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COMPOSITIONAL VARIATIONS IN SYNTHETIC TOPAZ

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ABSTRACT

Topaz has been synthesized in the quaternary system AlF_3–Al_2O_3–SiO_2–H_2O between 350° and 950°C largely at 2000 bars using conventional hydrothermal techniques. Compositional variations of two principal types have been recognized on the basis of refractive index and *d*-spacing measurements, defining two series, a "natural" series having variable F/OH ratios and an OH-free solid solution series containing excess Al and F.

In the natural series, stable in F-deficient assemblages, topaz hydrolyzes with decreasing temperature according to the equation $Al_2SiO_4F_2 + XH_2O = Al_2SiO_4F_{2-x}(OH)_x + X HF$. Thus, topaz F/OH ratios are dependent on the fugacities of HF and H_2O which are buffered by assemblages of four phases including vapor.

In the solid solution series stable in F-rich assemblages, Al^{3+} and F^{1-} substitute for Si^{4+} and O^{2-} respectively. Where Al^{3+} is not readily available anion substitutions may be compensated for by tetrahedral vacancies.

Isobarically univariant curves have been determined for topaz in assemblages with 1) quartz (or corundum), mullite (or pyrophyllite), vapor; 2) quartz, AlF_3, vapor; 3) corundum, AlF_3 (or ralstonite), vapor. Zunyite appears below 500° C in silica-deficient assemblages.

Application to natural topaz-bearing assemblages is limited because natural systems are usually open with respect to the vapor phase.

INTRODUCTION

Until recently few attempts had been made to study F/OH exchange in the silicates experimentally. In the past several years a number of studies involving micas have appeared (*e.g.*, Noda and Ushio, 1964; Munoz, 1968; Munoz and Eugster, 1969; Rieder, 1971) but micas are structurally and compositionally complex and therefore, the results of these studies have been difficult to interpret, and in some cases conflicting. The mineral topaz, $Al_2SiO_4(F, OH)_2$ is relatively simple both compositionally and structurally and is well suited to serve as a model for F/OH exchange in the silicates.

Topaz is a diagnostic product of so-called "pneumatolytic" processes which are believed to be due to crystallization from and reactions with F-rich fluids derived from late-stage, residual magmas or from F-bearing minerals by F/OH exchange during regional metamorphism (Deer, Howie, and Zussman, 1962). Topaz occurs in greisens and pegmatites associated with granitic rocks in assemblages with quartz and other minerals including micas, tourmaline, *etc.* A knowledge of the stability relations of topaz would help to define the range of physical conditions during the formation of these assemblages. Furthermore, since a wide range in F/OH ratios has been observed (Deer, Howie, and Zussman, 1962; Ribbe and Rosenberg, 1971), the composition of topaz may be a sensitive indicator of environmental conditions during its formation.

In 1887 Freidel and Sarasin (in Morey and Ingerson, 1937) synthesized topaz by reacting a fluorosilicic acid solution with a mixture of silica and alumina at 500°C. Since this first synthesis topaz has been prepared many times under a wide range of experimental conditions using a variety of starting materials. To date these studies have been concerned mainly with the synthesis of topaz (*e.g.*, Michel-Levy and Wyart, 1946; Schober and Thilo, 1940; Coess, 1955) or, more recently, with other minerals, the synthesis of topaz being purely incidental to the main purpose of the study (*e.g.*, Yoder and Eugster, 1955; Althaus, 1966). Despite these experimental studies no attempt has yet been made to determine the stability relations and compositional variations of topaz under a range of conditions simulating those in natural environments.

As a contribution to this problem topaz-bearing assemblages have been synthesized in the quaternary system AlF_3–Al_2O_3–SiO_2–H_2O in the presence of excess water between 350° and 950°C largely at total pressures of 2000 bars. Topaz equilibria under these conditions are believed to provide an adequate model for crystallization in some natural environments.

This paper concerns variations in the chemical composition of synthetic topaz and their significance. Detailed discussion of the thermal stability of topaz-bearing assemblages in the above system will be presented in a later paper now in preparation.

EXPERIMENTAL DETAILS

Procedure

Conventional hydrothermal equipment and techniques were used throughout this study. Most of the experiments were carried out in sealed gold tubes and cold-seal pressure vessels; gold-lined Morey vessels were used in a few of the earlier experiments.

In order to test the influence of starting materials in experimental products, bulk compositions (Fig. 1) were prepared in duplicate, as mechanical mixtures of reagent grade Al_2O_3 or recrystallized $Al(OH)_3$, natural quartz (Minas Gerais, Brazil) or Cab-O-Sil (amorphous silica) and AlF_3 which was used as the source of F in all mixtures. Several compositions were also prepared by mixing kaolinite (API No. 9, Mesa Alta, Calif.) and AlF_3 with enough quartz or Al_2O_3, where necessary, to give the required bulk composition. A series of early experiments using quartz, Al_2O_3, and fluorosilicic acid were carried out with the same purpose. The same final phase assemblage was obtained for bulk compositions in the silica-rich portion of the system regardless of starting materials. Some inconsistencies in run products (*e.g.*, presence or absence or zunyite, $Al_{13}Si_5O_{20}(OH, F)_{18}$) were observed in the Al_2O_3-rich portion of the system particularly below 500° C which, unfortunately, have some effect on the composition of coexisting topaz.

Samples of these mixtures were sealed, along with excess water, into gold capsules which proved to be inert to the corrosive experimental atmosphere. Most experiments were at a total pressure of 2000 bars except those above 800°C, 1000 bars and above 900°C, 500 bars. The duration of the experiment was from 3 days to 3 months. In general, equilibrium was assumed to have been attained when an increase in the duration of a particular experiment by a factor of three failed to produce a change either in the final phase assemblage or in the *d*-spacings of topaz, within the precision of the measurements. This criterion was useful for experiments above about 500°C since most phase assemblages reach a steady state within 30 days above this temperature. Below 500°C most experiments reported have a duration of 2–3 months and are believed to represent a close approach to equilibrium as defined above. Although experiments of longer duration were not attempted as a rule, several six month runs appear to confirm this con-

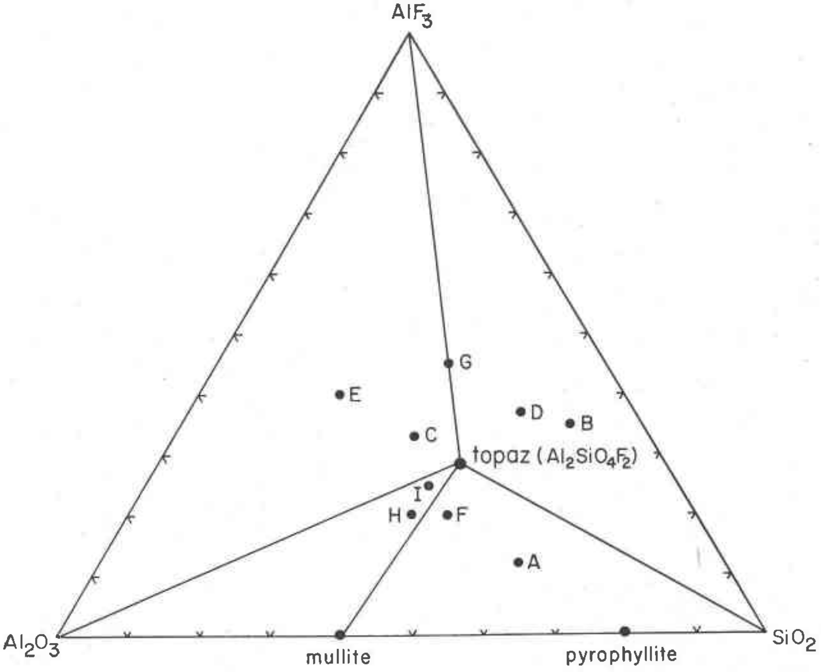

FIG. 1. Anhydrous bulk compositions (mole per cent) of starting materials. Each composition represents two or more mixtures. Composition triangles show phase compatibilities in the system with H_2O above 600°C. Note that topaz is represented only by end-member composition.

clusion. As a further check on equilibrium the F/OH ratio of topaz produced by direct synthesis was approached from two directions above 600°C using natural topaz having high and low F/OH ratios as starting materials. These experiments will be discussed in detail in a later section.

A series of experiments involving water-free, "dry" compositions resulted in the encrustation of the samples against the walls of the gold capsules; the capsules were etched and some gold was deposited within the samples. Although this phenomenon was not investigated, it appears to be due to the formation of a corrosive fluid which adheres to gold and quenches to an imperfect glass-like substance. These relations were never observed in the presence of water.

Phase Characterization

After quenching, products were identified by means of their X-ray powder diffraction patterns using Ni-filtered, Cu-radiation and where possible, by their optical properties. Topaz and AlF_3 were characterized by X-ray and optical measurements and by infra-red spectrophotometry.

Topaz (021) and (211) X-ray reflections, two of the three invariably observed, were measured against an internal standard, CdF_2, which has a conveniently located reflection at 28.70° Cu $K\alpha$. Ralstonite (311)-spacings were also measured against this peak. $\Delta 2\theta$ values were obtained by averaging four or more measurements (scan rate, ¼°/min.) per reflection and are known within 0.005° 2θ. The (220)-spacing of AlF_3 was measured (scan rate, ½°/min.) against a CdF_2 reflection at 56.7° Cu $K\alpha$; $\Delta 2\theta$ values are based on averages of two or more measurements and are known to within 0.01° 2θ.

Since individual topaz crystals could not be resolved under the polarizing microscope, mean refractive indicies of topaz aggregates were measured in Na-light. Mean values are significant because of the rather low birefringence of topaz (and AlF_3) and the relative sensitivity of refractive index to variations in F/OH ratios. Mean values were also obtained for AlF_3 refractive indicies, although in many cases it was possible to resolve individual crystals optically. Measured values have a precision of $\pm.002$. For purposes of comparison with synthetic topaz mean refractive indicies were calculated for a series of natural samples of known composition (Ribbe and Rosenberg, 1971) using the formula $n = \sqrt[3]{\alpha\beta\gamma}$ (Van Valkenburg, 1961).

The relationship of Δ_{021} and of refractive index to the F-content in natural topaz have been determined by Ribbe and Rosenberg (1971). Variations in Δ_{220} and mean refractive index of AlF_3 as well as Δ_{311} of ralstonite with F/OH ratios are implied from data given in this paper.

Infra-red spectrophotometry was used to study $(OH)^-$-stretching bands in topaz and AlF_3. Samples were prepared using conventional KBr pellet techniques (Lyon, 1967) and run on a Beckman IR-8 infra-red spectrophotometer with a blank KBr pellet in the reference beam.

Experimental Results and Their Implications

AlF_3-Vapor Equilibria

AlF_3-vapor equilibria can serve as a simplified model of topaz-vapor equilibria in the system AlF_3-Al_2O_3-SiO_2-H_2O.

X-ray, refractive index, and infra-red data indicate that AlF_3 hydrolyzes with decreasing temperature by partial replacement of F^- by

(OH)⁻. Direct evidence of hydrolysis is provided by the infra-red absorption pattern of AlF_3 after equilibration with water at 600°C and 2000 bars which clearly shows the presence of an (OH)⁻-stretching band (Fig. 2). Hydrolysis in the system AlF_3-Al_2O_3-SiO_2-H_2O results in progressive decrease in Δ_{220} with decreasing temperature (Fig. 3) corresponding to a decrease in *d*-spacing which is probably due to H-bonding. The extent of hydrolysis is greater when AlF_3 is in equilibrium with topaz, corundum, and vapor (Fig. 3, filled circles) than

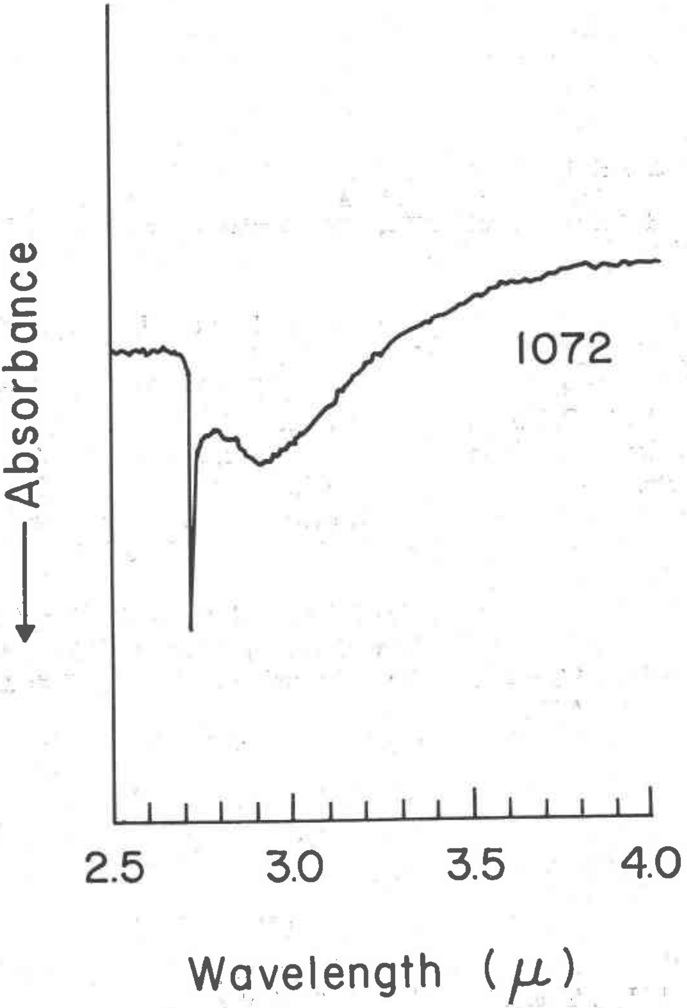

FIG. 2. Infra-red absorption pattern of hydrolyzed AlF_3.

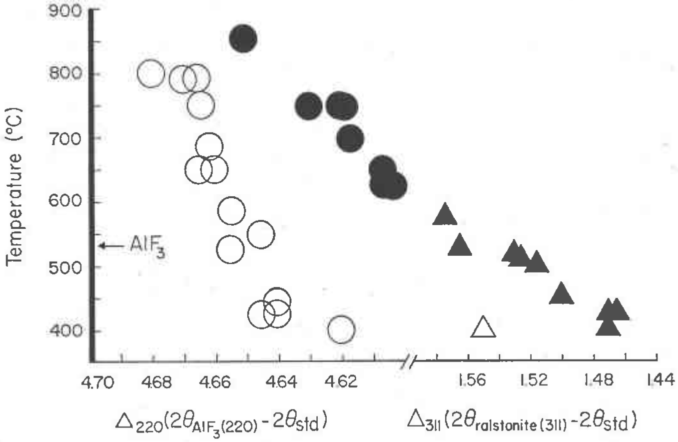

FIG. 3. Variations in AlF_3 Δ_{220} and ralstonite Δ_{311} X-ray measurements with temperature. Open circles; topaz with $AlF_{3-x}(OH)_x$, quartz, vapor (Fig. 1, B and D). Filled circles; topaz with $AlF_{3-x}(OH)_x$, alumina, vapor Fig. 1, E). Triangles; ralstonite replaces $AlF_{3-x}(OH)_x$.

when AlF_3 coexists with topaz, quartz, and vapor (Fig. 3, open circles). The maximum hydrolysis of AlF_3 in the former assemblage occurs at about 600°C; at lower temperatures $(OH)^-$-bearing AlF_3 inverts to yalstonite, $Al(OH, F)_3$ (pyrochlore structure), (Fig. 3, triangles) which also hydrolyzes with decreasing temperature, as shown by Δ_{311} measurements. The intervention of an additional phase, $AlF_2(OH)$ (P. H. Ribbe, personal communication), over a short temperature interval between 600° and 575°C inclusive is neglected here but will be discussed in a later paper.

Predictably, mean refractive indicies of $(OH)^-$-bearing AlF_3 increase progressively with decreasing Δ_{220} values and temperatures, ranging from 1.379 ± .001 for end-member AlF_3 to 1.405 ± .002 for hydroxyl-rich AlF_3.

The hydrolysis of AlF_3 may be expressed by the equation,

$$AlF_3 + X\,H_2O = AlF_{3-x}(OH)_x + X\,HF.$$

Topaz, an aluminum fluoride, may be expected to undergo a similar hydrolysis given by the equation.

$$Al_2SiO_4F_2 + X\,H_2O = Al_2SiO_4F_{2-x}(OH)_x + X\,HF.$$

Thus, the F/OH ratios of AlF_3 and topaz depend on the fugacities of HF and H_2O. These fugacities are fixed at a given temperature and pressure due to the buffering capacity of four-phase assemblages (including vapor) in the quaternary system. The greater extent of AlF_3 hydrolysis in the presence of excess alumina (Fig. 3, filled symbols) than in the presence of excess silica (Fig. 3, open symbols) suggests that f_{HF} is lower in alumina-rich assemblages. The reaction

$$SiO_2 + 4HF = SiF_4 + 2H_2O$$

buffers the fugacity of SiF_4 in the system.

Compositional Variability of Topaz

The relationship between Δ_{021} and the F-content of topaz (Ribbe and Rosenberg, 1971) can be assumed to hold only for synthetic samples approximating natural compositions. Early in this study, it was observed that many synthetic topaz samples have mean refractive indicies lower than that of the F-rich end-member. Two distinct series of topaz compositions can be distinguished by comparing mean refractive indicies wth Δ_{021} values (Fig. 4). Synthetic topaz coexisting with quartz, mullite, and vapor (Fig. 4, open circles) approaches the line based on measurements of natural topaz (Fig. 4, small filled circles). For these samples the linear relationship between Δ_{021} and F-content (Ribbe and Rosenberg, 1971) is believed to hold; they are referred to here as the "natural" topaz series.

In samples synthesized "dry" from end-member composition,

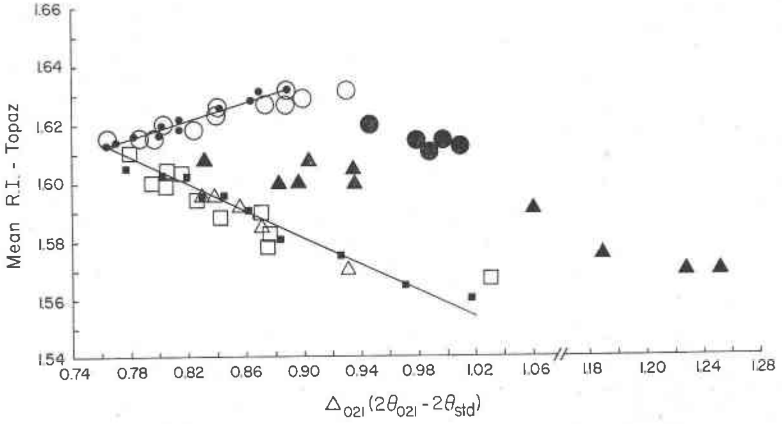

FIG. 4. Variation of mean refractive indices with Δ_{021} X-ray measurements of topaz. Small symbols: filled circles, natural topaz; filled squares, topaz "dry" experiments (Fig. 1, topaz comp.). Large Symbols: Open circles, topaz with quartz, mullite and vapor (Fig. 1, A and F); filled circles, topaz with zunyite, alumina, vapor (Fig. 1 H); filled triangles, topaz with alumina, vapor (Fig. 1 C); Open squares, topaz with $AlF_{3-x}(OH)_x$ ± quartz, vapor (Fig. 1, B, D, and G).

$Al_2SiO_4F_2$, (Fig. 4, small, filled squares) quartz coexists with topaz which is characterized by slightly expanded lattice dimensions and lower mean refractive indicies than that of the end-member. This topaz is thought to represent a solid solution series resulting from the coupled substitution of Al^{3+} and F^{1-} for Si^{4+} and O^{2-} and having the general formula

$$Al_2(Si_{1-x}Al_xO_{4-x}F_x)F_2.$$

An extrapolation of the line drawn through these data points (Fig. 4, lower line) intersects the natural topaz series at fluorotopaz composition, $Al_2SiO_4F_2$ being the end-member of both series.

Topaz synthesized in the presence of excess AlF_3 and water (Fig 4, open squares and triangles) lies close to the lower line representing hydroxyl-free topaz solid solutions and, therefore, belongs to this series. Δ_{021} values for these topaz samples are a measure of the extent of substitution of Al^{3+} and F^{1-} for Si^{4+} and O^{2-} rather than $(OH)^-$ for F^-.

The two series in Figure 4 represent extremes in the mean refractive indicies of topaz; numerous intermediates have been synthesized. Where AlF_3 or its hydrolysis products (*e.g.*, ralstonite) are absent, topaz compositions in zunyite-bearing assemblages (Fig. 4, filled circles) are believed to represent hydroxyl-bearing intermediate solid solutions while in alumina-rich zunyite-free assemblages topaz compositions (Fig. 4, filled triangles) are hydrolyzed members of the solid solution series (see Fig. 6). The extent of the latter series is much greater than that of the end-members due to the combined effects of coupled substitution and hydrolysis.

Infra-red absorption patterns of typical samples from each series are shown in Figure 5. Sharp $(OH)^-$-stretching bands are observed for synthetic samples approximating natural topaz compositions (Fig. 5, 1315); these bands are indistinguishable from those obtained for natural topaz. Broadening is observed in the $(OH)^-$-stretching band of hydroxyl-bearing topaz solid solutions (Fig. 5, 1321; Fig. 4, filled triangles) suggesting an unresolved doublet which may reflect the substitution of $(OH)^-$ for F^- in two dissimilar structural sites.

Although Figure 4 clearly defines the two compositional series, refractive index measurements were not possible for a great many samples particularly those synthesized at lower temperatures. The two series can also be distinguished on the basis of Δ_{021} and Δ_{211} X-ray measurements (Fig. 6), which, in general, confirm the relationships observed in Figure 4. Since these parameters were measurable for virtually every topaz sample, the entire range of compositions synthesized in this study can be illustrated. Samples 1315 and 1321 are located on this diagram.

The natural topaz series (Fig. 6) is defined by the solid line representing Δ values (correlation coefficient = −.963) calculated from unit-cell dimensions of fourteen natural samples (Rosenberg, 1967) and, assuming that the linear relationship is maintained for topaz with lower F/OH ratios, by its dashed extension. Δ values obtained for

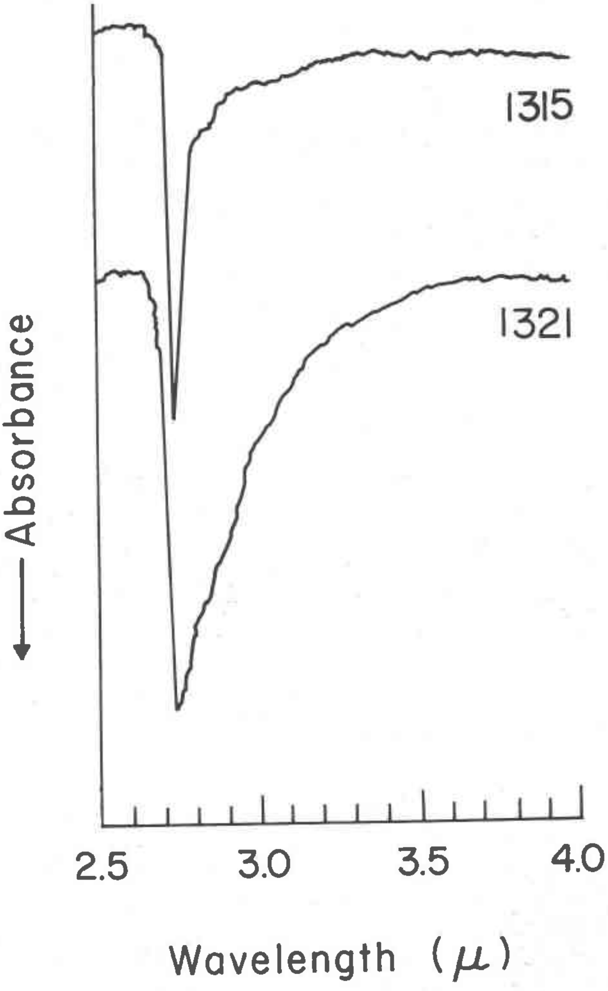

Fig. 5. Infra-red absorption patterns of synthetic topaz. Sample 1315, topaz with quartz, mullite, vapor (Fig. 1, A); sample 1321, topaz with corundum, vapor (Fig. 1, C).

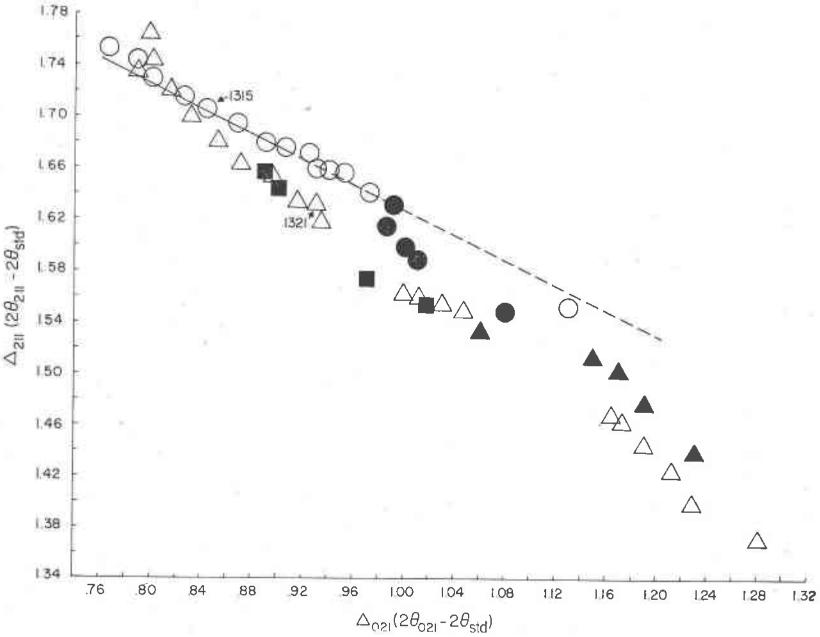

FIG. 6. Variations in Δ_{211} and Δ_{021} X-ray measurements of topaz. Straight line based on 14 natural samples, see text. Open circles; topaz with quartz, mullite (or pyrophyllite), vapor (Fig. 1, A and F). Filled circles; topaz with zunyite, alumina, vapor (Fig. 1, H). Open triangles; topaz with alumina, $AlF_{3-x}(OH)_x$ (or ralstonite), vapor (Fig. 1, E) or topaz with alumina vapor (Fig. 1, C). Filled triangles; topaz with zunyite, ralstonite (or alumina) vapor (Fig. 1, C and E).

synthetic topaz coexisting with quartz, mullite (or pyrophyllite), and vapor (Fig. 6, open circles) closely approach this line. The gap in the synthetic series is due to the relatively constant Δ values obtained for topaz in pyrophyllite-bearing assemblages. Equilibria involving pyrophyllite are not fully understood at present and are currently under further investigation.

Δ values for topaz synthesized in the absence of water (Fig. 6, filled squares) again define the topaz solid solution series; topaz synthesized in the presence of excess AlF_3 and water (Fig. 6, open triangles) closely approaches this series. However, Δ values of topaz synthesized in the absence of excess AlF_3 or its hydrolysis products, in zunyite-free, alumina-rich assemblages also plot (Fig. 6, open triangles) along this trend and are assumed to belong to the topaz solid solution series. Their higher refractive indicies (Fig. 4, filled triangles) suggests that they are hydroxyl-bearing. In agreement with relationships shown in

Figure 4, Δ values of topaz in quartz-free zunyite-bearing assemblages (Fig. 6, filled circles and triangles) appear to represent hydroxyl-bearing intermediate solid solutions.

The topaz solid solution series crosses the natural topaz series (Fig. 6) rather than meeting it at end-member topaz composition ($Al_2SiO_4F_2$). Δ values lying above those of the natural topaz series and representing decreased lattice dimensions are believed to be due to topaz solid solutions in which the substitution of F^{1-} for O^{2-} is compensated by vacancies in Si^{4+} lattice sites. These defect solid solutions have the general formula

$$Al_2(Si_{1-x/4}O_{4-x}F_x)F_2.$$

Similar coupled substitutions have been reported in the humites (Jones, Ribbe, and Gibbs, 1969) which are structurally analogous to topaz.

Topaz synthesized in the presence of excess AlF_3 is apparently always a solid solution. Defect solid solutions are crystallized when insufficient alumina is available (SiO_2-rich compositions) to form "normal" Al-rich topaz solid solutions. Δ values for stable defect solid solutions plot close to the intersection of the natural and solid solution series in Figure 6. The extent of this solid solution may be metastably enhanced by use of starting materials containing an unreactive form of alumina, α-Al_2O_3, to give Δ values lying above those of the natural topaz series (Fig. 6).

THE EFFECT OF TEMPERATURE

Natural Topaz Series

For the natural topaz series, synthesized from compositions low in AlF_3, Δ_{021} values are a measure of the hydrolysis of topaz which is shown by the progressive change in these values with temperature (Fig. 7). For assemblages of four phases including vapor the relationship is isobarically univariant, all values lying close to a single curve. Silica-rich compositions (Fig. 7, open circles) produce the assemblage topaz, quartz, mullite, vapor above 500°C and topaz, quartz, pyrophyllite, vapor at and below 500°C. Alumina-rich compositions (Fig. 7, filled circles) yield the assemblage topaz, corundum, mullite, vapor above 650°C; mullite is weak below 700°C and absent below 650°C. corundum is replaced by Al_2O_3-form *KI*[1] (Torkar, 1960) below 600°C except where α-Al_2O_3 was used as a starting material. Zunyite appears below 500°C in assemblages without quartz.

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[1] Same as AS(H)-I (Aramaki and Roy, 1963).

Δ_{021} measurements for topaz synthesized from alumina-rich and from silica-rich compositions are quite similar at any given temperature. Although there is no reason to expect the temperature dependence of F/OH ratios to be the same in both cases, present data cannot resolve a difference. Predictable changes in slope with the appearance of pyrophyllite and zunyite are also unresolved. Topaz in several pyrophyllite-bearing assemblages lies below the trend in Figure 7, apparently due to disequilibrium between pyrophyllite and the vapor phase. Due to the paucity of data, the curve for silica-rich compositions is difficult to trace below 450°C. Topaz in zunyite-bearing assemblages is an intermediate solid solution (see Figs. 4 and 6).

The F/OH ratio of topaz proved to be highly refractory and attempts to approach the curve (Fig. 7) from both directions met with limited success. Significant changes in Δ_{021} (and Δ_{211}) were observed using natural topaz mixed with a small amount of kaolinite and reacted at 750°, 700°, and 625° (Fig. 7, arrows), to give the assemblage topaz, quartz, mullite, and vapor. Natural topaz from Topaz Mountain, Utah ($\Delta_{021} = .765$) which is nearly $(OH)^-$-free (Penfield and Minor, 1894; Ribbe and Rosenberg, 1971) and Chesterfield Co.,

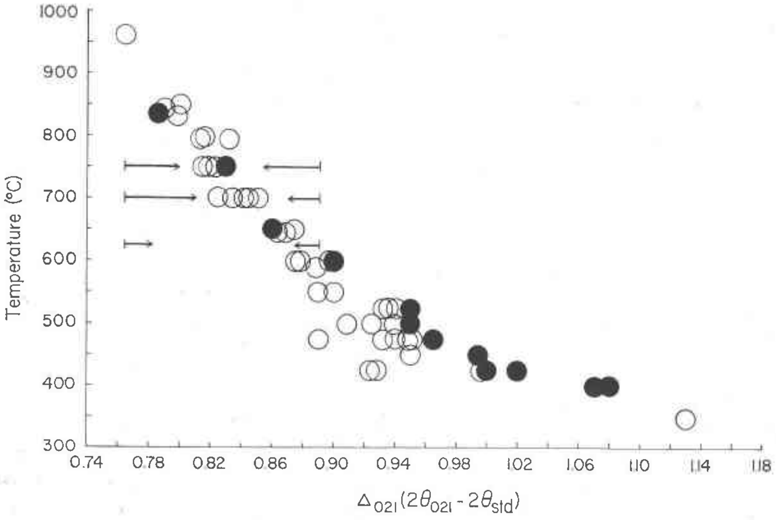

FIG. 7. Variation of Δ_{021} with temperature for the natural topaz series. Open circles; topaz with quartz, mullite (or pyrophyllite), vapor (Fig. 1, A and F). Filled circles; topaz with corundum, mullite (or zunyite) vapor (bulk composition; mole per cent; AlF_3 6, Al_2O_3 53, SiO_2 41). Arrows; reversal experiments, see text.

South Carolina ($\Delta_{021} = .890$), the most hydroxyl-rich topaz ever reported (Pardee, Glass, and Stevens, 1937) were used as starting materials. Δ_{021} (and Δ_{211}) for these samples was found to change in the direction of the values obtained by direct synthesis under the same experimental conditions (Fig. 7, arrows) suggesting that a close approach to equilibrium has been attained at least at higher temperatures. Similar attempts to reverse the hydrolysis of topaz at lower temperatures were unsuccessful.

In view of these results, the hydrolysis of the natural topaz series, as shown by the curve in Figure 7 is regarded as well-established above 600°C and as an approximation below 500°C. The extent of $(OH)^-$ substitution for F^- in synthetic samples may be estimated by extrapolating the linear relationship between Δ_{021} and F-content established by Ribbe and Rosenberg (1971) for natural samples. The synthetic series extends beyond the maximum substitution reported in nature, ($\Delta_{201} = .890$, 15.7 wt. percent F; Ribbe and Rosenberg, 1971) to a Δ_{021} value of 1.130 (7.5 wt. percent F) at 350°C with no indication that this represents the maximum substitution possible in the topaz structure.

Topaz Solid Solution Series

For the topaz solid solution series, synthesized in the presence of excess AlF_3, Δ_{021} values are a measure of the extent of the coupled substitution of Al^{3+} for Si^{4+} and F^{1-} for O^{2-}. The temperature dependence of Δ_{021} values observed in "dry" experiments and in experiments with excess alumina, AlF_3, and water are shown in Figure 8 (squares and circles respectively). These measurements lie close to a single curve which represents increasing solid solution with decreasing temperature. Topaz solid solutions synthesized in the presence of excess AlF_3 and water are hydroxyl-free at temperatures at least as low as 500°C since Δ_{021} and refractive index measurements for these solid solutions coincide with those of the "dry" series at and above this temperature (Fig. 4).

"Dry" experiments using end-member topaz composition ($Al_2SiO_4F_2$) yielded topaz and quartz; thus topaz composition lies in the triangle $Al_2SiO_4F_2$-Al_2O_3-AlF_3 (Fig. 1). In the presence of excess water, bulk compositions containing excess Al_2O_3 and AlF_3 yield the assemblage topaz solid solution, corundum, $AlF_{3-x}(OH)_x$ and vapor above 570°C, the extent of solid solution in topaz and the degree of hydrolysis of AlF_3 (Fig. 3) increasing with decreasing temperature. At lower temperatures ralstonite appears in place of $AlF_{3-x}(OH)_x$ and hydrolyzes with decreasing temperature (Fig. 3). The presence of zunyite below

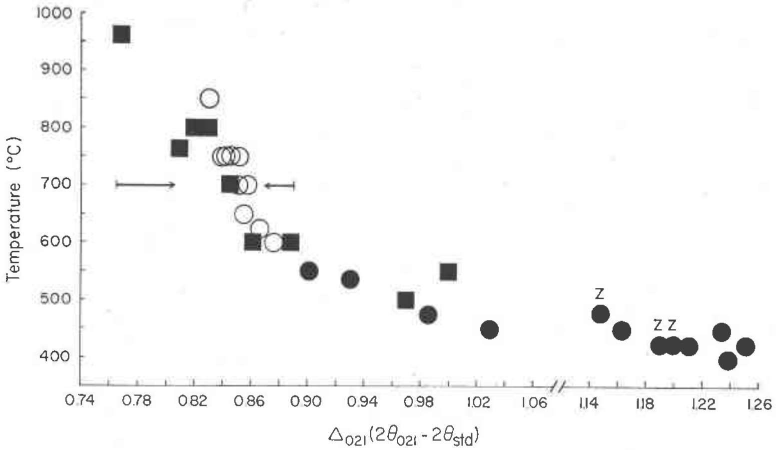

FIG. 8. Variation of Δ_{021} with temperature for the topaz solid solution series in the presence of excess alumina. Filled squares; topaz "dry" experiments (Fig. 1, topaz comp.). Open circles; topaz with alumnia $AlF_{3-x}(OH)_x$, vapor (Fig 1, E). Filled circles; topaz with alumina, ralstonite, vapor (Fig. 1, E). Z; zunyite present. Arrows; reversal experiments, see text.

500°C is dependent on the nature of starting materials. Bulk compositions made with α-Al_2O_3 gave the assemblage topaz solid solution, ralstonite, corundum, and vapor (Fig. 8, filled circles) whereas topaz solid solution, ralstonite, and zunyite were synthesized from the same bulk compositions using $Al(OH)_3$ (Fig. 8, filled circles with "Z"). The refractory nature of α-Al_2O_3 probably accounts for this discrepancy which does affect the composition of coexisting topaz to some degree (see Fig. 6). Diaspore replaced corundum in several experiments at 400°C which are not shown in Figure 8.

Topaz solid solutions coexisting with corundum and vapor are partially hydrolyzed; they appear as intermediates between the two compositional series in Figure 4 (filled triangles) but lie close to the hydroxyl-free topaz solid solution series in Figures 6 and 8. The curve in Figure 8 was approached from two directions at 700°C by starting with mixtures of natural topaz (Topaz Mountain, Utah; $\Delta_{021} = .765$ and Chesterfield Co. S. C.; $\Delta_{021} = .890$) alumina, AlF_3, and excess water, (Fig. 8, arrows). Similar attempts at lower temperatures were not successful.

The temperature dependence of topaz Δ_{021} values for the assemblages topaz solid solution, quartz, $AlF_{3-x}(OH)_x$, vapor and topaz solid solution, $AlF_{3-x}(OH)_x$, vapor is shown in Figure 9 (open circles and filled circles respectively). Topaz in these assemblages also lies on the curve for anhydrous solid solutions (Fig. 4, open triangles) and is, therefore, hydroxyl-free. Although a similar temperature dependence exists, the extent of topaz solid solution and the degree of hydrolysis of AlF_3 (Fig. 2) are both less than for the assemblage topaz solid solution, corundum, $AlF_{3-x}(OH)_x$, vapor (Fig. 8). Solid solution is probably limited by the absence of free alumina; Al^{3+} is not readily available to replace Si^{4+}. This explanation is in accord with the tendency to compensate for anion substitutions by creation of tetrahedral vacancies suggested by Δ_{211} measurements. Solid solution is slightly more extensive when topaz coexists only with $AlF_{3-x}(OH)_x$ and vapor (Fig. 9, filled circles); topaz in this assemblage is hydroxyl-free to temperatures at least as low as 425°C. Due to the lesser degree of AlF_3 hydrolysis, ralstonite is present only at 400°C.

Attempts were made to approach the curve for topaz solid solutions coexisting with $AlF_{3-x}(OH)_x$ and vapor from two directions by starting with natural topaz, AlF_3, and excess water. Although this procedure was partially successful using topaz from Chesterfield Co., S. C.

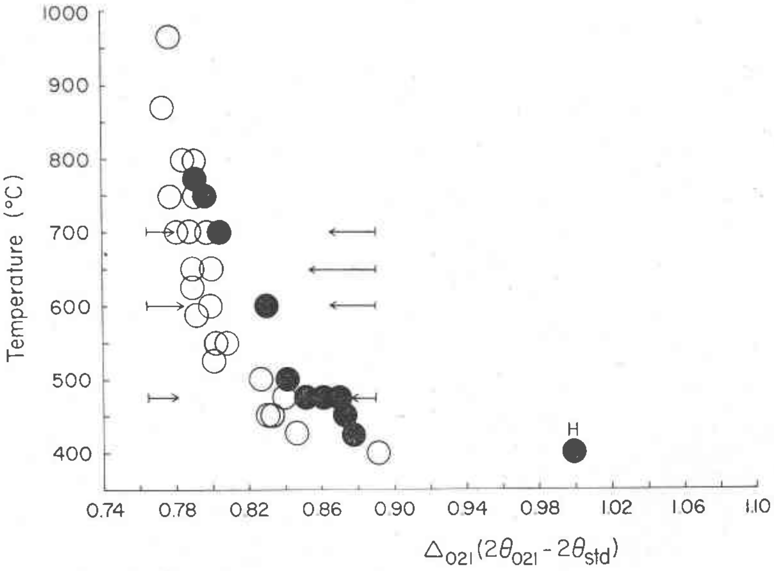

Fig. 9. Variation of Δ_{021} with temperature for the topaz solid solution series with and without excess quartz. Open circles; topaz with quartz $AlF_{3-x}(OH)_x$, vapor (Fig. 1, B and D). Filled circles; topaz and $AlF_{3-x}(OH)_x$, vapor (Fig. 1, G). H; ralstonite replaces $Al_{3-x}(OH)_x$. Arrows; reversal experiments, see text.

(Fig. 9, right arrows) no changes in Δ_{021} of topaz from Topaz Mountain, Utah, were observed. "Reversals" were obtained when concentrated HF was sealed quickly into gold tubes containing the latter material; the assemblage topaz solid solution, $AlF_{3-x}(OH)_x$, vapor was observed in every case (Fig. 9 left arrows).

THE EFFECT OF PRESSURE

Since the substitution of $(OH)^-$ for F^- in the natural topaz series and the coupled substitution of Al^{3+} for Si^{4+} and F^{1-} for O^{2-} in the topaz solid solution series are both accompanied by an increase in volume, the extent of these substitutions should be somewhat greater at lower pressures than at higher pressures. The tendency to compensate for anion substitutions by the creation of tetrahedral vacancies in the topaz solid solution series may be enhanced at higher pressures due to the smaller volumes of these solid solutions.

Although no attempt was made to study the effect of pressure on compositional variations in topaz, the assemblage topaz, quartz, mullite, vapor was synthesized at 1000 bars in a few experiments between 800°C and 600°C. Within the precision of the measurements, topaz Δ_{021} values were the same at 1000 bars as at 2000 bars.

RELATION TO NATURAL ASSEMBLAGES

Compositional variations of topaz discussed in this paper apply strictly only to alkali-free assemblages whereas most natural topaz-bearing assemblages contain significant amounts of alkalis; mica, for example, is an important constituent of greisens. However, preliminary studies (Rosenberg, 1969, and unpublished data) suggest that small amounts of K ($\sim$5 wt. percent K_2O) have little effect on topaz-vapor equilibria. Since topaz compositions in synthetic and natural assemblages are comparable, the univariant curve for the natural topaz series would appear to have applications to geothermometry.

The composition of topaz is determined by the fugacities of HF and H_2O, pressure, and temperature. Experimental gas fugacities were internally buffered by stoichiometric solid phases (quartz, mullite, *etc.*); these fugacities are fixed at a given temperature and pressure for assemblages of four phases including vapor. Preliminary data suggest that a change in pressure by a factor of two has little effect on topaz-vapor equilibria. However, natural topaz-bearing assemblages typically lack internal buffer assemblages as indicated by the predominance of solid phases with variable F/OH ratios in greisen (*e.g.*, topaz, mica, tourmaline, apatite, *etc.*) (Rieder, 1971). Thus, natural greisen assemblages (*e.g.*, quartz, muscovite, topaz) usually crystallize in a system that is open with respect to the vapor phase, the fugacity of HF being imposed by an external source. Under these conditions no simple relationship between topaz composition and temperature is to be expected and the experimentally determined univariant curve for the natural topaz series is not applicable.

Despite this serious limitation temperature estimates may be possible in some cases. F-buffered assemblages with bulk compositions approaching the quaternary system (topaz; quartz; andalusite, sillimanite, or kyanite) have been found in nature; for example, topaz, quartz, sillimanite assemblages have been reported from Tanzania (Kempe, 1967) and Evergreen, Colorado (Sheridan *et al.*, 1968). Neglecting the probable effects of pressure, topaz F/OH ratios in these assemblages suggest temperatures of 850°C ($\Delta_{021} = .789$) and 750°C ($\Delta_{021} = .826$) respectively. These temperatures must be regarded as approximations because pressures during the crystallization of topaz may have greatly exceeded 2000 bars. While most natural systems appear to have been open with respect to the vapor phase during fluorine metasomatism and greisenization, topaz in some assemblages may have crystallized under closed system conditions.

It would be of considerable interest to know the experimental gas fugacities in order to reconstruct the composition of the natural vapor phase in equilibrium with F-buffered assemblages. Unfortunately, this information cannot be obtained from the experimental data reported here. The buffer method (Munoz and Eugster, 1969) offers the best potential approach, although the range of HF fugacities established by buffers that have been calibrated to date is probably too low to be of value in studying topaz–vapor equilibria.

Topaz solid solutions have not been reported in nature but they may exist where bulk compositions are unusually high in fluorine and low in alkalis. For example, topaz coexisting with ralstonite should be a member of the solid solution series. This association has never been reported in nature to the author's knowledge but both minerals have been found in the vicinicity of St. Peter's Dome in Colorado (Cross and Hillebrand, 1885). It is possible that natural intermediates between the two series have been described but not recognized in the literature because, typically, insufficient data are provided for their characterization.

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