

## Amblygonite-montebbrasite optics: Response to (OH<sup>-</sup>) orientation and rapid estimation of F from 2*V*

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### ABSTRACT

For 11 crystals of the amblygonite-montebbrasite series, LiAlPO<sub>4</sub>(F,OH), ranging in composition from 4.0 to 91.8 mol% F (and only 2 containing significant Na), 2*V* and principal refractive indices were determined to 0.5° and 0.0005, respectively, by spindle-stage methods. If the F content is <60 mol% and therefore 2*V*<sub>z</sub> < 116°, as is true for the vast majority of natural specimens, the F content can usually be estimated to within 2 mol% from evaluating [F] = -66.3 + 1.08 × 2*V*<sub>z</sub> as well as from similar regression equations involving the refractive indices α, β, and γ. Above 60 mol% F, the optical properties are less sensitively (and nonlinearly) related to F content. Estimates of F content are feasible despite significant substitution of Na for Li. By contrast, this substitution may introduce significant errors when estimating F content by methods involving lattice parameters.

Progressive substitution of (OH), a natural dipole involving a covalent bond, for the relatively nonpolarizable F anion causes all three principal refractive indices to increase; γ increases more than α or β because its corresponding principal vibration direction Z becomes subparallel to the O-H vector in the structure as (OH) content increases.

### INTRODUCTION

For the amblygonite-montebbrasite solid-solution series, <sup>v</sup>(Li,NaCa)<sup>v1</sup>(Al,Fe,Mg)<sup>v</sup>PO<sub>4</sub>(F,OH), the elements in boldface represent the primary constituents. Thus, in the common representatives of this series, less than 10% of the five-coordinated Li sites contain Na and/or Ca and less than 0.1% of the six-coordinated Al sites contain Fe and/or Mg. Thus these specimens represent essentially binary solid solutions between the end members, amblygonite (amb), LiAlPO<sub>4</sub>F, and montebbrasite (mtb), LiAlPO<sub>4</sub>(OH). Natural members of the series range from amb<sub>0</sub> to amb<sub>92</sub>, but specimens more F-rich than amb<sub>65</sub> are rare.

Members of the amblygonite-montebbrasite series are triclinic and biaxial. If negative in sign, they are called amblygonites, and if positive, montebbrasites. Phillips and Griffen (1981) indicated that the optic sign changes from (+) to (-) at amb<sub>35</sub>, but present evidence, as will be demonstrated, places the change closer to amb<sub>30</sub>. The structural similarity between amblygonite and titanite becomes apparent when a nearly monoclinic cell is chosen as suggested by Simonov and Belov (1958) and as employed recently by Hawthorne (pers. comm.) during refinements of amblygonite-montebbrasite structures.

The dependence of the physical properties of the series on the dominant F-(OH) substitution has been studied by many investigators. The usual goal has been to find one or more physical properties to serve as reliable estimators of the F content. In such event, particularly if the

physical property were quickly and precisely measurable, monitoring the F contents in members of the amblygonite-montebbrasite series could permit recognition of the F-(OH) zoning in pegmatites, where these minerals exclusively occur.

Although initiated by Bragg (1924), studies relating a crystal's optical properties to its composition and structure are infrequent in mineralogy, often due to the imprecision of available data. Thus, prior to the development of microprobe and spindle-stage techniques, a chemical analysis of a 1- or 2-g sample of a biaxial mineral—itsself rendered suspect because of the possible presence of impurities in the sample—was often coupled with a refractive index α measured from one grain, β from another, and γ from still a third. Moreover, the precision of their measurement, usually ±0.002 or ±0.003, was insufficient and frequently overly optimistic. Now, however, from one and the same grain it is possible to measure all indices to ±0.0005 by spindle stage, transfer the goniometer head containing the grain to an X-ray camera for such X-ray studies as desired, and, ultimately, determine this same grain's composition by microprobe analysis.

Tight relations among optics, composition, and structure can thus be established and have led to an increasing number of recent studies (Selkregg and Bloss, 1980; Armbruster and Bloss, 1982; Su et al., 1984; Mereiter and Preisinger, 1986; Lager, 1986; to cite only a few). Combined X-ray, spindle-stage, and microprobe studies of the members of a solid-solution series have been of particular interest. With the substitution of one atomic species for

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TABLE 1. Sample descriptions and pegmatite localities

Sample nos.	Description and locality
1. AF-47	5841* Bluish water-clear crystals from pegmatite vugs with quartz and cleavelandite; F content not determined (Plumbago, Newry, Maine)
2. AF-43-2	117775* Grayish-white cleavage fragment (Gunnison Co., Colorado)
3. A-22**	Brownish translucent, massive
4. A-98**	Pale yellow translucent mass
5. A-1**	Pale pink core of a zoned crystal (see A-2), slightly contaminated by secondary montebrasite (~5%)
6. AF-46	105914* Pale bluish cleavage fragments (Karibib, South Africa)
7. AF-55	62576* Colorless cleavable mass (Hebron, Maine)
8. AF-65	14274† Translucent fragments with faint bluish tint (Chursdorf, Saxony)
9. A-2‡	Yellow outer rim of a zoned crystal (see A-1)
10. A-5‡	Yellow translucent, veined by A-4.
11. AF-50	10432* Pale brown transparent mass (Coolgardie, Western Australia)

Note: Modified from Černá et al. (1973). All crystals removed from these samples and studied optically were clear, contained few inclusions, and showed no evidence of zoning. Crystals for AF-43, A-22, AF-50, and AF-65 each contained a few lamellae of a polysynthetic twin component. The crystal studied optically for sample AF-43 is the same crystal for which Hawthorne (pers. comm.) performed a structure analysis.

\* U.S. National Museum sample number.

† British Museum of Natural History sample number.

‡ Sample number of specimens from the Tanco pegmatite, Bernic Lake, Manitoba, Černá et al. (1973).

another in a solid-solution series, the optical properties often change, because the substitution may involve changes in atomic number and electronic shell structure, polarizability, ionic radius, valence, electronegativity, charge transfer, disposition and distances of nearest neighbors around the site of the substituent, and/or even the proportion of one bond type relative to another.

The amblygonite-montebrasite series was thus of interest, because it involved the replacement of a relatively nonpolarizable anion,  $F^-$ , by a natural dipole,  $(OH)^-$ , containing an appreciably covalent bond that tended to be directionally oriented in the structure.

### EXPERIMENTAL METHODS

The experimental methods used have been described fully by Greiner (1986). In summary, optical constants were determined for each crystal (Table 1) by spindle-stage methods. Estimated precisions are  $2V$  ( $\pm 0.5^\circ$ ), refractive indices ( $\pm 0.0005$ ), and location of the principal vibration axes  $X$ ,  $Y$ , and  $Z$  ( $\pm 0.5^\circ$  or better). Transfer of the goniometer head from the Supper spindle stage to an X-ray precession camera permitted determination of the angular attitude of the triclinic axes (Palache, 1943) relative to  $X$ ,  $Y$ , and  $Z$ .

### CHEMISTRY

The amblygonite-montebrasite crystals examined were from the same specimens studied by Černá et al. (1973), ranging from translucent to gem quality and relatively homogeneous in composition throughout each single specimen (P. Černý, pers. comm.). Microprobe analyses

of these crystals showed Mg and Fe to be below detectable limits and Ca to be below 0.1 mol%. Na was below detectable limits for all samples except numbers 7 and 8, in which it exceeded 2 wt%. Al and P were nearly constant. This suggested that the eight crystals contained no significant substitutions other than F for (OH). Attempts to determine F content by calculation from microprobe analyses were unsuccessful. An initial spindle-stage study of several different crystals from each specimen yielded  $2V$  values, as calculated by EXCALIBR (Bloss, 1981), that differed by two degrees at most except for one sample in which they differed by four degrees. Thus, it seemed valid to assume that crystals from a given specimen differed little in optical properties and composition from each other. Accordingly, the F compositions (neutron activation) and (OH) compositions (gravimetric analysis) obtained by Černá et al. (Table 2, 1973) were accepted as valid for these crystals. For sample 8, Moss et al. (1969) determined F from its distillate using the zirconium-Eriochrome-cyanine method of Megregian (1954). No complementary (OH) analysis has been performed on sample 8.

In this paper the F content will be expressed as mole percent F [F]—that is, as 100 times the atomic frequency of F in the formula unit. [F] and [OH] (mole percent hydroxyl) were calculated by Černá et al. (1973) from the weight percentages they obtained for F and  $H_2O$ . The values for [F] and [OH] were adjusted for the presence of minor Na, Ca, K, Mg, and Fe. Complete chemical analysis of sample 8 has not been performed. Accordingly, for sample 8, [F] was calculated from the equation

$$[F] = 7.7845 \times \text{wt\% F.}$$

This equation correctly relates mole percent to weight percent F for samples wherein only the F-(OH) substitution occurs. Such a condition is not strictly valid for sample 8, since it contains significant ( $> 2$  wt%) Na. Still, any errors introduced by falsely assuming a lack of substitutions other than F for (OH) for these samples will be very small. The equation

$$\text{wt\% F} = 0.12846 \times [F]$$

will convert these values to weight percent F for all amblygonites and montebrasites in which substitutions except (OH) for F can be considered minimal. Table 2 summarizes the content of [F] and [OH] in the specimens from which the crystals studied were drawn.

### VARIATIONS OF OPTICAL PROPERTIES WITH MOLE PERCENT F

#### Previous work

Research on the optical properties of the amblygonite-montebrasite series is limited. Winchell and Winchell (1951) plotted refractive index and the optic axial angle  $2V$  versus (OH) content, using data from the literature, but the data points were widely scattered. Dubois et al. (1972) performed least-squares regressions on  $2V$  and refractive-index data measured for samples in the amb<sub>0</sub> to amb<sub>20</sub> range. The data show considerable scatter about the

TABLE 2. F and OH contents

Sample	[F] (mol%)	[OH] (mol%)	[F] + [OH] (mol%)	[F] <sub>w</sub> (wt%)	H <sub>2</sub> O <sub>+</sub> <sub>w</sub> (wt%)	H <sub>2</sub> O <sub>-</sub> <sub>w</sub> (wt%)
1	4.0*	96.5	—	0.30	5.98	0.10
2	10.8	85.3	96.1	1.40	5.25	0.07
3	14.4	83.4	97.8	1.88	5.11	0.06
4	26.5	70.2	96.7	3.44	4.43	0.05
5	42.7	54.8	97.5	5.56	3.39	0.10
6	55.3	47.0	102.3	7.24	2.92	0.05
7	79.2	25.0	104.2	10.17	1.53	0.09
8	91.8	—	—	11.80	—	—
9	27.9	65.9	93.8	3.65	4.09	0.04
10	34.8	53.6	88.4	4.51	3.30	0.08
11	54.5	53.5	108.0	7.07	3.29	0.23

\* Calculated value; see Černá et al. (1973).

trends, and these regressions indicated, for the most part, lower  $2V$  and refractive-index values than those predicted by Winchell and Winchell's graphs over the same compositional range. Černá et al. (1973) measured the index  $\gamma'$  for crystals lying on the {100} cleavage and found that it exceeded those that Winchell and Winchell had reported for  $\gamma$ . This underscored the need for a more accurate set of optical data for the series. The application of spindle-stage techniques to the chemically well-characterized specimens assembled by Černá et al. (Table 1) thus seemed in order.

### Optic orientation

Burri (1956) introduced the use of Euler angles to express quantitatively the optic orientation of the optical indicatrix's principal vibration axes ( $X$ ,  $Y$ , and  $Z$ ) relative to the crystallographic axes of a triclinic crystal. In essence, he related the intrinsically orthogonal set of axes ( $X$ ,  $Y$ , and  $Z$ ) to a second orthogonal set obtained by choosing (1) a reciprocal crystallographic axis; (2) one of the two direct crystallographic axes perpendicular to it; and (3) a third axis that is perpendicular to both (1) and (2). The cleavage planes for the amblygonite-montebbrasite series made it expedient to select from the crystallographic axes chosen by Palache et al. (1943) the orthogonal set (1)  $a^*$ ; (2)  $c$ ; and (3)  $B$ , where  $B$  symbolizes a direction perpendicular to both  $a^*$  and  $c$ . Euler angles for Na light (Table 3) were calculated (Greiner, 1986) such that if the corresponding rotations were performed,

$X$  would coincide with  $B$ ,  $Y$  with  $a^*$ , and  $Z$  with  $c$  (Fig. 1).

For the six crystals for which the optic orientation had been determined relative to the crystallographic axes chosen by Palache et al. (1943), optic orientation changed systematically as [F] varied from 4 to 92 (Fig. 1). Note that with increasing [F], the two optic axes ( $OA_1$  and  $OA_2$ ) move away from  $Z$  and approach  $X$  so that the optic sign changes from (+) to (-). For [F] = 79 and 92, however, note that  $OA_1$  and  $OA_2$  no longer move directly toward  $X$  but turn slightly away. Thus,  $2V_x$  ceases to decrease (and  $2V_z$  to increase) as rapidly with increased F when [F] exceeds ~60. With increased F, one optic axis ( $OA_1$ ) changes relatively little in position, whereas  $OA_2$  changes markedly. The situation is reminiscent of another triclinic solid-solution series, the plagioclases (Reinhard, 1931), in which one optic axis changes markedly in position as Ca content changes, whereas the other does not (Bloss, 1978).

### Refractive indices and $2V$

Principal refractive indices ( $\alpha$ ,  $\beta$ , and  $\gamma$ ) and values of  $2V_z$  calculated by EXCALIBR for Na light (Table 3) were determined for specimens 1 to 11. Except for samples 1 and 8, an F analysis and an independent (OH) analysis had been reported for each (Černá et al., 1973). These F and (OH) analyses were consistent for specimens 2 to 7 in that [F] + [OH]  $\approx$  100. For specimens 9, 10, and 11, however, the sum deviated by more than 5% from 100%. Accordingly, the data for specimens 9, 10, and 11 were omitted from the calculations when regressions were performed. The following models relating optical parameters to [F] (= mole percent F), and indeed all subsequent ones, were derived by a combined use of the STEPWISE and RSQUARE (Cp option) procedures of the SAS Institute (Ray, 1982).

$$\alpha = 1.61755(78) - 5.31(27) \times 10^{-4}[F] + 1.14(33) \times 10^{-10}[F]^4 \quad R^2 = 0.996 \quad (1)$$

$$\beta = 1.62570(11) - 3.07(11) \times 10^{-4}[F] + 3.98(29) \times 10^{-6}[F]^2 + 3.60(22) \times 10^{-8}[F]^3 \quad R^2 = 0.999 \quad (2)$$

TABLE 3. Refractive indices,  $2V$ , and Euler angles  $\Phi$ ,  $\Theta$ , and  $\Psi$  as observed for Na light

Sample	[F]	$\alpha^\dagger$	$\beta^\dagger$	$\gamma^\dagger$	$2V_z^\dagger$	$\Phi$	$\Theta$	$\Psi$
1	4.0*	1.61476	1.62440	1.64589	66.27	82.4	-26.0	77.8
2	10.8	1.61088	1.62190	1.64026	71.63	—	—	—
3	14.4	1.61043	1.62067	1.63800	72.82	—	—	—
4	26.5	1.60536	1.61533	1.62963	85.15	86.3	-23.9	76.4
5	42.7	1.59530	1.60816	1.61784	100.76	92.0	-20.8	77.8
6	55.3	1.58856	1.60263	1.60913	112.57	100.5	-14.3	81.0
7	79.2	1.57923	1.59417	1.59749	125.98	43.0	14.7	18.0
8	91.8	1.57723	1.59180	1.59560	129.47	55.5	18.2	30.0
9	27.9	1.60052	1.61283	1.62488	92.87	—	—	—
10	34.8	1.59532	1.60840	1.61753	99.31	—	—	—
11	54.5	1.59123	1.60536	1.61273	106.98	—	—	—

$\dagger$   $\alpha$ ,  $\beta$ , and  $\gamma$  should be rounded to the 4th and  $2V_z$  to the 1st decimal place.

\* Calculated value, see Černá et al. (1973).

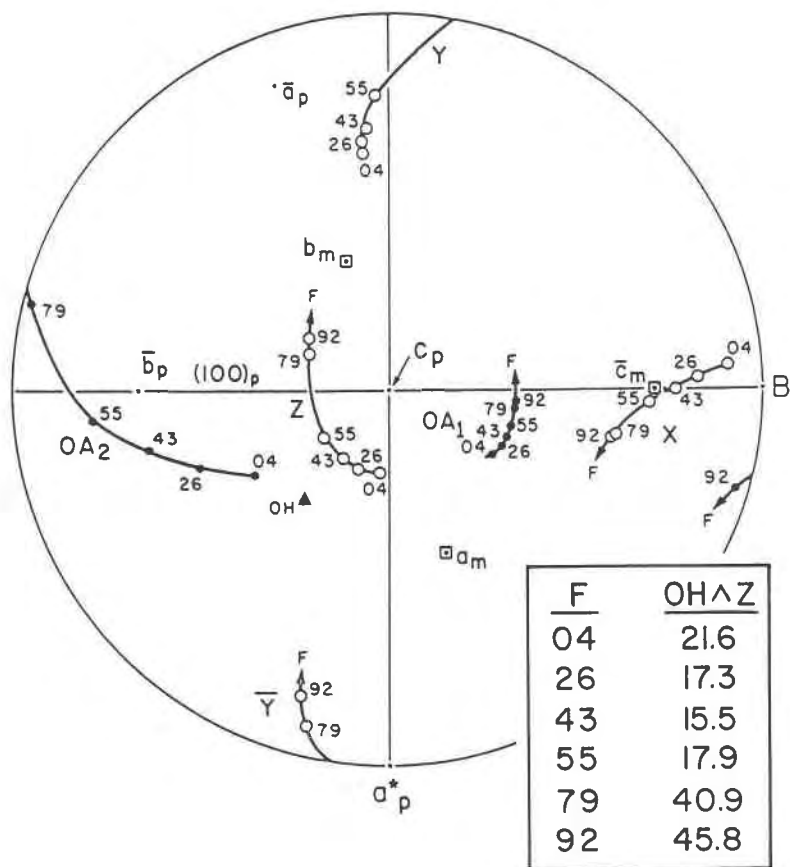


Fig. 1. Stereographic depiction of the variation in orientation of the two optic axes ( $OA_1$  and  $OA_2$ ) and the three principal vibration axes ( $X$ ,  $Y$ , and  $Z$ ) relative to  $c$  and  $a^*$  as mole percent  $F$  varies in the amblygonite-montebbrasite series. The dots represent data for the six crystals whose optic orientations were determined empirically; the numbers adjacent to the dots represent mole percent  $F$  for these crystals. The subscript  $p$  indicates crystal axes chosen by Palache et al. (1943); the subscript  $m$  and the small squares designate the almost monoclinic axes employed by Hawthorne (pers. comm.). The triangle represents the O-H bond direction as determined by Hawthorne. The inset represents the angle between  $Z$  and the O-H vector for the six crystals whose  $[F]$  values are listed. The Palache axes  $a^*$  and  $c$  were chosen because they are defined by the perfect  $\{100\}$  cleavage and the good  $\{110\}$  cleavage. Thus,  $a^*$  is normal to the perfect cleavage and  $c$  represents the trace of the good cleavage on this perfect cleavage.

$$\gamma = 1.64884(31) - 7.50(11) \times 10^{-4}[F] + 2.17(16) \times 10^{-10}[F]^4 \quad 0.999 \quad (3)$$

$$2V_Z = 60.86(95) + 0.96(3)[F] + 2.73(40) \times 10^{-7}[F]^4 \quad 0.998 \quad (4)$$

actually vary linearly between 0 and 60  $[F]$ . Indeed, of regressions tested on only the optical data for specimens 1 to 6, linear models, with  $F$  content as the dependent variable, most aptly fit the data and are given below:

These models and the data from which they were derived, along with the data for specimens 9, 10, and 11, are plotted in Figure 2. The dashed curve ( $2V_{RI}$ ) represents  $2V_Z$  as calculated from the refractive-index curves below it. Note that it closely conforms to the solid curve ( $2V_{EX}$ ) representing a regression (Eq. 4) on the  $2V_Z$  values calculated by EXCALIBR.

Although the nonlinear refractive-index and  $2V_Z$  curves in Figure 2 appear to suitably relate sample 1 through 8 to  $F$  content, similar relations could not be established with  $F$  content taken as the dependent variable. It appears from Figure 2, however, that  $2V$  and the principle refractive indices for the amblygonite-montebbrasite series may

$$\alpha = 1.61727(71) - 5.10(23) \times 10^{-4}[F] \quad R^2 \quad 0.996 \quad (5)$$

$$\beta = 1.62651(20) - 4.29(6) \times 10^{-4}[F] \quad 0.999 \quad (6)$$

$$\gamma = 1.64834(22) - 7.11(7) \times 10^{-4}[F] \quad 0.999 \quad (7)$$

$$2V_Z = 61.30(81) + 0.92(3)[F] \quad 0.998 \quad (8)$$

If these models were also plotted in Figure 2, their lines would closely follow along the nonlinear models until  $[F]$  exceeded  $\sim 60$  (Fig. 3). Above  $[F] = 60$ , the linear models begin to deviate markedly from the nonlinear curves of Figure 2 and do not adequately fit the  $2V$  and refractive-index data.

Upon examination of Figure 3, one might suspect that

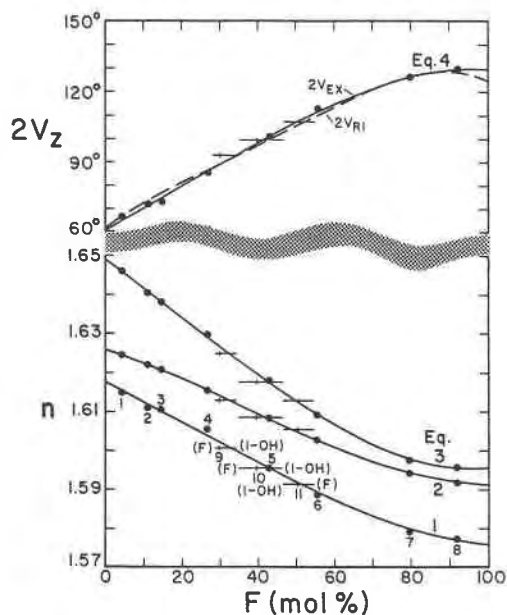


Fig. 2. Nonlinear models for  $2V_z$  and refractive indices vs.  $[F]$  (mole percent F). Solid refractive-index curves obtain from regression Equations 1, 2, and 3. The solid curve denoted  $2V_{EX}$  represents a regression (Eq. 4) of EXCALIBUR-derived  $2V_z$  values vs.  $[F]$ ; the dashed curve (denoted  $2V_{RI}$ ) represents  $2V_z$  as calculated from the refractive-index curves below. For samples 9, 10, and 11, whose F contents were uncertain, horizontal lines extend from analyzed  $[F]$  to 100 minus the analyzed  $[OH]$  value [symbolized  $(1 - OH)$ ]. The vertical ticks indicate the values of mole percent F for these samples if  $[F]$  plus  $[OH]$  is normalized to 100 mol%.

the F contents of samples 7 and/or 8 may actually be lower and that the linear models of refractive index are valid across the entire series. If this were true, the  $\gamma$  and  $\beta$  refractive-index curves would intersect and result in the existence of a pseudo-uniaxial amblygonite at the composition having  $\gamma = \beta$ . Examination of Figure 1, however, clearly shows that the migration curves of the two optic axes do not converge so as to eventually coincide with a principal direction,  $X$  in this case, as would be required of a biaxial mineral approaching uniaxiality.

### PREDICTION OF MOLE PERCENT F

#### Previous work

Moss et al. (1969), using uncalibrated powder films and diffractometer tracings, determined the relationship of F content to cell parameters and to  $2\theta_{131}(\text{CuK}\alpha_1)$  for the amblygonite-montebbrasite series. Černá et al. (1973) used diffractometer tracings of amblygonite and montebbrasite powder, intermixed with quartz, as an internal standard, to accomplish this. Even though the unit-cell parameters showed only small variations in response to F content, the F contents proved predictable to  $\pm 4$  mol% from values of  $2\theta_{131}(\text{CuK}\alpha_1)$ . Černá et al. also plotted, relative to F content, the peak differences ( $2\theta_{hk1} - 2\theta_{011}$ ), where  $2\theta_{hk1}$  successively represented the 121, 110, 021, 011, and 120

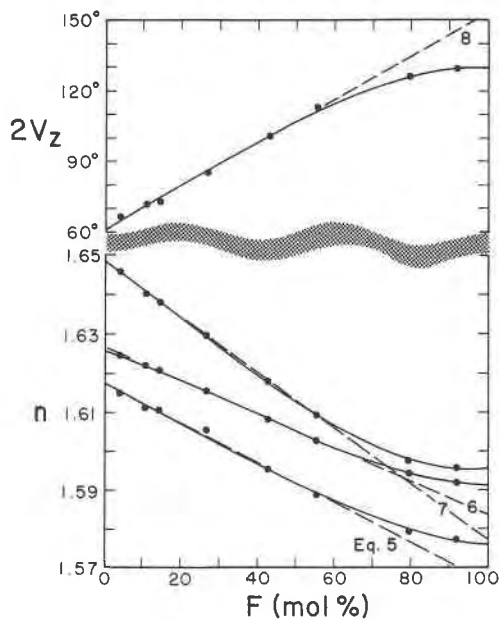


Fig. 3. Linear models (dashed) compared to the nonlinear models for  $2V_z$  and refractive indices vs.  $[F]$ . The linear models represent Equations 5–8.

peaks. Again, estimates of F content to  $\pm 4$  mol% resulted. Although the method is faster than the  $2\theta_{131}$  method, these peaks may overlap within several compositional ranges. Kallio (1978) utilized four uncalibrated reflections between  $46^\circ$  and  $54^\circ 2\theta$  ( $\text{CuK}\alpha_1$ ) to estimate F contents to  $\pm 5.5$  mol%.

Fransolet and Tarte (1977) studied infrared spectra of this series and established linear relationships between F content and the frequencies of both the stretching ( $\nu_{OH}$ ) and bending ( $\delta_{OH}$ ) vibrations of the (OH) molecule. Thus,  $\nu_{OH}$  and  $\delta_{OH}$  served to estimate F content to  $\pm 4$  mol% and  $\pm 3$  mol%, respectively. Černá et al. (1973) examined the applicability of specific gravity and of differential thermal analysis as determinative techniques. Neither proved useful because, as they stated, “specific gravity is too sensitive to the presence of impurities, and differential thermal behavior is too strongly dependent on the experimental setup.”

#### This study

Regressions, performed on the data for specimens 1 to 6 using  $[F]$  as the dependent variable, yielded the following models, which are only valid for  $[F] < 60$  mol% and thus for  $\alpha > 1.587$ ,  $\beta > 1.601$ ,  $\gamma > 1.606$ , and  $2V_z < 116^\circ$ :

	$R^2$	
$[F] = 3148(139) - 1946(87)\alpha$	0.992	(9)
$[F] = 3785(56) - 2327(35)\beta$	0.999	(10)
$[F] = 2317(22) - 1405(14)\gamma$	0.999	(11)
$[F] = -66.3(2.6) + 1.08(3) \times 2V_z$	0.997	(12)

Of these models, Equation 12 seems the most practical

TABLE 4. Observed and estimated F contents in mol% for samples with  $[F] < 60$ 

Sample	F observed from		F predicted from			
	$[F]_{100-[OH]}$	$[F]_{DIR}$	$[F]_{\alpha}$ (Eq. 9)	$[F]_{\beta}$ (Eq. 10)	$[F]_{\gamma}$ (Eq. 11)	$[F]_{2V}$ (Eq. 12)
1*	3.5	4.0	5.1	5.0	3.5	5.5
2	14.7	10.8	12.6	10.8	11.4	11.3
3	16.6	14.4	13.5	13.6	14.5	12.6
4	29.8	26.5	23.4	26.0	26.3	25.9
5	45.2	42.7	43.0	42.7	42.9	42.8
6	53.0	55.3	56.1	55.6	55.1	55.6
9	34.1	27.9	32.8	31.8	32.9	34.3
10	46.4	34.8	42.9	42.1	43.3	41.3
11	46.5	54.5	50.9	49.2	50.0	49.6
A**	—	17.0	31.9	36.1	34.2	23.0
B†	—	45.0	59.1	—	52.4	—
C‡	—	10.0	4.6	—	14.5	—

\*  $[F]_{100-[OH]}$  is from direct  $[OH]$  measurement, and  $[F]_{DIR}$  is calculated from  $100 - [OH]$  for this sample.

\*\* Haapala (1966).

† Mookherjee et al. (1979).

‡ Gallagher (1967).

because (1)  $2V_z$  can be quickly measured to a fraction of a degree by using a simple detent spindle stage (Bloss, 1981) to collect extinction data for Na light and then processing the data with EXCALIBUR; and (2) accordingly, if  $2V_z < \sim 116^\circ$ , F should be predictable to within 2 mol%. Thus, unless  $[F]$  exceeds 60 mol%, which is rare, Equation 12 probably represents the most rapid method yet known for precisely calculating the F content of a montebrasite or amblygonite from a physical property.

Table 4 compares the observed F contents—namely, those determined directly by chemical analysis  $[F]_{DIR}$  or by hydroxyl difference,  $100 - [OH]$  or  $[F]_{100-[OH]}$ —with the F contents determined by inserting the measured optical parameters of samples 1 to 6 and 9 to 11 into Equations 9 to 12. Clearly,  $2V_z$  and all three refractive indices are successful estimators of F contents between 0 and 60 mol%. However, if the chemically determined F contents taken from the literature for specimens 1 to 6 were systematically high or low, the same will be true of the values determined from Equation 12.

For specimens 9, 10, and 11, wherein a discrepancy existed between  $[F]_{DIR}$  and  $[F]_{100-[OH]}$ , the value predicted from  $2V_z$  almost coincided with  $[F]_{100-[OH]}$  for specimen 9 and fell between  $[F]_{DIR}$  and  $[F]_{100-[OH]}$  for specimens 10 and 11. Note also that the optical properties of sample 10 closely conform to those of sample 5.

A search of the literature disclosed three specimens (A, B, and C in Table 4) for which F contents and partial optical analyses were available (Haapala, 1966; Mookherjee et al., 1979; Gallagher, 1967). However, significant discrepancies exist between their reported F contents and those predicted by inserting their reported optical parameters into Equation 9, 10, 11, or 12. These discrepancies may have resulted from incorrect chemical and/or optical data, or there may actually have been differences in F content between the samples examined optically and those chemically analyzed.

Černá et al. (1973) carefully selected homogeneous material for each of the samples used in their study and, subsequently, in several other studies, including this one. Such attentive preparation of samples may have been absent in previous optical work, and thus, as stated by Černá et al., “the differences between the analyzed and the optically studied materials in many earlier studies are the most probable explanation for the poor correlation of optics with fluorine content in Winchell and Winchell’s (1951) graph.” Concerning differences in F content between samples analyzed chemically and samples subjected to measurement of physical properties, Černá et al. (1973) stated, “grains and crystals of amblygonite-montebrasite minerals frequently show primary compositional zoning and/or secondary replacement by members of the same series with different fluorine contents.”

Discrepancies between optically and chemically determined F contents may also be due to the presence of fluid inclusions and daughter minerals that contain F in concentrations greater or less than that of the host mineral. F contained within fluid inclusions and daughter minerals would be incorporated into the F analysis of a sample by a technique such as neutron activation. By contrast, F estimates based on optical properties refer only to that contained in the host mineral, assuming that the equations used for estimation were derived, as they indeed were, from a suite of samples with few inclusions. Černá et al. (1973) reported their specimen AF-1, which contained abundant inclusions, to contain 62.7 mol% F by neutron activation ( $= [F]_{DIR}$ ) but 73.0 mol% by hydroxyl difference ( $= [F]_{100-[OH]}$ ). The angle  $2V$ , measured for a crystal of AF-1, estimated  $[F]$  by use of Equation 12, at 57.0. The sample is very cloudy; thus, refractive indices could only be roughly estimated. Estimations from them placed  $[F]$  at 55 to 60. Finally, the optic orientation of AF-1 is nearly identical to that of sample 6 ( $[F] = 55.3$ ). Thus, it appears that the host amblygonite for AF-1 contains 55 to 60 mol% F and that possibly F is present in a higher concentration in the fluid inclusions and daughter minerals. Microscopic examination of the fluid inclusions in AF-1 revealed the presence of a cubic daughter mineral, possibly villiaumite (NaF) (R. J. Bodnar, pers. comm.). Thus, for samples of amblygonite and montebrasite that contain a significant amount of included material,  $2V_z$  measurement is clearly superior to chemical analysis in evaluating the F content of the host mineral.

#### Influence of Na content on F prediction

Most natural amblygonites and montebrasites contain minor Na via substitution for up to 10 mol% Li (Dubois et al., 1972); thus, an evaluation of the influence of Na content on the accuracy of Equations 9–12 seems in order. The substitution of Na for Li in this series results in minor changes in density and involves ions that have very similar polarizabilities (Pirenne and Kartheuser, 1964) and electronegativities (Pauling, 1960). This suggests that Na content should have very little effect on the

relationships between optical properties and F content established in this study. Indeed, the refractive indices 1.594, 1.603, and 1.615 reported by Nriagu and Moore (1984), for a sample containing ~56.0 mol% Na and ~46.5 mol% F, agree well with the values 1.594, 1.607, and 1.615 predicted by Equations 5, 6, and 7, when  $[F] = 46.5$  was inserted. Thus, unless Na content only affects the  $\beta$  refractive index, which seems very unlikely, the Na content of most natural samples will not affect F predictions based on Equations 9–12.

The difference in ionic radius between Na and Li is at least 0.26 Å (Shannon and Prewitt, 1969) if Li is six-coordinated. This is rather large when considering the 1.30-Å radius of three-coordinated  $F^-$  (Shannon and Prewitt) and the 1.34-Å radius of three-coordinated  $(OH)^-$  (Ribbe and Gibbs, 1971). Thus, predictions of F content based upon subtle variations in lattice parameters will be significantly in error if the measured sample contains even minor Na. Measurements of cell volume by Dubois et al. (1972) support this conclusion.

#### RELATION OF OPTICAL PROPERTIES TO STRUCTURE AND POLARIZATION

Černá et al. (1973) and Hawthorne (pers. comm.) have shown that as  $(OH)^-$  content increases in the amblygonite-montebbrasite series, the cell volume increases slightly, whereas the density decreases slightly. Both structural effects are ordinarily associated with a decrease in refractive indices. In this series, however, their effect appears to be overwhelmed by the increase in refractive indices resulting from substitution of the highly polarizable anion  $(OH)^-$  for the relatively nonpolarizable  $F^-$ .

#### Influence of the polarizability of $(OH)^-$ on optics

For hydroxyl-rich members of the amblygonite-montebbrasite series, the principal vibration direction  $Z$  lies reasonably close to the O–H bond direction (triangle, Fig. 1) located by Hawthorne (pers. comm.). Increases in  $(OH)^-$  content thus cause  $\gamma$  to increase at a greater rate than  $\alpha$  or  $\beta$ . Conversely, the decrease in  $(OH)^-$  from left to right in Figure 2 causes  $\gamma$  to decrease faster than  $\alpha$  or  $\beta$ . This causes the birefringence ( $\gamma - \alpha$ ) to decrease with increasing F content and also contributes to the change in optic sign from (+) for montebbrasites to (–) for amblygonites. Positional changes in the two optic axes and  $X$ ,  $Y$ , and  $Z$  appeared much more abrupt as  $[F]$  increased from 55 to 79 (Fig. 1) than when it increased from 79 to 92.

#### CONCLUSIONS

1. For montebbrasite-amblygonite crystals for which  $[F] < 60$  mol%, their F content can be estimated to ~2 mol% from their measured values for  $2V$ ,  $\alpha$ ,  $\beta$ , or  $\gamma$ . Results seemed relatively unaffected by Na content.

2. Substitution of  $(OH)^-$  for  $F^-$  in the amblygonite-montebbrasite structure causes the principal vibration direction  $Z$  to align subparallel to the O–H vector in the

structure and causes the corresponding refractive index  $\gamma$  to increase at a faster rate than  $\alpha$  or  $\beta$ .

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