

## Fluorine distribution in the hydrous silicate minerals of the Franklin Marble, Orange County, New York

LANCE E. KEARNS, LUCILLE E. KITE<sup>1</sup>

*Department of Geology, James Madison University  
Harrisonburg, Virginia 22807*

PETER B. LEAVENS

*Department of Geology, University of Delaware  
Newark, Delaware 19711*

AND JOSEPH A. NELEN

*Department of Mineral Sciences, Smithsonian Institution  
Washington, D. C. 20560*

### Abstract

Fifty specimens of the hydrous silicates norbergite, chondrodite, phlogopite, tremolite, edenite, and pargasite from 34 localities in the Franklin Marble of Orange County, New York, were analyzed quantitatively, and their F/(F + Cl + OH) ratios ( $X_F$ ) determined. The average F/(F + Cl + OH) ratio ( $\bar{X}_F$ ) determined for each species follows the sequence:  $\bar{X}_F$  Trem <  $\bar{X}_F$  Phlog <  $\bar{X}_F$  Amph <  $\bar{X}_F$  Chond <  $\bar{X}_F$  Norb where  $\bar{X}_F$  Amph is the average  $X_F$  for amphibole species other than tremolite. The fluorine contents of the hydrous silicate minerals formed within the Franklin Marble are high by comparison with analyses of the same species from other localities. The Franklin Marble is a high-temperature ( $836 \pm 40^\circ\text{C}$ ), high-pressure (4–7 kbar) metacarbonate. We suggest that the high fluorine content of the tremolite samples has increased the upper thermal stability limit for this species, thus preserving the assemblage tremolite + quartz + calcite under granulite facies conditions. There is an inverse relationship between the F/(F + Cl + OH) ratio and titanium content for chondrodite. This relationship has been noted by earlier investigators for other members of the humite group. The inverse relationship is not evident for Ti values below 0.02 atoms per formula unit.

### Introduction

The Franklin Marble is a late Precambrian (Grenvillian age) metacarbonate which crops out in a narrow belt in Sussex County, New Jersey and Orange County, New York, as part of the Hudson Highlands. Hague *et al.* (1956) and Offield (1967) have mapped portions of the Highlands and determined the conditions of metamorphism to be upper amphibolite to granulite facies. However, a number of hydrous silicate species, including tremolite and other amphiboles, norbergite, and chondrodite, occur

widely in the marble. The occurrence of tremolite in particular is not compatible with the postulated metamorphic conditions.

Earlier work on the humites of the Franklin Marble by Jones *et al.* (1969) suggests that the hydrous silicates are rich in fluorine. We undertook to determine the amount and distribution of fluorine in the hydrous silicates of the Franklin Marble in Orange County, New York, and to study the relationship of fluorine content to the stability of hydrous silicates under conditions of high-grade metamorphism. We conclude that high fluorine contents stabilize the hydrous silicates under these conditions and are responsible for their persistence in this granulite facies metacarbonate.

<sup>1</sup> Present address: Department of Geoscience, North Carolina State University, Raleigh, North Carolina 27607.

### Experimental

Fifty mineral specimens were selected for analysis from 34 localities distributed throughout the Franklin Marble in Orange County, New York (Fig. 1). Mineral species selected were norbergite, chondrodite, phlogopite, tremolite, tremolitic hornblende, edenite, pargasite, and pargasitic hornblende (amphibole nomenclature after Leake, 1978).

Chemical analyses of the minerals were performed by several different methods at three different institutions. Norbergite, chondrodite, phlogopite, and some amphiboles were analyzed with an ARL-SEMQ electron microprobe at the Smithsonian Institution. Take-off angle on this probe is 52.5°. Analyses were

performed with 0.30 microamp current at 15 kV. Beam size was 10–20 micron, signal counting time 10 seconds. Each analysis represents an average of at least six spots in different locations across sample. All counts were corrected for background and refined by applying the Bence–Albee correction procedure.

Additional amphibole specimens were analyzed by energy-dispersive X-ray analysis (EDAX) at the University of Delaware. A Cambridge-Stereoscan SEM was used in conjunction with the EDAX analyzer. A computer interfaced with the analyzer provided quantitative analyses for eight selected elements. The computer software is the EDIT/7EP program which corrects for background, interelement absorption,

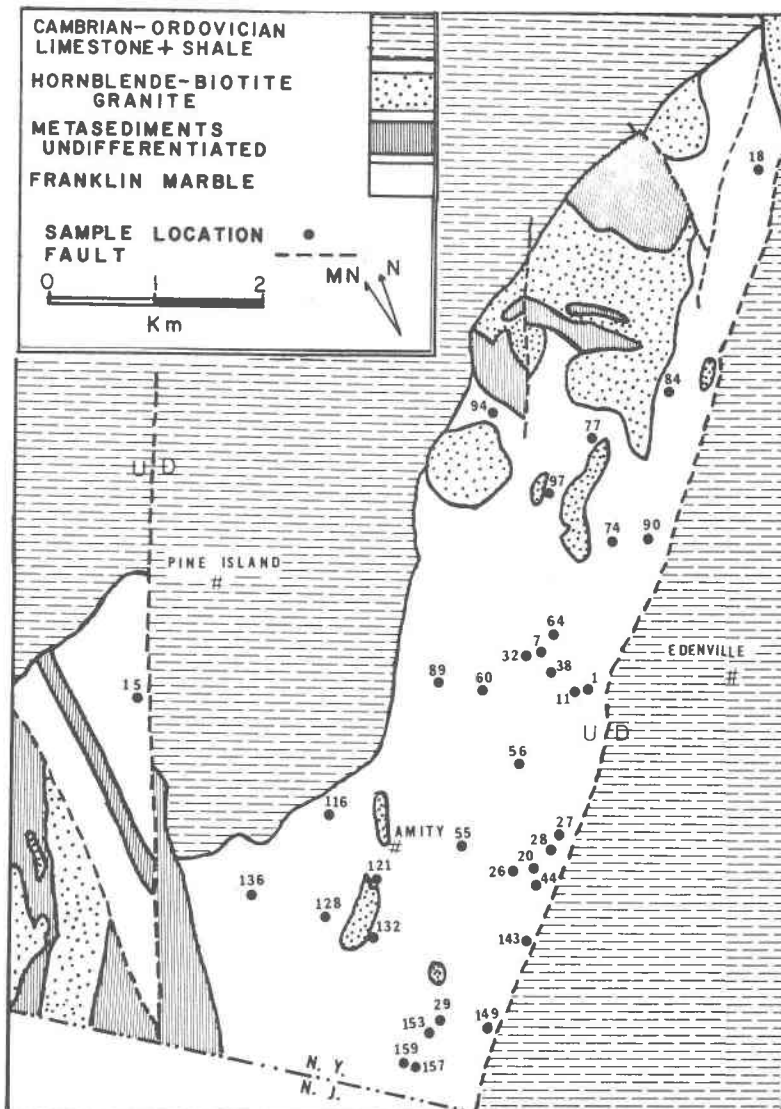


Fig. 1. Sample location map; geology modified from Offield (1967).

Table 1. Selected chemical analyses of hydrous silicate species from the Franklin Marble, Orange County, New York

Analysis No.	1	2	3	4	5	6
Species	Norbergite	Chondrodite	Tremolite	Edenite	Pargasite	Phlogopite
Original No. *	H-56-2	H-143-11	A-32-2	A-29-10	A-89-16	P-15-5
WEIGHT PERCENT OXIDES						
SiO <sub>2</sub>	29.21	33.87	56.23	50.55	41.80	42.53
Al <sub>2</sub> O <sub>3</sub>	<0.05	<0.05	1.51	6.90	17.13	12.93
TiO <sub>2</sub>	0.23	0.44	<0.05	0.51	0.66	0.04
MgO	58.51	56.20	23.72	22.06	18.51	26.51
FeO**	0.21	1.75	0.45	1.30	2.20	2.55
MnO	0.06	0.10	---	0.07	0.04	0.03
CaO	---	---	13.20	13.30	13.40	0.01
Na <sub>2</sub> O	---	---	1.62	2.35	3.05	0.44
K <sub>2</sub> O	---	---	0.05	0.54	0.45	9.89
H <sub>2</sub> O <sup>+</sup>	2.71	1.89	1.43	1.27	0.94	1.95
F	12.55	6.63	1.55	1.86	2.45	4.82
Cl	<0.13	<0.01	---	---	0.04	0.11
-(F+Cl)=0	103.61	100.88	99.76	100.71	100.67	101.81
	5.31	2.79	0.65	0.78	1.32	2.05
Total	98.29	98.09	99.11	99.93	99.35	99.76
ATOMS PER FORMULA UNIT						
Si	1.00	1.99	7.76	7.05	5.94	5.98
Al <sup>4+</sup>	---	---	0.24	0.95	2.06	2.02
Al <sup>6+</sup>	---	---	0.01	0.18	0.81	0.12
Ti	0.01	0.02	---	0.05	0.07	---
Mg	2.97	4.91	4.88	4.58	3.92	5.56
Fe	0.02	0.09	0.05	0.15	0.26	0.30
Mn	---	---	---	0.01	0.01	---
Ca	---	---	1.94	1.99	2.04	---
Na	---	---	0.43	0.63	0.84	0.12
K	---	---	0.01	0.10	0.08	1.77
OH <sup>+</sup>	0.62	0.74	1.32	1.18	0.89	1.83
F	1.35	1.23	0.68	0.82	1.10	2.14
Cl	---	---	---	---	0.01	0.03
F						
F+Cl+OH	0.68	0.62	0.34	0.41	0.55	0.54

\* First No. indicates sample location; second No. refers to original analysis.  
 \*\* Total iron.  
 +OH calc.: Analyses 1 and 2: after method of Jones et al., 1969.  
 Analyses 3-5: (F+Cl+OH)=2.00  
 Analysis 6: (F+Cl+OH)=4.00

and fluorescent effects. Single, broad-beam analyses were used with a 400-second counting period. Operating conditions were 20 kV, 60 degree tilt angle, and a take-off angle of 37.8°. Elemental percentages were converted to oxide percent and corrected to 96.82%, representing a calculated average anhydrous total for the amphiboles.

The EDAX analyses of amphiboles did not include determination of fluorine. The fluorine contents of these samples were determined at James Madison University by wet-chemical analysis. The method used was a modification of the lead chlorofluoride method of Hillebrand and Lundell (1953, p. 744) coupled with the use of a constant-temperature, steam-distillation apparatus for fluorine isolation as described by Huckabay et al. (1947). Standardized NaF samples were run with each batch of samples to determine and verify the accuracy of the method.

Analyses are corrected for standards by multiplying by the quotient [(fluorine in standard)/(fluorine determined for standard)]. The magnitude of the correction did not exceed 3.0 percent of determined fluorine for any batch of samples.

## Results

The analytical results show the hydrous silicate minerals of the Franklin Marble to be high in fluorine. Table 1 shows a typical analysis of each mineral species analyzed.<sup>2</sup> The range in F/(F + Cl + OH) ratios ( $X_F$ ) among the different species indicates assimilation of fluorine into their structures in varying proportions.

<sup>2</sup> To receive a copy of complete analyses, order document AM-80-129 from the Business Office, Mineralogical Society of America, 2000 Florida Avenue, NW, Washington, D.C. 20009. Please remit \$1.00 in advance for the microfiche.

Table 2. Summation of F/(F + Cl + OH) ratios

Mineral Species	No. Samples Analyzed	F/(F + Cl + OH)		
		High	Low	Average ( $\bar{X}_F$ )
Humites				
Norbergite	4	.68	.68	.68
Chondrodite	8	.65	.56	.61
Amphiboles				
Tremolite	4	.40	.15	.31*
Tremolitic Hornblende	2	.57	.34	.46*
Edenite	4	.59	.41	.47*
Pargasitic Hornblende	2	.57	.33	.45**
Pargasite	4	.55	.26	.43*
Phlogopite	22	.54	.20	.38

\*Cl was not determined in fifty percent of the analyses.  
 \*\*Cl was not determined.

A summary of the fifty analyses is shown in Table 2, which indicates the magnitude and variation of fluorine content for each mineral species. The fluorine distribution coefficient  $\bar{X}_F$ , where  $\bar{X}_F$  = average  $X_F$ , is lowest for tremolite among the hydrous silicates analyzed. Phlogopite, though showing a higher fluorine content than the tremolite, contains somewhat less fluorine than the remaining mineral species. Among the amphiboles (other than tremolite) fluorine appears to be nearly equally distributed. The greatest degree of fluorine replacement of hydroxyl is found in the humite species, with norbergite containing a slightly higher proportion of fluorine than chondrodite. Thus the fluorine distribution among the hydrous silicates is  $\bar{X}_F$  Trem <  $\bar{X}_F$  Phlog <  $\bar{X}_F$  Amph <  $\bar{X}_F$  Chond <  $\bar{X}_F$  Norb where  $\bar{X}_F$  Amph indicates the average  $X_F$  of the 12 analyses of tremolitic hornblende, edenite, pargasitic hornblende, and pargasite. We are making further systematic studies of a number of these species.

## Discussion

### Comparisons of fluorine content

The analyses of this study show that the hydrous silicate minerals of the Franklin Marble contain substantial amounts of fluorine. Although pure fluorine analogs of a number of the species studied herein are known (Van Valkenberg, 1961; Troll and Gilbert, 1972; Cameron and Gibbs, 1973), there are relatively few analyses of natural fluorine-bearing members.

Bourne (1974) gives analyses of minerals from the Grenville marbles of Ontario and Quebec, which are perhaps correlative with the Franklin Marble, and Moore and Kerrick (1976) provide analyses, including fluorine, of minerals of the siliceous dolomites of the Alta aureole, Utah. Minerals analyzed in these two studies can be compared with those from the Franklin Marble.

Although tremolite contains the lowest proportion of fluorine among species we analyzed, the  $\bar{X}_F$  of 0.31 for tremolite is high compared to that for tremolite from other localities. Bourne (1974) gives a tremolite with  $X_F$  of 0.13; Moore and Kerrick (1976) analyzed ten tremolites, which show an  $\bar{X}_F$  of 0.24. Of four tremolite analyses given by Deer *et al.* (1963, p. 251), only one shows the presence of fluorine, with  $X_F$  of 0.12.

The  $\bar{X}_F$  for phlogopites in this study is 0.38. Bourne (1974) gives 13 phlogopite analyses from the Canadian Grenville marbles with  $\bar{X}_F$  0.33. Of eleven analyses of phlogopites from worldwide localities cited by Deer *et al.* (1962b, p. 46-47), one has an  $X_F$  ratio of 0.75, but of the remaining ten only six show the presence of fluorine, and these have an  $\bar{X}_F$  of 0.20.

Pargasite and edenite from the Franklin Marble also show high  $\bar{X}_F$ , 0.43 and 0.47 respectively, when compared to samples taken from other localities. Three pargasites analyzed by Bourne (1974) average 0.28, and edenite 0.39. Only two of the ten pargasite analyses from Deer *et al.* (1963, p. 286-287) yield an  $X_F$  above 0.09.

In this study chondrodite and norbergite have an  $\bar{X}_F$  of 0.61 and 0.68 respectively. Analyses of humite minerals from the Canadian Grenville marbles (Bourne, 1974) show  $X_F$  similar to those of chondrodite and norbergite from the Franklin Marble. Chondrodite from the Alta aureole, analyzed by Moore and Kerrick (1976), shows a somewhat lower fluorine content, with  $X_F$  of 0.34. However, analyses of humite minerals from other localities (Deer *et al.*, 1962a, p. 52-53) show  $X_F$  similar to those of norbergite and chondrodite from the Franklin Marble. The highest known fluorine content for a natural chondrodite is 0.94 for a specimen from the Franklin Marble at Franklin, New Jersey (Jones *et al.*, 1969), about 20 miles south of our study area.

Hinthorne and Ribbe (1974), reporting on original data of Jones *et al.* (1969), give an analysis of chondrodite from Amity, Orange County, New York with an  $X_F$  ratio of 0.86 (National Museum of Natural History #36081). This is considerably higher than

the ratio of any of the eight chondrodites we analyzed. We suggest that this sample might be mislabelled and may be from the vicinity of Franklin, New Jersey, where chondrodites of high fluorine concentration do exist.

#### Fluorine relationship to titanium

The amount of fluorine in the humite minerals may be affected by the presence of Ti in their structure. Jones *et al.* (1969) state that clinohumite shows an inverse relationship between the amount of  $\text{TiO}_2$  and the  $F/(F + \text{Cl} + \text{OH})$  ratio, but that such a relationship is not evident below 1.9%  $\text{TiO}_2$ . Bourne (1974) verified the independence of the  $F/(F + \text{Cl} + \text{OH})$  ratio of clinohumite for low  $\text{TiO}_2$  content and showed a similar inverse relationship for chondrodite. Ribbe (1979) suggests a structural explanation for this phenomenon. Results from our study (Fig. 2) also support the inverse relationship between Ti and  $F/(F + \text{Cl} + \text{OH})$  ratio for chondrodite with a Ti content greater than 0.02 atoms/molecule. Such a relationship could not be determined for norbergite because all analyses showed Ti contents below 0.02 atoms/molecule.

#### Metamorphism

The metamorphic conditions affecting the Franklin Marble in Orange County have been determined to be of upper amphibolite to granulite facies, with temperatures reaching approximately  $836 \pm 40^\circ\text{C}$  as determined by carbonate-solvus geothermometry, total pressures of 4 to 7 kbar, and elevated  $\text{CO}_2$  of 0.75 to 1.00 (Kearns, 1977). The occurrence of the assemblage sillimanite-potassium feldspar in the surround-

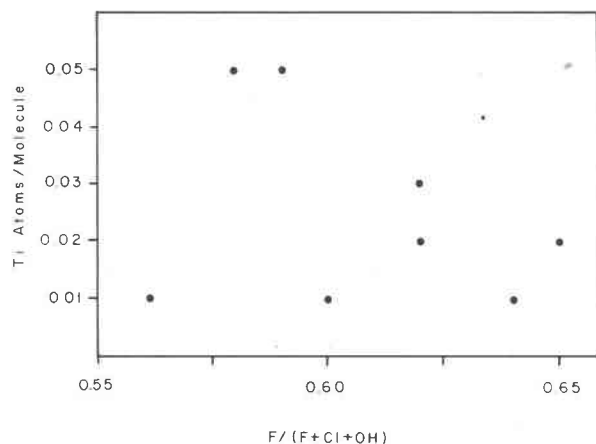


Fig. 2. Relationship of  $F/(F + \text{Cl} + \text{OH})$  vs. Ti atoms/molecule for eight chondrodite analyses. Inverse relationship suggested for  $\text{Ti} > 0.02$ .

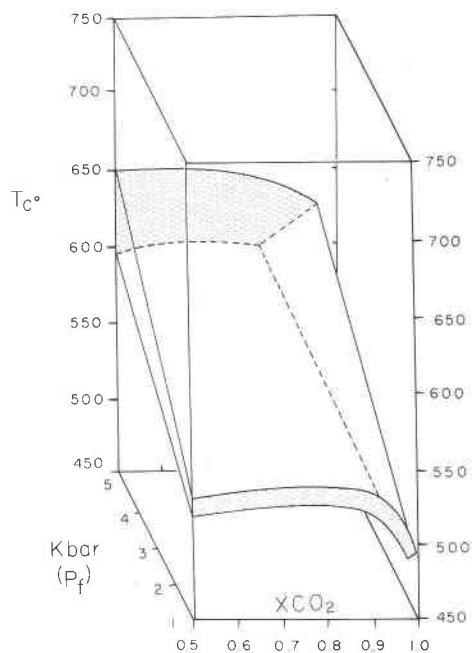
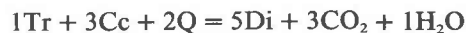


Fig. 3. Projected stability field in  $P$ - $T$ - $\text{XCO}_2$  for the assemblage tremolite + calcite + quartz. Data for stippled area (front—1 kbar, back—5 kbar) from Winkler (1976, p. 141, 121).

ing gneisses (Hague *et al.*, 1956; Offield, 1967), and common evidence of anatexis of silicate bodies within the marble (Kearns, 1977) are compatible with these figures. Comparable values have been inferred for metamorphism of the Franklin ore body by other workers (Fron del and Klein, 1965). Radiometric ages indicate that the area has been affected by only one episode of metamorphism, occurring  $840 \pm 35$  m.y. (Long and Kulp, 1962).

Assemblages typical of the Franklin Marble in Orange County include tremolite-calcite, tremolite-calcite-quartz, and tremolite-calcite-dolomite. Diopside is generally confined to aureoles around felsic bodies in the marble; reactions such as



have occurred only rarely. Forsterite occurs locally. At one locality it is rimmed with chondrodite.

Amphibole-bearing assemblages, especially those with tremolite, are not characteristic of the granulite facies and are not generally considered compatible with the pressure-temperature conditions we propose. In particular, the reaction above, consuming tremolite to produce diopside, occurs at a maximum of about  $650^\circ\text{C}$  at 5 kbar fluid pressure (Fig. 3; Winkler, 1976, p. 114, 121). An increase in the maximum temperature of this reaction of at least  $150^\circ\text{C}$  is

needed to account for the occurrence of tremolite–calcite–quartz in the Franklin Marble in Orange County. Some of this increase may be attributed to fluid pressure higher than 5 kbar; data in Winkler (1976, p. 141, 121) indicate that the maximum temperature for the reaction increases by about 50°C per kbar. Substitution of fluorine for hydroxyl clearly increases the stability of tremolite and other hydrous silicates. At 1 kbar total pressure, Moore and Kerrick (1976) calculate that for tremolite with  $X_F = 0.4$  ( $X_{OH} = 0.6$ ), the maximum temperature of the reaction will be elevated about 15°C. To account for the assemblage tremolite–calcite–quartz at the temperature measured for the Franklin Marble, substitution of fluorine for hydroxyl must have increased the thermal stability of tremolite in this assemblage at high pressure by about 100°C.

Forsterite occurs sparingly in the Franklin Marble; norbergite and chondrodite are widespread. High fluorine contents are characteristic of naturally-occurring norbergite and chondrodite (Jones *et al.*, 1969); in fact, hydroxy-chondrodite has been synthesized only at high pressure, and hydroxy-norbergite has not been synthesized and may be unstable except at very high pressure (>150 kbar?) (van Valkenberg, 1961; Ribbe, 1979). Humite and clinohumite have a somewhat lower average fluorine content (Jones *et al.*, 1969; Moore and Kerrick, 1976). High  $X_F$  is necessary to stabilize members of the humite group relative to forsterite at high  $X_{CO_2}$  (Moore and Kerrick, 1976), and increasing  $X_F$  would presumably stabilize members of the group with higher proportions of volatiles. Thus, the sequence of stability with increasing  $X_F$  at the pressures of metamorphism of the Franklin Marble would be humite → clinohumite → chondrodite → norbergite. The absence of humite and clinohumite in the Franklin Marble, and the abundance of norbergite and chondrodite relative to forsterite are consequences of abundant fluorine coupled with ideal metamorphic conditions for assimilation of fluorine by the hydrous silicate minerals.

#### Acknowledgments

This work was supported in part by a grant from the James

Madison University Program of Grants for Faculty Research and in part by a University of Delaware Faculty Research Grant.

#### References

- Bourne, J. H. (1974) *The Petrogenesis of Humite Group Minerals in Regionally Metamorphosed Marbles of the Grenville Supergroup*. Ph.D. Thesis, Queens University, Kingston, Canada.
- Cameron, M. and G. V. Gibbs (1973) The crystal structure and bonding of fluor-tremolite: a comparison with hydroxyl-tremolite. *Am. Mineral.*, 58, 879–888.
- Deer, W. A., R. A. Howie and J. Zussman (1962a, 1962b, 1963) *Rock-Forming Minerals*. Vol. 1, Ortho- and Ring Silicates; Vol. 3, Sheet Silicates; Vol. 2, Chain Silicates. Longmans, London.
- Frondel, C. and C. Klein (1965) Exsolution in franklinite. *Am. Mineral.*, 50, 1670–1680.
- Hague, J. M., J. L. Baum, L. A. Hermann and R. J. Pickering (1956) Geology and structure of the Franklin–Sterling Area, New Jersey. *Bull. Geol. Soc. Am.*, 67, 435–474.
- Hillebrand, W. F. and G. E. F. Lundell (1953) *Applied Inorganic Analysis*. Wiley, New York.
- Hinthorne, J. R. and P. H. Ribbe (1974) Determination of boron in chondrodite by ion microprobe mass analysis. *Am. Mineral.*, 59, 1123–1126.
- Huckabay, W. B., E. T. Welch and A. V. Metler (1947) Constant-temperature steam-distillation apparatus for isolation of fluorine. *Anal. Chem.*, 19, 154–156.
- Jones, N. W., P. H. Ribbe and G. V. Gibbs (1969) Crystal chemistry of the humite minerals. *Am. Mineral.*, 54, 391–411.
- Kearns, L. E. (1977) *The Mineralogy of the Franklin Marble, Orange County, New York*. Ph.D. Thesis, University of Delaware, Newark, Delaware.
- Leake, B. E. (1978) Nomenclature of amphiboles. *Am. Mineral.*, 63, 1023–1052.
- Long, L. E. and J. L. Kulp (1962) Isotopic age study of the metamorphic history of the Manhattan and Reading prongs. *Bull. Geol. Soc. Am.*, 73, 969–996.
- Moore, J. N. and D. M. Kerrick (1976) Equilibria in siliceous dolomites of the Alta aureole, Utah. *Am. J. Sci.*, 276, 502–524.
- Offield, T. W. (1967) *Bedrock Geology of the Goshen–Greenwood Lake Area, New York*. New York State and Sci. Serv., Map and Chart Ser. 9.
- Ribbe, P. H. (1979) Titanium, fluorine, and hydroxyl in the humite minerals. *Am. Mineral.*, 64, 1027–1035.
- Troll, G. and M. C. Gilbert (1972) Fluorine–hydroxyl substitution in tremolite. *Am. Mineral.*, 57, 1386–1403.
- Van Valkenberg, A. (1961) Synthesis of humites  $nMg_2SiO_4 \cdot Mg(F,OH)_2$ . *J. Res. Nat. Bur. Stand.*, 65A, 415–428.
- Winkler, H. G. F. (1976) *Petrogenesis of Metamorphic Rocks*. Springer-Verlag, New York.

Manuscript received, August 20, 1979;  
accepted for publication, December 6, 1979.