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The Fluorine Content and Some Physical Properties of the Amblygonite-Montebrasite Minerals

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Abstract

Specific gravities, refractive indices, differential thermal behavior, unit cell dimensions, and sensitive X-ray powder diffraction reflections were studied on a series of analyzed amblygonites-montebrasites, to find a reliable method for indirect determination of the F-content, and to check the existing determinative graphs reported as doubtful by some authors. Specific gravities were found to comply with the relations established earlier, but they proved to be very sensitive to alteration and inclusions. The variation of the refractive index γ' differs from that given by Winchell and Winchell (1951), and a thorough study of the optics is desirable. Differential thermal analyses show gradual changes in the number and temperature of the reaction peaks, and in the composition and proportions of the metastable heating products; however, the thermal behavior seems to be strongly dependent on the experimental setup. Unit cell dimensions, refined with high accuracy and precision, show small but regular changes with the F-content, and they appear to be not affected by Na_2O contents up to about 1.5 wt percent. Two determinative graphs were constructed, one based on separations of the uncalibrated X-ray powder reflections $\bar{1}01$, $\bar{1}10$, $\bar{1}\bar{2}1$, 011, $0\bar{2}1$, and 120, and the other on the 131 peak (Moss *et al.*, 1969) calibrated against $CuK\alpha_1$ quartz reflections. These two methods seem to be the most practical for determining indirectly the F-content, provided the examined samples contain less than about 1.5 wt percent Na_2O, and are optically homogeneous. The chemistry of the amblygonites-montebrasites used for structure determinations (Simonov and Belov, 1958; Baur, 1959) and the possible existence of high- and low-temperature forms are discussed.

Introduction

In 1969–1970, the first author investigated the distribution and composition of the amblygonite-montebrasite minerals, $(Li, Na)AlPO_4(F, OH)$, in the Tanco pegmatite deposit at Bernic Lake, S. E. Manitoba (Černá, 1970; Černá *et al.*, 1972). The study was prompted by the wide range of amblygonite-montebrasite compositions in this Li-Ta-Cs deposit and their potential petrological significance, but it also helped to establish methods for separating amblygonites-montebrasites from refractory-grade spodumene in which they are a highly undesirable contaminant.

During the previous study, the large number of specimens to be examined underscored the need to estimate their (F,OH) content indirectly instead of by lengthy direct chemical determinations. However, the then available physical methods were found to be either experimentally difficult and time-consuming (specific gravity), or unreliable because of the wide scatter of the known data (optical properties, Winchell and Winchell, 1951; see objections by Ginzburg, 1950; Staněk, 1960).

In the present study, the specific gravities, refractive indices γ', differential thermal records, X-ray powder diffraction data, and unit cell dimensions have been determined for 15 chemically analyzed amblygonites-montebrasites. We describe our results obtained by these methods, we estimate the practical value of different methods for indirect determination of F contents, and we draw the attention of pegmatite investigators to the widespread chemical inhomogeneities of both primary and secondary origin in amblygonites-montebrasites.

Selected Specimens and Their Chemical Compositions

About half of the specimens examined came from the Tanco pegmatite, a convenient source of large quantities of fresh material which gives some indication of the compositional changes by variations in color. All these specimens are deposited in the mineral collections of the Department of Earth Sciences, University of Manitoba. Other samples have been obtained from various collections. The list of specimens is given in Table 1.

TABLE 1. List of Specimens

Specimens from the Tanco pegmatite, Bernic Lake, Manitoba:

A-1:	Pale pink core of a zoned crystal (see A-2), slightly contaminated by secondary montebrasite (~5%).
A-2:	Yellow outer rim of a zoned crystal (see A-1).
A-3:	Waterclear colorless crystal; analyzed by P. Povondra, F-content by J. L. Dalton.
A-4:	White material surrounding and veining A-5; chemical analysis by R. M. Hill *et al.* (A-4B) and P. Povondra *et al.* (A-4A).
A-5:	Yellow translucent, veined by A-4.
A-13:	White to pinkish cleavable mass.
A-22:	Brownish translucent, massive.
A-29:	Milky white cleavable mass.
A-60:	Milky white cleavage fragment.
A-98:	Pale yellow translucent mass.

Other Specimens:

AF-1:	Montebras, France, Dept. Earth Sciences, Univ. of Manitoba No. M-4421; milky white opaque mass stuffed with dusty anisotropic inclusions.
AF-43:	Nesbitt spodumene mine, Gunnison County, Colorado; U.S.N.M. No. 117,775; grayish-white cleavage fragment.
AF-44:	Moguk, Upper Burma, U.S.N.M. No. 10,734; colorless to yellowish, waterclear fragments; F-content not determined.
AF-46:	Karibib, South Africa, U.S.N.M. No. 105914; pale bluish cleavage fragments.
AF-47:	Plumbago, Newry, Maine, U.S.N.M. No. 5841; bluish waterclear crystals from pegmatite vugs, with quartz and cleavelandite; F-content not determined.
AF-48:	Newry, Maine, U.S.N.M. No. 5906; waterclear colorless crystals from a pegmatite vug; no chemical data available.
AF-50:	Coolgardie, West Australia, U.S.N.M. No. 10432; pale brownish transparent mass.
AF-55:	Hebron, Maine, U.S.N.M. No. 62,576; colorless cleavable mass; the only sodium-rich specimen examined.
AF-65:	Chursdorf, Saxony, B.M.N.H. 14, 274; translucent fragments with faint bluish tint; partial chemical analysis by Moss *et al.* (1969).
AF-66:	Newry, Maine, Dept. of Geological Sciences, Harvard University; waterclear colorless crystals from a vug; no chemical data available.

As shown in Table 2, full chemical analyses were obtained for 15 specimens; two other samples were analyzed for all major components except F (AF-44, AF-47), and the partially analyzed specimen Z of Moss *et al.* (1969) was included in the examined series (AF-65). Two other specimens (AF-48 and AF-66) were checked only for physical properties because lack of material precluded chemical analyses. Since most of the Na-rich varieties examined in this study did not yield material sufficient for chemical analysis, this report is concerned only with Na-poor (<1 wt percent Na_2O) amblygonites-montebrasites; the Hebron sample (AF-55 with 2.55 wt percent Na_2O) is shown to give some indication of the influence of higher Na contents.

In the samples analyzed by K. Ramlal and R. M. Hill, Al_2O_3 and P_2O_5 were analyzed by X-ray fluorescence spectrometry, alkali metals and alkaline earths by atomic absorption spectrography, and H_2O gravimetrically. Fluorine contents were determined by J. L. Dalton (Mines Branch, Ottawa) using neutron activation. In the specimen analyzed by P. Povondra, P_2O_5 and H_2O were determined gravimetrically, alkali metals and alkaline earths by flame photometry, Al_2O_3 by potentiometric titration, and F by pyrolytic decomposition and complexometric titration.

In the following sections, the changes in individual physical characteristics are related directly to wt percent F as found by the chemical analysis, since the recalculation to atomic content is slightly influenced by errors in the determination of other components and by assumptions involved in calculation of crystallochemical formulae. The theoretically most useful atomic ratio $F/(F + OH)$ is considerably affected by errors in the determination of H_2O (*cf.* Ribbe and Rosenberg, 1971) and the plots of physical properties against this ratio show poorer correlation than when F content alone is used.

The linear regression equations and the correlation coefficients for most of the plots of physical constants *vs* wt percent F are given in Table 3. They were calculated on the basis of only those specimens for which the F content was directly determined chemically, except for the Na-rich specimen AF-55.

Specific Gravity

The specific gravities were measured with a Berman torsion balance, using toluene checked for temperature as a suspension medium. Three to five grains were used for each sample, the specific gravity being determined two to four times per grain. The purest grains available were selected for each specimen for this determination, and their refractive indices were checked. However, in some cases only milky, clouded grains were available. Microscopic examination showed that liquid inclusions were the main impurity in all cases, with clay-like and/or mica-like particles observed only occasionally.

The averaged specific gravities plotted against wt percent F in Figure 1 fall close to the widely used

TABLE 2. Chemical Composition and Physical Properties

	AF-47	A-22	AF-44	AF-43	A-98	A-2	A-4 A**	A-4 B***	A-5	A-1
Al_2O_3	35.26	35.10	35.90	34.60	34.46	35.53	34.45	34.75	34.86	34.53
Fe_2O_3						.11	.02		.028	.11
CaO		.085		.13	.030	.17		.166	.074	.17
MgO		.003		.005	.002	.002		.014	.002	.005
Li_2O	9.47	9.52	9.98	9.47	9.90	9.86	10.14	9.47	10.29	9.86
Na_2O	.08	.139	.012	.124	.015	.025	.055	.039	.044	.054
K_2O	.004	.005	.001	.020	.004			.003		
P_2O_5	49.38	49.11	49.38	49.66	49.26	49.21	49.48	48.98	49.26	49.32
H_2O-	.10	.07	.09	.06	.05	.04	.08	.07	.08	.10
H_2O+	5.98	5.25	5.45	5.11	4.43	4.09	3.85	4.34	3.30	3.39
F	.30*	1.40	1.45*	1.88	3.44	3.65	3.65	4.05	4.51	5.56
	100.274	100.682	100.81	101.059	101.591	101.687	101.725	101.882	102.448	103.099
-O=2F		-0.59		-0.70	-1.45	-1.536	-1.536	-1.71	-1.898	-2.341
Total	100.174	100.092	100.72	100.359	100.141	100.151	100.159	100.172	100.550	100.758
Li	.921	0.933	.964	.924	.969	.959	.995	.928	1.010	.964
Na	.004	.007				.001	.002	.002	.002	.004
Ca		.004			.001	.004		.004	.002	.004
(Li+Na+Ca)	(.925)	(.944)	(.964)	(0.924)	(.970)	(.964)	(.997)	(.934)	(1.014)	(.972)
Fe^{3+}	-	-	-	-	-	.002	-	-	-	.002
Al	1.005	1.008	1.016	.989	.989	.985	.992	.998	1.003	.989
(Fe^{3+}+Al)	(1.005)	(1.008)	(1.016)	(0.989)	(.989)	(.987)	(.992)	(.998)	(1.003)	(.991)
P	1.011	1.013	1.003	1.019	1.015	1.008	1.023	1.010	1.018	1.015
O	4.00	4.039	4.000	4.022	4.033	4.062	4.092	3.984	4.116	4.025
F	.04	.108	.130	.144	.265	.279	.282	.312	.348	.427
(OH)	.965	.853	.870	.834	.702	.659	.626	.704	.536	.548
Sp. gr. meas.	3.024	2.992	3.015	3.007	3.022	3.008	3.022		3.037	3.037
	± .010	± .005	± .008	± .010	± .003	± .008	± .002		± .008	± .010
Sp. gr. calc.		3.033		3.022	3.037	3.042	3.036		3.059	3.067
γ'	1.6367	1.638	1.635	1.636	1.626	1.626	1.624		1.626	1.615
a_o(Å)	5.1957	5.1896	5.1872	5.1924	5.1801	5.1798	5.1783		5.1792	5.1681
	± 09	± 08	± 08	± 09	± 07	± 08	± 07		± 09	± 10
b_o(Å)	7.1681	7.1685	7.1699	7.1689	7.1755	7.1685	7.1770		7.1736	7.1816
	± 10	± 10	± 92	± 10	+ 11	± 13	± 12		± 14	± 10
c_o(Å)	5.0397	5.0407	5.0424	5.0422	5.0448	5.0438	5.0468		5.0451	5.0501
	± 10	± 07	± 07	± 08	± 06	± 07	± 09		± 10	± 09
α	112°19.4'	112°27.1'	112°28.7'	112°26.7'	112°43.7'	112°41.9'	112°49.3'		112°45.5'	113°5.6'
	± 0.9'	± 0.7'	± 0.7'	± 0.7'	± 0.7'	± 1.0'	± 0.7'		± 0.9'	± 0.7'
β	97°53.3'	97°55.9'	97°54.2'	97°57.3'	98°0.1'	98°0.4'	98°4.8'		98°00.5'	98°11.2'
	± 1.2'	± 0.7'	± 0.8'	± 1.0'	± 0.7'	± 0.9'	± 0.9'		± 1.0'	± 0.9'
γ	67°48.6'	67°48.5'	67°50.1'	67°47.3'	67°43.8'	67°45.1'	67°42.5'		67°43.6'	67°35.6'
	± 0.9'	± 0.1'	± 0.8'	± 0.7'	± 0.6'	± 0.7'	± 0.7'		± 1.0'	± 0.7'
V(Å^3)	160.76	160.46	160.48	160.59	160.04	159.91	159.95		159.94	159.39
	± .03	± .03	± .03	± .03	± .03	± .03	± .03		± .04	± .03
°$2\theta_{131}$ meas.†	52.14	52.24	52.22	52.22	52.35		52.42		52.42	52.56
°$2\theta_{131}$ calc.†	52.146	52.229	52.234	52.217	52.361	52.386	52.412		52.391	52.558

* Calculated values, ** anal. P. Povondra, *** anal. K. Ramlal et al., † for CuK$_{\alpha_1}$ radiation

line which connects the specific gravities of montebrasite and amblygonite end members (2.98 and 3.11 respectively) as given by Palache *et al.* (1951). However, different grains from a single specimen show considerable spread, and the measurement of three to five grains seems to be the only way of obtaining reasonable averages. (The differences among individual grains of a single specimen appear to be real, since repeated measurements of a single grain fall within ±.0015 and variations among different grains reach up to .03). Most of the specimens that plot below the 2.98 – 3.11 line contain abundant inclusions, particularly the samples AF-1 and AF-46.

These results appear to confirm the views of Nicolas (1968) who concluded, after a detailed study of actinolite, that inclusions and other crystal imperfections may play a much more important role than does the chemical composition in causing slight variations in specific gravities.

For amblygonites-montebrasites, these problems can be demonstrated by comparing the measured specific gravities to the values calculated from unit cell volumes and contents. Using the values of 161 Å^3 and 158 Å^3 for volumes of montebrasite and amblygonite, respectively (*cf.* the X-ray powder diffraction section below), the calculated densities are 3.01 for $LiAlPO_4(OH)$ and 3.11 for $LiAlPO_4F$. The calculated density of montebrasite is higher by .03 than that estimated by Palache *et al.* (1951). As shown in Figure 1, all the calculated densities are distinctly higher than the measured data, and the

TABLE 2, Continued

	A-60	A-29	A-3	A-13	AF-50	AF-46	AF-1	AF-65	AF-66	AF-48
Al_2O_3	33.53	32.86	34.63	34.18	34.26	35.16	31.62			
Fe_2O_3			.007							
CaO	.146	.132	.22	.015	.08	.013	.025			
MgO	.003	.002	.008		.015	.010	.005			
Li_2O	9.90	9.90	10.22	9.52	9.30	9.60	8.93	8.8		
Na_2O	.128	.047	.039	.082	.174	.097	.97	1.2		
K_2O	.005	.004		.005	.003	.004	.004			
P_2O_5	48.85	49.26	49.22	49.11	48.85	49.27	48.85			
H_2O-	.05	.06	.08	.06	.23	.05	.11			
H_2O+	3.32	3.21	2.70	3.37	3.29	2.92	4.93			
F	6.17	6.30	6.30	6.43	7.07	7.24	7.85	11.8		
	102.102	101.775	103.424	102.775	103.272	104.364	103.32			
-O=2F	-2.59	-2.65	-2.65	-2.70	-2.97	-3.06	-3.31			
Total	99.512	99.125	100.774	100.075	100.302	101.304	100.01			
Li	.997	.980	1.001	.934	.913	.933	.906			
Na	.003	.002	.002	.004	.008	.004	.047			
Ca	.004	.003	.006		.002					
(Li+Na+Ca)	(.984)	(.985)	(1.009)	(.938)	(.923)	(.937)	(0.953)			
Fe^{3+}	-	-	-	-	-	-	-			
Al	.969	.954	.994	.982	.985	1.001	.941			
(Fe^{3+}+Al)	(.969)	(.954)	(.994)	(.982)	(.985)	(1.001)	(.941)			
P	1.014	1.026	1.015	1.013	1.008	1.007	1.04			
O	3.977	3.903	4.076	3.956	3.920	3.977	4.003			
F	.479	.490	.486	.496	.545	.553	.627			
(OH)	.544	.527	.438	.548	0.535	.470	.270			
Sp. gr. meas.	3.031 ± .012	3.039 ± .008	3.048 ± .020	3.032 ± .009	3.000 ± .010	3.035 ± .010	3.007 ± .010	3.094 ± .012	3.030 ± .012	3.025 ± .010
Sp. gr. calc.	3.052	3.052	3.072	3.050	3.057	3.065	3.043			
γ'	1.614	1.616	1.614	1.616	1.612	1.609	1.605	1.5923	1.638	1.637
a_o(Å)	5.1694 ± 19	5.1691 ± 12	5.1668 ± 11	5.1705 ± 15	5.1670 ± 10	5.1643 ± 08	5.1606 ± 11	5.1483 ± 17	5.1960 ± 09	5.1946 ± 09
b_o(Å)	7.1815 ± 12	7.1782 ± 11	7.1807 ± 09	7.1799 ± 14	7.1825 ± 07	7.1863 ± 09	7.1879 ± 13	7.2071 ± 20	7.1694 ± 20	7.1712 ± 13
c_o(Å)	5.0507 ± 10	5.0513 ± 09	5.0482 ± 07	5.0509 ± 11	5.0497 ± 07	5.0533 ± 09	5.0499 ± 17	5.0601 ± 12	5.0378 ± 07	5.0430 ± 12
α	113°9.1' ± 0.8'	113°5.8' ± 1.1'	113°4.7' ± 0.6'	113°4.9' ± 1.0'	113°11.5' ± 0.6'	113°17.3' ± 0.7'	113°23.7' ± 1.3'	114°0.3' ± 1.3'	112°18.1' ± .8'	112°21.5' ± 1.0'
β	98°11.2' ± 1.5'	98°10.7' ± 1.3'	98°8.8' ± 0.9'	98°9.6' ± 1.4'	98°10.8' ± 1.0'	98°15.4' ± 0.8'	98°17.3' ± 1.7'	98°38.3' ± 1.6'	97°53.1' ± .9'	97°54.8' ± 1.3'
γ	67°32.6' ± 1.2'	67°35.4' ± 1.0'	67°37.3' ± 0.9'	67°36.3' ± 1.2'	67°34.4' ± 0.7	67°31.9' ± 0.7'	67°32.0' ± 1.4'	67°14.5' ± 1.6'	67°49.5' ± .9'	67°51.6' ± 1.0'
V(Å^3)	159.32 ± .05	159.38 ± .04	159.32 ± .04	159.48 ± .05	159.22 ± .03	159.18 ± .03	158.86 ± .05	158.15 ± .05	160.79 ± .03	160.92 ± .04
$^{\circ}2\theta_{131}$ meas.†	52.61	52.59	52.56	52.57	52.62	52.63		53.00	52.13	52.15
$^{\circ}2\theta_{131}$ calc.†	52.593	52.575	52.558	52.557	52.619	52.653	52.730	53.009	52.131	52.146

trend of their change with F-content follows reasonably well the 3.01-3.11 line connecting the theoretical end-member values.

The fairly large difference between the measured and calculated densities of F-poor montebrasites seems to be due to the secondary nature of most of these minerals, which usually contain a high content of impurities. The gem-quality montebrasites from drusy vugs that should be very poor in F (according to γ' and X-ray diffraction data) show specific gravities fitting the OH-rich end of the regression line for calculated densities (Table 2).

Refractive Index γ'

The refractive index γ' was measured in white light by the Becke method. The refractive index of the immersion liquids was measured by means of a Zeiss refractometer. The highest index of cleavage fragments showing the highest birefringence was measured and designated γ'. The true γ index is distinctly higher in most cases, since the optical direction *Z* deviates for most amblygonite-montebrasite compositions from the {100} cleavage.

Our data plotted in Figure 2 show very good alignment which considerably deviates from the γ/F relation derived from widely scattered data by Winchell and Winchell (1951). Our γ' values are significantly higher than the γ values given by them for about two thirds of the range of F-contents. Since the errors inherent in our technique could only decrease the γ' values, the difference between our and the Winchells' best fit lines for true γ should actually be still larger, and thus the plot of F *vs* refractive indices given by the quoted authors is undoubtedly erroneous (as suggested earlier by, *e.g.*, Ginzburg, 1950, and Staněk, 1960).

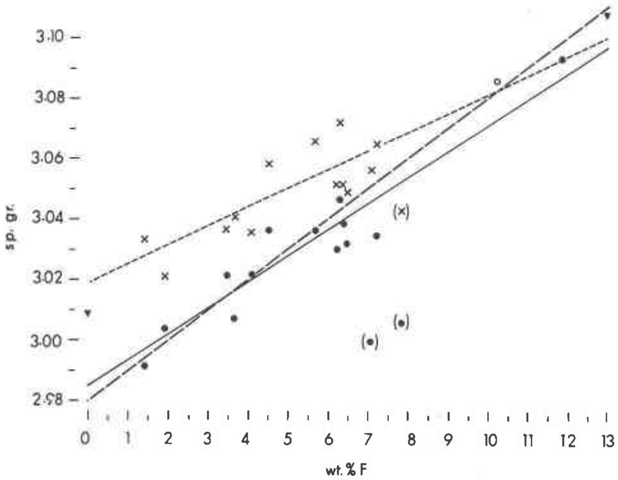

FIG. 1. Specific gravities (measured—dots; calculated—x; theoretical for ideal end members—triangles) plotted against F contents. Points in parentheses were not used in calculations of regression equations. Solid line—regression line for the measured data; heavy broken line—connects the 2.98 and 3.11 values given by Palache *et al.* (1943) for the end members; light broken line—regression line for the calculated data. Empty circle is the plot of the Na-rich Hebron sample (AF-55).

This conclusion is supported also by the γ values of 1.638 for a montebrasite with 1.29 wt percent F (Gallagher, 1967), and 1.645 for a montebrasite with sp gr 2.98 (Haapala, 1966).

Differential Thermal Analysis

The thermal behavior of 11 specimens has been studied using the automatic apparatus DTA-13M (R. L. Stone Co.). About 0.1 g of a 0.104-0.177 mm fraction (150–80 mesh) was heated in a platinum dish; Al_2O_3 was used as a reference standard. The rate of heating in air varied only negligibly about 100°C/10 min. The records were corrected for unbalance in the weights of sample and standard which causes vertical shifts, and for changes in the conductivity of the sample during heating by deducting the zero curve of a second run from that of the previously analyzed specimen.

The d.t.a. records (Figure 3 and Table 4) show several characteristic endothermic reactions: (1) A very weak reaction at 636 to 698°C seems to be more pronounced in F-poor minerals. (2) The major reaction at 751 to 793°C forms only a broad shoulder on a higher-temperature endotherm in the two F-richest specimens, then increases in intensity up to around 3 wt percent F, and decreases again for the F-poorest samples. This endotherm shifts from higher to lower temperatures with decreasing F-content. (3) A reaction at 795–811°C is the most prominent for the F-richest specimens. Although rather broad, it sharpens and increases in intensity in the 7 to 4 percent F range, then fades out rapidly. In the range 3.3 to 2.5 wt percent F it becomes perceptibly doubled, and then is united again. (4) A closely-spaced doublet, absent in the two F-richest specimens, de-

TABLE 3. Regression Equations and Correlation Coefficients

Specific gravity	=	.0087	x	wt.% F	+	2.9849	(.989)
γ'	=	-.00435	x	wt.% F	+	1.64223	(.989)
$°2\theta_{131}$ $CuK_{\alpha 1}$ meas.	=	.0750	x	wt.% F	+	52.1060	(.997)
$°2\theta_{131}$ $CuK_{\alpha 1}$ calc.	=	.0774	x	wt.% F	+	52.0919	(.993)
$°2\theta$ CuK_{α} $(\bar{1}01 - \bar{1}10)$	=	.0058	x	wt.% F	+	.4699	(.810)
$°2\theta$ CuK_{α} $(\bar{1}01 - \bar{1}\bar{2}1)$	=	-.0593	x	wt.% F	+	1.1099	(.985)
$°2\theta$ CuK_{α} $(\bar{1}01 - 0\bar{2}1)$	=	-.0511	x	wt.% F	+	1.6302	(.987)
$°2\theta$ CuK_{α} $(\bar{1}01 - 011)$	=	.0170	x	wt.% F	+	1.0077	(.958)
$°2\theta$ CuK_{α} $(\bar{1}01 - 120)$	=	-.0140	x	wt.% F	+	1.4781	(.942)
a_o	=	-.0043	x	wt.% F	+	5.1960	(.983)
b_o	=	.0029	x	wt.% F	+	7.1631	(.927)
c_o	=	.0018	x	wt.% F	+	5.0384	(.966)
α	=	.1516	x	wt.% F	+	112.1735	(.991)
β	=	.0651	x	wt.% F	+	97.7833	(.966)
γ	=	-.0531	x	wt.% F	+	67.9190	(.974)
V	=	-.2374	x	wt.% F	+	160.8696	(.986)

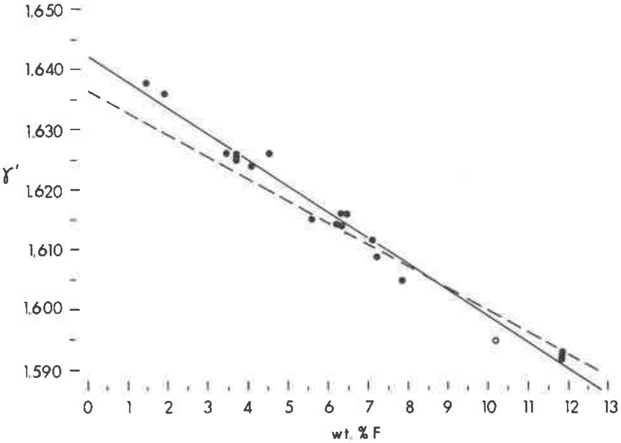

FIG. 2. The refractive indices γ' plotted against the F contents. The solid line is the regression line calculated from these data; the broken line is that given by Winchell and Winchell (1951) for true γ. Empty circle is the plot of the Na-rich Hebron sample (AF-55).

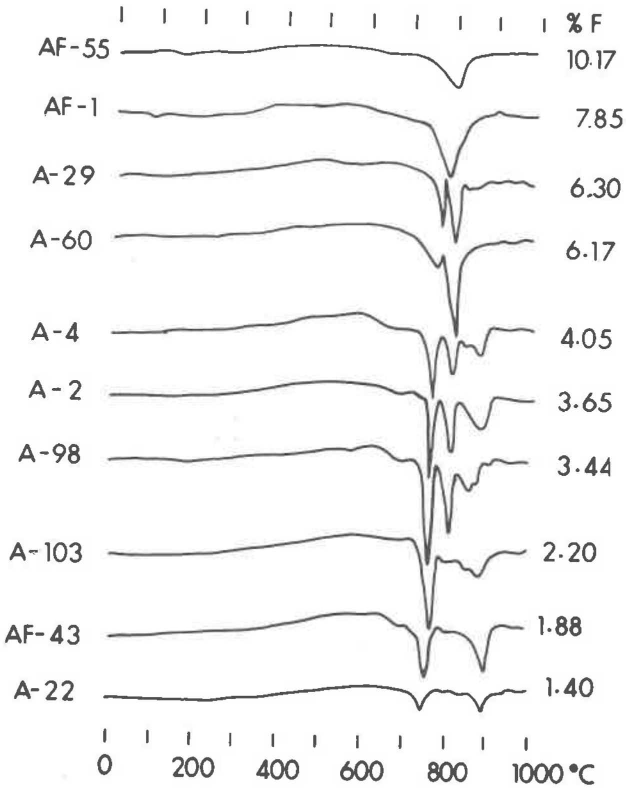

FIG. 3. Differential thermal analysis records of 10 chemically analyzed specimens; weight percentages of F are given at the right-hand side. Temperatures of reaction peaks are listed in Table 4.

velops gradually in the 6.5 to 3.4 wt percent F range in the 850–879°C region. From 3.4 wt percent F downwards, the first reaction becomes reduced to a mere shoulder and a broad slope on the higher-temperature reaction, which becomes much more intense for specimens with the F-content lower than 3 wt percent F and occurs at 896°C.[1]

The products of the d.t.a. treatment after heating to 1000°C have been identified by X-ray powder diffraction as $Li_4P_2O_7$, the high-temperature form of Li_3PO_4, and the berlinite-, tridymite-, and cristobalite-type forms of $AlPO_4$. Figure 4 shows the relative amounts of individual phases produced by the heating of a given specimen as estimated from the relative intensities of their most prominent peaks. The heights of the blocks for any one specimen are proportional to the amounts of the phases present; no absolute amounts are implied, and they are intended to show only the changes in mutual proportions among the five phases in different specimens. The tridymite- and cristobalite-type forms of $AlPO_4$ always occur together and in nearly equal amounts, their most prominent powder diffraction peaks being roughly of the same intensity; thus they are shown together in Figure 4.

For sample A-60 with 6.17 wt percent F, the heating products after each endotherm were X-rayed (at room temperature), and the phases identified and semiquantitatively estimated. The results illustrated in Figure 5 show the complicated reactions that take place during the heating of an intermediate amblygonite-montebrasite.

The phase assemblages obtained at 1000°C after the differential thermal treatment are understandably not equilibrated. Moreover, products of d.t.a. runs repeated on previously run samples differ considerably from the assemblages shown in Figure 4. This suggests that the relative phase abundances could be expected to be quite different not only after equilibrium heating, but also under different experimental conditions of the differential thermal analysis itself. This is documented by the d.t.a. results published by Manly (1950) and Boruckij (1966). Manly reported fusion of his sample at 850°C, whereas Boruckij found much of his charge unchanged at 900°C. Their d.t.a. patterns, as well as those published by Ginzburg (in Vlasov *et al.*, 1964), Ivanova (1961), and Correia Neves and Lopes Nunes (1968), either generally deviate from our records or approach those with different F-percentages.

TABLE 4. Temperatures of Differential Thermal Reactions*

Specimen	F% wt.	∿650°C	∿700°C	∿750°C	∿800°C	∿850°C	∿900°C
AF-55	10.17	(657)			(793) $\underline{811}$		
AF-1	7.85	(636)			(780) $\underline{797}$		
A-29	6.30				780 $\underline{810}$	(854) (870)	
A-60	6.17				777 $\underline{805}$		
A-4	4.05		(698)	$\underline{764}$	807	(850) 879	
A-2	3.65		(688)	$\underline{761}$	808	884	895
A-98	3.44		(689)	$\underline{760}$	812	862 879	
A-103	2.2**		(690)	$\underline{760}$	(795) (805)	(850) 881	
AF-43	1.88		(688)	$\underline{757}$	(800)		897
A-22	1.40		(684)	751	(800)		896

* ( ) = weak reaction; ___ = strong reaction.
** F-content estimated by X-ray powder diffraction method.

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[1] The only exception from these trends are the samples A-60 (6.17 wt% F) and A-29 (6.30 wt% F) that would fit the general scheme better if their positions in Figure 3 (and also in Figure 4) are interchanged. Perhaps their actual F-contents are reversed, since the determined values lie within the limits of analytical error.

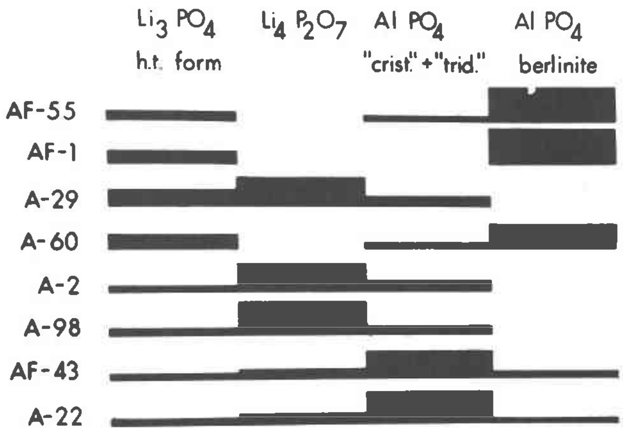

FIG. 4. Heating products of 8 chemically analyzed samples, as determined at room temperature by X-ray powder diffractometry in the products of d.t.a. treatment to 1000°C. Heights of blocks indicate the relative abundances of the individual phases. The tridymite and cristobalite forms of $AlPO_4$ are always present in about equal amounts.

X-Ray Powder Diffraction Methods

Reflection 131

Moss *et al.* (1969) give a graph for the determination of F-content based on the changes in $2\theta_{CuK\alpha}$ angle of the 131 reflection. Their diffractograms, however, were not calibrated and the data plotted in their Figure 3 show considerable spread.

In the present study, the diffractograms were calibrated with quartz as an internal standard. They were recorded using a slow scanning speed and a moderate chart driving speed which gave 1° 2θ per 5 cm. The absolute value of $2\theta_{131}$ for amblygonite-montebrasite was corrected using Frondel's (1963) calculated 2θ CuKα_1 angles for the $11\bar{2}2$ and $20\bar{2}2$ reflections of quartz. The graph presented in Figure 6 shows a much smaller scatter of individual plots than does that of Moss *et al.*, but the best fit line matches very well our lines drawn for both measured and calculated values (see Table 2). The maximum errors in readings of F should be lower than .5 percent.

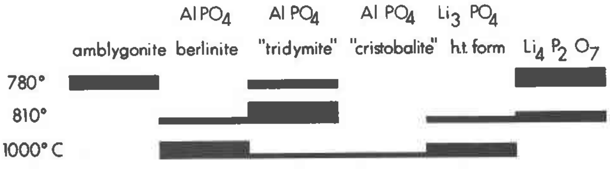

FIG. 5. Heating products of sample A-60 (6.17 wt percent F) as determined by X-ray powder diffractometry at room temperature after each endotherm in d.t.a. treatment. Heights of blocks indicate the relative abundances of the individual phases.

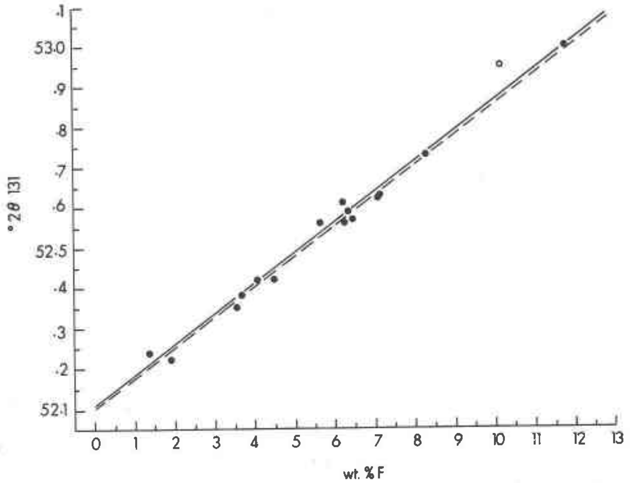

FIG. 6. Measured values of the 2θ CuKα_1 angles for the 131 reflection plotted against the F contents. The solid line is the regression line calculated for the measured data, the dashed line is that derived from values calculated from unit cell dimensions (see Tables 2 and 3).

Characteristic group of reflections

Moss *et al.* (1969) have shown that a group of X-ray powder reflections between 26 and 29° 2θ CuKα is sensitive to slight changes in the F content. We have developed a method for using this group of reflections for quantitatively estimating the F contents from uncalibrated X-ray powder diffractograms.

At the low-angle side of this group, the $\bar{1}01$ reflection is always well defined and not affected by overlap with other peaks. Thus it serves as a zero point from which the angular distances to the other reflections ($\bar{1}\bar{2}1$, $\bar{1}10$, $0\bar{2}1$, 011, and 120) are read. These distances, plotted on the appropriate scale on a paper strip, are then compared with our Figure 7 which relates the

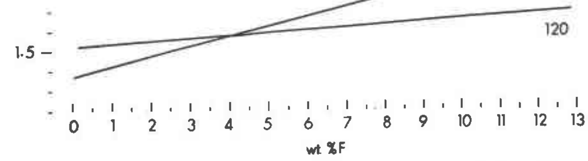

FIG. 7. The variations in angular distances of the X-ray powder diffraction reflections $\bar{1}\bar{2}1$, $\bar{1}10$, $0\bar{2}1$, 011, and 120 from the $\bar{1}01$ reflection. Regression equations are quoted in Table3.

$2\theta_{\mathrm{CuK}\alpha}$ positions of the six reflections to the F contents. With the "zero point" $\bar{1}01$ reflection of the examined record sliding on the $\bar{1}01$ line of the graph, the wt percent F in the examined mineral can be found in the position of best fit of the other five reflections; we regard the accuracy as ±.5 wt percent F or better.

The only disadvantage of this method is the partial or complete overlap of two reflections in several compositional ranges. However, with some practice it is possible in most cases to estimate correctly the positions of individual reflections in partially overlaping pairs, and there is always at least one resolved reflection present which aids in this estimate (*cf.* Figure 8). X-ray powder diffractograms of high resolution are of course needed to permit reading of the 2θ values to within ±.02°.

Unit cell dimensions

Glass-slide mounts of powdered amblygonites-montebrasites, with admixtures of subordinate quartz as internal standard, were run on a Philips Norelco diffractometer (Cu/Ni radiation, scanning speed ¼° 2θ/min. and chart driving speed 10 giving approximately 5cm/1°2θ, 400 counts/sec., time const. 4 sec.). Each sample was X-rayed three times, the powder being remounted for each run. All peaks were measured as close to the top as was reasonable, and 2θ values were then corrected using the theoretical $\mathrm{CuK}\alpha_1$-values for quartz calculated in Frondel (1963). Partial indexing was done using the data published by Haapala (1966) and Moss *et al.* (1969).

A least-squares refinement of unit cell dimensions was performed using the self-indexing program by Evans *et al.* (1963), modified by D. E. Appleman, with an input of 25 to 37 reflections for each specimen. The computer-calculated standard errors of the unit cell dimensions (Table 1) are mostly very small and even if doubled, as deemed more reasonable for feldspars by Wright and Stewart (1968), would still be smaller than the precision attained in earlier amblygonite-montebrasite studies. The large number of uniquely indexed and well shaped peaks obtainable from amblygonites-montebrasites likely accounts for this high precision, and the calibration by 6 to 8 quartz peaks distributed throughout the whole pattern makes us believe that the accuracy is also high.

The plot of unit cell dimensions *vs* F contents is shown in Figure 9. The calculated lines of best fit represent in our view a very good approximation in the range of the lower F contents, but are of a rather doubtful value in the high F range because of scarcity of data. It is possible that the plots of some unit

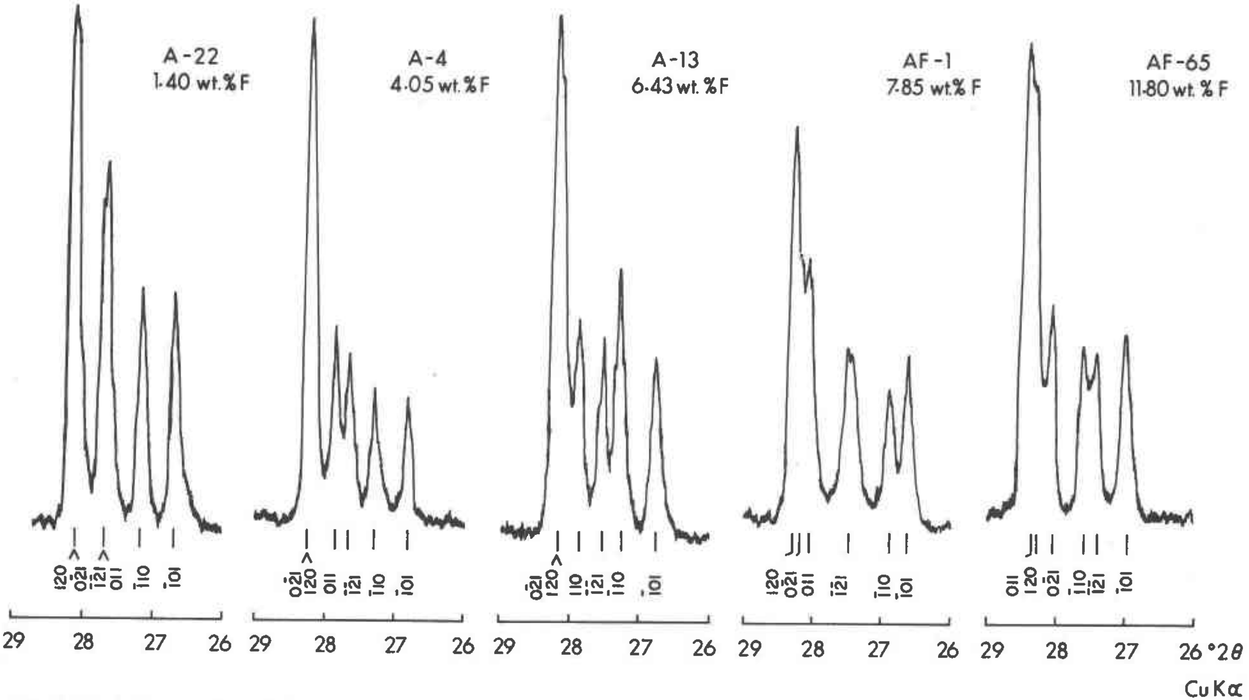

FIG. 8. Typical examples of the group of 6 reflections used for indirect determination of the F content by aid of Figure 7. Note the very good definition of all the $\bar{1}01$ reflections, used as zero points in reading the angular distances.

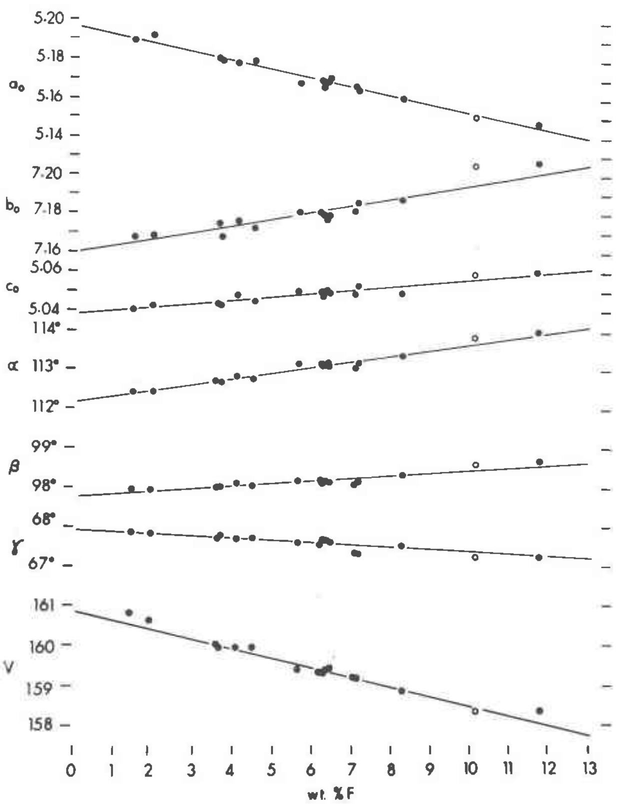

FIG. 9. Unit cell dimensions plotted against the F contents. Regression lines are calculated from equations given in Table 3. Empty circles are the plots of the Na-rich Hebron sample (AF-55).

cell dimensions follow very flat arcs (particularly those of b_o, β, and V), but this can be established only by collecting more data on F-rich amblygonites. For this reason it is not advisable to take the regression intercepts at $F = .00$ as accurate unit cell dimensions of pure montebrasite.

The deviations of individual plots from the best fit lines largely exceed the standard error values. They are probably caused by analytical errors in the determination of F, and by chemical substitutions other than F/OH and/or deviations from stoichiometry. Nevertheless the general agreement is distinctly better than that obtained by Moss *et al.* (1969), although most of their best fit lines are close to our regressions. Thus the graph presented in Figure 9 should yield estimates of the F-content correct to within ±0.5 wt percent F (see Table 2). Not to obscure the possibly curved alignment of our plots, the earlier data by Haapala (1966) and by Moss *et al.* (1969) shown in Figure 5 of the latter authors, are not included in our Figure 9.

Discussion

(1) From the different physical properties and determinative techniques used in this study, specific gravity and d.t.a. seem least suitable for the indirect determination of F contents in the examined mineral group. Specific gravity is too sensitive to the presence of impurities, and differential thermal behavior is too strongly dependent on the experimental setup.

(2) Optical properties are likely to be very useful once they are properly studied. The preliminary results obtained during the present study are good for only approximate estimates of the F contents. Nevertheless, we feel sure that these estimates would be much better than those based on earlier graphs of optical properties which have been shown to be unreliable (Winchell and Winchell, 1951). A detailed re-examination of the amblygonite-montebrasite optics is highly desirable.

(3) X-ray powder diffraction is evidently the best method available at present. The 2θ values of the 131 reflection, calibrated against quartz peaks, seem to be the most accurate. The "six-peak method" shows lower correlation coefficients but is faster in investigations where many dozens of samples are to be examined. Accurate unit cell dimensions should also yield quite reliable estimates, at least in the montebrasite half of the series, but the data collecting and computing process is time-consuming.

(4) It must be stressed, however, that fundamental prerequisites for the reliable use of the relationships and graphs presented in this study are Na_2O content lower than about 1.5 wt percent and optical homogeneity of the specimens. The influence of higher Na_2O contents is illustrated by the plots of the specimen AF-55. Since the determination of Na on minute samples is easily accomplished in most chemical laboratories, a series of specimens representative of all paragenetic types of amblygonites-montebrasites in a studied locality should be analyzed for Na before the indirect checks on F-contents are performed.

(5) As shown by Černá (1970) and Černá *et al.* (1972), grains and crystals of amblygonite-montebrasite minerals frequently show primary compositional zoning and/or secondary replacement by members of the same series with different F contents. Both zoning and replacement may betray themselves in hand specimens by slight changes in color, but usually they can be detected only microscopically. Thus thin section study and checks in immersion

liquids of material destined for X-ray diffraction work are necessary to ensure reliable results.

(6) In detailed investigations of individual specimens of amblygonite-montebrasite, great care should be taken to use only homogeneous material. A specimen being considered for chemical analysis should be studied in thin sections before crushing, and the required amount of the cleanest material separated out. The separated grains should be checked in oil immersion before final grinding, and material for the determination of physical properties should be sampled from them at random.

Differences between the analyzed and the optically studied material in many earlier studies are the most probable explanation for the poor correlation of optics with F content in Winchell and Winchell's (1951) graph. Differences between the analyzed and physically examined material can be demonstrated on Haapala's (1966) Hunnako montebrasite, which yielded 2.06 wt percent F in chemical analysis but its refraction index γ (1.624), specific gravity (3.023), and unit cell dimensions correspond to 4–5 wt percent F, when compared with our Figures 1, 2 and 9 (*cf.* also Moss *et al.*, 1969). The decrease in volume with increasing F content explains (at least partly) the discrepancy between Haapala's measured (3.023) and calculated (3.065) specific gravity.

(7) The structure of the amblygonite-montebrasite minerals has been studied by Simonov and Belov (1958) and by Baur (1959). Baur (1959) suggested the possible existence of high-temperature and low-temperature phases in the series, since the distributions of Li found in the two structure determinations were distinctly different. However, the chemical compositions of the minerals used in both structural studies were not known, and Baur concluded from indirect evidence that his crystal had a F/OH ratio 1:1. Moss *et al.* (1969) used their graph of F contents *vs.* unit cell dimensions to derive compositions for the specimens of Simonov and Belov and of Baur. They found that the Simonov and Belov values fall into the high-F half of the diagram, and that Baur's data approach closely the montebrasite composition.

We determined the unit cell dimensions and other physical characteristics of a crystal (AF-66) from the same suite of Newry specimens (Palache *et al.*, 1943, deposited in the mineral collections of the Harvard University) from which Baur obtained his material. All the properties fit a montebrasite with about 1 wt percent F, and we support the conclusion of Moss *et al.* that the difference between the two structures is probably due to compositional differences between the two minerals. Crystal structure refinements of analyzed amblygonites-montebrasites with different F/OH ratios would help to elucidate the crystal chemistry of this series.

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