The thermodynamic properties of topaz solid solutions and some petrologic applications

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Abstract

Reversed experiments were performed on the reaction andalusite + water = hydroxyltopaz component (in solid solution) in the intervals $600-900^{\circ}$ C and 650-2000 bars using conventional cold seal apparatus. The results allow discrimination among various activity models for topaz solid solutions and calculation of the thermodynamic properties of (hypothetical) hydroxyl-topaz. A proton-avoidance activity model agrees well with the experimental data and gives reasonable extrapolations to lower temperatures. Combined thermodynamic data for hydroxyl-topaz (OHT), fluor-topaz (FT) (from Barton *et al.*, 1982), and the solid solution are:

	$G^\circ_{\mathrm{fm},298,1}\mathrm{J}$	$S^{\circ}_{298,1}$ J/K-mol	$C_{\rm p}$ J/K-mol	а
OHT	-2693251	112.04	504.413 - 0.08737T +	$X_{\rm OHT}^2/(1 - 2X_{\rm OHT})$
			$1358330T^{-2} - 5869.53T^{-0.5}$	
FT	-2910660	105.40	471.414 - 0.08165T +	$2X_{\rm FT} - 1$
			$1269470T^{-2} - 5485.54T^{-0.5}$	

Calculations based on these data are in good agreement with observation of natural assemblages. In the presence of topaz, muscovite may be stable on the solidi of some granites to pressures as low as 1–2 kbkar. Calcic plagioclase is incompatible with topaz, especially in the presence of potassium feldspar. Hydroxyl-topaz contents of topaz coexisting with other aluminous phases increases with increasing pressure and decreasing temperature. With decreasing temperature at constant composition topaz removes HF from a water-rich fluid.

Introduction

Topaz $(Al_2SiO_4(F,OH)_2)$ occurs as an accessory mineral in some granites and associated hydrothermally altered rocks as well as in pegmatites, rhyolites, and other aluminous rocks. As one of the principal carriers of fluorine (along with fluorite, apatite, amphiboles, and micas), topaz offers a key to understanding the role of fluorine and, to a lesser extent, water in the genesis of these rocks. In contrast to the micas and the amphiboles, topaz has a simple composition and thus is an easier phase to deal with experimentally and theoretically. Fluorite, while chemically simple, is commonly the only calcium-rich mineral in high-fluorine environments which limits its usefulness, while topaz contains components $(Al_2O_3 \text{ and } SiO_2)$ nearly always present in associated phases.

Topaz is a solid solution between fluor-topaz $(Al_2SiO_4F_2)$ and (hypothetical) hydroxyl-topaz $(Al_2SiO_4(OH)_2)$. Natural topaz compositions range from nearly pure fluor-topaz, in rhyolites, to about $Al_2SiO_4F_{1.4}OH_{0.6}$, in hydrothermal deposits, although Rosenberg (1972a) has synthesized topaz with greater than 50% hydroxyl-topaz component. Other than fluoride-hydroxyl exchange, natural topazes exhibit little compositional variation. Iron and chromium, probably substituting for aluminum, occur in small amounts (<0.05 wt.%) in some rhyolitic topazes (Ribbe and Rosenberg, 1971; Deer *et al.*, 1962). Glyuk and Anfilogov (1973a) synthesized green topaz which they thought contained a considerable amount of iron, and Beus and Dikov

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(1966) synthesized an aluminum-iron fluoro-silicate which they thought was related to topaz. Rosenberg (1972a) synthesized topazes in silica-deficient assemblages involving the probable exchange $Si^{4+} + O^{2-} = Al^{3+} + F^-$. This substitution is very minor, if present at all, in natural topazes.

Ribbe (1980) discusses the crystal structure of topaz, which was determined independently by Pauling (1928) and Alston and West (1928) and refined by Ribbe and Gibbs (1971). Briefly, the structure is based on alternating close-packed anion layers of composition F₂O and O and contains crankshaft chains of edge-sharing AlO₄F₂ octahedra. Isolated SiO₄ tetrahedra connect the octahedral chains. Ideal topaz has the space group Pbnm in which all the fluorine-hydroxyl sites are equivalent. Fluorine-hydroxyl ordering was proposed by Akizuki et al. (1979) to explain the anomalous optical properties observed in some topazes. Structure refinements of OH-bearing topaz by Parise (1980) discussed by Ribbe (1980) confirmed that in low-temperature topaz the hydroxyl anion may be ordered onto as few as one of the eight positions in the topaz unit cell.

In all topazes the crystallographic and optical properties vary significantly with composition. These variations form the basis of several methods of compositional determination (Ribbe and Rosenberg, 1971).

While there are abundant data in the literature on the natural occurrences and chemography of topaz (see the Applications section below), relatively little experimental work has been done. Freidel and Sarasin in 1887 first synthesized topaz (Morey and Ingerson, 1937). Most work since then has also dealt with synthesis, intentional (e.g. Michel-Levy and Wyart, 1946; Coes, 1955) or unintentional (e.g. Althaus, 1966; Yoder and Eugster, 1955). Topaz figures prominently in experiments on the "system" granite-HF (Glyuk and Anfilogov, 1973a) and in studies of beryllium mineral stabilities (Beus and Dikov, 1967). In neither of these studies, however, was equilibrium demonstrated (e.g. by reversal of reactions), nor were the topaz compositions determined. Rosenberg (1972a, 1978) has done extensive experiments on topaz in the system Al₂O₃-SiO₂- $H_2O-F_2O_{-1}$ in which he has determined the compositions. Unfortunately, most were synthesis experiments and as such are inappropriate for extracting thermodynamic data. A few experiments of a quasireversed nature in Rosenberg (1972a) did vield results consistent with the direct synthesis data.

Synthesis experiments (Rosenberg, 1978, personal communication) give the equilibrium constant as a function of temperature for fluoride-hydroxyl exchange between topaz and aqueous vapor in the presence of quartz.

In order to quantitatively understand the petrologic role of topaz, phase equilibrium and/or calorimetric data are needed. Barton *et al.* (1982) presented calorimetric data for fluor-topaz. In this study hydroxyl-buffering experiments provide data which allow calculation of the thermodynamic properties of topaz solid solutions. In turn, calculations are made with these data to help interpret the conditions of formation of some greisens, pegmatites, and related rocks.

Experimental methods and results

The experimental portion of this study consists of hydoxyl-buffering experiments which permit estimation of an entropy and a standard enthalpy of formation for hydroxyl-topaz and also allow evaluation of alternative activity models for the solid solution.

Starting materials

A reliable method for the determination of topaz compositions is critical to the experiments on topaz solid solutions. Ribbe and Rosenberg (1971) developed several X-ray and optical determinative curves for topaz. In this study, after unsatisfactory preliminary results using their Δ_{021} method, cell refinements were done for each topaz used for starting material and for each run product. The volume and b cell edge regression equations of Ribbe and Rosenberg were then used to determine the compositions (the b cell edge equation was modified slightly to split the difference between the composition predicted by Ribbe and Rosenberg for the Topaz Mountain topaz and the wet chemical analysis done by Penfield and Minor, 1894). As expected the two regression equations gave similar results. Crystallographic data were collected using powder diffractometer methods (Ni-filtered CuKa radiation with a corundum internal standard a =4.75929(13)Å, c = 12.99168(49)Å). The program of Burnham (1962) was used to refine the data. Except for the starting materials the same set of peaks was used in all the refinements (hkl = 114,133,232,143,153,006,303,320,223).

Akizuki *et al.* (1979) suggest that the ordering that they postulate to explain the anomalous optical properties may also affect the X-ray determinative

Table 1. Chemical and crystallographic data for topaz starting materials

			(Comp.3		
Mater	ial ²	<u>a</u> (Å)	<u>b</u> (A)	<u>c</u> (Å)	v (Å ³)	X _{OHT}
Topaz	(TM)	4.6475(3) 4.6465(4)	8.7897(4) 8.7897(13)	8.3920(4) 8.3918(8)	342.81(2) 342.71(5)	0.014 0.014
Topaz	(OM)	4.6544(6) 4.6527(4)	8.8094(9) 8.8088(11)	8.3900(7) 8.3900(6)	344.01(4) 343.86(4)	0.108 0.105
Topaz	(BR)	4.6594(3) 4.6596(3)	8.8248(6) 8.8252(8)	8.3871(4) 8.3885(5)	344.86(2) 344.95(3)	0.181 0.183
Topaz	(OP)	4.6650(10) 4.6630(5)	8.8408(18) 8.8371(16)	8.3849(9) 8.3815(16)	345.81(7) 345.37(6)	0.257 0.240
Andalu	site (SD)	7.7928(14)	7.8980(18)	5.5539(19)	341.83(12)	-

¹ Errors given in parentheses (1σ)

² TM = Tpaz Mountain, OM = Omi, BR = Brewer Mine, OP = Ouro Preto, SD = South Dakota

³ Calculated from the <u>b</u> cell edge regression equation of Ribbe and Rosenberg (1971) modified slightly to better agree with the wet chemical analysis of Barton <u>et al</u>. (1982) for Topaz Mountain topaz

curves. The optically anomalous topaz studied by Akizuki *et al.* came from Ouro Preto, Minas Gerais, Brazil where the mineral associations (Olsen, 1971) suggest a low temperature of formation. Sector growth ordering, such as Akizuki *et al.* suggest, is more likely at low temperature; and the magnitude of such ordering at the temperatures of the experiments in this study is probably very small. However, indiscriminate application of the results of this study should not be made to anomalous topazes or to equilibria below about 400° C until this problem has been resolved.

Four topazes were used in the hydroxyl-buffering experiments. Nearly end member fluor-topaz crystals from Topaz Mountain, Thomas Range, Juab County, Utah were used both for this study and for the calorimetric measurements of Barton et al. (1982). This topaz occurs in lithophysae in rhyolites where it is associated with quartz, sanidine, fluorite, beryl, hematite, bixbyite, pseudobrookite, and spessartine (Ream, 1979). Light blue, gemmy topaz from Omi, Tanakami Yama, Japan which had no associated minerals, (University of Chicago collection #2231) was coarsely crushed and inclusion-free pieces were selected. White, fine-grained massive topaz from the Brewer mine, Chesterfield County, South Carolina was taken from the collections of the Field Museum of Natural History (FMNH #18049). This topaz occurs with quartz, pyrite, and gold (Fries, 1942). Topaz from Ouro Preto, Minas Gerais, Brazil occurs with kaolinite, quartz, euclase, muscovite, and orthoclase (Olsen, 1971). Brown gemmy crystals were obtained from the Field Museum (FMNH #13130). Inclusion-free fragments of andalusite from the Black Hills, South Dakota were also used (specimen collected by P. B. Moore).

Electron microprobe analysis was done on an automated ARL-EMX instrument at the University of Chicago using a ZAF correction program written by I. M. Steele of the University of Chicago. Beam currents were 1.5 μ A at accelerating voltages of 15 kV. Andalusite served as the standard for aluminum and silicon. The water and fluorine analyses for the Topaz Mountain topaz are from Penfield and Minor (1894) and Barton et al. (1982). The Topaz Mountain topaz was used as the microprobe standard for the fluorine analyses in the other samples of topaz. The precision of the fluorine analyses on the other topazes was approximately $\pm 10\%$ of the amount present. As a result the fluorine and hydroxyl contents for these samples are taken to be those obtained from the b cell edge determinative curve of Ribbe and Rosenberg. Although other elements were searched for none was found. Table 1 shows the chemical and crystallographic data.

Hydroxyl-buffering experiments

Hydroxyl-buffering experiments offer information on the stability of topaz solid solutions and in particular on the stability of hydroxyl-topaz. These experiments are based on the reaction:

$$Al_2SiO_5 + H_2O = Al_2SiO_4(OH)_2^{ss}$$
 (1)
andalusite hydroxyl-topaz

where the hydroxyl-topaz is in solid solution with fluor-topaz. With data on the equilibrium content of hydroxyl-topaz at a given temperature and pressure and an activity model for fluorine-hydroxyl mixing, one can calculate the thermodynamic properties of hydroxyl-topaz given thermodynamic data on andalusite and water. Figure 1 illustrates the reaction showing the experimental assemblage as the three phase field of topaz, aluminum silicate, and waterrich vapor. The reaction was reversed by doing matched sets of experiments at the same temperatures and pressures but starting with topazes which had initially higher or lower hydroxyl contents than the final, equilibrium concentrations.

These experiments are hydroxyl-buffering experiments because it is only the hydroxyl-component of the solution which is buffered, unlike the conventional fluorine-hydroxyl buffering experiments (Munoz and Eugster, 1969) where the chemical potentials of both HF and water are fixed externally to the mineral of interest. As a result only data for the hydroxyl end-member may be directly extracted from this type of experiment. Attempts to do conventional fluorine-hydroxyl buffering experiments failed for lack of a suitable buffer stable at the high temperatures and HF fugcities required by topaz.

Starting mixes of 60% topaz, 35% and alusite, and 5% quartz were prepared from the materials listed in Table 1. Optically pure, natural quartz was added to insure that the solid assemblage remained silicasaturated. A silica-deficient assemblage would be undesirable because Rosenberg (1972a) has shown that, at least in synthesis experiments, topaz may contain excess alumina and fluorine in such assemblages, which affects the X-ray determinative curves. The mixtures were ground in an agate morter until the average grain size, determined by optical examination, was in the range 1-3 μ . Even though reaction rates at the lower temperatures were quite low the materials were not ground more finely to avoid introducing substantial surface energy and strain energy effects.

Approximately 10 mg of starting mix and 2 mg of distilled water were sealed in gold capsules. Up to five capsules were run simultaneously in conventional cold-seal bombs with internal chromel-alumel thermocouples. Pressures were monitored by Bourdon-tube gauges. The temperature and pressure measurements are believed to be accurate to within $\pm 5^{\circ}$ C and ± 40 bars. Run times varied from 5 days at 900° C to 6 months at 600° C. Daily monitoring of the runs assured that the pressures and temperatures never varied by more than the estimated accuracy and were usually kept within a degree or two and 20 bars of the nominal temperatures and pressures.

At the end of a run the bombs were quenched at pressure by cooling with an air blast. Using this method temperatures fell to less than 200° C in the first 2 minutes. Capsules were examined for signs of leakage on removal from the bomb. Although the capsules could not be weighed to check for leakage because they tended to weld themselves to one another during the course of the experiment, it was generally possible to tell if any had leaked. On opening, those that had not leaked generally emitted a spurt of pressurized water; also, those that had leaked almost always reacted to give coarsely crystalline, thin plates of alumina which were very distinct from the very fine-grained powder resulting from the successful experiment.



Fig. 1. Composition plot showing the limiting buffering assemblage for topaz solid solutions on the join $Al_2SiO_5-H_2O-F_2O_{-1}$ in the $Al_2O_3-SiO_2-H_2O-F_2O_{-1}$ system. Note that the compositions to the F_2O_{-1} side of the line between HF and $Al_2SiO_5 + 5F_2O_{-1}$ are physically unattainable. The tie lines are schematic. The abbreviations are: v = vapor, tpz = topaz, and = andalusite.

Even though many of the experiments were done in the sillimanite stability field, and alusite was used in all the experiments to eliminate the need to take the ordering state of sillimanite into account. A powder diffraction scan was made for each charge from 19 to 35° 2θ and examined for the presence of extraneous peaks (in particular sillimanite, mullite, and corundum) and the peaks of the starting phases. In none of the experiments was there any evidence of sillimanite or mullite. Only those experiments which were rejected for leakage had any extraneous peaks or did not show peaks of topaz and andalusite (the quartz peak was quite small in most cases and was not observed in some otherwise normal runs and in all runs checked quartz was optically determined to be present). After the first scan a portion of the charge was used for a cell refinement. Direction of reaction was determined by comparison of the composition of the final topaz with the composition of the initial topaz (both compositions determined by application of the slightly modified b cell edge regression equation of Ribbe and Rosenberg, 1971). The experimental results are listed in Table 2 along with calculated compositions.

Thermodynamics and discussion

The thermodynamic properties of topaz solid solutions can be derived from the experimental data presented here, and the standard state properties of fluor-topaz from Barton *et al.* (1982).

In order to derive the thermodynamic properties of hydroxyl-topaz and to be able to apply any of the thermodynamic results to most natural topazes, it is necessary to develop a mixing model for topaz solid solutions. Given this model the equilibrium constant data collected from the hydroxyl-buffering experiments may be used to estimate the properties of (hypothetical) hydroxyl-topaz.

The heat capacity and entropy of hydroxyl-topaz can be estimated from the values for fluor-topaz and data on other fluoride-hydroxide pairs. The entropy of hydroxyl-topaz was estimated using six fluoride-hydroxide pairs (Robie *et al.*, 1978) and the data for fluor-topaz (Barton *et al.*, 1982) in exchange reactions of the type:

$$2XOH + Al_2SiO_4F_2 = 2XF + Al_2SiO_4(OH)_2$$
(2)

where ΔS° was assumed to be 0 and a volume correction was applied (Helgeson *et al.*, 1978). The estimated entropy of hydroxyl-topaz is 112.8 J/Kmol or 7% greater than the entropy of fluor-topaz. The heat capacity of hydroxyl-topaz is also arbitrarily taken to be 7% greater than the heat capacity of fluor-topaz, although this is probably a slight overestimate.

In all calculations the fugacity of water is assumed to equal the fugacity of pure water at the pressure and temperature of the experiment. Other possible vapor species include HF and a variety of fluoride and hydroxide complexes of Si and Al. Calculations based on the thermodynamic data for fluor-topaz suggests that the fugacity of HF amounts to at most a few bars. While thermodynamic data are not available to evaluate the concentrations of the other species at the conditions of the experiments they are unlikely to be more than perhaps an order of magnitude greater than the concentration of HF. They then should have no more than a small effect on the equilibrium constant and hence on the derived free energies. Considering that the relative uncertainty in the mole fraction of hydroxyl-topaz is 10% or greater, changes in the fugacity of water of this degree would not add greatly to the uncertainty in the derived parameters.

The simplest mixing models for topaz are those that involve ideal mixing of the fluorine and hydroxyl on the fluorine sites in the topaz structure. In ideal orthorhombic topaz (*Pbnm*) all eight fluorine sites in the unit cell are equivalent. If the fluorine and hydroxyl mix ideally on all these sites the activities of fluor-topaz and hydroxyl-topaz are given by the expressions:

$$a_{\rm FT} = X_{\rm FT}^2 \tag{3a}$$

$$a_{\rm OHT} = X_{\rm OHT}^2 \tag{3b}$$

for the formula units $Al_2SiO_4F_2$ and $Al_2SiO_4(OH)_2$. If the fluorine sites are not crystallographically equivalent (as in topaz of lower symmetry) the activity relations would be the same in the absence of inter-site fluorine-hydroxyl partitioning. Any activity model must render the results from the hydroxyl-buffering experiments internally consistent. The equilibrium condition for reaction (1) is:

$$\Delta G_{\mathrm{T},1}^{\circ} = -R\mathrm{T}\ln\frac{a_{\mathrm{OHT}}}{f_{\mathrm{H}_{2}\mathrm{O}}} + \int_{\mathrm{P}}^{1} \Delta V \mathrm{d}P \qquad (4)$$

Two related tests of internal consistency can be made on the activity models. The first is to check that experiments at different pressures but at the same temperature give the same value for the standard state free energy. The second test is to plot all the free energies versus temperature to see if the results at the various temperatures are consistent with one another given reasonable values for heat capacities and the entropies of the phases. Values for $\Delta G^{\circ}/RT$ for the ideal activity model are given in the second to the last column of Table 2. These data satisfy the above criteria for internal consistency; a curve that gives reasonable values for the entropy and heat capacity of reaction can be fit through the brackets.

While the ideal mixing model fits the experimental data within uncertainty, the ideal model is not satisfactory for extrapolation of the results to much lower temperatures or to high water pressures. The reason for this is that the model allows the hydroxvl-topaz content of a topaz to reach unity. This would imply, given the experimental results, that andalusite plus water is unstable relative to pure hydroxyl-topaz at a few hundred degrees celsius, a conclusion which clearly conflicts with natural assemblages. Natural topazes have at most about 30% hydroxyl-topaz component even when coexisting with andalusite, pyrophyllite, or kaolinite. Rosenberg (1972a) did synthesize topazes at low temperatures having more than 50% hydroxyl-topaz component, but he started with highly metastable materials and his final assemblage (quartz + topaz + pyrophyllite) was mestastable over most of the temperature interval of his experiments. Parise (1980) argues that due to the proximity of pairs of fluorine sites in topaz occupation of one site in a pair by hydroxyl would preclude the occupation of the other by hydroxyl. To have hydroxyls on adjacent sites would require the hydrogen atoms to be too close to one another. This leads to a "protonavoidance" restriction on the occupation of adjacent sites limiting the mole fraction of hydroxyltopaz to less than 0.5

Given this restriction on the distribution of hydroxyl within the topaz structure an alternative "ideal" activity model can be derived which gives an equally good fit to the experimental data, but also gives very reasonable results when used to extrapolate the experimental results to lower temperatures.

Ideal mixing models are derived through the Boltzmann relation (Kerrick and Darken, 1975):

$$S = k \ln \Omega \tag{5}$$

which relates the entropy of a state S to the multiplicity of that state Ω , where k is the Boltzmann constant. In this problem the activities of the components are related to the entropy of mixing through the relation:

$$S_{i}^{\circ} - \overline{S}_{i} = R \ln a_{i} \tag{6}$$

where S_i° is the entropy of the pure phase and \overline{S}_i is the partial molar entropy of the component in the solution. The entropy that needs to be determined in equation (5) is the entropy of mixing because the entropy of mixing and the activity are related through the expression:

- 0

$$R\ln a_{i} = \frac{\partial S_{\min}}{\partial X_{i}} (1 - X_{i}) + S_{\min}$$
(7)

. . .

where X_i is the mole fraction of component i. Ω , the multiplicity for mixing in topaz solutions with the proton-avoidance restriction, is given by:

$$\Omega = 2^{2NX_{\text{OHT}}} \frac{N!}{(2NX_{\text{OHT}})!(N(1-2X_{\text{OHT}}))!}$$
(8)

where N is the number of "molecules" of Al_2SiO_4 (F,OH)₂ and X_{OHT} is the mole fraction of hydroxyltopaz. This multiplicity is composed of two parts. The first, the power of 2, is the number of ways that pairs of sites of which one member is hydroxyl may be arranged. The second term accounts for the number of ways that the *pairs* of sites may be arranged (F-F vs. F-OH, remembering that OH-OH combinations are not allowed). Substituting (8) into (5) and letting N be Avogadro's number:

$$S_{\rm mix} = k \ln \Omega = R[2X_{\rm OHT} \ln 2 + 2X_{\rm OHT} \ln 2X_{\rm OHT} + (1 - 2X_{\rm OHT}) \ln (1 - X_{\rm OHT})]$$
(9)

Substituting (9) into (5) and simplifying one arrives at the expressions for the activities of hydroxyltopaz and fluor-topaz in topaz solid solution.

$$a_{\text{OHT}} \propto 16 \frac{X_{\text{OHT}}^2}{(1 - 2X_{\text{OHT}})}$$
 (10a)

$$a_{\rm FT} \propto (2X_{\rm FT} - 1) \tag{10b}$$

These proportionalities may be converted to equalities by considering what the activities must be at boundary conditions. In the limit of low hydroxyl content in the solid solution the activity of hydroxyl-topaz using the proton-avoidance model must equal that of the ideal model. This results because at low hydroxyl contents the probability of a pair of sites both being occupied by hydroxyls is very small and therefore the dominant contribution to the entropy of mixing in both models comes from the F-OH combinations. Similarly, for pure fluor-topaz the activity of fluor-topaz must be unity. The correct activity expressions for the "proton-avoidance" model are:

$$a_{\rm OHT} = \frac{X_{\rm OHT}^2}{(1 - 2X_{\rm OHT})}$$
 (11a)

$$a_{\rm FT} = (2X_{\rm FT} - 1)$$
 (11b)

Some comments are in order on these activities. Clearly they are not completely correct representations of the activities because they give values of ∞ and 0 for a_{OHT} and a_{FT} , respectively, at X_{OHT} = 0.5. These "unreasonable" answers result from the "unreasonable" restriction that no two hydroxyls may occupy both sites in any adjacent pair of sites. As a consequence of this on the molecular level it becomes very difficult to add another hydroxyl as X_{OHT} approaches 0.5 (alternatively, it is very easy to substitute a fluorine). At $X_{OHT} = 0.5$ it is impossible to substitute any more hydroxyl because it would violate the proton-avoidance principle. This is what requires the activity of hydroxyl-topaz to be infinite and the activity of fluor-topaz to be zero at this composition. A completely equivalent formulation can be done using the components $Al_2SiO_4F_2$ and $Al_2SiO_4F(OH)$. If this is done there is a zero-point (configurational) entropy for Al₂SiO₄ F(OH) of Rln2 which arises from the disorder of the fluorines and hydroxyls on the pairs of sites. Note that this is equal to the entropy of mixing for X_{OHT} = 0.5 in equation (9).

These mixing relations are very similar to those that would be derived for the Ca–Mg pyroxenes if Ca is considered to be restricted to the M2 site. The activity of wollastonite would be infinite and the activity of enstatite would be zero at diopside composition (Grover, 1980). The only difference in the two cases is that in the topaz model there is an additional entropic contribution due to the two ways that pairs of F–OH can be arranged (F–OH vs. OH–F). In both the pyroxenes and topaz it is clear that this extreme case is unreasonable, the true solution being one where there is intra-crystalline partitioning between the two sites; some Ca on M1 or OH–OH pairs.

Grover and Orville (1969) have discussed intracrystalline partitioning for cases like this, but appli-

Table 2. Results for the hydroxyl-buffering experiments

Run ¹	т	Р	Time	b	X _{OHT}	-lnK - V(P-1)/RT	
	°c	bars	days	Å		ideal ² [-avoid ³
K-10b(BR)	620	2000	191	8,8183(18)	0 149	10 72	10 37
K-10c(0M)	620	2000	191	8 8120(26)	0 119	11 18	10.98
K~14a(BR)	700	1000	125	8 8140(30)	0 128	10 71	10.90
K-14b(OM)	700	1000	125	8 8070(10)	0.005	11 20	10.41
K-1/10(TM)	700	1000	1.25	0.00/0(10)	0.055	12.70	12.70
R-140(111)	100	1000	125	0.7307(14)	0.045	12.19	12.70
K-15a(BR)	750	2000	28	8.8155(16)	0.135	11.13	10.90
K-15b(BR)	750	2000	28	8.8177(39)	0.146	11.07	10.72
K~15c(OM)	750	2000	28	8.8076(10)	0.098	11.86	11.64
K-15d (TM)	750	2000	28	8.7984(12)	0.053	13.09	12.98
K-16a(OM)	750	1000	27	8.8059(10)	0.089	11.50	11.30
K-16b(OM)	750	1000	27	8,8049(15)	0.085	11.59	11.40
K-16c(TM)	750	1000	27	8.7969(6)	0.046	12.82	12.72
K-16d(TM)	750	1000	27	8.7973(9)	0.048	12.73	12.63
K-17a(OM)	800	1000	14	8,8034(10)	0.077	11.94	11.67
K-17b(TM)	800	1000	14	8.7959(8)	0.042	13.07	12.96
				. ,			
K-18a(TM)	700	2000	101	8,8002(16)	0.062	12.67	12.54
K-18c(OM)	700	2000	101	8,8098(17)	0.108	11.56	11.32
K-18d(BR)	700	2000	101	8,8183(15)	0.149	10.92	10.57
K-18e(BR)	700	2000	101	8.8188(13)	0.151	10.90	10.54
K-19a(TM)	800	1000	37	8.7986(8)	0.054	12.53	12.42
K-19c(OM)	800	1000	37	8,8027(11)	0.074	11,91	11.75
K-20a (TM)	850	650	31	8.7955(11)	0.040	12.79	12.73
K-20b(TM)	850	650	31	8,7966(10)	0.045	12.57	12.48
K-20c(OM)	850	650	31	8,8031(9)	0.076	11.52	11.36
K-20d (OM)	850	650	31	8.7995(11)	0.059	12,04	11.91
K-21a(OM)	750	1000	65	8.8037(8)	0.079	11.73	11.56
K-21b(TM)	750	1000	65	8.7966(11)	0.045	12.85	12.76
K-22a(BR)	750	2000	63	8.8138(18)	0.127	11.34	11.05
K-22b(OM)	750	2000	63	8.8055(6)	0.088	12.07	11.88
K-22c(TM)	750	2000	63	8.7989(14)	0.056	13.16	12.87
K-23a(TM)	850	650	44	8.7979(13)	0.051	12.32	12,21
K-23b(OM)	850	650	44	8,7985(8)	0.054	12.21	12,10
K-23c(TM)	850	650	44	8.7952(10)	0.038	12,91	12.83
K-23d(OM)	850	650	44	8,8020(14)	0.071	11.56	11.51
K-24a(TM)	900	650	5	8.7945(10)	0.035	13.09	13.02
K=245(0M)	000	650	5	9 9019/12)	0 070	11 71	11 56
K-25a(OM)	600	1000	96	8 8003(1/)	0.106	10.90	10.65
K-25b(OM)	600	1000	96	8 8009(11)	0.100	10.09	10.05
K=250(0H)	600	1000	90	0.0090(11)	0.100	10.85	10.01
K-254(BR)	600	1000	90	0.0229(14)	0.171	9.94	9.52
K-230(BK)	000	1000	90	8.8233(14)	0.1/3	9.92	9.49
K-26a(OM)	6000	2000	49	8.8125(20)	0.121	11.08	10.80
K-26d(BR)	600	2000	49	8.8212(15)	0.163	10.50	10.10
K-26e(BR)	600	2000	49	8,8228(10)	0.170	10.41	9.99
l TM = Topaz Mountain: OM = Omi: BR = Brewer Mine: see Table 1							
$2 v = v = \frac{2}{6} = \frac{3}{6} v = \frac{2}{6} = \frac{3}{6} v = \frac{2}{6} = \frac{2}{6} = \frac{3}{6} v = \frac{2}{6} $							
$K = X_{OHT} / t_{H_2O}$ $K = X_{OHT} / [f_{H_2O}(1 - 2X_{OHT})]$							

cation here of a more complex model is not justified for the following reasons. The experimental data can be fit equally well with either the ideal model or the proton-avoidance model because the two models give similar activities for fluorine-rich topazes such as those stable at the high temperatures of the experiments. Even for the lowest temperature experiments (600° C, containing the most hydroxylrich topaz) the error due to the uncertainty in the composition is larger than the calculated difference between the two activity models. Therefore, on the basis of experiment, this is no way to choose between the alternative models. However, calculations based on the proton-avoidance model agree well with natural assemblages, whereas those based on the ideal model do not. Therefore, given the present degree of resolution in the experimental data, the proton-avoidance model, although an approximation, provides a satisfactory basis for extrapolating the results of the experiments.

Table 2 gives values for $\Delta G^{\circ}/RT$ for reaction (1) calculated using the proton-avoidance model. These values are plotted versus 1/T in Figure 2. From these values, the estimates of the heat capacity and entropy of hydroxyl-topaz and thermodynamic data on andalusite and water (Haas et al., 1981; Burnham et al., 1969) the standard state thermodynamic properties of hydroxyl-topaz may be calculated. Numerous curves could be fit through the data within the experimental uncertainty, but the one chosen was picked because it gives an entropy very close to the estimated entropy and violates the fewest brackets. A least squares fit was not done because data of this type do not belong to normal distributions. The standard state thermodynamic data for hydroxyl-topaz are given in Table 3. The following (conservative) method was used for the estimation of errors. First, the error in the entropy for hypothetical hydroxyl-topaz was assumed to be ± 8.0 J/K-mol, which is the combination of the error in the fluor-topaz entropy and the F-OH exchange correction. Second, the error in the standard free energy formation of hydroxyltopaz (for the proton-avoidance model) was estimated from the uncertainty in the experimental brackets (on the order of 8 kJ due to ± 0.025 uncertainty in X_{OHT} and the width of the brackets the former contribution predominates) and the uncertainties in the free energies for the other phases. The standard state free energy for hydroxyl-topaz calculated for the ideal solution model would be about 5500 J more positive; within error of the



Fig. 2. $-\Delta G^{\circ}/RT$ versus 1/T plot for the hydroxyl-topaz buffering experiments (values calculated using the protonavoidance model; see text). Arrows indicate the direction of change. The uncertainty is approximately ± 0.4 at the hightemperature end decreasing to ± 0.15 at the low-temperature end. The line is also calculated from the proton-avoidance model and represents the preferred fit.

proton-avoidance value (there is no special significance to this agreement). Parentheses enclose the value for the standard free energy of formation of hydroxyl-topaz (Table 3) to emphasize that the value is model dependent.

From the activity model and from thermodynamic data on hydrogen fluoride, water, and the topaz end members, the fugacity ratio of the gaseous species coexisting is related to topaz composition through the expression (T in K; P in bars):

$$2RT\ln\frac{f_{\rm H_2O}(1-2X_{\rm OHT})}{f_{\rm HF}X_{\rm OHT}} = 133697 + 606.946T + 0.0318354T^2 - 5.0728 \times 10^{-6}T^3 - 4012.56T^{0.5} - 170507T^{-1} + 72.8278T\ln T - 0.239(P-1)$$
(12)

This expression can not be directly compared with the results of Rosenberg (1978) on fluoride-hydroxyl exchange in topaz. However, the predicted fugacity ratios differ greatly from Rosenberg's. His equation predicts that with increasing temperature at constant composition the coexisting fluid becomes poorer in HF. This is contrary to the results predicted here and also conflicts with other experiments on fluoride-hydroxyl exchange in silicates (e.g. the mica exchange experiments of Munoz and Ludington, 1974, 1977). There does not seem to be a simple numerical reason for this discrepancy such as the use of different formula units. However, the discrepancy may be within the experimental errors of the two studies. The method used by Rosenberg (1978) involved determination of the HF content of the fluid by mass balance (Rosenberg, personal communication). Because only a very small fraction of the fluorine is partitioned into the liquid, small errors in the determination of the composition of the topaz could lead to large errors in the relative amount of HF and hence large error in the equilibrium constant. The presence of other fluoride species

G⁰298K,1 bar Phase C_** S⁰298K Volume Source a Ь d ë J/mol J/K.mol J/K·mol J/bar S Cp V G Andalusite -2442807 93.77 543.227 -0.20790 2.28751 6.68751 -6754.36 5.153 4 4 4 4 (484)(0.73)Fluor-topaz -2910660 105.40 471.414 -0.08165 1,26947 -5485.54 5.153 5 5 5 5 (4400)(0.15)Hydroxy1-topaz⁺ (-2693251)112.04 504.413 -0.08737 1.35833 -5869.53 5.392 1 1 1 1 (12000)(8.00)HF (ideal gas) -275400 173.78 30.352 -0.00302 0.31404 -10.38892479. 2 2 3 3 (828)(0.04)H₂O (ideal gas) -228611 188.73 10.438 0.02596 -0.13108 -0.44689 299.19 2479. 4 4 4 4 (100)(0.08)

Table 3. Thermodynamic properties of some phases in the Al₂O₃-SiO₂-H₂O-F₂O₋₁ system

 st Errors given here are for the Gibbs free energies of formation.

** $C_p = a + bT + c \times 10^6 T^{-2} + d \times 10^{-5} T^2 + eT^{-0.5}$

 † The Gibbs free energy for hydroxyl-topaz is for the proton-avoidance model.

¹ This study, ² Robie et al. (1978). ³ Stull and Prophet (1971). ⁴ Haas et al. (1981). ⁵ Barton <u>et al</u>. (1982)

in solution, such as suggested by the low-temperature data of Roberson and Barnes (1978), would result in unusually high apparent HF contents. The pressure effect on log $f_{\rm HF}/f_{\rm H,O}$ at constant topaz composition (6.24/*T* in units of kbar⁻¹) is negligible given the uncertainty in the thermodynamic data.

The synthesis experiments of Rosenberg (1972a) are roughly compatible with the results obtained here finding that the buffered content of hydroxyltopaz in topaz solid solution increases with decreasing temperature. His results show hydroxyl contents which are systematically higher than those calculated from the results of this study. This is consistent with the fact that Rosenberg's mullite and pyrophyllite buffering assemblages were metastable compared to the andalusite + topaz (+ quartz) assemblage used here. Interestingly, the shape of Rosenberg's T-X results agrees with calculations using the ideal activity model suggesting that the topaz produced in his study was highly disordered. This results perhaps as a consequence of the synthesis nature of his experiments.

Petrologic applications

Topaz compositions in nature may be controlled in one of two ways: by local equilibria with coexisting solids and vapor, or by externally imposed vapor compositions. In the case of local equilibrium the topaz in turn buffers the vapor composition. Most parageneses result from metasomatic process-



Fig. 3. Projection of the compositions of some of the phases in the Al_2O_3 -SiO₂-H₂O-F₂O₋₁ system (parallel to the join H₂O-F₂O₋₁). Abbreviations (used throughout this paper) are: tpz = topaz, and = andalusite, cor = corundum, di = diaspore, ka = kaolinite, kya = kyanite, py = pyrophyllite, qz = quartz, rs = alkali-free ralstonite, sil = sillimanite, v = vapor, zu = chlorinefree zunyite.

es. Hence the compositions of the topazes and the resulting assemblages are governed in large part by externally derived fluids. This section emphasizes equilibrium calculations on topaz-bearing assemblages and what these equilibria can reveal about closed and open system topaz parageneses.

Topaz occurs in a wide variety of granitic and related hydrothermally altered rocks. Topaz-bearing rhyolites and hypabyssal equivalents are quite common in some environments (Burt et al., 1980; Christiansen, 1981; Eadington and Nashar, 1978; Kovalenko et al., 1972). Closely related topazbearing granites are also common as are topazbearing pegmatites (reviewed in Bailey, 1977). Gradational with igneous rocks containing "primary" topaz, and often developed within them, are topazbearing metasomatic rocks. These include greisens, porphyry molybdenum or tin mineralization, various types of vein deposits, and some aluminous skarns (Thomas, 1979; Hemley et al., 1980; Wallace et al., 1978; Vlasov, 1967; Smirnov, 1977). Detailed discussion of all the associations of topaz in these rocks is beyond the scope of this study, but a number of generalizations can be made concerning the petrology of topaz.

Topaz equilibria in the Al_2O_3 -Si O_2 -H₂O-F₂O₋₁ system

The composition of topaz can be buffered by reaction with many phases in the Al_2O_3 -SiO₂-H₂O- F_2O_{-1} system (Figure 3). The simplest reactions are divariant fluoride-hydroxyl exchange reactions such as represented by reaction (4). Other, heterogeneous reactions such as (1), (13)-(16) may also control topaz compositions. Many other buffering

$$\begin{array}{rcl} Al_2 SiO_4 (OH)_2^{ss} + 3SiO_2 = Al_2 Si_4 O_{10} (OH)_2^{ss} & (13) \\ topaz & quartz & pyrophyllite \end{array}$$

4A

$$l_{2}SiO_{4}(OH)_{2}^{ss} = topaz 6AlO(OH)^{ss} + Al_{2}Si_{4}O_{10}(OH)_{2}^{ss} (14) diaspore pyrophyllite$$

$$2Al_{2}SiO_{4}(OH)_{2}^{ss} + H_{2}O =$$

topaz
$$Al_{2}Si_{2}O_{5}(OH)_{4}^{ss} + 2AlO(OH)^{ss}$$
(15)
kaolinite diaspore

$$\begin{array}{c} \text{Al}_2\text{SiO}_4(\text{OH})_2^{\text{ss}} + \text{SiO}_2 + \text{H}_2\text{O} = \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4^{\text{ss}}\\ \text{topaz} \quad \text{quartz} \quad \text{kaolinite} \\ \end{array}$$
(16)

reactions could be written involving the minerals in



Fig. 4. Calculated isopleths of hydroxyl-topaz in topaz solid solution as a function of pressure and temperature for reaction (1). Abbreviations are the same as for Fig. 3. The uncertainty in composition varies as a function of the temperature and the pressure *and* isopleths are model dependent; but is on the order $\pm 35^{\circ}$, except for the highest temperatures (>750° C) at low pressures (<800 bars).

Figure 3, but they would not represent known assemblages. Figure 4 shows isopleths of hydroxyl-topaz buffered by an aluminum silicate and a waterrich vapor. These isopleths are calculated from equation (3) assuming that the vapor is pure water. The hydroxyl-topaz isopleths are similar in shape to normal dehydration curves as expected from the fact that they represent the dehydration reaction of hydroxyl-topaz diluted by fluor-topaz to aluminum silicate + water.

Topaz compositions will be buffered by reactions (13)–(16) at temperatures below 400° C as a consequence of the instability of andalusite and kyanite relative to pyrophyllite- and then kaolinite-bearing assemblages. Figure 5 somewhat schematically shows the buffering of topaz by these reactions at 500 bars. Calculation of the displacement of the reaction:

$$Al_2Si_4O_{10}(OH)_2 = Al_2SiO_5 + 3SiO_2 + H_2O$$
 (17)
pyrophyllite andalusite quartz

with the addition of fluorine shows that at the fluorine content where andalusite reacts to give topaz the fluorine content of the pyrophyllite is only about a tenth of a weight percent and that the temperature of (17) has been raised by less than 2°. For this calculation the F–OH exchange between

pyrophyllite and vapor was assumed to be the same as Munoz and Ludington (1977) found for muscovite-vapor exchange. With the first addition of fluorine pyrophyllite is slightly stabilized. With subsequent reaction of andalusite to give topaz at a higher fluorine concentration the stability of pyrophyllite is governed by reaction (13) and decreases in temperature with increasing fluorine content. If, with increasing fluorine content reaction (13) moved to higher temperatures in the limit of complete fluoride for hydroxyl substitution, fluor-topaz would break down to fluor-pyrophyllite plus quartz. This is incompatible with known topazkaolinite assemblages and with the normally observed chemography of the phases (F/OH in topaz is much greater than F/OH in coexisting pyrophyllites). From this it would appear that the pyrophyllite-bearing experiments of Rosenberg (1972a) must be metastable and thus is consistent with the unusually high hydroxyl contents of his topazes.

Figure 5 also illustrates other reactions involving topaz, including compositional limits for silica undersaturated conditions. Note that at temperatures lower than those of reaction (18) the maximum



Fig. 5. Schematic temperature versus OH/(OH + F) diagram showing some, but not all, of the reactions which limit topaz compositions in the system Al_2O_3 -SiO₂-H₂O-F₂O₋₁ at 500 bars total pressure. The lines represent the compositions of the various phases coexisting with the phases in the parentheses (*i.e.*, tpz(py,qz) is the projected composition of topaz in equilibrium with pyrophyllite and quartz). The abbreviations are the same as for Fig. 3.

$$(2 - r)Al_2Si_4O_{10}(OH_xF_{2-x}) =$$
pyrophyllite
$$(x - r)Al_2SiO_5 + 3(2 - r)SiO_2$$
andalusite
quartz
(18)

$$(2 - x)Al_2SiO_4(F_{2-r}OH_r) + (x - r)H_2O$$

topaz

hydroxyl-content for topaz is found in silica-undersaturated assemblages; the topazes in silica-saturated assemblages contain more fluorine. Implicit in the construction of Figure 5 is the assumption that F/OH in topaz \gg kaolinite > diaspore > pyrophyllite. This sequence is arbitrary except for the position of topaz which always has F/OH much greater than that of the other phases (*cf.* Deer *et al.*, 1962).

Topaz-bearing assemblages in the Al₂O₃-SiO₂- $H_2O-F_2O_{-1}$ system are quite common. And alusitetopaz-quartz has been reported by Sykes and Moody (1978) and Hildebrand (1961), and might be expected in regions of advanced argillic alteration in hydrothermal ore deposits (Hemley et al., 1980). Kempe (1967) describes sillimanite (kyanite) + topaz + quartz assemblages from Tanzania, and Sheridan et al. (1968) describe topaz + sillimanite + quartz from the Front Range in Colorado. Topaz, pyrophyllite, and alusite and quartz have been described in vein assemblages from hydrothermal ore deposits (Meyer and Hemley, 1967; Hemley et al., 1980) and pyrophyllite developed by alteration of pre-existing topaz-andalusite-quartz rock is described by Sykes and Moody (1978). Olsen (1971) and Sainsbury (1964) specifically describe kaolinite-topaz-quartz associations and such associations are common in supergene or late hypogene alteration of topaz-bearing granites and greisens. Silicaundersaturated "apo-carbonate" greisens often have coexisting topaz and diaspore (Vlasov, 1967). All these assemblages are consistent with the model for the low-temperature phase relations of topaz represented by Figure 5. Although calculated topaz compositions at low temperatures are suspect due to the uncertainties in the thermodynamic data, such calculations should give a reasonable qualitative understanding of topaz behavior, because of the large activity coefficients of hydroxyl-topaz near $X_{OHT} = 0.5$.

Few topazes from well-documented buffering assemblages in this system have been analyzed. Those that have are generally consistent with the present results. Topaz from Ouro Preto, Minas Gerais, Brazil is found with kaolinite and quartz and contains 25 mole % hydroxyl-topaz (Table 1), roughly consistent with Figure 5. Thomas (1979) reports that fluid inclusion filling temperatures for topaz from Ouro Preto are in the range 260–280° C. The topaz from the Hillsborough pyrophyllite deposit also contains about 25 mole % hydroxyl-topaz component (Sykes and Moody, 1978) consistent with the composition expected near reaction (18) (Figs. 4 and 5). It is interesting to note that the pyrophyllite composition calculated for this assemblage has a fluor-pyrophyllite component of but a few percent, in reasonable agreement with the composition reported by Sykes and Moody.

Kempe (1967) provides optical and crystallographic data for several topazes from sillimanite + topaz + quartz + kyanite assemblages from Tanzania. Estimated compositions from Kempe's data fall in the range of 11–16% hydroxyl-topaz component. However, Rosenberg (1972a) reports that at least some of this topaz has as little as 5% hydroxyltopaz component. If these are stable assemblages then $P_{\rm H_2O} \ll P_{\rm tot}$ (*cf.* Fig. 4). Topaz in a sillimanite + quartz assemblage from Colorado (Sheridan *et al.*, 1968) contains about 10% hydroxyl-topaz component (Rosenberg, 1972a) which would be consistent with formation under vapor-saturated conditions above about 1 kbar and 675° C.

Without independent pressure or temperature estimates the topaz composition from a buffered assemblage can at most give the temperature as a function of pressure (or *vice versa*). Only for univariant reactions can the temperature and pressure both be estimated from the composition of the topaz. The uncertainties in derived pressures and temperatures would be highly correlated even for the univariant reactions such as (18) and hence it would be difficult to tightly constrain the pressure or the temperature in the absence of some independent information.

For fluorine-rich, silica-undersaturated portions of this system topaz compositions may be buffered by reactions involving alkali-free ralstonite (Al(F,OH)₃) and chlorine-free zunyite (Al₁₃Si₅ $O_{20}(OH,F)_{18}(F,OH)$) (Fig. 3). Rosenberg (1972a) observed these phases in his synthesis experiments and suggested that natural ralstonite-topaz assemblages might occur in places like the St. Peter's Dome area, Colorado, where both minerals have been reported. Zunyite plus pyrophyllite or kaolinite is equivalent to topaz plus vapor and is found in some ore deposits characterized by intense acid leaching (such as Red Mtn., Colorado; Butte, Mon-

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tana; Meyer and Hemley, 1967). This suggests that zunyite + topaz + pyrophyllite (or kaolinite) + vapor may be a stable assemblage under some conditions. Zunyite + quartz + kaolinite (or pyrophyllite) would be incompatible with the commonly observed assemblage topaz + kaolinite + (inferred) vapor suggesting that zunyite, like pyrophyllite, could have a limited temperature range of stability at least under high silica activities.

Topaz equilibria in more complex systems

Although many topaz-bearing rocks can be described in terms of the four-component system discussed above most topaz-bearing assemblages include a variety of other minerals requiring the addition of other components, notably alkalies. Burt (1979, 1980, 1981), Beus and Dikov (1967), Glyuk and Anfilogov (1973a), Kalyuzhnaya and Kalyuzhni (1963), Kogarko (1966), Kupriyanova (1970), and others have discussed the paragenesis of topaz under a variety of conditions on the basis of field observations and synthesis experiments.

Under alkali-rich and/or silica-poor conditions topaz decomposes to alkali-aluminum fluorides such as cryolite (Na₃AlF₆) or chiolite (Na₅Al₃F₁₄) (Burt, 1979; Kogarko, 1966). This explains the absence of topaz in syenites and the reaction relations observed between topaz and these fluorides in very alkalic granites and granitic pegmatites.

Other reactions involving topaz include reactions with beryllium minerals (Burt, 1975a) where with increasing fluoride activity the aluminous beryllium minerals decompose to give topaz plus phenakite or bertrandite. Reactions of this type have been proposed as natural fluorine buffers for some pegmatite and greisen assemblages (Burt, 1975b). For example, beryl + phenakite + topaz + quartz and beryl + bertrandite + topaz + quartz assemblages occur in the pegmatites and greisens in the Mt. Antero region, Chaffee Co., Colorado (Adams, 1954). These assemblages buffer the HF fugacities by the heterogeneous reactions:

$$2Be_{3}Al_{2}Si_{6}O_{18} + 4HF = 3Be_{2}SiO_{4}$$
beryl phenakite
$$+ 2Al_{2}SiO_{4}F_{28}^{ss} + 2H_{2}O + 7SiO_{2}$$
topaz quartz
$$4Be_{3}Al_{2}Si_{6}O_{18} + 8HF = 3Be_{4}Si_{2}O_{7}(OH)_{2}$$
beryl bertrandite

+
$$4Al_2SiO_4F_2^{ss} + H_2O + 14SiO_2$$
 (19b)
topaz quartz

If the topaz composition and a temperature or pressure were known for one of these assemblages, and the activity of water could be assumed to be nearly equal to unity, the temperature or pressure, and HF fugacity could be calculated. Analogous reactions can be written for the decomposition of aluminous phases of other minor components with increasing activity of HF to less aluminous phases and topaz. However, such reactions are probably not common fluorine buffers because the bulk of the fluorine buffering will be performed by the major component compounds in the rock—i.e. the alkali aluminosilicates.

Of the alkali aluminosilicates the most important here are the feldspars and the micas. Numerous fluorine buffering reactions can be written in terms of reactions involving the feldspars, micas, aluminum silicates, and one or more fluorides. Fluorite is the only one of the common alkali or alkaline earth halides stable with topaz. Fluorination reactions for calcium-bearing feldspars produce fluorite plus an aluminous phase \pm quartz. They extract the anorthite component in a manner analogous to metamorphic reactions involving (clino)zoisite or calcite. Three of the most common buffering reactions involving anorthite component are:

$$CaAl_2Si_2O_8^{ss} + 2HF =$$

anorthite

 Al^2SiO^5 + SiO_2 + CaF_2 + H_2O (20a) andalusite quartz fluorite sillimantite

$$CaAl_2Si_2O_8^{ss} + 4HF =$$

 $\begin{array}{rcl} Al_2SiO_4F_2^{ss} &+ & SiO_2 &+ & CaF_2 &+ & 2H_2O \ (20b)\\ topaz & & quartz & fluorite \\ CaAl_2Si_2O_8^{ss} &+ & KA1Si_2O_8^{ss} &+ & 2HF \\ anorthite & & K-feldspar \end{array}$

$$\begin{array}{rcrcr} KA1_2[A1Si_3O_{10}](OH)_2^{ss} &+ CaF_2 &+ 2SiO_2 (20c) \\ muscovite & fluorite & quartz \end{array}$$

Reaction (20a) is the buffering reaction for fluorine in some metamorphic rocks (Bohlen and Essene, 1978) and represents the AFSQ fluorine buffer (Munoz and Eugster, 1969). This reaction represents the low-fluorine complement of reaction (20b) which is the buffering reaction for anorthite component (in feldspars) in some greisens and rhyolites. Figure 6 illustrates the effect of fluorination on the anorthite content of plagioclase in the presence of



Fig. 6. Reactions (1), (20a), (20b), (20c), (21a), and (21b) plotted for the log of the activity of anorthite versus $\log f_{\rm HF}/f_{\rm H_2O}$ at 500 bars and 400 and 600° C. $X_{\rm An}$ is the mole fraction of anorthite at the temperature of interest (calculated from the solution model of Newton *et al.*, 1980). Abbreviations are ksp = K-feldspar, mu = muscovite, an = anorthite (in plagioclase), and as for Fig. 3.

common granitic phases. These calculations are based on the thermodynamic data for topaz (this study) and the data for the other phases (Haas *et al.*, 1981; Robie *et al.*, 1978). Under most conditions at HF fugacities high enough to stabilize topaz the activity of anorthite must be fairly low, especially in the presence of potassium feldspar. Figure 6 was calculated assuming pure K-feldspar, if one considers the most sodic composition (coexisting with albite) the shift in the curve is <0.1 log units to higher HF.

Desborough *et al.* (1980) have recently proposed that (20c) could account for unusually low temperatures derived from feldspar geothermometry on fluorite-bearing, two-mica granites from the Pikes Peak batholith. Siderophyllite component in biotite is another plausible sink for alumina in these fluorination reactions. Because of these fluorination reactions, greisenization and other phenomena related to the generation of relatively high HF activities are restricted to low-calcium granitic rocks. Conversely, rocks with greisen-style alteration, be they granites, rhyolites, pegmatites, or aluminous sediments have albitic plagioclase. As Burnham (1979) points out, the strict association of certain types of ore deposits with alkalic rocks may be more a consequence of their bulk composition than of any original enrichment in trace ore components. Calcic rocks will buffer the *acid* fluoride species at low concentrations precluding the significant involvement of these species in the ore-forming process.

Topaz-bearing assemblages could however arise from calcic source magmas given the following scenario: fluids derived from the magma must start with relatively low HF/H_2O ratios, below the field of topaz stability for the magmatic conditions. If the fluid then cools without being able to react with the calcium-rich host it will move into the field of topaz (*cf.* Figs. 6 and 7). On encountering a low-calcium host it could then produce topaz.

Figure 6 also indicates that the AFSQ buffer is only marginally stable with respect to anorthite + fluorite + topaz + quartz, and could be metastable given the errors in the thermodynamic data. Bohlen and Essene (1978) have discussed some of the chemographic consequences of this.

Two common fluorine buffers involving feldspars and related to topaz are:

$$\frac{\text{KAl}_2[\text{AlSi}_3\text{O}_{10}](\text{OH})_2^{\text{ss}} + \text{SiO}_2}{\text{muscovite}} \qquad (21a)$$

 $\begin{array}{ll} KAlSi_{3}O_{8}^{ss} + Al_{2}SiO_{4}F_{2}^{ss} = \\ K-feldspar & topaz \end{array}$

$$\begin{array}{rcl} \text{KAl}_2[\text{AlSi}_3\text{O}_{10}]\text{F}_2^{\text{ss}} + \text{SiO}_2 & (21b) \\ \text{muscovite} & \text{quartz} \end{array}$$

These reactions relate the three minerals characteristic of greisen-style alteration—muscovite, topaz, and quartz. Figure 7 shows the stability fields of these phases relative to reactions involving andalusite and potassium feldspar. This figure was calculated by extracting the thermodynamic properties of muscovite and potassium feldspar from the experiments of Chatterjee and Johannes (1974) on (fluorine-free) reaction (21a). The minimum slope through their brackets was chosen in order to minimize the difference between the extracted entropy of reaction and that determined from calorimetry (see discussion of Krupka *et al.*, 1979). No correction has been made for the ordering of the potassium feldspar with decreasing temperature or for possible ordering in the muscovite; these corrections are small compared with the other uncertainties. The muscovite F–OH exchange data of Munoz and Ludington (1977) were used to calculate new values for the thermodynamic properties of fluor– muscovite. New f_{HF}^2/f_{H_2O} ratios for the AFSQ buffer (used by Munoz and Ludington) were calculated from the data of Robie *et al.* (1978) for fluorite and the data of Haas *et al.* (1981) for the other phases. This recalculation shows that the preferred fugacity ratios for the muscovite–vapor exchange are approximately 0.6 log units less than the values derived by Munoz and Ludington.

Reactions (1), (21a), and (21b) are plotted in Figure 7. The addition of fluorine to the vapor stabilizes muscovite plus quartz relative to andalusite plus K-feldspar plus vapor, while at high fluorine concentrations muscovite plus quartz becomes unstable relative to topaz plus K-feldspar (reactions (21a) and (21b) respectively). The point where all three of these reactions intersect gives the maximum temperature for the stability of the assemblage muscovite and quartz at that pressure. The region between the andalusite-muscovite-quartz-K-feldspar reaction and the topaz-muscovite-quartz-Kfeldspar reaction is the region where topaz, muscovite, and quartz are stable together. This field represents many greisens. Addition of other components to the system will affect the absolute positions of the curves by small amounts while leaving the topology the same.

Burt (1976) correctly argues that $\mu_{\rm HF}$ increases with increasing $\mu_{\rm H_2O}$ for reaction (21b), however from chemography alone it is not possible to determine the direction of reaction with decreasing temperature. Although the present calculations do indicate that on cooling topaz±kspar±vapor produces muscovite + quartz in agreement with Burt's conclusion, small changes in the entropies of the F-OH exchange reactions could produce the opposite effect. Consequently, the agreement between the calculations and observation (below) gives further support to the applicability of the thermodynamic model.

Rosenberg (1972b) documents an example of this in the Brown Derby pegmatite (Colorado) where early topaz + K-feldspar (+quartz) has been replaced by micas (muscovite/lithium micas). Muscovite commonly replaces topaz in greisens and related deposits (e.g. Panasquiera, Kelley and Rye, 1980; and in other deposits, summarized in Vlasov, 1967). The addition of other components (such as Li or Fe) will increase the stability of mica relative to topaz + K-feldspar. In many cases the micas replacing topaz depart significantly in composition from muscovite; as a result, they may replace topazes of higher fluorine content. For instance, the lithian muscovites in the Brown Derby pegmatite replace topaz with $X_{OHT} = 0.090$ (Rosenberg, 1972b).

Granitic porphyry molybdenum deposits are characteristically enriched in fluorine and usually contain zones in which topaz is a major component (Mutschler *et al.*, 1981). Broadly speaking, the zoning in these deposits ranges from (deep to shallow) potassic to silicic/greisen to sericitic to propylitic. In many deposits several mineralizing events are superimposed and locally alteration may depart from the typical sequence (Carten *et al.*, 1981; Wallace *et al.*, 1968, 1978; White *et al.*, 1981).

Gunow et al. (1980) studied the compositions of micas from the alteration zones in the Henderson (Colorado) porphyry molybdenum deposit. The F/ (F + OH) ratios in the muscovites are highest in the potassic zone and decrease with decreasing temperatures of origin. These ratios vary from >0.25 to about 0.10 over a temperature range from $>500^{\circ}$ to <350° C (Gunow et al. (1980) based on the fluid inclusion data of Kamilli (1978)). The topaz varies in composition from $X_{OHT} = 0.14$ to 0.04 and is not known to be correlated with temperature in its more restricted paragenesis. Comparison of these values with Figure 7 shows reasonable agreement. The Henderson muscovites, in some cases, contain appreciable amounts of magnesium which greatly increases their tendency to hold fluorine (Munoz and Ludington, 1974). The discrepancy between the fluorine contents found by Gunow et al. and the values calculated here can be largely attributed to this factor.

The greisen assemblages which constitute characteristic part of porphyry-style molybdenum (tungsten-tin) mineralization, and occur in many other kinds of deposits, represent a fluorine-rich variety of advanced argillic alteration (Meyer and Hemley, 1967). Fluid inclusion and other geologic evidence indicates that these deposits probably formed at pressures less than 1 kbar and at temperatures generally less than 500° C, although the early alteration in some cases took place at higher temperatures (Hall *et al.*, 1974; Ivanova *et al.*, 1978; Kelley and Rye, 1980; Thomas, 1979; Wallace *et al.*, 1978 and many others). Boiling of the hydrothermal



Fig. 7. Log f_{HF}/f_{H_2O} versus 1/T plot showing the calculated positions of some reactions in the silica-rich portion of the K₂O-Al₂O₃-SiO₂-H₂O-F₂O₋₁ at 500 bars. Also shown are isopleths for hydroxyl-muscovite (dotted) and hydroxyl-topaz (dashed). Abbreviations are the same as for Fig. 3 and 6.

fluids is also a common feature (e.g. Landis and Rye, 1974; Ivanova et al., 1978; and others). These observations may be combined to interpret, very crudely, the sequence of alteration assemblages in terms of the Figure 7. The aqueous fluids produced by crystallization of a fluorine-rich alkalic magma would be rich in halogen acids and alkali halides (Burnham, 1979). On entering the surrounding rocks these fluids could react with the feldspars to produce potassium feldspar at the expense of the earlier minerals. Continued cooling, perhaps accompanied by boiling, would drive the fluid composition into the stability field of the aluminum silicates (Montoya and Hemley, 1975; Burnham, 1979; Burt, 1981) which, in the presence of significant amounts of acid fluoride species, would be represented by topaz. Further cooling and reaction with the primary minerals farther out would make the solutions more alkaline and move from the topaz field into the muscovite field. Projected onto Figure 7 this trajectory would start in the upper right-hand corner and move to the lower left-hand corner. In essence, the shift from the topaz field into the mica field is governed by progressive removal of acid fluoride species from the fluid by reaction with the primary minerals. If the HF/H2O fugacity ratio were not reduced by either fixation of fluorine in a solid phase or by hydrogen-alkali exchange then the fluid composition would remain in the topaz field on cooling. This removal of fluorine from the fluid by formation of fluorine-bearing solids distinguishes the behavior of fluorine in these systems from that of chlorine which is not incorporated to a significant degree in the solids. Topaz veinlets

cutting K-feldspar alteration in the Henderson deposit have sericitic envelopes (E. Seedorff, pers. comm.) a sequence consistent with simple acidbase exchange (cf. Figure 4 in Burt, 1981) and similar to the patterns seen in many greisens (Vlasov, 1967).

Addition of fluorine increases the stability of muscovite + quartz with respect to K-feldspar + aluminum silicate + quartz (Figure 8). The maximum stability of muscovite is achieved at topaz saturation where muscovite + quartz = K-feldspar + andalusite + topaz + vapor. Increasing the HF fugacity at lower temperatures results in complete decomposition of the mica (cf. Figs. 7 and 5). The topaz phase relations in Figures 6–8 are topologically consistent with the acidity-salinity diagrams presented by Burt (1981).

The addition of fluorine as HF (Wyllie and Tuttle, 1961; Glyuk and Anfilogov, 1973a; Kovalenko, 1977; Manning, 1981) or as a salt (Anfilogov *et al.*, 1973; Glyuk and Anfilogov, 1973b; P. J. Wyllie, personal communication) to granitic bulk composition has a dramatic effect on the solidus, lowering it by at least several tens of degrees even at low (a few percent) total fluorine contents. Fluorine-free (taken from Wyllie, 1977) and schematic fluorine-bearing (buffered by topaz + andalusite) solidi for the system $K_2O-Al_2O_3-SiO_2-H_2O$ and for a muscovite granite are illustrated in Figure 8. These reactions



Fig. 8. Calculated positions for the muscovite + quartz breakdown reaction for the fluorine-free system and for fluorine buffered by andalusite + topaz + vapor. Schematic solidii are shown for melting in the fluorine-free and topaz-buffered systems for a muscovite granite and for the $K_2O-Al_2O_3-SiO_2 H_2O-F_2O_{-1}$ system. See the text for further discussion. Abbreviations are: L = liquid, als = aluminum silicate, w = water, and as for Fig. 3 and 6.

intersect with the muscovite + quartz breakdown reactions to give invariant points for the respective systems. The curves between the pairs of invariant points represent the topaz-missing reactions. Not shown are several other melting reactions that radiate from each of these invariant points. The extra lines connecting the two pairs of invariant points for the potassium system and for the muscovite granite are the topaz-missing melting reactions for the respective fluorine-bearing systems. One of the consequences of this topology is that the minimum pressure for the existence of muscovite on the solidus is lowered by about one-half, helping to explain the presence of muscovite in many twomica granites which have features incompatible with higher pressures (see Miller et al., 1981). Another consequence is that subsolvus (two alkalifeldspar) granites can form down to quite low pressures. Pichavant (1981) draws similar conclusions for boron-rich magmas based on melting experiments.

Topaz-bearing hypabyssal and volcanic rocks, are known in some areas (Eadington and Nashar, 1978; Burt *et al.*, 1980; Kovalenko *et al.*, 1972; Lindsey, 1979). The topaz from these rocks tends to have a very low hydroxyl content which is compatible with a high-temperature, low-pressure, but not necessarily magmatic, origin.

Summary

Thermodynamic data for topaz solid solutions provide a means for understanding the conditions of formation of the wide variety of rocks which contain topaz. In this study experiments on the reaction andalusite + water = hydroxyl-topaz component in topaz solid solution permit calculation of the thermodynamic properties of (hypothetical) hydroxyltopaz and evaluation of the applicability of alternative activity models for the solid solution. Both ideal and proton-avoidance mixing models agree with the experimental data, but the proton-avoidance model gives much more reasonable results on extrapolation to lower temperatures.

Combined thermodynamic data on topaz solid solutions from this study and that of Barton *et al.* (1982) allow calculation of many reactions involving topaz and some coexisting fluid compositions. These calculations show that topaz is efficient at removing HF from a coexisting vapor phase, an efficiency which increases with decreasing temperature. Topaz is richer in fluorine than coexisting sheet silicates, although such silicates may incorporate substantial amounts of fluorine up to the point where topaz becomes stable, increasing the thermal stabilities of these sheet silicates by up to several tens of degrees. The hydroxyl content of topaz buffered by andalusite, kyanite, and sillimanite increases with increasing pressure and decreasing temperature. Low-temperature stability relations of topaz are uncertain, but calculations based on the thermodynamic model indicate that topaz is stable to low temperatures with a variety of minerals in the Al_2O_3 -SiO₂-H₂O-F₂O₋₁ system. The calculations predict compositions ($X_{OHT} < 0.35$) and assemblages that accord well with observation.

Under fluorine-rich conditions in more complex systems topaz usurps the role of the aluminum silicates. For fluorine contents buffered by topaz, muscovite may be stable on the solidii of some granites in the pressure range of one to two kilobars. Muscovite plus quartz become unstable with respect to topaz plus K-feldspar with increasing fluoride activity. Presence of topaz is generally restricted to rocks with low calcium contents or where the calcium is restricted to fluorite. The anorthite content of plagioclase coexisting with topaz must be quite low under nearly all conditions. This fact restricts the development of topaz-rich rocks to those which either have initially low calcium contents or those in which most of the calcium has already been incorporated in fluorite, corresponding to the general restriction of greisens and related deposits to low-calcium rocks and the rarity of topaz in skarns.

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