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SYNTHESIS AND FLUORINE-HYDROXYL EXCHANGE IN THE AMBLYGONITE SERIES

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ABSTRACT

The amblygonite series includes the solid solution between the end members, amblygonite, $LiAlPO_4F$, and montebrasite, $LiAlPO_4OH$. The most common composition range is between Amb_{10} and Amb_{50}, where this series occurs in Li-rich pegmatites.

The end members and four intermediate compositions were synthesized by standard hydrothermal techniques at 600°C and 2 kbar water pressure. All six cell parameters vary linearly across the compositional range. Amblygonite cell dimensions are *a* 5.103, *b* 7.221, *c* 5.506Å, α 114°22′, β 98°54′, γ 67°02′; and montebrasite, *a* 5.185, *b* 7.161, *c* 5.040Å, α 112°18′, β 97°51′, γ 67°52′. These cell dimensions indicate that the unit cells of the pure Li series are slightly smaller than those of the natural mineral series. Refractive indices are essentially identical with comparable natural minerals.

Equilibrium compositions of the amblygonite phase in the exchange reaction $LiAlPO_4F + H_2O = LiAlPO_4OH + HF$ were approached from both sides, using pure synthetic end members as starting materials. Gas compositions were controlled by solid buffers. The results, x_{Amb} for several levels of f_{HF}, can be fit to the equilibrium constant in the form, $\log K^{600°C}_{2\,kba} = -4.58\ (\pm 0.22) = \log (f_{HF}/_{H_2O}) + \log [(1 - x_{Amb})/x_{Amb}]$ which allows calculation of gas compositions for natural amblygonite compositions beyond the range of the buffers. If $\Delta G_r/\Delta T \simeq 0$ and $\Delta G_r/\Delta P \simeq 0$, as in the LiF-LiOH exchange reaction, then $\log K = -4000/T(°K)$.

Equilibrium constants at pegmatitic temperatures are very small, indicating strong fractionation of F into the amblygonite phase. Isothermal crystallization of amblygonite will cause a decrease in the F content of the gas, and crystal zoning will be toward montebrasite compositions. Zoning with increases of F content result from (1) increases in f_{HF}, accompanying increases in gas pressure caused by silicate phase crystallization and/or (2) by decreasing temperature leading to smaller equilibrium constants.

SOMMAIRE

La série amblygonite consiste en une solution solide entre les pôles extrêmes, l'amblygonite ($LiAlPO_4F$) et la montébrasite ($LiAlPO_4OH$). La composition la plus courante que l'on retrouve dans les pegmatites riches en Li se situe entre Amb_{10} et Amb_{50}. Les compositions limites et quatre compositions intermédiaires ont été synthétisées par voie hydrothermale à 600°C et 2 kbar de pression d'eau. Tous les six paramètres de la maille varient de façon linéaire. Les dimensions de la maille de l'amblygonite sont, *a* 5.103, *b* 7.221, *c* 5.506Å, α 114°22′, β 98°54′, γ 67°02′; pour la montébrasite, *a* 5.185, *b* 7.161, *c* 5.040Å, α 112°18′, β 97°51′, γ 67°52′. Les paramètres de ces composés purement lithiques sont un peu plus petits que ceux des minéraux naturels. Les indices de réfraction coïncident essentiellement avec ceux des minéraux naturels. Les compositions d'équilibre de la phase amblygonite dans la réaction d'échange $LiAlPO_4F + H_2O = LiAlPO_4OH + HF$ ont été approchés des deux côtés à l'aide des membres extrêmes synthétiques purs comme matériaux de départ. Les compositions gazeuses ont été contrôlées par des solutions tampons solides. Les résultats, x_{Amb} pour les différents niveaux de f_{HF}, peuvent être adaptés à la constante d'équilibre par $\log K^{600°C}_{2\,kbar} = -4.58\ (\pm 0.22) = \log (f_{HF}/f_{H_2O}) + \log [(1 - x_{Amb})/x_{Amb}]$ ce qui permet le calcul des compositions gazeuses pour les compositions d'amblygonites naturelles au delà des solutions tampons. Si $\Delta G_r/\Delta T \simeq 0$ et $\Delta G_r/\Delta P \simeq 0$, comme dans la réaction d'échange alors $\log K = -4000/T(°K)$. Les constantes d'équilibre, à des températures pegmatitiques, sont très petites indiquant ainsi un fractionnement de F dans la phase amblygonite. La cristallisation isothermique de l'amblygonite abaissera le contenu en F du gas, et la zonation du cristal sera dans la direction d'une augmentation en montébrasite. Une zonation qui démontre une augmentation en F résultera (1) d'une hausses en f_{HF}, qui accompagne l'augmentation de la pression gazeuse causée par la cristallisation de silicates et/ou (2) d'un abaissement de la température menant à des constantes d'équilibre plus petites.

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INTRODUCTION

Amblygonite series

A continuous, isomorphous series exists between the end members, amblygonite, $LiAlPO_4F$,

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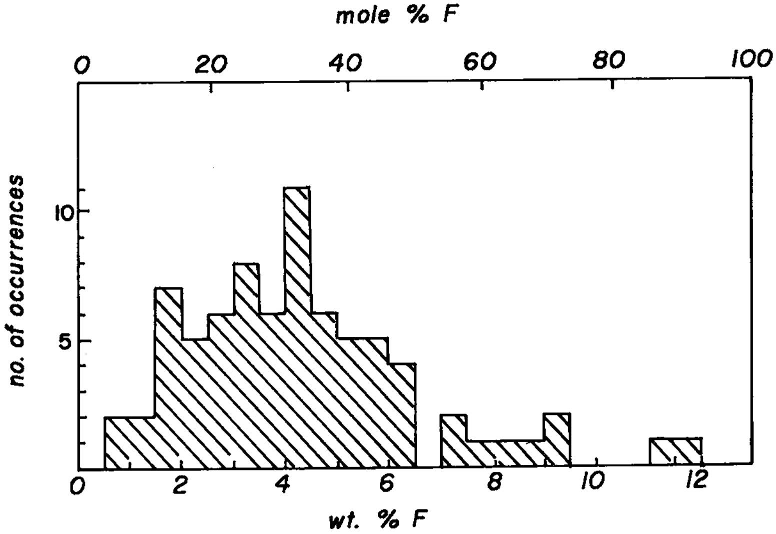

FIG. 1. Histogram of the compositions of natural members of the amblygonite series from data compiled by Loh (1975).

and montebrasite, $LiAlPO_4OH$. Generally, the name amblygonite or amblygonite series has been used to represent any member of the series. Neither pure amblygonite nor montebrasite has been found in nature. The highest reported fluorine content is 11.8 wt. % (92 mole %) from Saxony (Moss *et al.* 1969) and the lowest is 0.85 wt. % (7 mole %) from Siberia (Vlasov 1966). Figure 1 illustrates the compositions of all the reported occurrences of amblygonite and montebrasite, 80% of which have less than 50 mole % fluorine. Sodium is the most common minor element replacing lithium, in amounts averaging near 0.5 mole %.

The members of this series occur chiefly in lithium- and phosphate-rich granitic pegmatites, commonly as ellipsoidal nodules or crude crystals up to 0.5 m in a paragenesis similar to that of spodumene (Moore 1973). The perfect {100} cleavage and milky-white color often lead to confusion with the feldspars. The minerals most commonly associated with amblygonite are spodumene, apatite, lepidolite, tourmaline, and other lithium phosphate minerals. Amblygonite has also been found in high-temperature veins and greisen with cassiterite, topaz, and mica. The minerals of the amblygonite series have been found at the famous pegmatite localities of Varutrask, Sweden; Karakhstan and Siberia, USSR; Montebras, France; Rhodesia; Black Hills, South Dakota, Eight Mile Park, Colorado; Pala, California; Newry, Hebron, Buckfield, and other localities in Maine; and Tanco Pegmatite, Bernic Lake, Manitoba (Quensel 1956; Ginzburg 1950; Gallagher 1967; Connolly & O'Hara 1929; Heinrich & Corey 1955; Černá *et al.* 1972).

Černá *et al.* (1973) presented detailed physical properties on twenty analyzed natural amblygonite minerals. Specific gravities, refractive indices, and differential thermal behavior all show gradual changes with F-content. X-ray powder diffraction methods provide efficient and accurate means for the indirect determination of F content. The $2\theta(CuK\alpha_1)$ values for the (131) reflection (Moss *et al.* 1969) show linear changes with the fluorine content in amblygonite minerals. The determination line was refined by Černá *et al.* (1973).

Purpose of the study

Since little experimental work has been done on this mineral series, pure end members and intermediate members of the amblygonite series have been synthesized to investigate some of the physical properties and to test the completeness of the solid solution. Comparison of properties of the synthetic and natural minerals will help to further define the mineral series especially for the end members. More important is the determination of the relationship between the F content of the amblygonite and the f_{HF} of the pegmatite magma. In this paper we present the properties of a series of synthetic amblygonites, and we show that most amblygonites crystallize from fluids with very low f_{HF}—less than 0.005 bars.

TABLE 1. COMPUTED DENSITIES, CELL DIMENSIONS, $CuK\alpha_1(131)$ AND MEASURED γ-REFRACTIVE INDEX OF SYNTHETIC AMBLYGONITE, MONTEBRASITE, AND ITS INTERMEDIATE MEMBERS*

	mnt	amb_{20}	amb_{40}	amb_{60}	amb_{80}	amb
a (Å)	5.185 (6)	5.175 (2)	5.167 (1)	5.151 (3)	5.134 (2)	5.130 (3)
b (Å)	7.161 (9)	7.164 (2)	7.171 (3)	7.175 (6)	7.213 (6)	7.221 (5)
c (Å)	5.040 (5)	5.042 (2)	5.047 (2)	5.045 (4)	5.056 (3)	5.056 (4)
α	112° 18(6)'	112° 37(2)'	112° 57(2)'	113° 23(4)'	114° 3(4)'	114° 22(4)'
β	97° 51(8)'	98° 0(2)'	98° 3(2)'	98° 15(4)'	98° 42(4)'	98° 54(5)'
γ	67° 52(7)'	67° 46(2)'	67° 42(2)'	67° 30(3)'	67° 12(2)'	67° 2(3)'
V $(Å)^3$	160.4 (2)	159.8 (6)	159.3 (7)	158.1 (1)	157.6 (1)	157.1 (1)
density (calc.)	3.020	3.041	3.058	3.089	3.108	3.126
2θ(131) (obs.)	52.22°	52.42°	52.58°	52.84°	53.07°	53.23°
2θ(131) (calc.)	52.23°	52.40°	52.57°	52.85°	53.07°	53.24°
γ-index	1.643 (1)	1.634 (1)	1.622 (1)	1.612 (1)	1.603 (1)	1.592 (1)

* Estimated deviations are given in parentheses and refer to last digit quoted.

SYNTHESIS OF MEMBERS OF THE AMBLYGONITE SERIES

Experimental procedure

The end members and four intermediate compositions of the amblygonite series were prepared from mixes of the proper proportions of LiF, $LiOH \cdot H_2O$, and $AlPO_4$.[1] Approximately 30 mg of mix and 15 mg of water were sealed in 2 cm long and 3 mm diameter gold tubes. The synthesizing runs were conducted at 600°C and 2000 bars water pressure in standard, externally heated, cold-seal pressure vessels. Temperatures were regulated to within ±3°, and pressure to within ±10 bars. These runs yielded approximately 30 mg of fine-grained crystalline aggregates, which were identified by X-ray diffraction and optical means. Run times of one week were sufficient to allow the lithium to react with all of the $AlPO_4$.

Physical properties of the amblygonite series

The synthetic crystals are very small ($\sim$1 μm), but appear to have homogeneous compositions, based on the sharpness of X-ray reflections. X-ray powder diffraction charts were obtained by scanning at ½°/minute and using Si as an external standard. The refractive index γ was measured by the Becke method in calibrated oils. The highest index of the synthetic crystals showing the highest birefringence was measured.

Complete X-ray powder patterns[2] were obtained for each composition, and the unit-cell dimensions were refined using the U.S. Geological Survey's FORTRAN IV computer program W7214 (see Table 1). Linear regressions of each parameter are given in Table 2 with the compositions expressed both as mole % F and wt. % F, which may be compared directly to those developed by Černá *et al.* (1973). The values of $2\theta(131)$ for each composition and

TABLE 2. REGRESSION EQUATIONS AND CORRELATION COEFFICIENTS OF MEASURED PARAMETERS OF A SYNTHETIC MONTEBRASITE-AMBLYGONITE SERIES

	equation	R
$2\theta_{131}CuK\alpha_1$ (meas.)(°)	= 0.0104 x F mole% + 52.208	(.998)
$2\theta_{131}CuK\alpha_1$ (meas.)(°)	= 0.0807 x F wt. % + 52.208	(.998)
a (Å)	= -0.00059 x F mole% + 5.187	(.989)
a (Å)	= -0.0046 x F wt. % + 5.187	(.989)
b (Å)	= 0.00064 x F mole% + 7.152	(.926)
b (Å)	= 0.0050 x F Wt. % + 7.152	(.926)
c (Å)	= 0.00017 x F mole% + 5.039	(.931)
c (Å)	= 0.0013 x F wt. % + 5.039	(.931)
α (°)	= 0.0215 x F mole% + 112.20	(.992)
α (°)	= 0.1676 x F wt. % + 112.20	(.992)
β (°)	= 0.0108 x F mole% + 97.75	(.964)
β (°)	= 0.0840 x F wt. % + 97.75	(.964)
γ (°)	= -0.0086 x F mole% + 67.93	(.981)
γ (°)	= -0.0672 x F wt. % + 67.93	(.981)
V $(Å)^3$	= -0.0345 x F mole% + 160.4	(.991)
V $(Å)^3$	= -0.2682 x F wt. % + 160.4	(.991)
γ-index	= -0.00051 x F mole% + 1.643	(.999)
γ-index	= -0.00378 x F wt. % + 1.643	(.999)

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[1] LiF and $LiOH \cdot H_2O$ are reagent-grade stock items; $AlPO_4$ was prepared by reaction of reagent-grade Al wire with diluted phosphoric acid and heating the precipitate for 24 hours at 600°C.

[2] Copies available from the authors.

regression constants are reported in Tables 1 and 2. Densities were calculated from the unit-cell volumes and ideal-member compositions. The maximum refractive index, γ, varies along a line almost identical with that of Černá *et al.* (1973).

The cell lengths and $2\theta(131)$ reflect unit-cell volumes that are 0.3 to 0.4% smaller than corresponding natural minerals. Most natural amblygonites contain small amounts of Na and Ca that probably account for the larger spacings. Since the refractive indices of the synthetic and natural minerals are essentially the same, the Na and Ca substitution must have little effect on these values.

FLUORINE-HYDROXYL EXCHANGE

Experimental methods

The exchange between a solid phase of the amblygonite series and an F-bearing gas can be expressed by the reaction: amblygonite+H_2O = montebrasite+HF, for which the equilibrium constant is

$$\frac{f_{HF} \cdot a_{Mnt}}{f_{H_2O} \cdot a_{Amb}} \qquad (1)$$

The exchange was studied by the buffer technique of Munoz & Eugster (1969), in which the solid is allowed to equilibrate with a fixed, buffered gas composition. In this study the exchange was studied at a single temperature (600°C±10°) and at 2000 bars vapor pressure.

The f_{HF} in the gas was buffered by the assemblages

wollastonite-fluorite-quartz (WFQ)
andalusite-fluorite-anorthite-quartz (AFAQ)
andalusite-villiamite-albite-quartz (AVAQ).

In order to spread the range further, the hydrogen hematite-magnetite (HM) was combined with the fluorine buffers (see Munoz & Eugster 1969). Table 3 lists the buffer assemblages and calculated fugacities in the O-H-F gas controlled by the buffers at 600°C and 2 kbar total gas pressure. With each buffer, both synthetic montebrasite and amblygonite were allowed to equilibrate with each buffered gas composition. Run times of four weeks were necessary for the solids to approach the equilibrium composition. The buffer-charge arrangement was similar to that of Munoz & Eugster (1969) except that the charge was separated from the buffer by Au foil disks; the wrapped packet for the charge used by Munoz & Eugster proved too difficult for complete gas exchange.

TABLE 3. CALCULATED FUGACITIES AND PARTIAL PRESSURES IN O-H-F GAS SYSTEM AT 600°C AND 2000 BARS TOTAL PRESSURE FOR SIX ASSEMBLAGES.

Buffer	log f_{HF}	log f_{H_2O}	log f_{H_2}	log f_{O_2}	log f_{F_2}	log P_{HF}
(AVAQ)	+1.482	3.026	-	-	-	+1.190
(AFAQ)	-0.213	3.029	-	-	-	-0.505
(WFQ)	-0.814	3.029	-	-	-	-1.106
(HM)(AVAQ)	+1.581	3.024	-2.257	-13.33	-27.84	+1.289
(HM)(AFAQ)	-0.098	3.028	-2.253	-13.33	-31.21	-0.390
(HM)(WFQ)	-0.646	3.028	-2.253	-13.33	-32.30	-0.938

Since most natural amblygonites contain small amounts of Ca and Na, it is to be expected that the synthetic amblygonite will not only equilibrate with the gas but also with the feldspar of the buffer and accept small amounts of Na or Ca into its structure. The F content of the equilibrated amblygonites was estimated from the refractive index, which is essentially independent of the Na and Ca content. Measurements of $2\theta(131)$ do not give concordant compositions, if the line for synthetic members is used. However, concordant compositions (estimated accuracy is ±2 mole %) are obtained from the $2\theta(131)$ line for natural minerals, clearly indicating compositions closely corresponding to natural minerals.

Run data are presented in Table 4 and plotted on Figure 2. Even though the resulting compositions are all F-rich, we believe that a meaningful curve, relating the F-content of the gas and the amblygonite, can be drawn through these points.

Thermodynamic properties based on the experimental results

By assuming that the mole fraction of amblygonite (x_{Amb}) is equal to the activity of ambly-

TABLE 4. RUN DATA FOR SYNTHETIC AMBLYGONITES AND MONTEBRASITES EQUILIBRATED WITH BUFFERED H-O-F GASES

Run No.	Start. Mat.	Buffers	Temp. (°C)	Press. (kbar)	Time (hrs.)	F mole %
199	M	(HM)(WFQ)	600(4)	2	672	90
149	A	(HM)(WFQ)	593(1)	2	610	95
214	M	(HM)(AFAQ)	600(5)	2	648	90
221	A	(HM)(AFAQ)	600(5)	2	630	90
215	M	(HM)(AVAQ)	600(5)	2	648	100
218	A	(HM)(AVAQ)	600(5)	2	648	100
183	M	(QFI)(WFQ)	595(3)	2	334	77
150	A	(QFI)(WFQ)	595(2)	2	610	95
217	M	(QFI)(AFAQ)	600(5)	2	648	95
222	A	(QFI)(AFAQ)	600(5)	2	630	90
216	M	(QFI)(AVAQ)	600(5)	2	648	100
219	A	(QFI)(AVAQ)	600(5)	2	744	97

* Starting material: M = synthetic montebrasite;
A = synthetic amblygonite

gonite (a_{Amb}), an expression of the equilibrium constant can be obtained. From (1)

$$\log K = \log \frac{f_{\mathrm{HF}}}{f_{\mathrm{H_2O}}} + \log \frac{1 - x_{\mathrm{Amb}}}{x_{\mathrm{Amb}}} \ldots\ldots \quad (2)$$

Using the relation, $f_i = f_i^{\circ} \cdot p_i$, where f_i is the fugacity of gas i in the gas mixture, f_i° is the fugacity of pure i at the same P and T, and p_i is the partial pressure of i in the mixture, we obtain

$$\log K = \log \frac{f_{\mathrm{HF}}^{\circ}}{f_{\mathrm{H_2O}}^{\circ}} + \log \frac{p_{\mathrm{HF}}}{p_{\mathrm{H_2O}}} + \log \frac{1 - x_{\mathrm{Amb}}}{x_{\mathrm{Amb}}} \ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

At 600°C and 2 kbar the value for $f_{\mathrm{H_2O}}^{\circ}$ from Burnham *et al.* (1969) is 1046 bars, and f_{HF}° from the reduced variable chart of Hougen & Watson (1946) is 3920 bars. A value for log K was calculated for each pair of experimental points. An average value of −4.58 with a standard deviation of 0.22 was obtained. The curve

$$\log K = -4.58\ (\pm.22) = .574 + \log \frac{p_{\mathrm{HF}}}{p_{\mathrm{H_2O}}} + \log \frac{1 - x_{\mathrm{Amb}}}{x_{\mathrm{Amb}}}, \ldots\ldots\ldots\ldots \quad (4)$$

with the standard deviation limits has been plotted through the experimental points on Figure 3.

The free energy for the exchange reaction at 600°C calculated from $\Delta G_r^{600°\mathrm{C}} = -RT\ln K = 18.3(\pm 0.9)$kcal.

Since $\Delta G_r^{600°} = \Delta G_{f,\mathrm{Mnt}} + \Delta G_{f,\mathrm{HF}} - \Delta G_{f,\mathrm{Amb}} - \Delta G_{f,\mathrm{H_2O}}$, substitution of the free energy for H_2O (Burnham *et al.* 1969), and for HF (Stull & Prophet 1970) yields the difference between the free energies of the two end members $\Delta G_{f,\mathrm{Mnt}} - \Delta G_{f,\mathrm{Amb}} = 37.0$ kcal. (This value is about 8 kcal lower than $\Delta G_{f,\mathrm{LiOH}} - \Delta G_{f,\mathrm{LiF}}$ at the same temperature).

Even though there are no thermodynamic data on the amblygonite end members, the ΔG_r of the exchange reaction as a function of temperature may be modeled after the $\mathrm{LiF+H_2O = LiOH+HF}$ reaction, because bonding in these compounds is similar to that in the amblygonite series. Using the free energies (in Stull & Prophet 1970), the ΔG_r of the LiF-LiOH reaction is essentially constant over the temperature range of 400° to 700°C. This is because the net change in entropy of the reactants and product is nearly zero, for the exchange takes place with no breaking and forming new kinds of bonds. Assuming that the ΔG_r of the ambly-

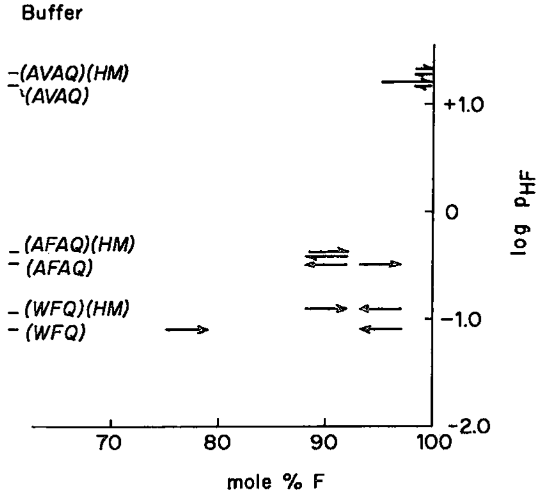

FIG. 2. Plot of the experimentally determined compositions of amblygonite as equilibrated with buffered gas phase at 600°C and 2000 bars total gas pressure. Buffers are shown along left edge. Gas compositions are given in Table 3 and experimental data in Table 4. Left-pointing arrows represent starting amblygonite material; right-pointing arrows, montebrasite. The length of the arrows represents the probable error in the composition determination.

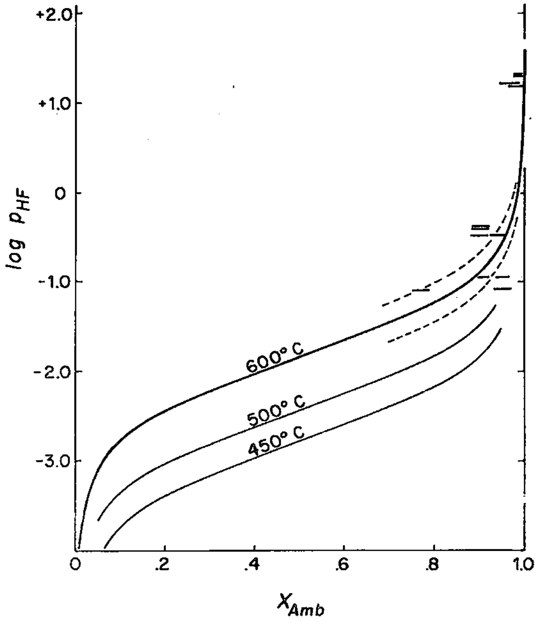

FIG. 3. Equilibrium-constant curve drawn through experimental points. The dashed curves illustrate the variation of ±0.22 in the log value of K. The 500° and 450° curves were calculated as explained in the text. Arrow symbols are the same as in Figure 2.

gonite-montebrasite exchange reaction is also nearly constant, an expression relating the equilibrium constant as a function of temperature can be calculated from $\Delta G_r = -RT\ln K$. Substituting values for ΔG_r and R, we obtain $\log K = -4000/T(°K)$. This expression allows the calculation of a curve relating x_{Amb} with P_{HF} at any temperature. Two such curves were calculated for temperatures of 500° and 450°C, and are plotted on Figure 3.

Application of experimental results

The relationships developed in the preceding section, illustrated in Figure 3, allow interpretations of the crystallization and zoning of amblygonites. Three processes leading to composition changes are:

1. Isothermal crystallization in a closed system depletes the gas with respect to F and causes zoning in the amblygonite with decreasing F. The simultaneous crystallization of other F-bearing phases, such as micas, will only accelerate the depletion of F in the gas.
2. Crystallization associated with decreasing temperature in an open or very large system will lead to substantial increases if F content in the amblygonite. In this situation the fugacity of HF is held constant; other F-bearing phases will have no effect on the composition of the amblygonite.
3. Coupled with a temperature decrease will be the crystallization of the silicate phases from the pegmatite increasing the gas pressure and also the fugacity of HF which will lead to higher F contents in the amblygonite. The degree of increase, of course, will depend on how much F is removed by other minerals.

These processes can be applied to the compositional changes in amblygonites in the Tanco Pegmatite at Bernic Lake, Manitoba. Briefly, the observations on these amblygonites, made by Černá *et al.* (1972), are: the amblygonites of the wall zone contain 30 mole % F, increasing to 30 to 50% in zone 4 and to 40 to 55% in zone 5, but decreasing in the upper parts of that zone. Zoning of crystals in each pegmatite zone is toward lower F contents. Secondary montebrasite veins many of the earlier-formed crystals.

The increases of F contents from zone 2 to 4 to 5 probably result from mechanisms 2 and 3 above. An increase of 25 mole % of F will correspond to a temperature decrease of about 50°C in an open system. The slight decrease in F in each zone of the pegmatite seems to suggest that each zone formed within a small temperature interval, and amblygonite crystallization caused a decrease in the HF content of the gas. After another temperature decrease with gas pressures up, higher amounts of F enter the amblygonite and again zone toward decreasing amounts as HF is removed from the gas phase.

The late montebrasite veining is a result of the solid amblygonite re-equilibrating with the late-stage gas phase. Crystallization of other F-bearing phases, such as apatite or lepidolite, will further deplete the HF in the gas. Since apatites and amblygonite have about the same exchange reaction free energies, there will be no particular partitioning of F by either one of the minerals. It would appear that the F-poor secondary montebrasite and the commonly associated fluorapatite (Černá *et al.* 1972, p. 658) did not equilibrate.

Lepidolites crystallizing in pegmatites, in which earlier-formed amblygonite has been removing F, will necessarily have compositional restrictions. Commonly, amblygonites contain less than 50 mole % F (Fig. 1), which means that the gas phase will have p_{HF} less than 0.0058 bar at 600°C, 0.0010 bar at 500°C, and 0.0003 bar at 450°C. These values are all below the lower stability of trilithionite+quartz (Munoz 1971).

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REFERENCES

BURNHAM, C. W., HOLLOWAY, J. R. & DAVIS, N. F. (1969): Thermodynamic properties of water to 1000°C and 10,000 bars. *Geol. Soc. Amer. Spec. Pap.* **132**.

ČERNÁ, I., ČERNÝ, P. & FERGUSON, R. B. (1972): The Tanco pegmatite at Bernic Lake, Manitoba. III. Amblygonite-montebrasites. *Can. Mineral.* 11, 643-659.

———, ——— & ——— (1973): The fluorine content and some physical properties of the amblygonite-montebrasite minerals. *Amer. Mineral.* 58, 291-301.

CONNOLLY, J. P. & O'HARA, C. C. (1929): The mineral wealth of the Black Hills. *South Dakota School Mines Bull.* 16, 245-246.

GALLAGHER, M. J. (1967): Phosphates and other minerals in pegmatites of Rhodesia and Uganda. *Mineral. Mag.* **36**, 50-59.

GINZBURG, A. I. (1950): Montebrasite and the process of its alteration. *Trans. Mineral. Museum Acad. Sci. USSR* 2, 72-85 (in Russ.).

HEINRICH, E. W. & COREY, A. S. (1955): Montebrasite from Eight Mile Park, Fremont County, Colorado. *Amer. Mineral.* 40, 1141-1145.

HOUGEN, O. A. & WATSON, K. M. (1946): *Chemical Processes Principles Charts.* John Wiley & Sons, New York.

LOH, S. E. (1975): *Synthesis and Fluorine-Hydroxyl Exchange in the Amblygonite Series.* M.A. thesis, Univ. California, Santa Barbara.

MOORE, P. B. (1973): Pegmatite phosphates. *Mineral. Record* 4, 103-130.

MOSS, A. A., FEJER, E. E. & EMBREY, P. G. (1969): On the X-ray identification of amblygonite and montebrasite. *Mineral. Mag.* 37, 414-422.

MUNOZ, J. L. (1971): Hydrothermal stability relations of synthetic lepidolite. *Amer. Mineral.* 56, 2069-2087.

———— & EUGSTER, H. P. (1969): Experimental control of fluorine relations in hydrothermal systems. *Amer. Mineral.* 54, 943-959.

QUENSEL, P. (1956): The paragenesis of the Varutrask pegmatite including a review of its mineral assembledge. *Arkiv Mineral. Geol.* 2, 9-125.

STULL, D. R. & PROPHET, H. (1970): *JANAF Thermochemical Tables.* 2nd ed. *NSRDS-NBS 37.*

VLASOV, K. A., *ed.* (1966): *Geochemistry and Mineralogy of Rare Elements and Genetic Types of Their Deposits.* Vol. 2 *Mineralogy of Rare Elements.* Transl. from Russ. by Z. Lerman. Daniel Davey & Co., N. Y.

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