>/ΣFe from SmX analysis in order to give a closer look at Adirondack geothermometry and partitioning of Fe<sup>3+</sup> 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<sup>3+</sup> content (table 1). To establish established baselines, fayalite, magnetite, and hematite standards (0%, 67%, and 100% Fe<sup>3+</sup>, 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<sup>2+</sup>. (2) SmX Fe<sup>3+</sup> data was used for both garnet and clinopyroxene. (3) Fe<sup>3+</sup> in garnet was assumed to be zero, and SmX Fe<sup>3+</sup> data was used for clinopyroxene. (4) Fe<sup>3+</sup> in garnet was calculated using stoichiometry (Fe<sup>3+</sup>=2-Al), and SmX data was used for clinopyroxene.

The garnet and clinopyroxene compositions were used to calculate 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<sup>3+</sup>/ΣFe of the four garnets analyzed (figure 7 and table 3). Those Fe<sup>3+</sup> concentrations result in overfilling of the two 6-fold sites in the structure, such that Al + Fe<sup>3+</sup> > 2. This would require that some Fe<sup>3+</sup> 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<sup>2+</sup> gave metamorphic temperatures in the range of 700-750°C, but factoring in Fe<sup>3+</sup> from the SmX analysis lowered the temperature to 575-600°C (figure 6). Since the garnet Fe<sup>3+</sup> SmX data may not be

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

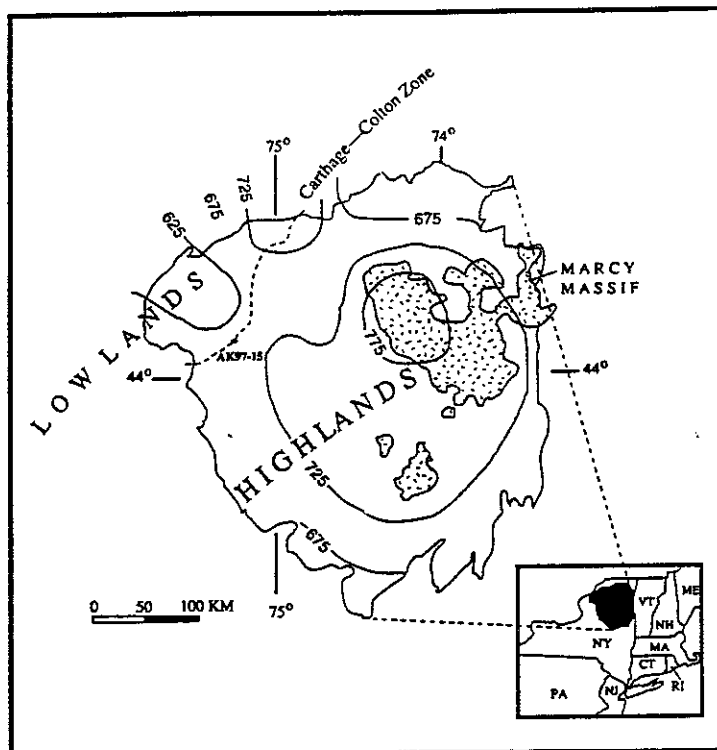


Figure 1. Adirondack Mountains, NY: Regional map with isotherms (metamorphic temperatures, °C): Samples AK97-15A and AK97-15B taken from the Carthage-Colton Mylonite Zone (CCMZ), which separates Adirondack Lowlands from Adirondack Highlands (Bohlen et al.1985).

valid, the geothermometry calculations were also done assuming no  $\text{Fe}^{3+}$  in garnet (method 3, above), giving 600-700°C, as well as method 4, above, that resulted in 600-675°C. The correction for  $\text{Fe}^{3+}$  in the compositions input into our geothermometry calculations lowered temperatures by 50-100°C, indicating that the effects of  $\text{Fe}^{3+}$  should not be ignored.

The calculated  $\text{Fe}^{3+}/\Sigma\text{Fe}$  for garnet was in the range of 3-5% and the SmX analysis of  $\text{Fe}^{3+}/\Sigma\text{Fe}$  for clinopyroxene gave 11%, 20%, and 38%, results which indicate a preferential partitioning of  $\text{Fe}^{3+}$  into clinopyroxene instead of garnet at these P-T conditions.

## DISCUSSION AND CONCLUSIONS

The SmX data for clinopyroxene fit stoichiometric constraints, but calibrations for  $\text{Fe}^{3+}$  in garnet do not yet appear reliable: aside from the crystallographic contradiction mentioned above, SmX analysis of garnet standards did not match the known chemical composition. Conversely, the SEM/EDS analysis does not yield enough cations in 6-fold coordination, indicating the presence of some  $\text{Fe}^{3+}$ . Thus, the calculated  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratios for garnet seem the most reliable. Further research with the SmX technique needs to be done to provide a more accurate calibration for garnet.

Our derived temperatures using the calculated  $\text{Fe}^{3+}$  in garnet (600-675 °C), however, are not consistent with previous studies of the area. Bohlen et al. (1985) reported temperatures of 750-800 °C, using geothermometers of both iron- and non-iron-bearing minerals. It is probable that the relatively low temperatures of our study do not record peak metamorphic conditions of this granulite facies region, but suggest that the cooling period of the metamorphic region was protracted. With the time for chemical re-equilibration at lower temperatures, the mineral compositions present today would represent a set of post-peak P-T conditions.

## REFERENCES

- Bajt S., Sutton S. R. and Delaney J. S. (1994) Micro-analysis of iron oxidation states in silicates and oxides using x-ray absorption near edge structure (XANES). *Geochim. Cosmochim. Acta* **58**, 5209-5214.
- Bohlen, S. R., Valley, J. W., and Essene, E. J. (1985) Metamorphism in the Adirondacks. I. Petrology, pressure and temperature. *J. Petrology* **26**, 971-92.

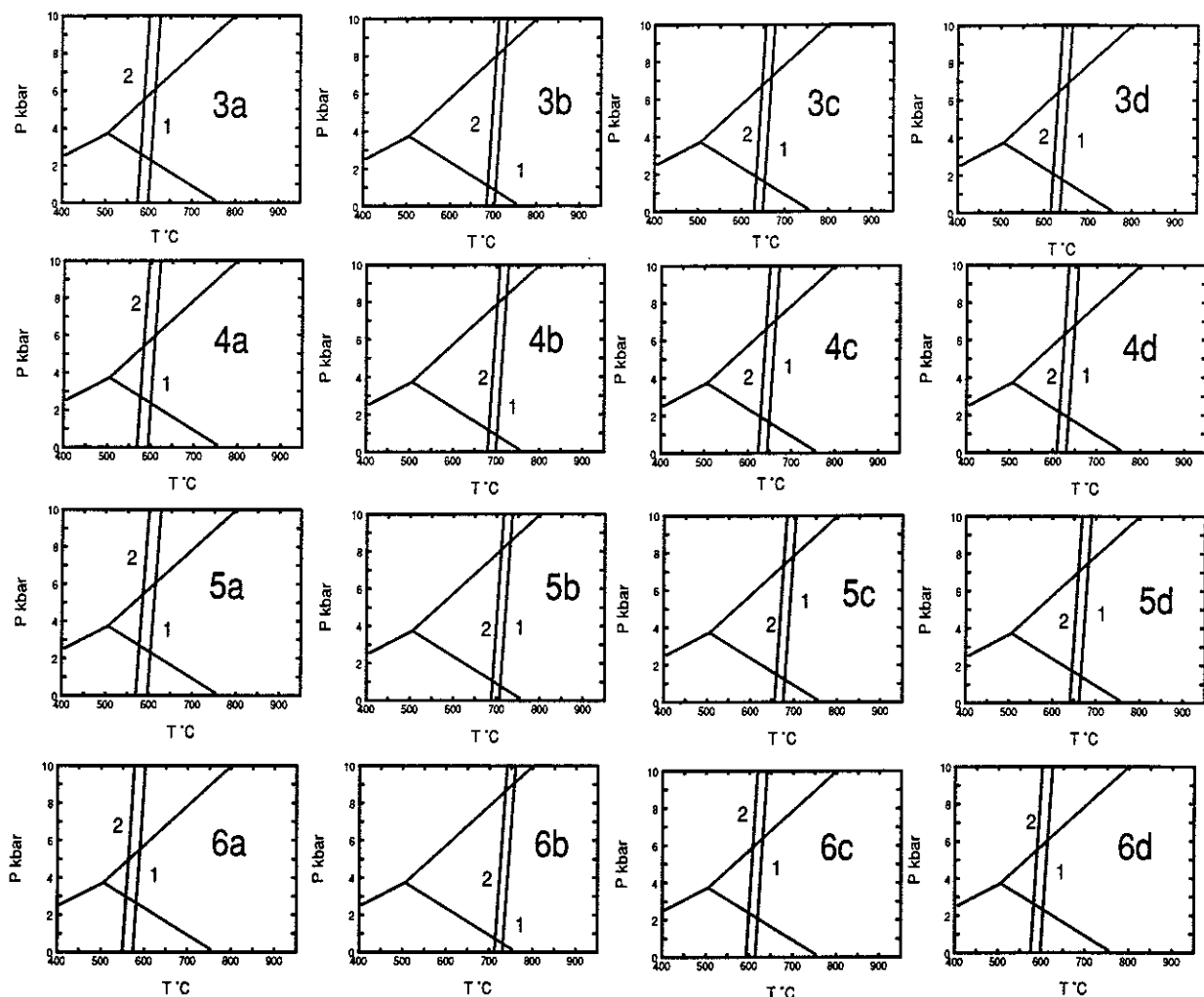


100 μm



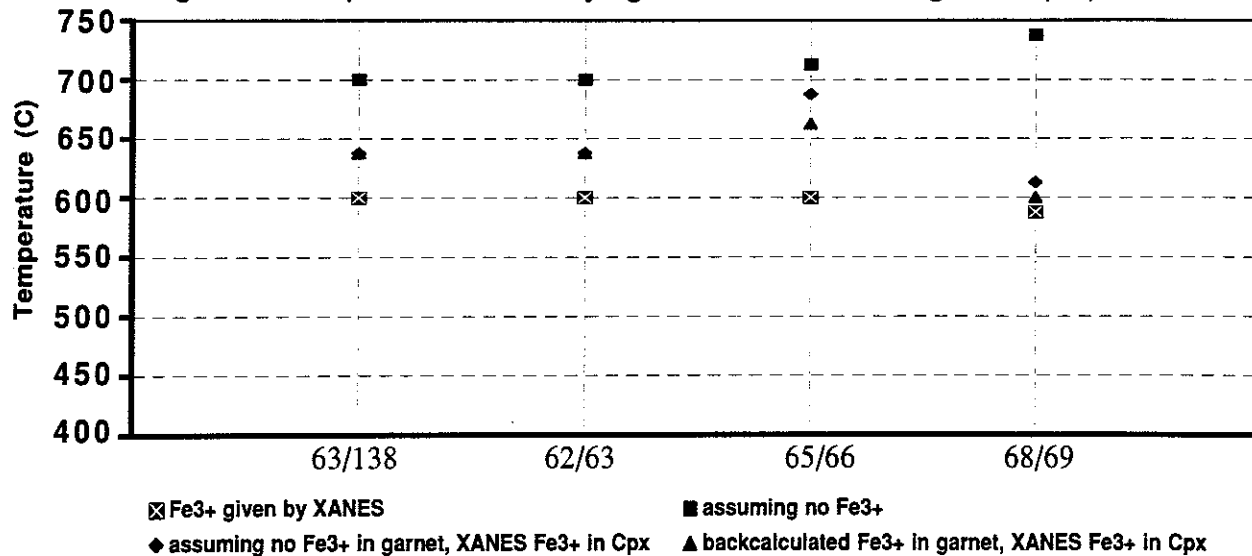
500 μm

Figures 1 and 2: Photomicrographs of garnet (light) and cpx (dark) pairs in sample AK97-3b



**Figures 3a-6d:** P-T diagrams for mineral pairs 63/138 (3), 62/63 (4), 65/66 (5), and 68/69 (6), generated using 4 iron partitioning calculations: a:  $Fe^{3+}/\Sigma Fe$  as given by SmX; b: assuming  $Fe^{3+}/\Sigma Fe=0$ ; c: SmX  $Fe^{3+}/\Sigma Fe$  in Cpx,  $Fe^{3+}/\Sigma Fe=0$  in garnet; d: SmX  $Fe^{3+}/\Sigma Fe$  in Cpx, backcalculated  $Fe^{3+}/\Sigma Fe$  in garnet. Thermometer lines are Ellis and Green (1979) (#1), and Powell (1985) (#2).

**Figure 7:** Temperatures for varying  $Fe^{3+}$  calculations--garnet/cpx pairs



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)

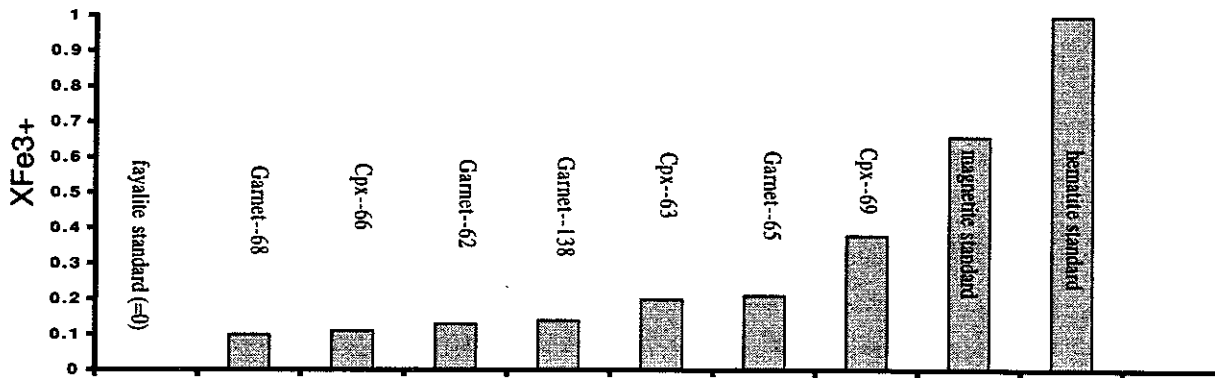
temp C @5kbar	63/138 #1	63/138 #2	62/63 #1	62/63 #2	65/66 #1	65/66 #2	68/69 #1	68/69 #2
xanes Fe <sup>3+</sup>	600	600	600	600	600	600	600	575
no Fe <sup>3+</sup>	700	700	700	700	725	700	750	725
no gt Fe <sup>3+</sup>	650	625	650	625	700	675	625	600
calc gt Fe <sup>3+</sup>	650	625	650	625	675	650	600	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
Fe <sub>2</sub> /ΣFe	0.86	0.87	0.80	0.79	0.89	0.90	0.62
Fe <sub>3</sub> /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



# 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

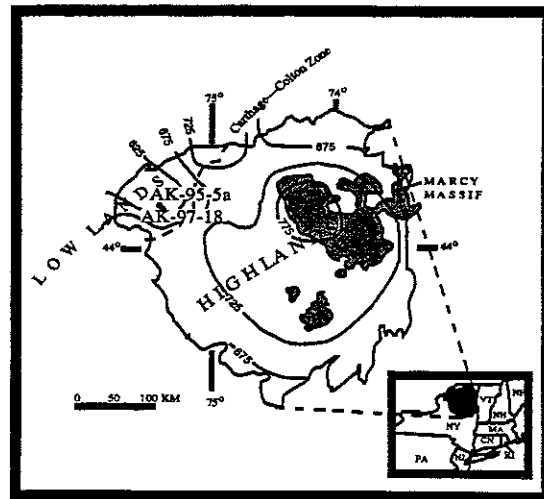


Figure 1. Area map (Bohlen *et al.*, 1985) with locations AK-97-18 and AK-95-5a.