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

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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 ± 40°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.

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ANALYSES OF HUMITES, AMPHIBOLES AND PHLOGOPITE FROM THE FRANKLIN MARBLE, ORANGE COUNTY, NEW YORK

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Analytical Results

Humites

The humite specimens were all analyzed by electron microprobe which yielded weight oxide percents for the cations (Si, Al, Ti, Mg, Fe, Mn) and for F and Cl.

Calculation of the chemical formula from the mineral analysis was done according to Deer, Howie and Zussman (1966), and based on six oxygen equivalents for the norbergite and ten oxygen equivalents for chondrodite. The atomic proportion of OH was determined by the formula (Jones, Ribbe and Gibbs, 1969):

$$OH = (2/(2n + 1)\ M_{Ti} - 2Ti - F$$

where n = 1 for norbergite, n = 2 for chondrodite, and M_{Ti} represents the sum of the atomic proportions of Fe, Mn, Mg, and Ti. From this atomic proportion of OH the weight of H_2O^+ was calculated.

The oxide percent total in some cases is somewhat lower than one would expect for a complete analysis and is perhaps due to the presence of small amounts of Na or K which were not analyzed for in this study. (See Tables 1a and 1b for humite analyses.)

Table 1a.

Index of Specimens for Humite Analyses.

Analysis	Sample #*	Mineral Species
1	H-15	Norbergite
2	H-56	Norbergite
3	H-64	Norbergite
4	H-55A	Norbergite
5	H-132	Chondrodite
6	H-15A	Chondrodite
7	H-200-44	Chondrodite
8	H-157	Chondrodite
9	H-20	Chondrodite
10	H-94	Chondrodite
11	H-143	Chondrodite
12	H-90	Chondrodite

*Indicates mineral locality (See Figure 1)

Table 1b.

Analyses of Humites

	#1	#2	#3	#4	#5	#6
SiO_2	29.17	29.21	28.25	28.92	33.63	33.74
Al_2O_3	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
TiO_2	0.47	0.23	0.11	0.28	0.36	0.30
MgO	58.02	58.51	58.61	57.93	51.09	53.44
FeO	0.57	0.21	0.41	0.40	5.19	3.07
MnO	0.05	0.06	0.03	0.02	0.17	0.17
H_2O^+	2.72	2.71	2.81	2.74	1.64	1.77
F	12.47	12.55	12.48	12.33	6.59	6.57
Cl	<0.01	<0.13	<0.01	<0.01	<0.01	0.01
Total	103.47	103.61	102.70	102.62	98.67	99.06
F+Cl=O	5.25	5.31	5.25	5.19	2.77	2.77
Corrected Total	98.22	98.29	97.44	97.43	95.90	96.29

Ions per formula unit based on 6(O, OH, F) for analyses 1-4, and 10(O, OH, F) for analyses 5,6

Si	1.00	1.00	0.98	1.01	2.05	2.02
Al	--	--	--	--	--	--
Ti	0.01	--	0.01	0.01	0.02	0.01
Mg	2.97	2.99	3.02	3.02	4.63	4.78
Fe	0.02	0.01	0.01	0.01	0.26	0.15
Mn	--	--	--	--	0.01	0.01
OH	0.62	0.62	0.65	0.64	0.67	0.71
F	1.35	1.36	1.36	1.37	1.27	1.25
Cl	--	0.01	--	--	--	--
Ratio $\frac{F}{F+Cl+OH}$	.68	.68	.68	.68	.65	.64

	#7	#8	#9	#10	#11	#12
SiO_2	33.39	34.17	33.82	33.23	33.87	33.34
Al_2O_3	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
TiO_2	1.08	0.15	1.18	0.73	0.44	0.27
MgO	51.61	55.61	54.92	53.55	56.20	57.19
FeO	4.78	1.84	1.97	3.78	1.75	0.91
MnO	0.15	0.05	0.06	0.21	0.10	0.05
H_2O^+	1.88	2.19	2.00	1.86	1.89	2.06
F	5.86	6.00	5.89	6.32	6.63	6.43
Cl	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Total	98.75	100.01	99.84	99.68	100.88	100.25
F+Cl=O	2.47	2.53	2.48	2.66	2.79	2.71
Corrected Total	96.28	97.48	97.36	97.02	98.09	97.54

Ions per formula unit based on 10(O, OH, F)

Si	2.02	2.01	2.00	1.99	1.99	1.95
Al	--	--	--	--	--	--
Ti	0.05	0.01	0.05	0.03	0.02	0.01
Mg	4.66	4.88	4.84	4.78	4.91	5.01
Fe	0.24	0.09	0.10	0.19	0.09	0.04
Mn	0.01	--	--	0.01	--	--
OH	0.76	0.86	0.79	0.74	0.74	0.81
F	1.12	1.12	1.10	1.20	1.23	1.19
Cl	--	--	--	--	--	--
Ratio $\frac{F}{F+Cl+OH}$	.59	.56	.58	.62	.62	.60

Amphiboles

The complete analyses of the amphibole specimens were obtained in three ways. Seven were analyzed by electron microprobe (denoted by * under Analytical Methods in Table 2a) which yielded weight oxide percents for the cations (Si, Al, Ti, Fe, Mg, Mn, Ca, Na, K) and for the anions F and Cl. Four were analyzed by electron microprobe to obtain weight oxide percents for the cations named above, while the F content was determined by wet chemical analysis (these specimens are denoted by ** under Analytical Method). The weight oxide percents of the cations for the remaining five specimens were determined by energy dispersive X-ray analysis (EDAX) with the F content being determined by wet chemical analysis (these specimens are denoted by + under Analytical Method). The number of OH ions per molecule was calculated on the assumption that the anion total (F + Cl + OH) in each molecule equalled 2.00. ND in the individual analyses indicates that the oxide percent for that element was not determined.

Table 2a.

Index of Specimens for Amphibole Analyses

Analysis	Sample #†	Mineral Species	Analytical Method
1	A-77	Tremolite	*
2	A-32	Tremolite	+
3	A-149	Tremolite	+
4	A-159	Tremolite	*
5	A-116	Tremolitic Hornblende	+
6	A-136	Tremolitic Hornblende	*
7	A-60	Edenite	*
8	A-84	Edenite	+
9	A-15	Edenite	*
10	A-29	Edenite	**
11	A-28	Pargasitic Hornblende	**
12	A-11	Pargasitic Hornblende	**
13	A-121	Pargasite	*
14	A-26	Pargasite	+
15	A-38	Pargasite	**
16	A-89	Pargasite	*

†Indicates mineral locality (See Figure 1)

Table 2b.

Analyses of Amphiboles

	#1	#2	#3	#4	#5	#6
SiO_2	56.00	56.23	55.72	56.47	53.90	53.90
Al_2O_3	1.18	1.51	1.47	2.26	3.43	4.20
TiO_2	0.06	<0.05	<0.05	0.06	0.10	0.17
FeO	1.00	0.45	1.34	0.43	0.30	0.81
MgO	23.38	23.72	23.48	23.89	23.72	23.23
Mn	0.05	ND	ND	0.03	ND	0.06
CaO	13.60	13.20	13.02	13.75	13.64	13.90
Na_2O	1.21	1.62	1.73	0.97	1.57	1.22
K_2O	0.16	0.05	0.05	0.41	0.15	0.38
H_2O^+	1.28	1.43	1.84	1.47	0.93	1.45
F	1.80	1.55	0.69	1.52	2.61*	1.54
Cl	0.09	ND	ND	0.03	ND	0.02
Total	99.81	99.76	99.34	101.29	100.35	100.88
F+Cl=O	0.78	0.65	0.29	0.65	1.10	0.65
Corrected Total	99.03	99.11	99.05	100.64	99.25	100.23

Ions per formula unit based on 23 oxygen equivalents

Si	7.77	7.76	7.73	7.69	7.48	7.42
Al^4	0.19	0.24	0.24	0.31	0.52	0.58
Al^6	--	0.01	--	0.05	0.04	0.10
Ti	0.01	--	--	0.01	0.01	0.02
Fe	0.12	0.05	0.15	0.05	0.03	0.09
Mg	4.84	4.88	4.85	4.85	4.90	4.76
Mn	0.01	--	--	--	--	0.01
Ca	2.02	1.94	1.94	2.01	2.03	2.05
Na	0.16	0.43	0.47	0.26	0.42	0.33
K	0.01	0.01	0.01	0.07	0.03	0.07
OH	1.19	1.32	1.70	1.34	0.86	1.33
F	0.79	0.68	0.30	0.65	1.14	0.67
Cl	0.02	--	--	0.01	--	--
Ratio $\frac{F}{F+Cl+OH}$	.40	.34	.15	.33	.57	.34

*Average of two F analyses by wet chemical procedure.

	#7	#8	#9	#10	#11	#12
SiO_2	53.70	50.86	51.55	50.55	44.78	42.75
Al_2O_3	4.02	6.75	6.66	6.90	13.44	13.66
TiO_2	0.20	<0.05	0.32	0.51	0.52	0.51
FeO	0.37	5.41	0.41	1.30	3.54	6.87
MgO	23.70	18.72	22.74	22.06	18.35	15.54
MnO	0.02	ND	0.02	0.07	0.06	0.14
CaO	13.68	12.56	13.79	13.30	13.14	12.77
Na_2O	1.71	1.38	1.87	2.35	2.76	2.06
K_2O	0.43	1.09	0.58	0.54	0.91	2.22
H_2O^+	1.18	0.87	1.20	1.27	0.92	1.43
F	2.09	2.60*	2.02	1.86	2.38*	1.31
Cl	0.02	ND	0.04	ND	ND	ND
Total	101.12	100.24	101.20	100.71	100.80	99.26
F+Cl+O	0.88	1.09	0.86	0.78	1.00	0.55
Corrected Total	100.24	99.15	100.34	99.93	99.80	98.71

Ions per formula unit based on 23 oxygen equivalents

Si	7.39	7.24	7.12	7.05	6.37	6.28
Al^4	0.61	0.76	0.88	0.95	1.63	1.72
Al^6	0.04	0.37	0.20	0.18	0.62	0.65
Ti	0.02	--	0.03	0.05	0.06	0.06
Fe	0.04	0.64	0.05	0.15	0.42	0.84
Mg	4.86	3.97	4.68	4.58	3.89	3.40
Mn	--	--	--	0.01	0.01	0.02
Ca	2.02	1.92	2.04	1.99	2.00	2.01
Na	0.46	0.38	0.50	0.63	0.76	0.59
K	0.08	0.20	0.10	0.10	0.17	0.42
OH	1.09	0.83	1.11	1.18	0.87	1.40
F	0.91	1.17	0.88	0.82	1.13	0.60
Cl	--	--	0.01	--	--	--
Ratio $\frac{F}{F+Cl+OH}$	.45	.59	.44	.41	.57	.33

*Average of two F analyses by wet chemical procedure.

	#13	#14	#15	#16
SiO_2	42.58	43.11	41.24	41.80
Al_2O_3	14.33	15.05	15.02	17.13
TiO_2	1.45	1.24	1.96	0.66
FeO	3.05	1.13	6.97	2.20
MgO	18.65	20.03	14.61	18.51
MnO	0.05	ND	0.20	0.04
CaO	13.10	12.79	12.46	13.40
Na_2O	2.78	3.28	2.56	3.05
K_2O	0.63	0.19	1.81	0.45
H_2O^+	1.52	1.34	1.00	0.94
F	1.12	1.63	2.19	2.45
Cl	0.14	ND	ND	0.04
Total	99.40	99.79	100.02	100.67
F+Cl=0	0.50	0.69	0.92	1.32
Corrected Total	98.90	99.10	99.10	99.35
Si	6.11	6.10	6.05	5.94
Al^4	1.89	1.90	1.95	2.06
Al^6	0.54	0.61	0.65	0.81
Ti	0.16	0.13	0.22	0.07
Fe	0.37	0.13	0.86	0.26
Mg	3.99	4.22	3.19	3.92
Mn	0.01	--	0.02	0.01
Ca	2.01	1.94	1.96	2.04
Na	0.77	0.90	0.73	0.84
K	0.12	0.03	0.34	0.08
OH	1.46	1.27	0.98	0.89
F	0.51	0.73	1.02	1.10
Cl	0.03	--	--	0.01
Ratio $\frac{F}{F+Cl+OH}$	.26	.39	.51	.55

Phlogopite

The phlogopite specimens were all analyzed by electron microprobe which yielded weight percent oxides for the cations (Si, Al, Ti, Fe, Mg, Mn, Ca, Na, K) and for F and Cl. The number of OH ions per molecule was calculated on the assumption that the anion total (F+Cl+OH) equalled 4.00.

Table 3a.

Index of Specimens for Phlogopite Analyses

Analysis	Sample #*	Mineral Species
1	P-7	Phlogopite
2	P-157	Phlogopite
3	P-18A	Phlogopite
4	P-200-44	Phlogopite
5	P-15	Phlogopite
6	P-77	Phlogopite
7	P-27	Phlogopite
8	P-153	Phlogopite
9**	P-84	Phlogopite
10	P-18	Phlogopite
11	P-28	Phlogopite
12	P-11	Phlogopite
13	P-462-44	Phlogopite
14	P-121	Phlogopite
15	P-97	Phlogopite
16	P-94	Phlogopite
17	P-1	Phlogopite
18	P-55A	Phlogopite
19	P-74	Phlogopite
20	P-29	Phlogopite
21	P-128	Phlogopite
22	P-26	Phlogopite

*Indicates mineral locality (See Figure 1).

**Average of two analyses.

Table 3b.

Analyses of Phlogopite

	#1	#2	#3	#4	#5	#6
SiO_2	43.18	43.09	42.78	42.25	42.53	42.39
Al_2O_3	12.24	12.75	12.60	11.56	12.93	13.25
TiO_2	0.13	0.04	0.06	0.21	0.04	0.18
FeO	1.17	0.75	1.19	0.79	2.55	0.74
MgO	26.35	27.84	27.42	27.96	26.51	27.23
MnO	0.02	0.01	0.01	0.02	0.03	0.01
CaO	0.01	0.01	0.06	0.04	0.01	<0.01
Na_2O	0.02	0.77	0.25	0.50	0.44	0.67
K_2O	10.23	9.26	10.00	8.90	9.89	9.20
H_2O^+	2.41	2.77	2.21	2.48	1.95	2.23
F	3.79	3.21	4.31	3.60	4.82	4.23
Cl	0.03	0.02	0.03	0.07	0.11	0.06
Total	99.58	100.52	100.92	99.38	101.81	100.19
F+Cl=0	1.60	1.36	1.82	1.53	2.05	1.79
Corrected Total	97.98	99.16	99.10	97.85	99.76	98.40

Ions per formula unit based on 22 oxygen equivalents

Si	6.14	6.02	6.01	6.01	5.98	5.97
Al^4	1.86	1.98	1.99	1.94	2.02	2.03
Al^6	0.19	0.12	0.10	--	0.12	0.17
Ti	0.01	--	0.01	0.02	--	0.02
Fe	0.14	0.09	0.14	0.21	0.30	0.09
Mg	5.58	5.78	5.74	5.93	5.56	5.72
Mn	--	--	--	--	--	--
Ca	--	--	0.01	0.01	--	--
Na	--	0.21	0.07	0.14	0.12	0.18
K	1.85	1.65	1.79	1.62	1.77	1.65
OH	2.29	2.58	2.07	2.36	1.83	2.11
F	1.70	1.42	1.92	1.62	2.14	1.88
Cl	0.01	--	0.01	0.02	0.03	0.01
Ratio $\frac{F}{F+Cl+OH}$	.43	.36	.48	.41	.54	.47

	#7	#8	#9*	#10	#11*	#12
SiO_2	42.62	42.10	42.07	41.31	41.58	40.97
Al_2O_3	13.33	13.40	13.38	13.11	13.62	14.13
TiO_2	0.19	0.36	0.44	0.47	0.31	0.70
FeO	1.26	0.80	3.94	6.02	3.61	5.81
MgO	27.28	26.99	25.23	23.58	25.27	23.02
MnO	0.01	0.01	0.03	0.05	0.04	0.07
CaO	0.01	0.02	<0.01	<0.01	0.01	0.01
Na_2O	0.65	0.20	0.41	0.19	0.69	0.46
K_2O	9.51	10.11	9.93	10.03	9.48	9.49
K_2O^+	2.34	2.26	2.39	2.46	2.49	2.74
F	4.09	4.16	3.58	3.48	3.60	2.99
Cl	0.04	0.09	0.05	0.27	0.11	0.12
Total	101.33	100.50	101.60	100.97	100.81	100.51
F+Cl=0	1.73	1.77	1.52	1.53	1.54	1.29
Corrected Total	99.60	98.73	100.08	99.44	99.27	99.22

Ions per formula unit based on 22 oxygen equivalents

Si	5.95	5.94	5.93	5.93	5.90	5.86
Al^4	2.05	2.06	2.07	2.07	2.10	2.14
Al^6	0.14	0.16	0.15	0.15	0.18	0.24
Ti	0.02	0.04	0.05	0.05	0.03	0.07
Fe	0.15	0.09	0.46	0.72	0.43	0.70
Mg	5.68	5.67	5.30	5.04	5.34	4.91
Mn	--	--	--	0.01	0.01	0.01
Ca	--	--	--	--	--	--
Na	0.18	0.05	0.11	0.05	0.20	0.13
K	1.70	1.82	1.78	1.84	1.71	1.73
OH	2.18	2.13	2.39	2.36	2.36	2.62
F	1.81	1.85	1.60	1.58	1.61	1.35
Cl	0.01	0.02	0.01	0.06	0.03	0.03
Ratio $\frac{F}{F+Cl+OH}$	.45	.46	.40	.40	.40	.34

*Average of two analyses.

	#13	#14	#15	#16	#17	#18
SiO_2	41.14	41.65	39.78	41.46	41.20	41.12
Al_2O_3	14.19	14.25	13.92	14.44	15.16	15.32
TiO_2	0.52	0.61	0.88	0.92	0.14	0.17
FeO	4.06	2.30	8.03	1.85	1.00	0.60
MgO	24.48	26.15	21.26	26.30	26.97	27.44
MnO	0.06	<0.01	0.12	0.02	0.01	<0.01
CaO	0.02	<0.01	0.01	<0.01	0.01	0.02
Na_2O	0.40	1.04	0.28	1.04	1.19	1.72
K_2O	9.83	9.00	9.63	8.97	8.98	7.71
H_2O^+	2.49	3.13	2.22	3.35	2.80	2.62
F	3.56	2.37	3.88	1.94	2.82	3.51
Cl	0.12	0.09	0.18	0.05	0.06	0.06
Total	100.87	100.59	100.19	100.34	100.33	100.29
F+Cl=0	1.53	1.02	1.67	0.83	1.20	1.49
Corrected Total	99.34	99.57	98.52	99.51	99.13	98.80

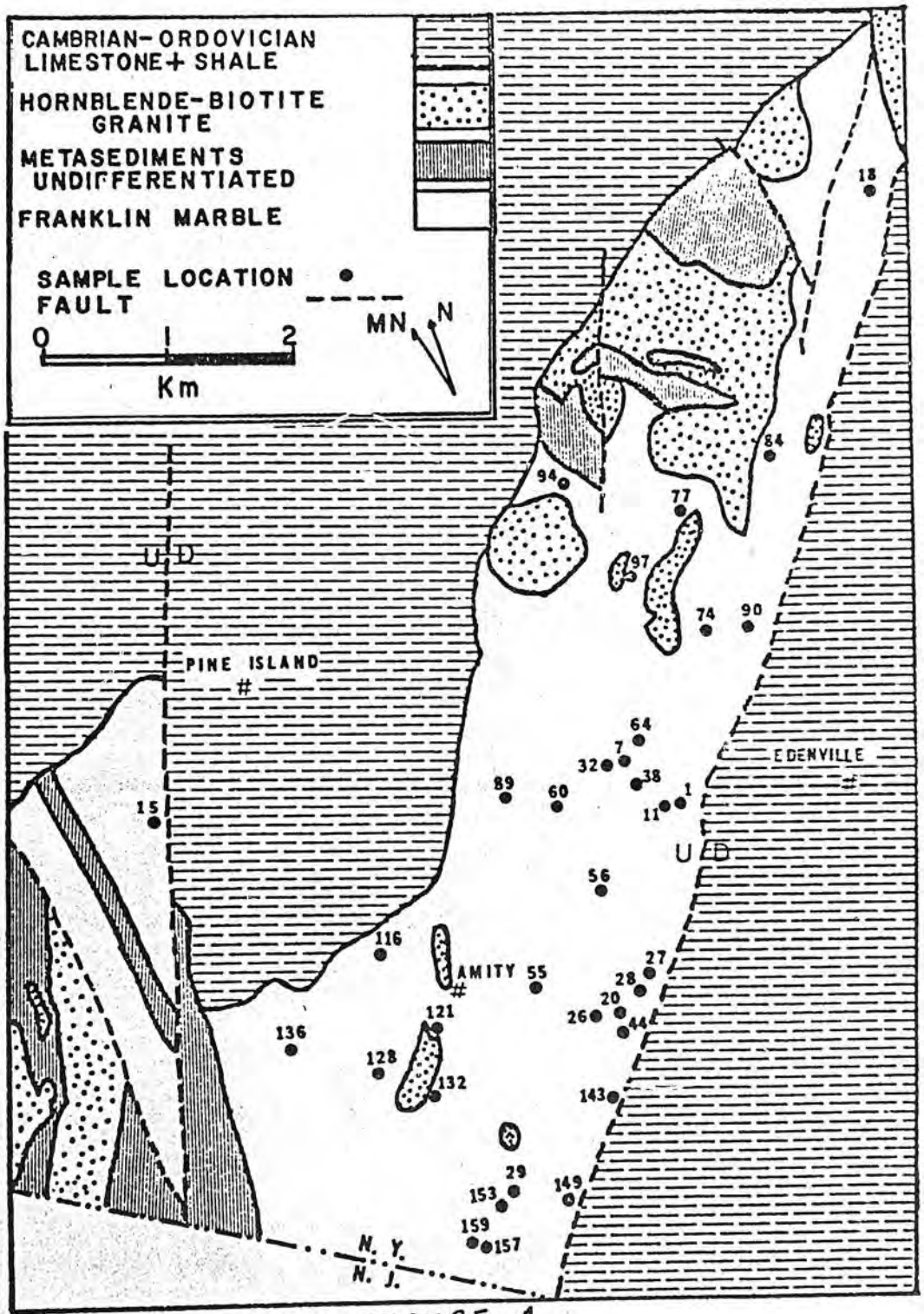
Ions per formula unit based on 22 oxygen equivalents

Si	5.85	5.83	5.82	5.80	5.76	5.74
Al^4	2.15	2.17	2.18	2.20	2.24	2.26
Al^6	0.23	0.18	0.22	0.18	0.26	0.26
Ti	0.05	0.06	0.10	0.10	0.01	0.02
Fe	0.48	0.27	0.98	0.22	0.12	0.07
Mg	5.19	5.46	4.63	5.48	5.62	5.71
Mn	0.01	--	0.01	--	--	--
Ca	--	--	--	--	--	--
Na	0.11	0.28	0.08	0.28	0.32	0.46
K	1.78	1.61	1.80	1.60	1.60	1.37
OH	2.37	2.93	2.17	3.13	2.61	2.44
F	1.60	1.05	1.79	0.86	1.25	1.55
Cl	0.03	0.02	0.04	0.01	0.14	0.01
Ratio $\frac{F}{F+Cl+OH}$	.40	.26	.45	.22	.32	.39

	#19	#20	#21	#22
SiO_2	41.15	40.29	39.96	38.96
Al_2O_3	15.19	16.10	16.33	17.46
TiO_2	0.03	1.00	1.21	1.64
FeO	0.23	1.15	2.87	0.93
MgO	28.33	26.17	25.09	25.49
MnO	0.01	0.0[illegible]	0.03	0.02
CaO	0.08	0.02	0.01	0.02
Na_2O	1.92	1.09	1.66	1.34
K_2O	7.07	8.93	7.80	8.53
H_2O^+	2.67	2.92	3.20	3.39
F	3.43	2.81	2.21	1.79
Cl	0.05	0.13	0.12	0.13
Total	100.16	100.63	100.49	99.70
F+Cl=0	1.45	1.21	0.96	0.78
Corrected Total	98.71	99.42	99.53	98.92

Ions per formula unit based on 22 oxygen equivalents

Si	5.73	5.63	5.60	5.47
Al^4	2.27	2.37	2.40	2.53
Al^6	0.22	0.28	0.30	0.36
Ti	--	0.10	0.13	0.17
Fe	0.03	0.13	0.34	0.11
Mg	5.88	5.46	5.24	5.33
Mn	--	--	--	--
Ca	0.01	--	--	--
Na	0.52	0.29	0.45	0.36
K	1.26	1.59	1.39	1.53
OH	2.48	2.73	2.99	3.18
F	1.51	1.24	0.98	0.79
Cl	0.01	0.03	0.03	0.03
Ratio $\frac{F}{F+Cl+OH}$	.38	.31	.25	.20



LOCATION MAP - FIGURE 1