

## The biotite-apatite geothermometer revisited

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### Abstract

The proposed biotite-apatite geothermometer of Stormer and Carmichael (1971) is refined by taking the effect of octahedral cation substitution in biotite into account and by incorporating some new thermochemical data for the phases involved. For the reaction, biotite(F) + apatite(OH)  $\rightleftharpoons$  biotite(OH) + apatite(F), it is proposed that  $T(\text{Kelvins}) = 1100/\log K^*$ , where  $\log K^* = \log [X_F/X_{OH}]_{\text{ap}} + \log [X_{OH}/X_F]_{\text{bit}} - 1.107(X_{\text{annite}}) - 1.444(X_{\text{siderophyllite}})$ . These revisions lead to higher calculated temperatures.

### Systematics

Coexistence of more than one fluoride-hydroxyl solid solution provides a theoretical basis for geothermometry, as pointed out by Stormer and Carmichael (1971).

Consider the general reaction:



For this reaction, the equilibrium constant is simply:

$$(2) \quad K_T = (a_{OH}^A \cdot a_F^B) / (a_F^A \cdot a_{OH}^B)$$

As a first approximation, mole fractions may be substituted for activities and the equilibrium constant calculated as a function only of the phase compositions. Then, at any pressure:

$$(3) \quad T = -\Delta G^0 / R \ln K$$

If  $\Delta G^0$ , the free-energy change when each substance is in its standard state, is known as a function of temperature, the temperature of equilibrium becomes a simple function of the composition of the two phases. Unfortunately, several complications are involved in the practical use of this technique:

(1) Free-energy data are poorly known for all geologically reasonable fluor-hydroxyl pairs. This limitation can probably be overcome by experimental calibration or by careful calorimetric measurement.

(2) In equation (3), temperature is very sensitive to small variations in  $K$ . Compositional uncertainties as small as  $\pm 5$  mole percent in each of the participating phases may result in temperature uncertainties of hundreds of degrees.

(3) Another serious limitation is that common to

all geothermometers: the temperature recorded by mineral equilibrium may not be the one we would like to know. A fluoride-hydroxyl thermometer should record the last equilibration of the minerals in question with an aqueous fluid. Therefore, one should have greater confidence in a calculated temperature when there is independent evidence for rapid quenching and no subsequent rock-water interaction.

(4) A related problem is differential exchange kinetics. If one of the indicator minerals exchanges ions more rapidly and/or to lower temperatures, the results are difficult to interpret.

(5) The minerals may not be homogeneous. Stormer and Carmichael (1971) reported strong zonation in phlogopite crystals, indicating local equilibrium at best. Roegge *et al.* (1974) and Jacobs and Parry (1973) reported similar features in apatite, including variation from crystal to crystal in the same hand specimen. Wherever such variations are present, thermometric interpretation becomes exceedingly complex. For this reason no fluoride-hydroxyl geothermometry should be attempted with mineral separates without a study of compositional homogeneity by the electron microprobe.

### Coexisting biotite and apatite

Several mineral pairs are potential F-OH geothermometers, including various combinations of biotite, muscovite, apatite, topaz, and amphibole. Few data are available for fluoramphibole, and the many possible compositional variations present a formidable calibration task. No data are available for topaz, and

Table 1. The effect of revisions on calculated temperatures

Sample No. *	F/F+OH(ap)	F/F+OH(bi)	log K	T <sub>1</sub>	X <sub>ann</sub>	log K*	T <sub>2</sub>	T <sub>3</sub>
L-118	0.50	0.03	1.51	220	0.38	1.09	410	740
Cal 13	0.58	0.04	1.52	220	0.34	1.14	380	690
Cal 19	0.52	0.03	1.54	210	0.40	1.10	400	730

\*Sample numbers are those in Stormer and Carmichael (1971).

T<sub>1</sub> calculated from T=743/log K (Stormer and Carmichael, 1971). T<sub>2</sub> calculated from T=743/log K\*.

T<sub>3</sub> calculated from T=1100/log K\*.

All temperatures in the table are reported in degrees Celsius.

When used in the text Capital 'T' refers to absolute temperature

(Kelvins). X<sub>ann</sub> is calculated on the basis of a structural

formula which requires 7 octahedral + tetrahedral cations

(Ludington and Munoz, 1975).

biotite-muscovite fluorine partitioning has been shown to be independent of temperature (Munoz and Ludington, 1977). This leaves biotite-apatite (or muscovite-apatite) as the only geothermometer presently amenable to calibration.

Combining equations (2) and (3), we have:

$$(4) \quad \frac{-\Delta G^0}{2.303 RT} = \log \frac{X_F^{ap}}{X_{OH}^{ap}} + \log \frac{X_{OH}^{bi}}{X_F^{bi}}$$

If the appropriate thermodynamic data are known, the equation can be solved for temperature. To approximate the needed data, Stormer and Carmichael (1971) used thermodynamic data for simple hydroxides and fluorides. They used a  $\Delta G^0 = -3.4$  kcal (log K = 743/T), but their approach met with limited success. The discrepancies which they found were attributed to late exchange of biotite with fluorine-poor fluids. I suggest that these discrepancies are due in part to the fact that they did not make allowance for the large effect of Fe, Mg substitution on fluorine partitioning in biotite (Munoz and Ludington, 1974; Ludington and Munoz, 1975).

Without experimental calibration there is little hope for making this thermometer truly quantitative, but the biotite-partitioning data, coupled with some recent determinations of thermodynamic data for fluor- and hydroxyapatite, may provide a means of approaching quantification more closely.

#### Effect of biotite composition

Ludington and Munoz (1975) determined log K in the range 700 to 1000K for:



$$(6) \quad \log K = \log (f_{\text{H}_2\text{O}}/f_{\text{HF}}) + \log (X_F^{\text{biO}}/X_{\text{OH}}^{\text{biO}}) \\ = 2100/T + 1.523(X_{\text{phg}}) + 0.416(X_{\text{ann}}) + \\ 0.079(X_{\text{sid}})$$

The mole fractions refer to the end members phlogopite,  $\text{KAlSi}_3\text{Mg}_3\text{O}_{12-x}\text{H}_{2-x}\text{F}_x$ , annite,  $\text{KAlSi}_3\text{Fe}_3\text{O}_{12-x}\text{H}_{2-x}\text{F}_x$ , and siderophyllite,  $\text{KAl}_{1.5}\text{Si}_{2.5}\text{Al}_{0.5}\text{Fe}_{2.5}\text{O}_{12-x}\text{H}_{2-x}\text{F}_x$ . The complex crystal chemistry of tri-octahedral micas precludes a simple methodology for calculating end members. A convenient, if arbitrary, method consists of assigning  $(\text{Mg}^{\text{VI}}/\Sigma\text{oct})$ ,  $[(\text{Fe}^{\text{VI}}-5\text{Al}^{\text{VI}})/\Sigma\text{oct}]$ , and  $(6\text{Al}^{\text{VI}}/\Sigma\text{oct})$  to the mole fractions of phlogopite, annite, and siderophyllite, respectively.

Given that log K for the reaction apatite (OH) + phlogopite(F)  $\rightleftharpoons$  apatite(F) + phlogopite(OH) is (7)  $\log K_{a-p} = 743/T$ , algebraic manipulation yields, for the general biotite-apatite exchange reaction, apatite(OH) + biotite(F)  $\rightleftharpoons$  apatite(F) + biotite(OH):

$$(8) \quad \log K_{a-b} = 743/T + 1.107(X_{\text{ann}}) + 1.444(X_{\text{sid}}),$$

so that:

$$(9) \quad T = 743/\log K^*,$$

where  $\log K^* = \log K_{a-b} - 1.107(X_{\text{ann}}) - 1.444(X_{\text{sid}})$ .

The effect of this change on predicted temperatures is shown in the column labeled T<sub>2</sub> in Table 1, which compares results for three biotite-apatite pairs used by Stormer and Carmichael (1971). Their results suggest that these rocks crystallized in the range 850–1000°C, and an allowance for the effect of iron substitution is seen to improve the correspondence between the F-OH temperature and the inferred crystallization temperatures.

#### Refinement of thermodynamic data

A different approach to improvement of the geothermometer involves some new thermodynamic data for apatite end-member compositions reported by Duff (1971), coupled with the revised data on F  $\rightleftharpoons$  OH exchange in biotite (Ludington and Munoz, 1975). From these sources, the standard free energy for equation (7) can be estimated to be approximately -5.0 kcal (log K<sub>a-p</sub> = 1100/T). Combining this temperature dependence with the compositional correc-

Table 2. The effect of compositional uncertainty on calculated temperatures

F/F+OH(ap)	F/F+OH(bi)	log K*	T(°C)
0.84	0.10	1.013	810
±5% {	0.80	0.872	990
	0.88	1.183	660
±10% {	0.76	0.748	1200
	0.92	1.404	510

tions discussed above yields some very realistic temperatures, labeled  $T_3$  in Table 1.

### Discussion

The most that can be claimed for the changes suggested herein is that any deduced temperatures will be higher than those estimated using Stormer and Carmichael's original method. My hope is that the higher, and *perhaps* more realistic, temperatures may encourage more petrologists to systematically investigate the halogen contents of biotite and apatite in rocks which they are studying and to publish this information.

If a large body of data was available for testing the temperature dependence of this equilibrium, some attention could be paid to other uncertainties in application of the geothermometer, including the following:

(1) Non-ideality of mixing in either or both solid solutions is possible.

(2) The crystal chemistry of both minerals is poorly known. With respect to biotite, an important problem is the generality of the  $R^{3+} \rightleftharpoons R^{2+} + H^+$  substitution scheme proposed by Wones and Eugster (1965). With respect to apatite, a similar problem exists with carbonate-apatite [ $Ca_5(PO_4,CO_3)_3(OH,F)$ ], as some analyses show greater than stoichiometric fluorine contents (Deer *et al.*, 1962, p. 328). These problems are particularly important when electron microprobe analyses are used.

(3) Variations in composition of the minerals in question may affect the equilibrium substantially. Specifically, the quantitative effects of Ti, Mn, Cr, Na, V, Cl, and, particularly, Li in biotite and Mg, Mn, Fe, V, As, and Cl in apatite are unknown.

The most serious remaining shortcoming of the geothermometer is its extreme sensitivity to analytical precision. Consider a typical igneous biotite,  $X_{phlog} = 0.4$ ,  $X_{ann} = 0.6$ ,  $F/(F + OH) = 0.10$ . If we assume this biotite and a coexisting apatite ceased exchange at 800°C,  $\log K^*$  should be 1.025, implying  $F/(F + OH)$  in the apatite is 0.84. Table 2 shows the effects of

uncertainties of  $\pm 10$  percent and  $\pm 5$  percent in the measured  $F/(F + OH)$ .

It seems likely, however, that if the same analytical method and structural-formula assumptions are consistently applied to minerals for a group of related rocks, important insight into temperature differences and gradients (or lack of equilibrium) may be delineated, even if the absolute values for temperature are not very accurate.

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