OPTICAL AND X-RAY DETERMINATIVE METHODS FOR FLUORINE IN TOPAZ

P. H. Ribbe, *Department of Geological Sciences, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061*

AND

P. E. Rosenberg, *Department of Geology, Washington State University, Pullman, Washington 99163.*

Abstract

Microprobe analyses for fluorine in the suite of 14 natural topazes studied by Rosenberg (1967) led to the calculation of the following determinative curves:

Weight percent fluorine equals $3.91 + 0.24 \ (2V_\gamma)$; $892.5 - 99.2$ (b cell edge); $155.6 - 35.7$ (Δ_{021}), where $\Delta_{021} \equiv 2\theta_{NaCl \ 200} - 2\theta_{topaz \ 021}$ with $CuK\alpha$ radiation. Using refractive indices for eight specimens, these polynomial regression equations were calculated:

Weight percent fluorine equals $-14434 + 18091 \ (\alpha) - 5660 \ (\alpha)^2$; $-15373 + 19232 \ (\beta)$ $-6007 \ (\beta)^2$; $-10247 + 12847 \ (\gamma) - 4018 \ (\gamma)^2$.

Introduction

In 1894 Penfield and Minor first demonstrated that the formula for topaz is $[Al(F, OH)]_2SiO_4$ and that differences in specific gravity, optical properties, and axial ratios of topaz are related to the replacement of fluorine by hydroxyl. If Deer, Howie, and Zussman (1962) had used all of Penfield and Minor's optic angle data to plot fluorine determinative curves, they would have obtained essentially the one we present here (see Fig. 1a).

However, they plotted optical properties and density for a variety of analyzed specimens against the ratio $OH/(OH+F)$. This was an unfortunate choice of an independent variable, both because of the propagation of error in calculating this ratio and because OH and F analyses are particularly difficult to make, as Penfield and Minor (1894) noted. Chaudhry and Howie (1970) also admit that the general deficiency of Si in *their* analyses " . . . probably may be attributed to negative error in the determination of the (OH+F) group." Since there are many topaz analyses in the literature whose (F, OH) values are inconsistent with various physical properties of topaz (*cf.* Fig. 1a), we determined to clarify the situation with a microprobe study of fourteen topazes characterized by Rosenberg (1967).

Rosenberg (1967) showed that the b and c cell dimensions (and volume) of topaz increase with increasing $OH/(OH+F)$, and that b and $2V_\gamma$ show a strong negative correlation. Because precise optical and lattice parameter measurements were available, this suite of specimens was chosen for microprobe analysis. The fluorine analyses listed in Table 1
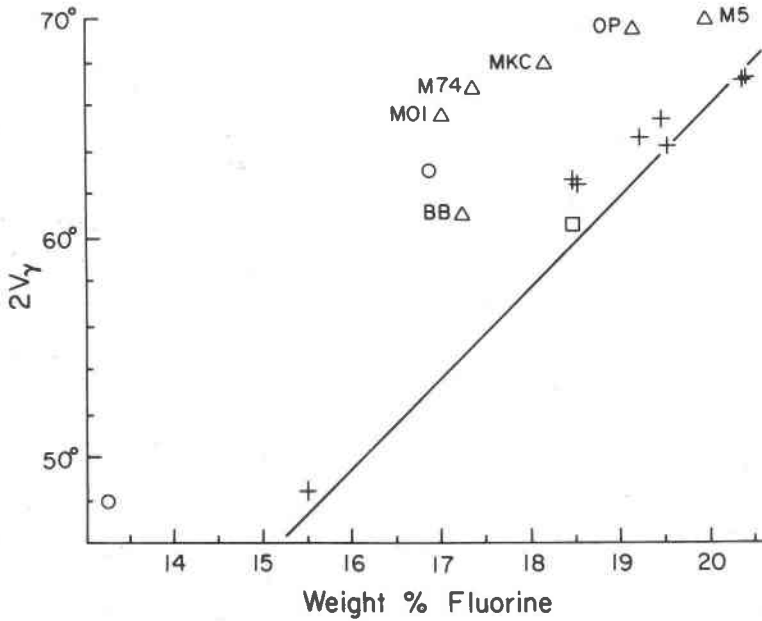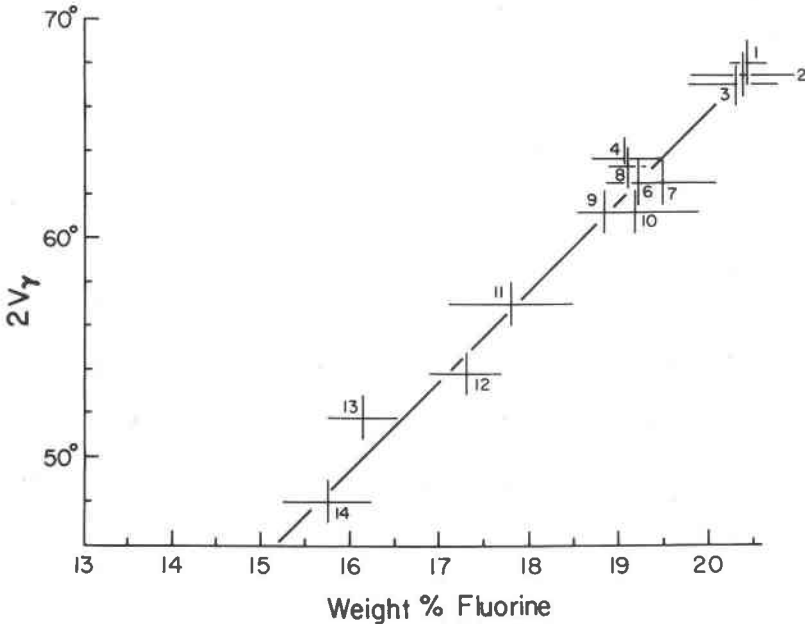
FIG. 1. (a) Optic axial angle $2V_\gamma$ plotted against weight percent fluorine for chemically analyzed topazes. The line is taken from Figure 1b. The crosses represent data from Penfield and Minor (1894); the open circles, data tabulated by Deer *et al.*, (1962, p. 146); the square, data from Ödman (1950); and the triangles, data from Chaudhry and Howie (1970).

(b) Optic axial angle $2V_\gamma$ plotted against weight percent fluorine for thirteen topazes analyzed with the microprobe. Size of the data points represent estimated standard errors of the measurements (see Table 1). $2V_\gamma$ from Rosenberg (1967).

were standardized to the topaz from Thomas Range, Utah (sample 2, 20.4 weight percent F), and individual values are probably known to within 3–4 percent of the amount of F present. This is about the same level of precision that Van Loon (1968) claims in determining the amounts of fluorine present in mineral fluorides using a specific ion electrode. The only other elements present in detectable amounts are Fe and Cr, notably in samples 1, 2, and 3 from cavities in rhyolites (Table 1). These probably substitute for Al in octahedral coordination (Thyer, Quick, and Holuj, 1967). Ca, Ti, V, Ni, and Co were not detected at the 0.01–0.02 weight percent level, and Mg was not detected at the 0.05 weight percent level (*cf.* El-Hinnawi and Hofmann, 1966).

With one exception microprobe analyses of Si proved to be within ± 1 percent of the amount calculated (± 0.15 weight percent) for stoichiometric $Al_2SiO_4(F, OH)_2$. The exception is sample 14, the most F-poor topaz in this suite, which is 0.3 to 0.5 weight percent Si-deficient. This sample yielded the highest Al counts of all specimens analyzed, but they were within the ± 1 percent (± 0.3 weight percent) variation observed from sample to sample. Sample 14 may be a natural example of the synthetic topaz solid solution series reported by Rosenberg (1969). However, the extent of this solid solution is very small in this sample, and it may be neglected as far as the determinative curves are concerned.

DETERMINATIVE METHODS

$2V_\gamma$ and Refractive Indices. The optic axial angle $2V_\gamma$ can be measured with ease on a universal stage or spindle stage (Wilcox and Izett, 1968). Fortunately for our purposes, $2V_\gamma$ shows very high correlation with F content (Fig. 1b; Table 2). The correlation coefficient is 0.988 and the range of residuals ($F_{obs} - F_{calc}$) is -0.42 to $+0.34$ weight percent F. Refractive indices measured for eight topazes across the composition range also produce useful second order polynomial determinative curves (Fig. 2; Table 2). These curves were fitted by least-squares methods to α, β, and γ, but they do not exactly predict the $2V_{obs}$ values measured on the same specimens and thus they probably should not be extrapolated far beyond the range shown. This is not surprising since an error of only 0.001 in $(\gamma - \alpha)$ or $(\gamma + \beta)$ produces errors of up to 8° in $2V_{calc}$.

Lattice parameters. In the topaz structure recently described by Ladell (1965) and Ribbe and Gibbs (1971a), the b cell-edge is normal to the close-packed anion layers of alternating $(F, OH)_2O_1$ and O_∞ Composition. Figure 3a shows that b increases with increasing substitution of OH for F. The reason for this is that two-coordinated OH is ~ 0.04 Å larger in

Table 1. Microprobe and lattice parameter data for topaz. Estimated standard deviations are in brackets and refer to the last decimal place.

Spec. No.	F(wt%)	b(Å)[a]	$2V_\gamma$[a]	Vol.(Å³)[a]	Calculated Δ_{021}[b]	Observed Δ_{021}	Refractive indices, n_D			Minor elements (wt%)[c]	
							α	β	γ	Fe	Cr
1	20.5(2)	8.789(1)	68.0°	343.20	3.788	3.789				.02	nd
2	20.4(6)	8.792(2)	67.4°	342.99	3.782	3.782	1.609	1.612	1.619	.04	tr
3	20.4(5)	8.794(1)	67.0°	343.40	3.800	3.800	1.612	1.614	1.621	.04	tr
4	19.1(4)	8.801(2)	63.6°	343.89	3.818	3.815	1.615*	1.617*	1.624*	tr	nd
5	-----	8.803(2)	64.0°	343.75	3.812	3.815				.02	nd
6	19.2(4)	8.806(2)	62.5°	343.84	3.812	3.808				.02	nd
7	19.5(6)	8.807(2)	62.5°	343.86	3.820	3.822	1.616	1.618	1.625	tr	tr
8	19.1(2)	8.808(2)	63.3°	343.69	3.810	3.810				nd	nd
9	18.8(3)	8.810(2)	61.2°	344.16	3.828	3.831	1.619	1.621	1.627	nd	nd
10	19.2(7)	8.811(2)	61.2°	344.08	3.832	3.816	1.615	1.618	1.625	nd	nd
11	17.8(7)	8.817(3)	57.0°	344.89	3.860	3.852	1.622	1.625	1.632	nd	nd
12	17.3(4)	8.826(2)	53.8°	345.59	3.881	3.881	1.625*	1.627*	1.634*	nd	.04
13	16.2(4)	8.833(2)	51.8°	345.55	3.887	3.901	1.628	1.630	1.638	nd	nd
14	15.7(5)	8.836(2)	48.0°	345.87	3.907	3.908	1.629	1.631	1.638	nd	nd

a. Data from Rosenberg (1967).
b. Calculated Δ_{021} determined using cell parameters from Rosenberg(1967). NaCl $d_{(200)}$ was taken to be 2.821Å in this study and in Rosenberg (1967).
c. "tr" symbolizes <0.01 wt.%, but at a level more than one standard deviation above background; "nd" indicates none detected.
* These indices measured after determinative curves were calculated.

Table 2. Equations for least-squares regression lines. Estimated standard
deviations for the intercept and regression coefficient are given in
brackets.

				Range of residuals	Correlation coefficient
wt. % F	=	3.91 [0.25]	+	0.24(2V$_\gamma$) [0.01]	-.42 to +.34	0.988
wt. % F	=	155.6 [0.4]	-	35.7(Δ_{021}) [2.7]	-.37 to +.51	-0.971
wt. % F	=	892.5 [0.4]	-	99.2(b) [7.9]	-.51 to +.60	-0.967
wt. % F	=	465.5 [0.8]	-	1.3(Volume) [0.2]	-.84 to +.57	-0.881

Polynomial regression equations for refractive index
determinative curves.

$$\text{wt. \% F} = -14434 + 18091(n_\alpha) - 5660(n_\alpha)^2$$
$$\text{wt. \% F} = -15373 + 19232(n_\beta) - 6007(n_\beta)^2$$
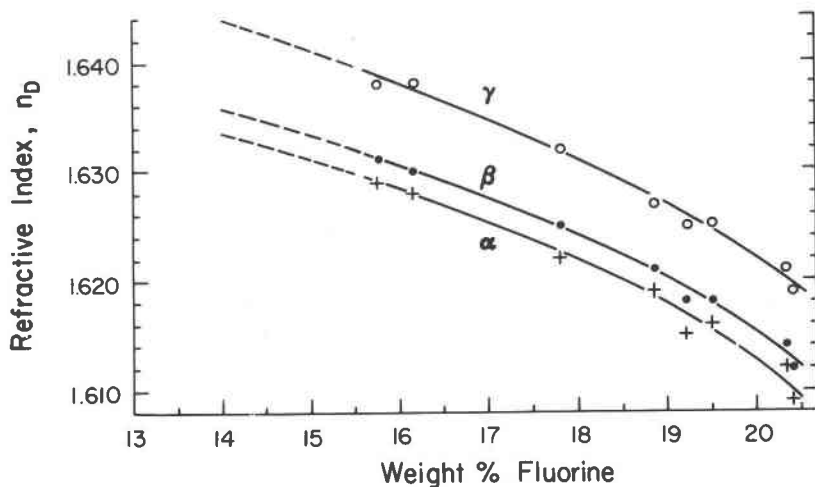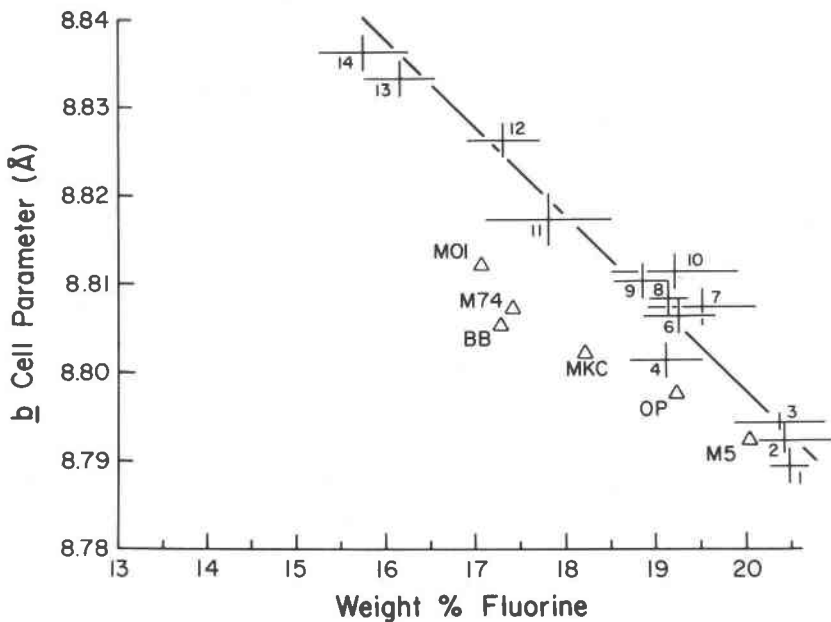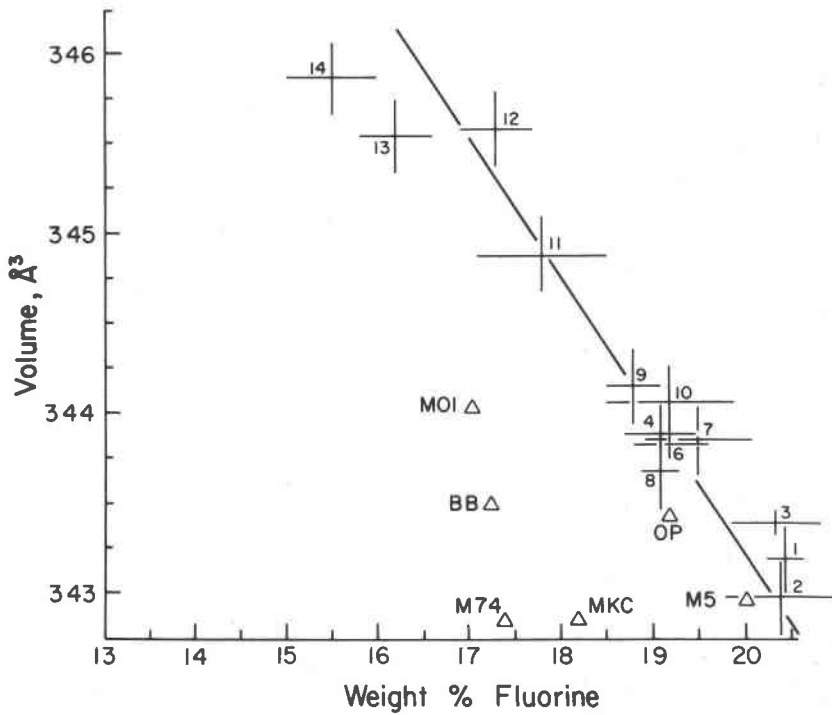$$\text{wt. \% F} = -10247 + 12847(n_\gamma) - 4018(n_\gamma)^2$$

FIG. 2. Refractive indices, n_D, plotted against fluorine content of eight specimens (see Table 1). Estimated precision of α, β, and γ is ± 0.001. The polynomial regression equations are listed in Table 2.

FIG. 3. (a) Variation of the b cell parameter and (b) unit-cell volume of topaz with fluorine content. Data from this paper (Table 1) and Rosenberg (1967) are represented by crosses whose sizes are indicative of the estimated standard errors of the measurements. The triangles represent data from Chaudhry and Howie (1970). Equations for the regression lines are listed in Table 2.

radius than two-coordinated F.[1] The equation for the least-squares regression line relating b to weight percent F is given in Table 2. The a cell edge (space group setting *Pmnb*) varies by only 0.006 Å (Rosenberg, 1967) and shows nearly zero correlation with F content; the c cell edge *vs.* F has a correlation coefficient of only -0.551. Thus, considering the propagation of errors, unit-cell colume is a poor estimator of F (Fig. 3b; Table 2).

$\Delta_{021} \equiv 2\theta_{NaCl\ 200} - 2\theta_{topaz\ 021}$. Another parameter for fluorine determination can be measured easily on powder diffraction patterns to topaz with reagent grade NaCl as an internal standard (see Rosenberg, 1969). Using CuK_α radiation, scan the 2θ range $26.5°-32.5°$ at a suitably slow speed and measure to the nearest 0.001° the separation of the topaz 021 peak 27.9° and the NaCl 200 peak near 31.7° to obtain Δ_{021}. Use the graph (Fig. 4) or the regression equation (Table 2) to calculate the F content. Our data showed a maximum deviation in Δ_{021} of 0.005° from the average of four measurements made on each of fourteen specimens. The regression analysis indicates that F can be predicted within 0.5 weight percent.

Evaluation. Specimen 5 (Table 1) was not analyzed by microprobe methods, but the three determinative methods discussed above predict the following fluorine contents: $2V_\gamma$, 19.3 weight percent; Δ_{021}, 19.4 weight percent b, 19.2 weight percent. It is obvious from Figure 1a that the F contents determined using $2V_\gamma$ for Penfield and Minor (1894) and Ödman's (1950) topazes agree very well with their chemical analyses. However, this is not true of the specimens examined by Chaudhry and Howie (1970). Except for specimen M_5, the predicted F contents differ significantly from their analytical values (see Table 3 and compare Figs. 1a, 3a, and 3b). Thus it is our opinion that their determinative curves are incorrect and should not be used.

The reported optical properties of their topazes and three others (Kempe, 1967; Table 3) yield F contents that are consistent within 0.5 weight percent. Since the errors in refractive index and $2V_\gamma$ measurements are likely to be small, it is probably best to rely on these for F values predicted using the b cell edge and Δ_{021} as calculated from reported determination. By contrast there are rather obvious inconsistencies in F

---

[1] This value was obtained from a comparison of the volumes of the essentially pure F end-member (specimen 1) and the most OH-rich specimen 14, which has the approximate formula $Al_2SiO_4F_{1.5}OH_{0.5}$. Assuming that $r_0III = 1.36$ Å and $r_FII = 1.285$ Å (Shannon and Prewitt, 1969), the radius of OH^{II} must be 1.325 Å if the difference in volume is due entirely to F=OH substitution. Using bond length differences in F and OH amphiboles, it can be shown that OH^{III} is likewise $\sim$0.04 Å larger than F^{III} (see Ribbe and Gibbs, 1971b).
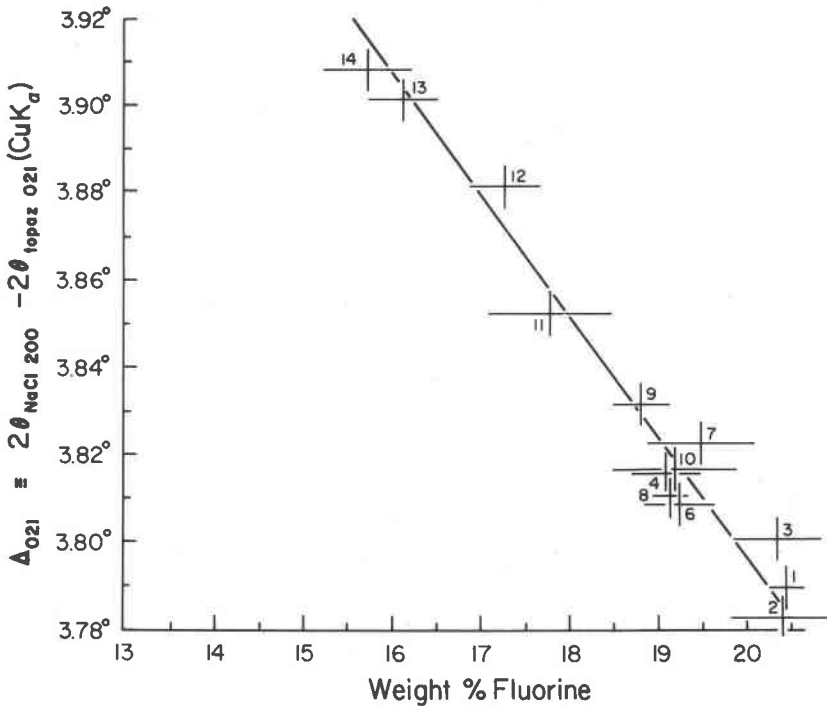
FIG. 4. $\Delta_{021} \equiv 2\theta_{\text{NaCl } 200} - 2\theta_{\text{topaz } 021}$ as a function of fluorine content. Data from Table 1. Maximum error in measurement of Δ_{021} is $0.005°$. The equation of the regression line is in Table 2.

values of b and c. These indicate errors in lattice parameters which may have arisen from misindexing or the failure to use internal standards. [Kempe (personal communication) has recently confirmed that his cell edges were in error.]

Saito and Ushio (1968) report cell dimensions and refractive indices for synthetic topazes of composition $Al_2SiO_4F_x(OH)_{2-x}$, where $2 > x > 0.8$. These data are totally inconsistent with both natural topazes (this study) and with synthetic topaz solid solutions (Rosenberg, 1969, and unpublished data).

CONCLUSION

Since most natural topazes are apparently free from chemical impurities which significantly effect optical properties or lattice parameters, it is felt that any of the methods presented here can be used successfully in determining F content. However, difficulties may arise if extensive solid

Table 3. Fluorine contents of topazes predicted from regression curves in Table 2 using physical properties reported by Chaudhry and Howie (1970) and Kempe (1967). Chaudhry and Howie's (1970) bulk chemical analyses of fluorine are listed for purposes of comparison.

Predicted fluorine contents (wt. %)

Parameter	Chaudhry and Howie (1970)						Kempe (1967)			
Spec. No.	M_5	OP	MKC	M_{74}	BB	MO_1	B_2	C	D	Granite
α	20.5	20.5	20.1	19.9	19.4	19.7	18.9	18.9	18.7	19.3
β	20.6	20.3	20.2	20.0	19.4	19.8				
γ	20.6	20.3	20.0	19.8	19.4	19.4				
2Vγ	20.9	20.8	20.5	20.2	18.9	19.9	18.9	18.6	18.2	
b	20.5	20.0	19.5	19.0	19.2	18.5		18.8	21.6	20.2
Δ_{021} (calc)	20.5	21.4	19.9	20.5	19.5	18.8		20.5	21.8	21.3
Chem. analysis wt. % F	20.01	19.20	18.19	17.40	17.24	17.05				

solutions of the type $Al^{3+} + (F, OH)^{1-} \rightleftharpoons Si^{4+} + O^{2-}$ described by Rosenberg (1969) are found to exist in nature.

REFERENCES

CHAUDHRY, M. N., AND R. A. HOWIE (1970) Topaz from the Meldon aplite, Devonshire. *Mineral. Mag.* **37,** 717–720.

DEER, W. A., R. A. HOWIE, AND J. ZUSSMAN (1962) *Rock-forming Minerals,* **I,** 145–150. John Wiley and Sons Inc., New York.

EL-HINNAWI, E. E., AND R. HOFMANN (1966) Distribution of trace elements in topaz. *Chem. Erde* **25,** 230–236.

KEMPE, D. R. C. (1967) Some topaz-, sillimanite-, and kyanite- bearing rocks from Tanzania. *Mineral. Mag.* **36,** 515–521.

LADELL, J. (1965) Redetermination of the crystal structure of topaz: a preliminary account. *Norelco Rep.* **12,** 34–39.

ÖDMAN, O. H. (1950) Manganese mineralization in the Ultevis District, Jokkmokk, North Sweden: Topaz. *Sveriges Geol. Unders., Ser. C,* **44,** 12.

PENFIELD, S. L., AND J. C. MINOR, JR. (1894) On the chemical composition and related physical properties of topaz. *Amer. J. Sci. Ser. 3,* **47,** 387–396.

RIBBE, P. H., AND G. V. GIBBS (1971a) The crystal structure of topaz and its relation to physical properties. *Amer. Mineral.* **56,** 24–30.

——— (1971b) The crystal structures of the humite minerals. III. Humite. *Amer. Mineral.* **56** (in press).

ROSENBERG, P. E. (1967) Variations in the unit-cell dimensions of topaz and their significance. *Amer. Mineral.* **52,** 1890–1895.

——— (1969) Topaz-vapor equilibria in the presence of excess silica and water. *Geol. Soc. Amer. Ann. Meet., Atlantic City* [abstr.], 192–193.

SAITO, H., AND M. USHIO (1968). Relationship between fluorine content and physical properties of synthetic topaz [$Al_2SiO_4F_x(OH)_{2-x}$]. *J. Ceram. Assoc. Jap.* **76,** 412–420.

SHANNON, R. D., AND C. T. PREWITT (1969) Effective ionic radii in oxides and fluorides. *Acta Crystallogr.* **B25,** 925–946.

THYER, J. R., S. M. QUICK, AND F. HOLUJ (1967) The E.S.R. spectrum of Fe^{3+} in topaz. *Can. J. Phys.* **45,** 3597–3610.

VAN LOON, J. C. (1968) Rapid determination of fluoride in mineral fluorides using a specific ion electrode. *Anal. Lett.* **1,** 393–398.

WILCOX, R. E., AND G. A. IZETT (1968) Optic angle determined conoscopically on the spindle stage: I. Micrometer ocular method. *Amer. Mineral.* **53,** 269–282.