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Pyroxene exsolution: An indicator of high-pressure igneous crystallization of pyroxene-bearing quartz syenite gneiss from the High Peaks region of the Adirondack Mountains

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ABSTRACT

Relict, coarse, high-temperature inverted pigeonite lamellae in host augite and augite lamellae in host inverted pigeonite are locally preserved in metamorphosed igneous rocks from the Adirondack Mountains of New York State. The exsolution history of these pyroxenes consists of (1) crystallization of high-temperature augite or pigeonite, (2) exsolution of coarse "001" lamellae of augite in host pigeonite and pigeonite in host augite, (3) faulting of lamellae and then of host along (100) as lattice parameters change during cooling, (4) inversion of pigeonite to orthopyroxene, and (5) decomposition of the lamellae to produce intergrowths of augite and orthopyroxene along (100) of host grain.

These textures have been observed in pyroxenes that span the full range of compositions found in Adirondack anorthositic and syenitic rocks. An inverted pigeonite from a pyroxene-bearing quartz syenite gneiss collected in the Mount Marcy quadrangle yields a reintegrated composition of $Wo_{15.1}En_{4.2}Fs_{80.7}$ indicating that igneous crystallization of this rock took place at pressures greater than or equal to approximately 9 kbar.

INTRODUCTION

This paper describes pyroxene exsolution textures found in metamorphosed igneous rocks from the Adirondack Mountains of New York State. These exsolution textures are petrologically significant in that they allow one to "see through" the effects of regional metamorphism and to study the igneous history of the rocks that contain them. Pyroxenes described in this report were found in rocks that range in composition from gabbroic anorthosite to pyroxene-bearing quartz syenite gneiss and were collected during our geologic mapping of the Mount Marcy and Santanoni quadrangles in the High Peaks region of the Adirondacks. Sample locations are shown on Figure 1, and sample descriptions are given in Appendix 1.

The Marcy anorthosite massif crops out in a roughly heart-shaped pattern and covers approximately 3000 km² (Fig. 1). It has generally been characterized as consisting of a core of anorthosite surrounded by gabbroic anorthosite (Buddington, 1939, 1969; Davis, 1971). Mapping by Ollila (1984), however, has shown that there are significant amounts of gabbroic anorthosite within the core regions of the massif. Core rocks are characterized by igneous textures. Subophitic gabbroic anorthosites and gabbros in which garnet coronas around mafic minerals are the only evidence of regional metamorphism are relatively common. Gabbroic anorthosite gneiss, characterized by plagioclase augen in a granoblastic matrix of plagioclase, pyroxene, hornblende, and garnet, occurs at the margins of the massif and in localized shear zones within the core of the massif. Syenite gneisses typically overlie the gabbroic anorthosite gneiss found at the margins of the anorthosite massif.

Valley and O'Neil (1982) and Valley (1985) presented evidence that anorthosite in the Adirondacks was intruded at relatively shallow levels (<10 km) and then later underwent granulite-facies metamorphism. This was a significant finding in that it was the first actual evidence that Adirondack anorthosite was not intruded under pressure-temperature conditions similar to those that occurred during regional metamorphism. This finding gave support to the suggestion, made on the basis of analogy with Labrador anorthosite massifs, that anorthosite in the Adirondacks may have intruded under anorogenic rather than synorogenic conditions (Berg, 1977; Emslie, 1978). Evidence presented in this paper suggests, however, that pyroxene-bearing quartz syenites closely associated with and commonly thought to be coeval with the Adirondack anorthosite were intruded at depths greater than 10 km and perhaps as great as 30 km. The most important evidence leading to this conclusion is igneous exsolution textures in Fe-rich pyroxenes from quartz syenites. Low-Ca pyroxenes that exhibit these textures are sufficiently Fe-rich that they only could have crystallized at high pressures. In order to develop this argument, it is first necessary to briefly describe exsolution in pyroxenes.

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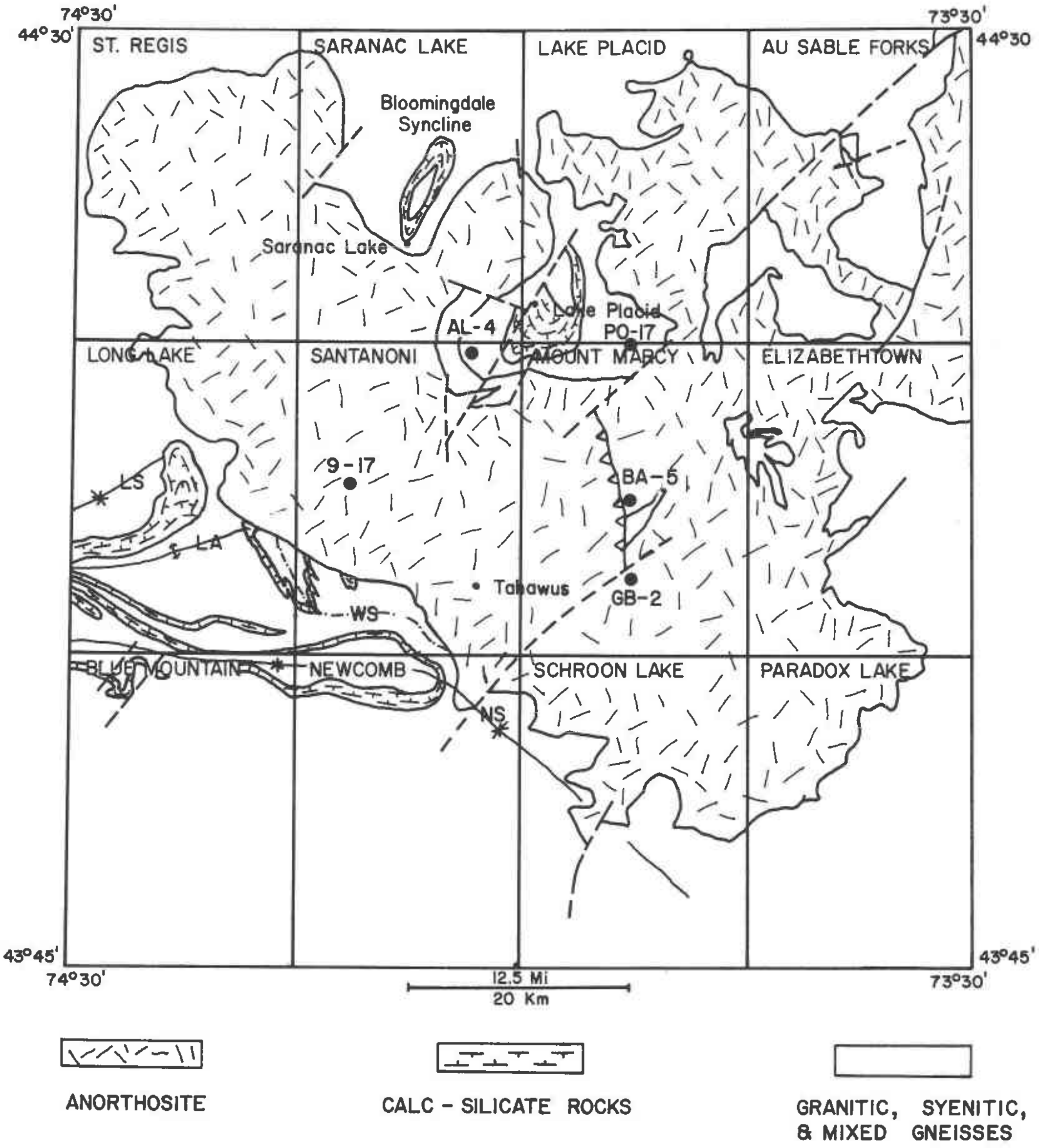

Fig. 1. Generalized geologic map of the Mount Marcy anorthosite massif. Locations for samples 9-17, AL-4, BA-5, GB-2, and PO-17 are indicated on the map.

Pyroxene exsolution

Optimal phase boundary theory was used by Robinson et al. (1971, 1977), Robinson (1980), and Jaffe et al. (1975) to explain why pigeonite lamellae in an augite host and augite lamellae in a pigeonite host are oriented along nonrational planes. The theory states that monoclinic pyroxenes with identical *b* dimensions and differing *a, c,* and β will have two planes of exact dimensional fit. One plane, "001," is close to (001), its orientation being controlled by the difference between the *a* dimensions of the host and lamellae pyroxenes. Another plane, "100," lies close to (100) and is controlled by the difference between the *c* dimensions of the pyroxenes. Since the lattice parameters are functions of pressure, temperature, and chemical composition, the orientation of the best-fit planes is also a function of these variables. The rapid expansion of pigeonite as it goes through the $P2_1/c \rightleftharpoons C2/c$ reversible, nonquenchable transition is of particular importance in interpreting exsolution temperatures. At temperatures above the stability of $P2_1/c$ pigeonite, *a* and *c* of pigeonite are greater than *a* and *c* of augite. At temperatures where $P2_1/c$ pigeonite is stable, the reverse is true. Because of these relationships, high-temperature lamellae of pigeonite in host augite or augite lamellae in host pigeonite orient in obtuse angle β [$c \wedge$ "001" $< c \wedge (001)$]; whereas low-temperature lamellae orient in acute angle β (Fig. 2). High-temperature lamellae are much coarser (approximately 10–100 μm thick) and spaced farther apart than lamellae formed at lower temperatures, which are less than 1 μm thick. Examples of high-temperature exsolution in low-Ca pyroxenes (inverted pigeonite) are relatively common in plutonic igneous rocks and have been described from many localities. This type of exsolution was originally described by Hess (1941, 1960) and has been described in Adirondack rocks by Davis (1971), Ashwal (1982), and Jaffe et al. (1983). Robinson et al. (1977) described high-temperature (~1000 °C) exsolution in host augites from the Bushveld complex in South Africa and the Nain complex in Labrador, and more recently Livi (1987) has described similar exsolution features in pyroxenes from the Laramie anorthosite massif. Before the work of Ollila et al. (1983, 1984), this type of exsolution had not been recognized in the Adirondacks.

In contrast to the exsolution textures visible in monoclinic pyroxenes, exsolution between orthorhombic and monoclinic pyroxenes is much simpler. The only plane that is at all similar between orthopyroxene and clinopyroxene is (100), and lamellae of clinopyroxene in orthopyroxene host or orthopyroxene in clinopyroxene host orient along this plane. As pointed out by Robinson (1980), this type of exsolution is common in metamorphic pyroxenes and in magnesian igneous pyroxenes that crystallized at temperatures below the stability of pigeonite. This type of exsolution also occurs during the late stages of exsolution of igneous pyroxenes.

Exsolution textures in Adirondack rocks are complicated by the fact that igneous rocks have been affected by a regional metamorphism. This metamorphism has resulted in complex exsolution textures that have been poorly understood. In a few locations, however, igneous rocks were only slightly deformed during regional metamorphism, and pyroxenes in rocks from these localities retain recognizable high-temperature exsolution textures that have proved to be the key in unraveling the exsolution history of Adirondack pyroxenes.

Figure 2 is a schematic diagram showing a model for the exsolution history of metamorphosed igneous augite. Stages 1 through 3 are based on descriptions of unmetamorphosed igneous pyroxenes (Robinson et al., 1977; Robinson, 1980). Stages 4 through 6 are based on observations of pyroxenes from Adirondack rocks. The diagram is applicable to both augite and pigeonite hosts, but inverted pigeonite that retains coarse "001" augite lamellae is much more common than host augite with relict, high-temperature "001" inverted pigeonite lamellae. Figures 3 through 5 are photomicrographs of grains that illustrate the exsolution processes outlined in Figure 2.

Relict, high-temperature exsolution lamellae in host augite were found initially in a coarse-grained gabbroic anorthosite from the central part of the Santanoni quadrangle (sample 9-17, Fig. 3). This rock is subophitic with both augite and inverted pigeonite interstitial to plagioclase. Subsequently, similar exsolution textures were found in rocks from the central part of the Mount Marcy quadrangle (GB-2 and BA-5, Figs. 4 and 5). These rocks are weakly foliated and consist of medium- to fine-grained granoblastic aggregates of garnet, pyroxene, and feldspar, but also contain coarser (>2 mm) pyroxene grains that retain relict igneous exsolution textures. Augite from sample 9-17 shows textures equivalent to stage 4 in Figure 2. Augite in samples BA-5 and GB-2 show textures intermediate between stages 4 and 5 of Figure 2. It should be emphasized that these sorts of exsolution textures are quite rare. Medium- to coarse-grained augite in metamorphosed igneous rocks from the Adirondacks most commonly shows exsolution textures corresponding to stage 6 of Figure 2. Augite in gabbroic anorthosite gneiss typically occurs in granoblastic aggregates and only contains fine, low-temperature "001" and "100" pigeonite lamellae such as illustrated between the coarser lamellae in part 6 of Figure 2.

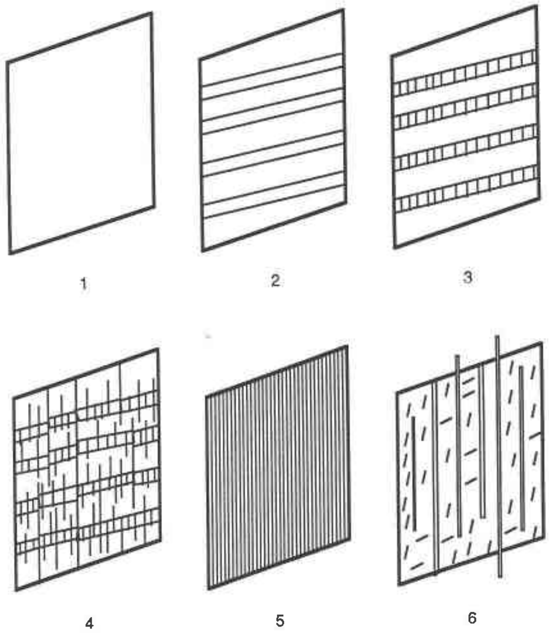

Fig. 2. A model based on observations of pyroxene textures for the exsolution history of igneous augite in the Adirondacks. The sequence is **(1)** crystallization of homogeneous augite; **(2)** exsolution of coarse "001" pigeonite lamellae, which orient in obtuse angle β of the host augite; **(3)** faulting of pigeonite lamellae during cooling (Robinson et al., 1977); **(4)** faulting of the host augite along (100), inversion of pigeonite and decomposition of "001" inverted pigeonite lamellae along (100) of the host augite; **(5)** formation of pyroxene "mesoperthite"—all the orthopyroxene that originally was in "001" lamellae now forms (100) lamellae in host augite; **(6)** orthopyroxene lamellae coarsen, and fine pigeonite lamellae, which orient in acute angle β of host augite, exsolve from host augite. Note that low-temperature (100) orthopyroxene lamellae may exsolve so as to protrude beyond the confines of the augite host.

Inverted pigeonite containing coarse "001" augite exsolution lamellae is common in Adirondack anorthositic rocks (Davis, 1971; Ashwal, 1982; Jaffe et al., 1983). Such is not the case for syenitic rocks. Davis (1971) stated that inverted pigeonite was never observed in syenitic

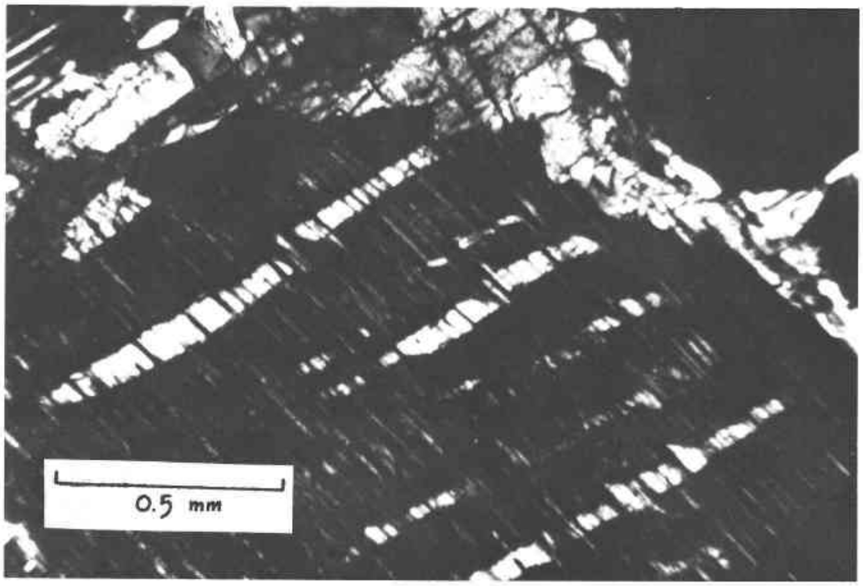

Fig. 3. Photomicrograph of host augite from sample 9-17. Host augite is at extinction, and relict high-temperature pigeonite lamellae now inverted to orthopyroxene are oriented from lower left to upper right. These lamellae are faulted and have partially broken down to produce an intergrowth of augite and orthopyroxene along (100) of host augite (upper left to lower right). This grain corresponds to stage 4 in Fig. 2.

gneisses from the Saint Regis quadrangle. Bohlen and Essene (1978) described inverted pigeonite from Adirondack pyroxene-bearing quartz syenite gneiss, but the pyroxenes they described lacked the distinctive exsolution textures of inverted pigeonite. Bohlen and Essene's conclusions were based on the reintegrated compositions of exsolved grains that contain abundant augite exsolution lamellae oriented along (100) of host orthopyroxene. As can be seen in Figure 2, the assumption that these grains were originally pigeonite is quite reasonable given the effect that regional metamorphism has had on exsolution textures.

There is one potential problem, however, in interpreting grains that only consist of augite and orthopyroxene intergrown along (100). Rietmeijer (1979), in an extensive study of pyroxene exsolution textures in syenitic rocks from the South Rogaland complex in Norway, pointed out that quite similar textures could be produced by both exsolution processes and by epitaxial overgrowths. Some of the criteria Rietmeijer used to distinguish between exsolution lamellae and epitaxial overgrowths included the width of the lamellae, the shape of the lamellae, and the presence or absence of inclusions along host-lamellae boundaries. These kinds of observations cannot be made if all high-temperature lamellae have broken down to produce augite-orthopyroxene "mesoperthite." It is uncertain how prevalent this phenomena is in Adirondack rocks, but this possibility decreases the certainty of igneous crystallization temperatures based on integrated compositions of grains that do not show relict high-temperature-type exsolution lamellae.

Syenitic gneisses that contain pyroxenes with relict, high-temperature exsolution lamellae were found in the northeastern corner of the Santanoni quadrangle and the northern part of the Mount Marcy quadrangle (Fig. 1). Inverted pigeonite with coarse "001" augite exsolution lamellae was found in sample AL-4 (Fig. 6), a medium- to coarse-grained pyroxene-plagioclase-quartz-microperthite gneiss. Compositionally similar, but finer-grained and more strongly foliated rocks located in the southern part of the Santanoni quadrangle do not contain relict high-temperature exsolution lamellae. Exsolution textures are not as well preserved in syenitic rocks from the Mount Marcy quadrangle as in sample AL-4, but sample SC-6 (Fig. 7) contains what are interpreted as epitaxial intergrowths of pigeonite (now inverted) and augite, and both samples PO-17 (Fig. 8) and SC-6 contain orthopyroxene grains with abundant augite exsolution lamellae oriented along (100) of the host orthopyroxene. Samples SC-6 and PO-17 also contain host augite with relict coarse "001" lamellae.

CHEMISTRY

Mineral analyses were obtained on an ETEC Autoprobe at the University of Massachusetts. Microprobe analyses were performed at 15-kV accelerating potential and an aperture current of 0.03 μA. Standards consisted of both synthetic and natural silicate and oxide minerals, and corrections were made following the procedure of Bence and Albee (1968) and using the correction factors of Albee and Ray (1970). Analytical results are listed in Table 1. Reintegrated analyses of exsolved pyroxenes were obtained by a number of techniques. Most reintegrated analyses were obtained by combining microprobe anal-

Fig. 4. Photomicrograph of host augite in sample GB-2. Fine (100) orthopyroxene exsolution lamellae are nearly vertical. Relict high-temperature pigeonite lamellae are horizontal. This grain is intermediate between stages 4 and 5 in Fig. 2. The thick orthopyroxene lamella in the bottom third of the grain is thought to represent an epitaxial overgrowth of pigeonite (now inverted) on the augite grain. Note how the augite host is depleted of orthopyroxene lamellae near the coarse orthopyroxene lamella. In other grains, epitaxial overgrowths such as this one have broken down to produce (100) "mesoperthite."

yses of host and lamellae with relative volumes determined from point counts of photomicrographs. Approximately 1000 points per grain were used for this technique. In one case (BA-5), the microprobe beam was widened to about 20 μm, and approximately 100 analyses were collected on a number of traverses across the grain. In this way a significant proportion of the grain was analyzed. For sample PO-17, mineral analyses of augite and orthopyroxene host determined by Jaffe et al. (1978) were used in conjunction with point-count data from photomicrographs. The assumption that augite and orthopyroxene host and lamellae compositions are similar in this rock was checked at Vassar College by means of energy-dispersive analyses of host and lamellae on a scanning electron microscope equipped with an energy-dispersive analyzer. Use of an SEM provided advantages in that a backscattered-electron image allowed more precise positioning of the electron beam. Lamellae compositions were determined by comparison with host spectra. Results from these analyses are listed in Table 1. Optical reintegration techniques of the grain shown in Figure 8 were evaluated by scanning crack-free areas as large as possible and analyzing for Fe, Mg, Ca, and Si. Results of these analyses are shown in Figure 9. These analyses indicate that the optical reintegration techniques provide very reasonable limits on pigeonite compositions in this rock.

TEMPERATURES AND PRESSURE OF CRYSTALLIZATION

Igneous crystallization temperatures for pyroxenes in anorthositic and syenitic rocks from the Adirondacks have been determined previously by Ashwal (1982) and Bohlen and Essene (1978). As first pointed out by Bohlen and Essene (1978), reintegrated pyroxene temperatures from a variety of metamorphosed igneous rocks from the Adirondacks yield temperatures well above regional metamorphic temperatures. Bohlen et al. (1985) estimated maximum regional metamorphic temperatures to be approximately 800 °C. Figure 10 shows integrated pyroxene compositions from Bohlen and Essene (1978) and this report. Crystallization temperatures range from approximately 1150 °C for gabbroic anorthosite (9-17) to 1100 °C for metagabbro (GB-2) and 950 to 850 °C for syenitic rocks (BA-5, PO-17, P-10). Pyroxene crystallized after plagioclase in anorthositic rocks, so liquidus temperatures must have been somewhat higher than the pyroxene temperatures would indicate.

The depth at which anorthositic rocks crystallized is difficult to determine in the Adirondacks, because regional metamorphism has overprinted any contact aureole assemblages that might have been useful in this respect. Martignole and Schrijver (1971, 1973) and Martignole (1979), however, presented arguments in favor of a deep-seated emplacement of anorthosite-charnockite suites in the Grenville province and the Adirondacks. Martignole and Schrijver's (1971, 1973) and Martignole's (1979) arguments, however, are largely based on garnet-bearing assemblages. Martignole (1979) left open the possibility that the garnet-bearing assemblages reflect metamorphic recrystallization of a shallowly intruded igneous rock, but suggested that the preservation of ophitic textures in mafic charnockites is most easily explained by intrusion during high-grade regional metamorphism. More recently, Martignole (1986) has presented a model that allows for both the shallow emplacement of anorthosite and the deep emplacement of charnockitic rocks.

Valley and O'Neil (1982) concluded, on the basis of O-isotope studies of the wollastonite deposit at Willsboro, New York, that anorthosite was intruded at shallow levels (<10 km) and then was metamorphosed at higher pressures during regional metamorphism. Valley (1985) strengthened this argument with a combined phase-equilibria and O-isotope study of Cascade slide, a monticellite marble locality found in the Mount Marcy quadrangle.

According to shallow-intrusion models, the orthoferrosilite originally described by Jaffe et al. (1978) from

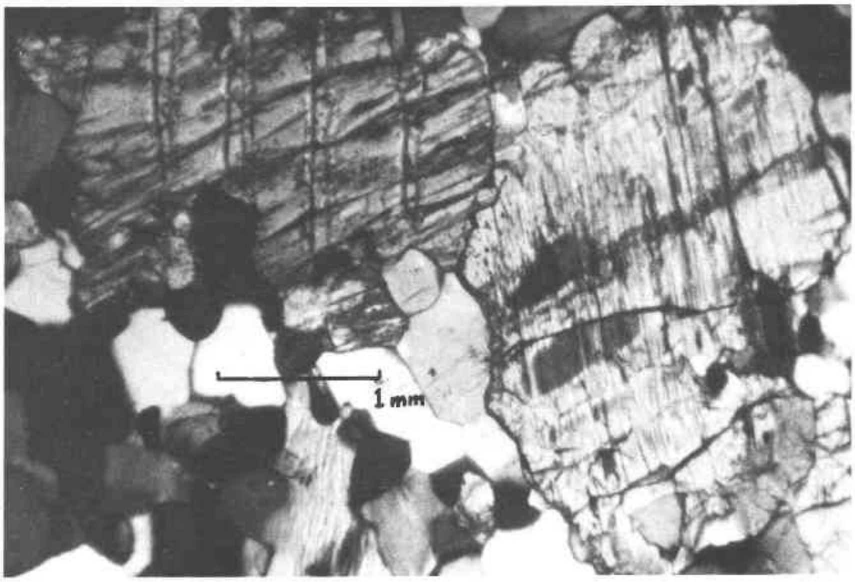

Fig. 5. Coexisting augite (right) and inverted pigeonite (left) from sample BA-5. The thick "001" augite lamellae in the inverted pigeonite and *c* of host augite are nearly vertical. The augite grain is intermediate between stages 4 and 5 of Fig. 2, whereas the inverted pigeonite corresponds to stage 3. This difference in textural development is typical in these rocks. Relict igneous textures are usually better preserved in inverted pigeonite than in host augite.

pyroxene-bearing quartz syenite gneiss in the Mount Marcy quadrangle is indicative only of minimum metamorphic pressures of approximately 8 kbar (Jaffe et al., 1978; Bohlen and Boettcher, 1981). As described above, however, re-examination of some of the specimens collected by Jaffe et al. (1978) has shown that Fe-rich orthopyroxene in these gneisses is, in fact, inverted pigeonite (Figs. 7 and 8). The composition of inverted pigeonite from sample PO-17, when compared to the "forbidden zone" boundaries in the solvi of Lindsley (1983), suggests that igneous crystallization of this rock must have taken place at a minimum of approximately 9 kbar (Fig. 10).

DISCUSSION

Valley (1985) has pointed out that there is a high degree of uncertainty associated with the position of "forbidden zone" boundaries in Lindsley's (1983) phase diagrams when applied to natural pyroxenes that contain nonquadrilateral components and has suggested that PO-17 could have crystallized at pressures as low as 3 kbar. It should be pointed out in this regard, however, that the argument in favor of deep crystallization for Adirondack pyroxene-bearing quartz syenites is not based solely on the composition of sample PO-17. Although sample PO-17 is the most Fe-rich sample yet studied, numerous other samples such as AL-4 and SC-6 show textures indicative of igneous pigeonite and are sufficiently Fe rich to require high-pressure crystallization. Samples P-10, IN-11, and SR-29 from the study of Bohlen and Essene (1978) likewise require crystallization pressures in excess of 3 kbar. These pyroxenes contain low percentages of nonquadrilateral components and are significantly more Fe rich than inverted pigeonites described by Ranson (1986) from the Nain anorthosite massif or by Frost and Lindsley (1981) from the Laramie anorthosite massif. Samples AL-4, SC-6, PO-17, and SR-29 (Bohlen and Essene, 1978) are also more Fe-rich than inverted pigeonites described by Smith (1974) from a portion of the Nain anorthosite massif that crystallized at higher pressure (Berg, 1977) than the area described by Ranson (1986). Ranson (1986) reintegrated pyroxenes in a pyroxene-bearing quartz monzonite from a part of the Nain complex that crystallized at approximately 3 to 4 kbar. This rock contains the assemblage augite + inverted pigeonite + olivine + quartz. Pyroxene compositions from this rock (Fig. 10) are consistent with Lindsley's (1983) "forbidden zone" boundaries and represent the compositions at which low-Ca pyroxene is replaced by olivine + quartz at the pressure (3–4 kbar) and temperature at which this pyroxene-bearing quartz monzonite crystallized. The relatively common occurrence of inverted pigeonite more Fe rich than that found in sample PL-187 (Fig. 10) in Adirondack syenitic rocks indicates crystallization at pressures well in excess of 3 kbar.

If crystallization pressures for syenitic rocks are applicable to anorthosite, then the conclusions presented above conflict with the shallow-intrusion hypothesis of Valley and O'Neil (1982) and with the models of Whitney (1983) and McLelland (1986). Although it is possible, given the uncertainties of metamorphic geothermometry and of phase relationships for natural pyroxenes, that Fe-rich pigeonite could have been produced during regional metamorphism, this is not thought likely. In order to evaluate this possibility, phase relations in the pyroxene quadrilateral have to be examined.

Figure 11 is a schematic representation—based on natural assemblages described by Smith (1974) and the ex-

Fig. 6. Inverted pigeonite from sample AL-4. Coarse "001" augite lamellae are oriented diagonally from lower left to upper right and *c* of host orthopyroxene is vertical. This grain illustrates the pigeonite equivalent of stage 4 in Fig. 2.

Fig. 7. Photomicrograph of intergrown augite (top) and orthopyroxene (bottom) from sample SC-6. The coarse augite lamella in orthopyroxene is interpreted as an epitaxial intergrowth of augite and pigeonite (now inverted) and suggests that pigeonite was the initial low-Ca pyroxene to crystallize in this rock.

perimental work of Huebner and Turnock (1980) and Turnock and Lindsley (1981)—of the phase relations between olivine (ol), quartz (q), orthopyroxene (opx), and clinopyroxene (cpx) at three different temperatures ($T1 < T2 < T3$). As can be seen in this diagram, Ca clearly increases the stability of orthopyroxene over olivine for the assemblage opx + ol + q. Ca, however, has a different effect on the assemblage opx + cpx + ol + q. In this assemblage, orthopyroxene is saturated with Ca, and any increase in Ca content of orthopyroxene or pigeonite reflects higher temperatures. These higher temperatures in turn favor the stability of olivine + quartz over orthopyroxene or pigeonite. These effects are evident in the solvi of Lindsley (1983) in which the "forbidden zone" for pyroxenes expands to more magnesian compositions as the Ca content of either orthopyroxene or pigeonite increases. This can be seen in Figure 10, which shows pyroxene compositions plotted on the 10-kbar solvus of Lindsley (1983).

The shallow-intrusion model as stated by Whitney (1983) requires that pyroxene-bearing quartz syenite gneiss be metamorphosed fayalite-rich olivine granite. If one uses the 10-km maximum depth of intrusion suggested by Valley and O'Neil (1982) for these rocks, then olivine should have replaced orthopyroxene in rocks with 100Fe/(Fe + Mg) ratios of >75 (Bohlen and Boettcher, 1981) and should have replaced pigeonite with 100Fe/(Fe + Mg) ratios of >78 at 825 °C (Lindsley and Grover, 1980). At higher temperatures, olivine should replace pigeonite at more magnesian compositions.

According to the shallow-intrusion model, low-Ca pyroxenes with 100Fe/(Fe + Mg) ratios of >78 should record metamorphic rather than igneous temperatures. Bohlen and Essene (1978) reintegrated compositions of exsolved, Fe-rich, low-Ca pyroxenes in Adirondack syenitic gneisses and concluded that these rocks had igneous precursors that crystallized between 900 and 1000 °C (Fig. 10). Any hypothesis of shallow intrusion, however, requires that these rocks were originally olivine-bearing granites and would require that the temperatures determined by Bohlen and Essene are metamorphic.

The requirement that metamorphic temperatures be

TABLE 1. Electron-microprobe analyses of pyroxenes and formulae based on six oxygens

	9-17						BA-5						AL-4
Sample:	Cpx H	Cpx L	Opx H	Opx L	Aug I	Pig I	Cpx H	Cpx L	Opx H	Opx L	Aug I	Pig I	Cpx H
SiO_2	50.38	50.39	50.05	49.26	50.01	50.15	50.80	50.82	49.10	48.57	50.03	49.44	48.28
Al_2O_3	2.43	2.86	1.90	1.65	2.18	2.20	1.91	1.87	0.73	0.53	1.43	0.95	1.23
TiO_2	0.15	0.23	0.07	0.03	0.11	0.12	0.21	0.24	0.09	0.12	0.18	0.12	0.23
Cr_2O_3													0.00
MgO	11.63	11.21	16.23	16.46	13.20	14.70	0.21	0.24	0.09	0.12	0.18	0.12	3.21
ZnO													0.09
FeO*	12.47	13.05	31.56	31.40	18.64	25.91	17.09	16.75	38.01	37.76	24.24	33.84	28.01
MnO	0.27	0.22	0.54	0.57	0.37	0.44	0.20	0.18	0.45	0.45	0.29	0.40	0.58
CaO	21.65	21.15	0.39	0.60	14.79	6.72	20.40	20.79	0.52	0.62	13.56	4.49	18.79
BaO													
Na_2O	0.58	0.53	0.04	0.03	0.40	0.19	1.01	1.05	0.01	0.06	0.68	0.21	0.68
Total	99.56	99.66	100.78	100.00	99.70	100.43	100.44	100.61	100.40	99.97	100.28	100.43	101.09
Si	1.925	1.923	1.937	1.926	1.925	1.932	1.957	1.954	1.971	1.961	1.958	1.968	1.949
Al	0.075	0.077	0.063	0.074	0.075	0.068	0.043	0.046	0.029	0.025	0.042	0.032	0.051
Fe^{3+}													
Total	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000
Al	0.034	0.053	0.023	0.002	0.024	0.032	0.044	0.039	0.005	0.000	0.024	0.012	0.008
Ti	0.004	0.007	0.002	0.001	0.003	0.003	0.006	0.007	0.003	0.004	0.005	0.004	0.008
Cr													0.000
Fe^{3+}**	0.075	0.050	0.039	0.072	0.074	0.042	0.062	0.072	0.019	0.023	0.058	0.029	0.083
Mg	0.662	0.638	0.936	0.960	0.757	0.844	0.507	0.511	0.687	0.714	0.576	0.651	0.193
Zn													0.003
Fe^{2+}	0.323	0.367	0.982	0.955	0.526	0.793	0.488	0.467	1.256	1.252	0.735	1.097	0.862
Mn	0.009	0.007	0.018	0.019	0.012	0.014	0.007	0.006	0.015	0.015	0.010	0.013	0.020
Ca	0.886	0.865	0.016	0.025	0.610	0.277	0.842	0.857	0.022	0.027	0.569	0.191	0.813
Ba													
Na	0.043	0.039	0.003	0.002	0.030	0.014	0.075	0.078	0.001	0.005	0.052	0.016	0.053
Total	2.036	2.026	2.019	2.036	2.036	2.019	2.031	2.037	2.008	2.040	2.029	2.013	2.042
Wo**	43.1	42.0	0.9	1.3	28.6	15.8	43.7	44.8	1.1	1.4	29.5	12.1	41.4
En	38.2	36.8	48.4	49.4	42.2	43.4	28.7	28.8	35.0	35.8	31.0	32.7	10.7
Fs	18.7	21.2	50.8	49.2	29.3	40.8	27.6	26.4	63.9	62.8	39.6	55.1	47.9

Note: H = host, L = lamellae, I = reintegrated bulk composition.

* Total Fe reported as FeO.

** Fe^{3+} and Wo, En, and Fs calculated according to the method of Lindsley (1983).

† Pigeonite compositions are based on optical reintegration of exsolved grains and host compositions published by Jaffe et al. (1978). Lamellae compositions were determined by means of energy-dispersive analysis on a scanning electron microscope. These analyses are not as accurate as the wavelength-dispersive analyses published by Jaffe et al. but do establish that there is no significant difference between host and lamellae compositions.

greater than 900 °C for large areas of the Adirondacks leads to a number of inconsistencies. One problem is with the pyroxenes themselves. If metamorphic temperatures were greater than 900 °C, pyroxenes with 100Fe/(Fe + Mg) ratios of >92 should be hypersolvus (Lindsley, 1983). This is clearly not the case in Fe-rich rocks from the Mount Marcy quadrangle (Fig. 10). A second problem is that numerous mineral assemblages and geothermometers that limit metamorphic temperatures to less than approximately 800 °C (Bohlen et al., 1985) are common in the areas where a 900 °C metamorphic temperature is required by the shallow intrusion model. A third problem is that integrated pyroxene compositions in these rocks indicate a range of temperatures. Although this is relatively easily explained by igneous processes, it is much more difficult to explain if the pyroxenes are the product of regional metamorphism. A fourth problem is that there is no evidence of olivine pseudomorphs in any of the rocks studied so far. Similar orthoferrosilite-bearing rocks from the Lofoten Islands of Norway retain clear-cut evidence that the orthoferrosilite replaced fayalite-rich olivine (Ormaasen, 1977). There is no textural evidence that this has taken place in the Adirondacks.

Another argument against a metamorphic origin for the Fe-rich pigeonite in these rocks is the nature of the exsolution textures. Pyroxenes from similar rocks in the Nain anorthosite massif (Ranson, 1981; Huntington, 1980) and the Laramie massif (Frost and Lindsley, 1981; Livi, 1987) and pyroxenes from many other plutonic suites (Robinson et al., 1977) show exsolution textures similar to the relict textures observed in the Adirondacks. The difference between Adirondack pyroxenes and unmetamorphosed plutonic pyroxenes is in the breakdown of high-temperature pigeonite or augite lamellae (stage 3, Fig. 2) to intergrowths of augite and orthopyroxene (stages 5 and 6, Fig. 2). Although it is difficult to assess the relative importance of thermal-induced versus stress-induced changes, the breakdown is most easily explained as resulting from deformation associated with regional metamorphism because of the correlation between rock fabric and degree of preservation of relict lamellae. Rocks with igneous textures or weak metamorphic fabrics locally contain pyroxenes with relict igneous exsolution textures, whereas pyroxenes from granoblastic rocks only contain low-temperature, fine exsolution lamellae. Exsolution textures in relatively undeformed rocks from the

TABLE 1—*Continued*

AL-4	GB-2						PO-17†						
Opx H	Cpx H	Cpx L	Opx H	Opx L	Aug I	Pig I	Cpx H	Cpx L	Opx H	Opx L	Aug I	Pig I	Pig I
46.74	50.36	50.51	48.68	49.18	49.92	49.31	48.69	49.72	45.50	44.67	47.86	45.97	46.18
0.25	2.04	2.06	0.92	0.86	1.91	1.31	0.65	0.91	0.36	0.36	0.83	0.45	0.50
0.09	0.27	0.26	0.09	0.06	0.18	0.15	0.06	0.015	0.11	0.12	0.13	0.11	0.12
0.00							0.06	0.06	0.06	0.02	0.06	0.06	0.06
3.95	9.25	9.36	12.06	12.49	10.15	11.13	1.17	1.21	1.36	1.03	1.22	1.33	1.32
0.24							0.19	0.19	0.37	0.41	0.24	0.34	0.33
47.30	15.87	16.03	36.85	36.63	22.05	29.71	29.18	29.63	49.81	49.92	34.52	46.78	45.44
0.62	0.17	0.18	0.50	0.47	0.32	0.39	0.43	0.30	1.10	1.38	0.60	1.00	0.96
0.69	20.64	20.11	0.87	0.44	15.18	7.47	19.07	19.53	0.84	0.66	14.35	3.52	4.70
							0.00		0.06				
0.00	1.10	1.13	0.20	0.09	0.68	0.51	0.73	0.71	0.03	0.03	0.54	0.13	0.18
99.88	99.70	99.64	100.17	100.22	100.39	99.98	100.65	102.41	99.60	98.60	100.37	99.74	99.84
1.990	1.948	1.953	1.954	1.965	1.942	1.954	1.984	1.990	1.983	1.975	1.984	1.983	1.983
0.010	0.052	0.047	0.044	0.035	0.058	0.046	0.016	0.010	0.017	0.019	0.016	0.017	0.017
			0.002							0.006			
2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000
0.002	0.041	0.046	0.000	0.005	0.029	0.015	0.032	0.033	0.001	0.000	0.025	0.006	0.008
0.002	0.008	0.008	0.003	0.002	0.005	0.004	0.004	0.005	0.004	0.004	0.004	0.004	0.004
0.000							0.002	0.002	0.002	0.001	0.002	0.002	0.002
0.002	0.078	0.071	0.052	0.033	0.070	0.061	0.029	0.022	0.009	0.007	0.025	0.012	0.014
0.251	0.533	0.539	0.722	0.744	0.589	0.657	0.071	0.072	0.088	0.068	0.075	0.086	0.084
0.008							0.006	0.006	0.012	0.013	0.007	0.011	0.010
1.682	0.435	0.448	1.183	1.191	0.648	0.923	0.965	0.970	1.806	1.833	1.172	1.676	1.618
0.022	0.006	0.006	0.017	0.016	0.011	0.013	0.015	0.010	0.041	0.052	0.021	0.037	0.035
0.031	0.855	0.833	0.016	0.019	0.633	0.317	0.833	0.830	0.039	0.045	0.637	0.163	0.216
									0.001		0.000	0.001	0.001
0.000	0.083	0.085	0.016	0.007	0.051	0.039	0.057	0.055	0.003	0.003	0.043	0.011	0.015
2.001	2.039	2.036	2.032	2.017	2.036	2.029	2.014	2.012	2.006	2.013	2.011	2.009	2.007
1.6	44.9	43.6	1.9	1.0	31.8	21.1	42.8	42.9	2.0	1.7	32.7	12.0	15.1
12.8	30.4	30.8	37.1	38.1	32.5	32.8	3.9	4.0	4.6	3.5	4.1	4.3	4.2
85.6	24.8	25.6	60.9	60.9	35.7	46.1	53.3	53.2	93.4	94.8	63.2	83.7	80.7

Santanoni quadrangle most closely resemble exsolution textures in pyroxenes from unmetamorphosed igneous rocks.

Regardless of their 100Fe/(Fe + Mg) ratios, all pyroxenes that contain relict high-temperature lamellae have partially broken down to intergrowths of augite and orthopyroxene oriented along (100) of the host grain. This breakdown suggests that regional metamorphism took place at temperatures below the stability of pigeonite. This conclusion is entirely consistent with metamorphic geothermometry (Bohlen et al., 1985) and with pyroxene phase relations (Lindsley, 1983).

If initial exsolution and inversion took place during cooling of these rocks from igneous conditions, as is consistent with the histories of pyroxenes from both the Nain and Laramie anorthosite massifs (Huntington, 1980; Frost and Lindsley, 1981; Ranson, 1986; Livi, 1987), then orthopyroxene as well as pigeonite equilibria apply to the igneous part of these rocks' histories. The orthopyroxene host in sample AL-4 (Fig. 6 and Table 1) requires a minimum pressure in excess of 4.6 kbar if inversion took place at approximately 800 °C, according to the geobarometer of Bohlen and Boettcher (1981). An ideal ionic model as described by Bohlen et al. (1981) was used to correct for components other than Mg and Mn. The minimum pressure of 4.6 kbar is a conservative estimate since it assumes that nonquadrilateral components are completely partitioned into orthopyroxene, that inversion took place at a temperature 25 °C below the minimum stability of pigeonite (Lindsley, 1983), and that the orthopyroxene contained 3% $CaSiO_3$ at 800 °C. Bohlen and Boettcher have suggested that this is the maximum $CaSiO_3$ component for Fe-rich orthopyroxene at temperatures below approximately 850 °C. A minimum crystallization pressure of approximately 6.3 kbar for sample AL-4 is a much more reasonable estimate according to Lindsley's (1983) forbidden-zone boundaries, but even if one uses the conservative pressure estimate based on orthopyroxene, the minimum pressure required for the crystallization of AL-4 is well in excess of the 3-kbar maximum suggested by Valley and O'Neil (1982) for anorthositic rocks at Willsboro, New York. Likewise, the metamorphic pressure determined for sample PO-17 (approximately 8 kbar) by Jaffe et al. (1978) and Bohlen and Boettcher (1981) also represents a minimum igneous pressure if inverted pigeonite in this rock inverted as it cooled from igneous conditions.

The association of anorthosites with granitic and syenitic rocks is a worldwide phenomenon, and although geochemical evidence has ruled out a comagmatic origin

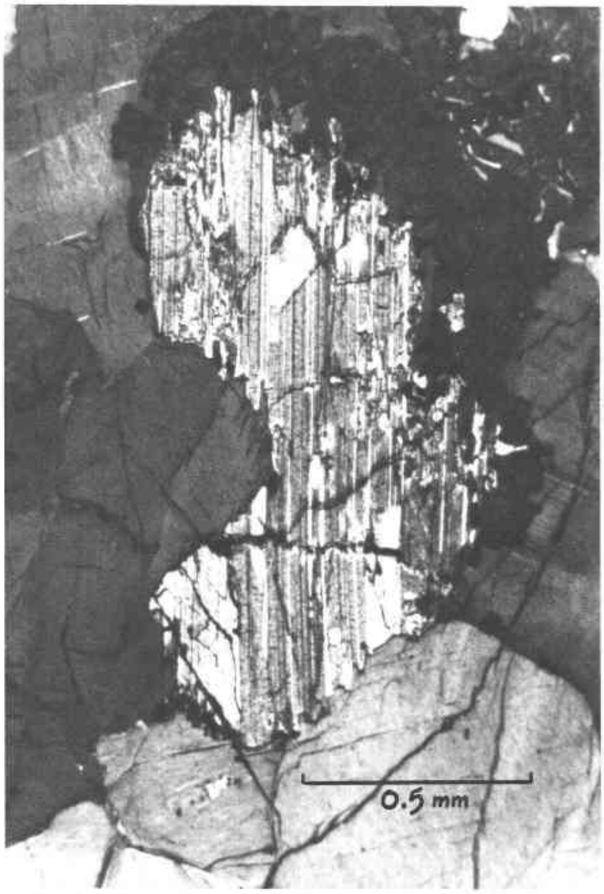

Fig. 8. Photomicrograph of inverted pigeonite from sample PO-17. Orthopyroxene host is at partial extinction, and (100) augite lamellae are vertical. This grain is the pigeonite equivalent of stage 6 in Fig. 2. No trace of original high-temperature lamellae are visible, and augite lamellae have coalesced and coarsened. This grain was chosen for optical reintegration because it is not in contact with an augite grain. Bulk compositions were determined both including and not including the larger areas of augite. Both compositions are listed in Table 1 and are within the pigeonite range. Optical reintegration values were checked by means of energy-dispersive analysis on a scanning electron microscope. Four areas that were as large as possible while avoiding cracks were scanned. Results are plotted in Fig. 9.

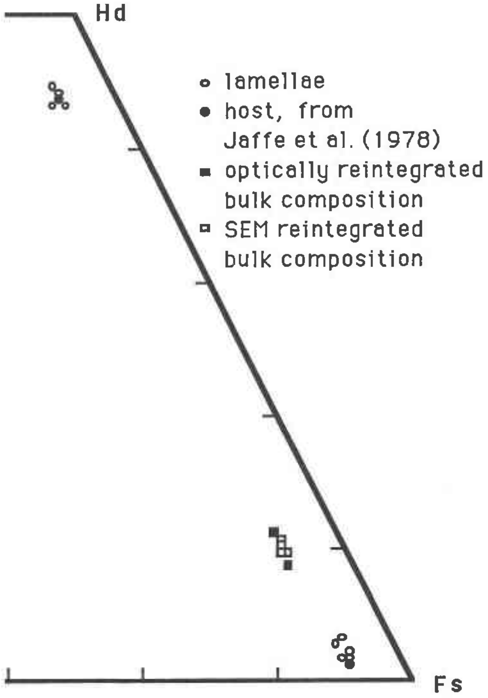

Fig. 9. Energy-dispersive analyses of exsolution lamellae and inverted pigeonite in sample PO-17 plotted on the Fe-rich part of the pyroxene quadrilateral. Analyses were obtained by use of a Kevex quantitative match routine using host compositions from Jaffe et al. (1978) as standards. Pyroxenes were analyzed for Ca, Mg, Fe, and Si and are plotted as mol% Wo [Ca/(Ca + Mg + Fe)], Fs [Fe/(Ca + Mg + Fe)], and En [Mg/(Ca + Mg + Fe)].

for these rocks, it is commonly thought that they are cogenetic or at least roughly coeval (Emslie, 1978; Morse, 1981; Philpotts, 1981; McLelland, 1986). Furthermore, it has commonly been assumed in the Adirondacks that the gradational contacts between anorthositic and syenitic rocks (de Waard and Romey, 1969; Davis, 1971; Jaffe et al., 1983) imply that these rocks were magmas at the same time and that mixing occurred between the two rock types. This sort of relationship has been documented for the Nain anorthosite massif by Wiebe (1980), and if such is the case for the Adirondacks, then crystallization pressures for pyroxene-bearing quartz syenites are applicable to anorthosite. Given the discrepancy, however, between the conclusions presented here and the conclusions of Valley and O'Neil (1982) and Valley (1985), the assumption that pyroxene-bearing quartz syenites intruded at the same time as anorthosite may have to be re-examined in more detail.

There is some isotopic evidence to support the contention that pyroxene-bearing quartz syenites were intruded at a different time than anorthosite. Silver (1969), on the basis of a U-Pb study of zircons from Adirondack syenitic rocks, concluded that these rocks had an igneous crystallization age of approximately 1130 Ma. In contrast, Ashwal and Wooden (1983) concluded, on the basis of a Nd-Sm study, that anorthosite in the Mount Marcy massif in the Adirondacks has a crystallization age of approximately 1288 Ma. Critical evaluation of these ages, based upon different decay systems, must await more data, but it at least appears possible that anorthositic and syenitic rocks were intruded at different times and under different conditions. A better understanding of the relationship between anorthositic and syenitic rocks awaits more detailed isotopic studies, a more complete understanding of the wollastonite deposit at Willsboro, New York, and an understanding of the relationship between the anorthosite found at Willsboro and that found in the Marcy massif. If, however, conclusions regarding shallow emplacement of anorthosite and the deep emplacement of syenitic rocks are both correct, then a model such as

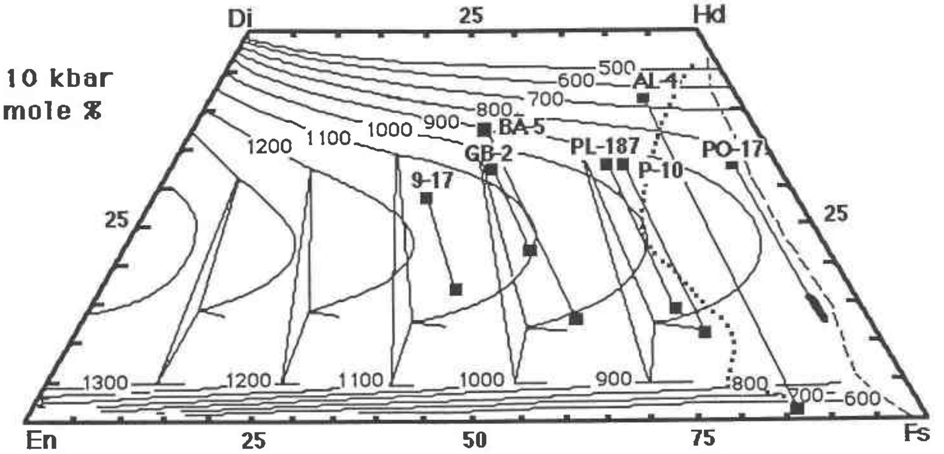

Fig. 10. Compositions of pyroxenes from anorthositic and syenitic rocks from the Adirondacks and Labrador (PL-187) plotted on the 10-kbar solvus of Lindsley (1983). P-10 is from Bohlen and Essene (1978) and PL-187 is from Ranson (1986). The dashed line is the 10-kbar boundary of the "forbidden zone" (Lindsley, 1983). Pyroxene compositions to the right of this line are metastable with respect to the assemblage augite + olivine + quartz. The 5-kbar "forbidden-zone" boundary (dotted line) is also shown. Reintegrated compositions of exsolved grains are plotted except for sample AL-4. Alteration made reintegration of inverted pigeonite impossible in sample AL-4; however, analyses of host augite and orthopyroxene were obtained. Exsolution textures (Fig. 8) clearly indicate that this sample contains inverted pigeonite. Sample PO-17 suggests that crystallization of these rocks took place at pressures greater than or equal to approximately 9 kbar.

presented by Martignole (1986) in which anorthosite intrusion is followed almost immediately by crustal thickening and in which syenites are intruded into thickened crust provides at least one solution to this problem.

CONCLUSIONS

The complex exsolution textures described above are interpreted to result from the combined effects of cooling from igneous conditions and regional metamorphism. Adirondack pyroxenes differ from typical igneous pyroxenes in that relict coarse exsolution lamellae have broken down to intergrowths of augite and orthopyroxene oriented along (100) of the host grain. Reintegrated compositions of magnesian to moderately Fe-rich pyroxenes (samples 9-17, GB-2, and BA-5) showing relict igneous exsolution textures record temperatures well above regional metamorphic temperatures and confirm that these are igneous rather than metamorphic pyroxenes. We interpret the mobilization of exsolution lamellae to be caused by regional metamorphism at temperatures below

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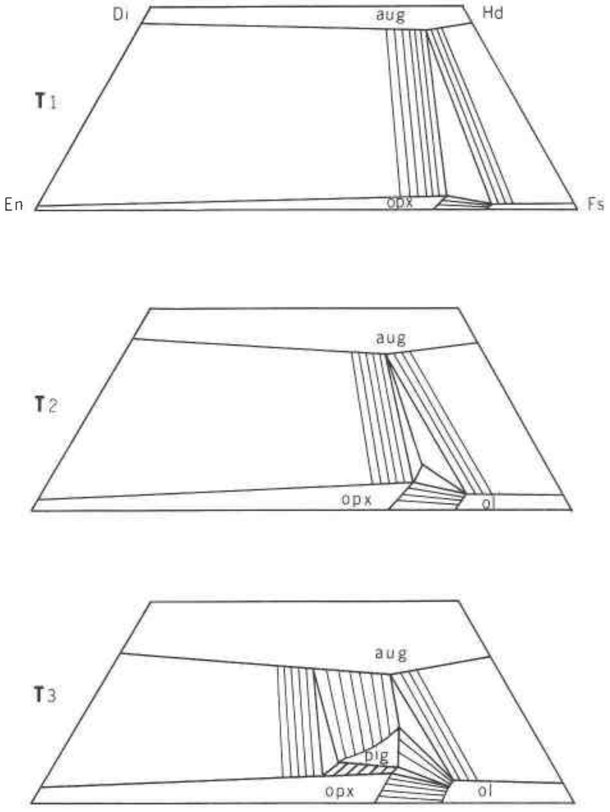

Fig. 11. Schematic phase relations among pyroxenes, and olivine + quartz (ol) at different temperatures ($T1 < T2 < T3$) and constant pressure. The three-phase triangle opx-aug-ol ($T1$) moves to the left, and the Ca content of opx increases as temperature increases. At $T2$, pigeonite becomes stable and forms via the reaction augite + orthopyroxene + olivine + quartz = pigeonite. As temperature further increases, the three-phase triangle pig-aug-ol moves to the left, and the gap in Ca content between pigeonite and augite narrows ($T3$). These trends are evident in the boundaries of the "forbidden zones" in the solvi of Lindsley (1983) and Fig. 10 of this paper. Increased Ca content stabilizes both orthopyroxene and pigeonite relative to olivine + quartz when the assemblage is not saturated with respect to augite. If the assemblage is saturated with augite, then increased Ca content of either orthopyroxene or pigeonite reflects an increase in temperature that in turn stabilizes olivine + quartz relative to low-Ca pyroxene.

those necessary to stabilize pigeonite during the Grenvillian metamorphic event. This conclusion is based on the differences between Adirondack pyroxenes and typical igneous pyroxenes, the ubiquitous occurrence of (100) intergrowths of augite and orthopyroxene regardless of the Fe/Mg ratio of the pyroxene, and the correlation between the degree of preservation of relict igneous exsolution textures and metamorphic fabric in the host rock.

Fe-rich inverted pigeonite from sample AL-4 contains coarse "001" augite lamellae that are most reasonably interpreted as resulting from cooling from igneous conditions, and these lamellae have partially broken down to intergrowths of augite and orthopyroxene. Low-Ca pyroxene from sample PO-17 has a bulk composition that clearly indicates original crystallization as pigeonite even though low-Ca pyroxenes in this rock now consist of intergrowths of orthopyroxene and augite with augite lamellae oriented along (100) of the host. The compositions of these pyroxenes, as well as pyroxenes described by Bohlen and Essene (1978), require crystallization pressures well in excess of 3 kbar, and the composition of low-Ca pyroxene in sample PO-17 (Fig. 10 and Table 1) suggests a minimum igneous crystallization pressure of greater than approximately 9 kbar. Fe-rich igneous pyroxenes indicate that models requiring shallow emplacement of Adirondack anorthosite cannot be applied to the syenitic rocks that surround the Marcy anorthosite massif.

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APPENDIX 1. SAMPLE DESCRIPTIONS

9-17. Coarse-grained subophitic gabbroic anorthosite consisting of plagioclase (An_{46}) 80%, augite 16%, inverted pigeonite 1%, and ilmenite 3%. Sample was collected near the summit of Donaldson Mountain, Santanoni quadrangle.

AL-4. Medium- to coarse-grained, pyroxene-plagioclase-quartz-microperthite gneiss consisting of quartz 16%, microperthite 61%, oligoclase 15%, augite 2.5%, inverted pigeonite 1.4%, hornblende 3.0%, garnet 0.3%, opaques 0.3%, apatite 0.4%, and zircon 0.1%. Sample was collected in the northeastern corner of the Santanoni quadrangle on the top of a hill 1 km south of Cameras Pond.

BA-5. Fine-grained pyroxene monzonite granulite consisting of microperthite 19%, plagioclase 25%, inverted pigeonite 13%, augite 14%, garnet 20%, apatite 4%, and opaques 5%. Medium to coarse grains of plagioclase and pyroxene, which retain relict igneous textures, are enclosed in a fine-grained granoblastic matrix consisting of microperthite, plagioclase, and garnet. The sample was collected on Basin Mountain in the Mount Marcy quadrangle.

GB-2. Medium- to fine-grained gabbro granulite consisting of plagioclase (An_{26} to An_{35}) 33%, orthopyroxene (includes inverted pigeonite) 15%, augite 19%, garnet 16%, ilmenite 11%, magnetite 2%, and apatite 4%. Pyroxenes occur both as granoblastic, fine-grained aggregates and as coarser (up to 2 mm) grains that retain relict igneous exsolution textures. The sample was collected in Guideboard Brook in the Mount Marcy quadrangle.