Fluorine–hydroxyl exchange in synthetic muscovite and its application to muscovite–biotite assemblages

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Abstract

Hydrothermal fluorine buffer techniques are used to measure the equilibrium constant for the exchange reaction: OH–muscovite + HF ⇌ F–muscovite + H_2O. At a total pressure of two kbar, $\log K = 2100/T - 0.11$ (T in kelvins). These data, when combined with similar data for biotite, permit evaluation of F ⇌ OH equilibrium between coexisting biotite and muscovite. The partitioning, which is independent of temperature and fluid composition, may be portrayed graphically, and provides a simple test of F ⇌ OH exchange equilibria in natural mica pairs.

Introduction

Fluorine is less abundant in dioctahedral micas than in biotite; nonetheless, its presence can be used to reconstruct fluid compositions (in terms of the ratio $f_{H_2O}/_{HF}$) if temperatures of muscovite equilibration with fluid are known. Experimental calibrations for muscovite have been completed using techniques identical with those previously described for biotite (Munoz and Ludington, 1974).

Experimental procedure

Each experiment consists of equilibrating synthetic muscovite with a fluid in contact with a fluorine buffer assemblage (Munoz and Eugster, 1969). The anorthite–fluorite–sillimanite–quartz–gas assemblage (AFSQ), which fixes the ratio f_{H_2O}/f_{HF} at constant temperature and pressure according to the equilibrium

$$CaAl_2Si_2O_8 + 2HF \rightleftharpoons CaF_2 + Al_2SiO_5 + SiO_2 + H_2O,$$
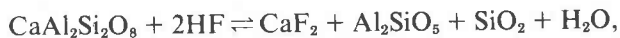
$$K_{buffer} = f_{H_2O}/f_{HF}^2,$$

was used for all muscovite experiments, because it generates hydrogen fluoride fugacities sufficiently high to produce easily measurable fluorine levels in muscovite. At the end of each experiment, the muscovite is separated from the buffer, checked by both X-ray diffraction and optical examination for purity, and is analyzed for fluorine by means of an indirect

spectrophotometric method (Shapiro, 1967). These analyses are converted to F/OH ratios, assuming F + OH = 2.0 for muscovite of stoichiometry $KAl_3Si_3O_{10}(F, OH)_2$. An equilibrium constant is calculated for each experiment: OH–muscovite + HF ⇌ F–muscovite + H_2O

$$\log K = \log(f_{H_2O}/f_{HF})_{fluid} + \log (a_F/a_{OH})_{muscovite}.$$

The fugacity ratio is obtained from thermodynamic data for the AFSQ buffer phases (Munoz and Ludington, 1974), revised using more recent values for anorthite (Thompson, 1974). Mole fractions are used as an approximation to activities for the fluorine and hydroxyl sites in muscovite.

Reversibility of F ⇌ OH exchange was demonstrated in two experiments (Runs MSE-5 and MSE-8 in Table 1), in which the starting material was a fluorine-bearing muscovite obtained by reacting OH–muscovite with AFSQ at a higher temperature. Both experiments showed a reduction of fluorine when equilibrated with AFSQ at a lower temperature (Fig. 1).

Experimental results

Table 1 and Figures 1 and 2 show that muscovite contains less fluorine than biotite equilibrated with AFSQ at similar temperatures. Reevaluation of thermodynamic data for buffer phases (Ludington and Munoz, 1975) has led to the conclusion that

no experimentally significant difference exists in the slopes of the previously determined annite ($KFe_3AlSi_3O_{12}H_2$), siderophyllite ($KFe_{2.5}Al_2Si_{2.5}O_{12}H_2$), and phlogopite ($KMg_3AlSi_3O_{12}H_2$) equilibrium constants, when the data are plotted in terms of log K vs. $1/T$ (Fig. 2). Similarly, the data for muscovite closely approximate a straight-line of this same slope. Although these lines are probably not perfectly straight, no curvature is indicated by the data. Any curvature that exists (reflecting changing reaction enthalpies with temperature) is masked by the stated uncertainties (*ca.* ± 0.2 log units) associated with each line. Considering both the reciprocal temperature scale and proximity of data points, extrapolation somewhat above the temperature range of the experiments is probably justified, but extrapolation to lower temperatures is less certain.

Because the slopes of all four mica exchange reactions are so similar, the implication is that the enthalpy for all four reactions is nearly identical. Apparently the differences in mica structure and octahedral cation occupancies have little effect on reaction enthalpy of the F ⇌ OH exchange. The differences in the intercepts on the log K axis between the various biotites and muscovite therefore must indicate that the entropies of the exchange reaction differ substantially between phlogopite and muscovite. Thus, there is a possibility of F, OH ordering differences between the different micas. Such a possibility is mentioned by Hazen and Burnham (1973) as a possible explanation for the elongation of the thermal ellipsoids for the OH site parallel to c^* in the phlogopite and annite structures. Indeed, the elon-
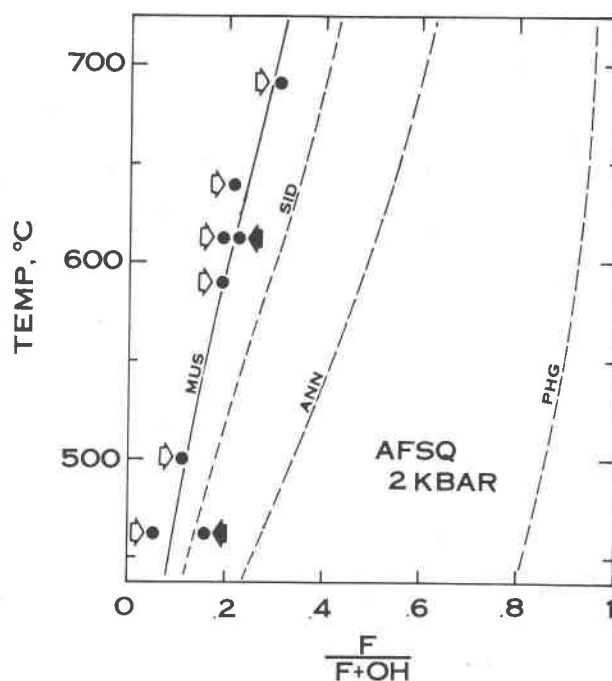

Fig. 1. Fluorine contents of synthetic muscovite (mus), siderophyllite (sid), annite (ann), and phlogopite (phg) in equilibrium with AFSQ at two kbars. Data for annite, siderophyllite, and phlogopite are calculated from exchange equations in Ludington and Munoz (1975); experimental data is shown only for muscovite. Arrowheads show direction from which equilibrium was approached. The solid arrowheads highlight the two reversal experiments.

gation is noticeably greater for annite than for phlogopite, suggesting that annite is more ordered. Further evidence for this possibility is given by Guggenheim and Bailey (1975), who postulate a low-

Table 1. Experimental data for F ⇌ OH muscovite exchange

Run Number	Temperature (°C.)	Run Time (days)	Starting Composition	Final Composition (wt. % F)	F/F+OH	log K
MSE-7	462	59	OH-ms	0.5%	0.05	2.49
MSE-8	462	59	2.0% F	1.5%	0.16	3.03
MSE-10	500	61	OH-ms	1.0%	0.11	2.59
MSE-12	590	68	OH-ms	1.8%	0.19	2.32
MSE-6	612	59	OH-ms	1.8%	0.19	2.22
MSE-5	612	59	2.9% F	2.1%	0.22	2.31
MSE-3	640	51	OH-ms	2.0%	0.21	2.13
MSE-1	690	36	OH-ms	2.9%	0.31	2.12

All experiments were conducted at a total fluid pressure of two kilobars; oxygen fugacity was imposed by the Stellite pressure vessel. Temperature uncertainty is ± 5°. OH-muscovite (OH-mus) was synthesized in 250 mg. lots from a stoichiometric mixture of kaolinite and KOH, at two kilobars and 500°C. The starting material was the 1M polymorph of muscovite; all exchange runs at 590°C. and above yielded entirely the $2M_1$ polymorph; lower temperature runs resulted in mixtures of polymorphs. Analytical uncertainties in fluorine analyses are always less than ± 10% (relative). Least squares fitting of log K vs. reciprocal temperature yields the following equation: log K = 2100/T - 0.11 (T in kelvins).
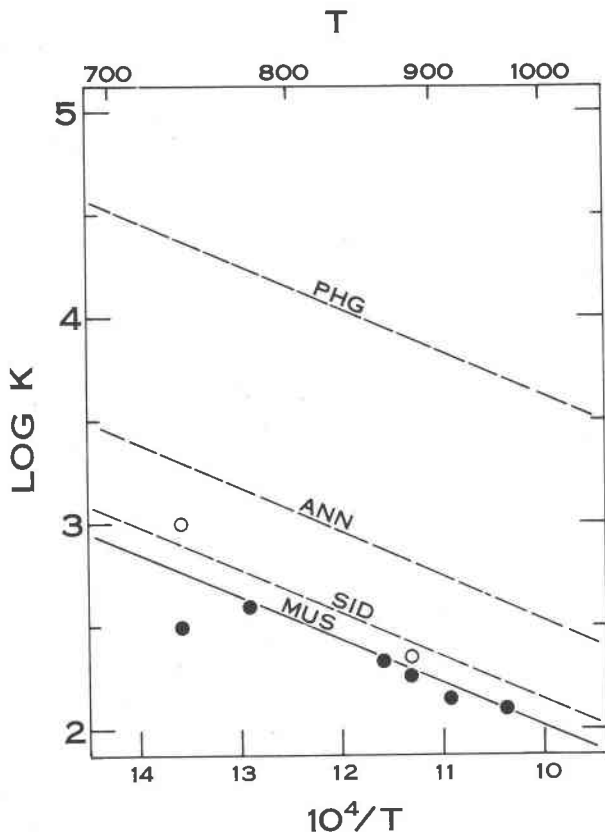
Fig. 2. Equilibrium constants for mica F $\rightleftharpoons$ OH exchange. Mineral abbreviations are as in Fig. 1. Filled circles represent experiments in which OH–muscovite was the starting material. Open circles represent the two reversal experiments. Log K = $2100/T - 0.11$. T measured in kelvins.

symmetry (Cm/c) space group for margarite, which leads to splitting of the OH site into two.

The data presented here cannot be rigorously applied to natural muscovites containing significant amounts of octahedral cations other than aluminum. For example, it is likely that both lithium and magnesium, two of the most common minor cations in dioctahedral micas, should increase fluorine partitioning into muscovite. A rough correlation exists between the fluorine and lithium contents of natural dioctahedral micas (Foster, 1960; Munoz, 1968). In the case of magnesium, it seems reasonable that the same marked preference for fluorine shown by magnesian biotite should also apply to dioctahedral micas.

Application

A practical result of the similarity in slopes of all the mica exchange reactions is that the fluorine

contents of coexisting muscovite and biotite may not be used as a geothermometer. Indeed, simultaneous solution of the log K equations for the pairs muscovite–phlogopite, muscovite–annite, and muscovite–siderophyllite yield numbers for biotite–muscovite exchange that are independent of both temperature and fluid composition. For the reaction:

$$\text{OH–biotite} + \text{F–muscovite} \rightleftharpoons \text{F–biotite} + \text{OH–muscovite},$$
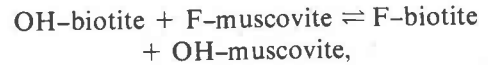
$$\log K^{\text{bio-mus}} = \log (a_F/a_{OH})^{\text{bio}} + \log (a_{OH}/a_F)^{\text{mus}}.$$

Combining the data for muscovite presented in this paper (Table 1, Fig. 2) with the revised data for the biotites reported in Ludington and Munoz (1975) allows solution of the above equation for all the biotite end-members studied, yielding:

$$\log K^{\text{phg-mus}} = 1.633, \log K^{\text{ann-mus}} = 0.526,$$

$$\text{and } \log K^{\text{sid-mus}} = 0.180.$$

These numbers were used to construct Figure 3, which shows the variability in log K for biotite–muscovite exchange as a function of octahedral
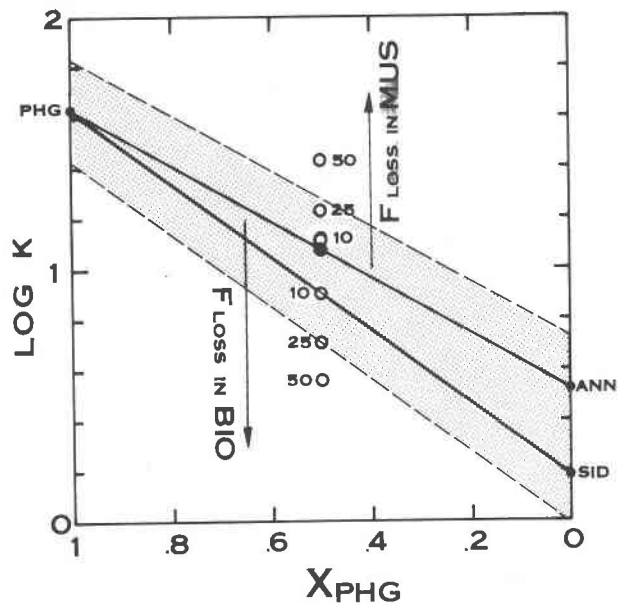

Fig. 3. Muscovite–biotite "equilibrometer," showing the effects of differential postcrystallization loss of fluorine from muscovite (mus) or biotite (bio). The equilibrium constant (K) refers to the distribution of F and OH between mus and bio. Filled circle represents a biotite of composition $\text{phg}_{50}\text{ann}_{50}(\text{F}_{75}\text{OH}_{25})$ coexisting with a muscovite of composition ($\text{F}_{20}\text{OH}_{80}$). Open circles represent 10, 25, and 50 percent fluorine loss from biotite (log K decreases) or muscovite (log K increases). Dashed lines represent the 0.2 log units uncertainty in K discussed in the text.

Table 2. Site occupancies and F$\rightleftharpoons$OH exchange equilibrium constants for biotite + muscovite assemblages reported by Müller (1966)

Sample No.	X_{Mg}^{bio}	F occupancy		OH occupancy		log K
		bio	mus	bio	mus	
2	0.30	0.120	0.052	1.424	1.948	0.499
4	0.20	0.164	0.058	1.318	1.942	0.620
5	0.08	0.387	0.376	1.055	1.624	0.200
17	0.22	0.386	0.129	1.525	1.871	0.565
46	0.04	0.688	0.408	0.573	1.592	0.671
53	0.23	0.168	0.052	1.405	1.948	0.651
59	0.34	0.157	0.060	1.365	1.940	0.570

Structural formulas were calculated on the basis of 7 (bio) and 6 (mus) tetrahedral + octahedral cations.

composition in biotite. Inherent in such a construction and in subsequent applications is the assumption that all activity coefficients for both octahedral and (F,OH) sites in muscovite and biotite are unity, and that the effect of minor substitutions in both muscovite and biotite can be ignored. If equilibrium constants are calculated for natural coexisting muscovite–biotite pairs, then all such pairs whose compositions reflect F $\rightleftharpoons$ OH exchange equilibrium should plot within the shaded area on Figure 3. Conversely, gross departures from the shaded area are a persuasive argument against intercrystalline equilibrium. Thus, we refer to the graph in Figure 3 as an "equilibrometer."

In order to plot coexisting micas on the equilibrometer, it is necessary to know both F and OH occupancies for muscovite and biotite and the composition of the octahedral layer of the biotite. Unfortunately, there is no unique method of proceeding from chemical analyses to ion occupancies; the method that we believe is most satisfactory is based on the assumption of full octahedral occupancy in biotite and muscovite (Ludington and Munoz, 1975).

In testing natural assemblages by this method, it is imperative to transfer analytical uncertainties through to the calculation of log K. Typically, an uncertainty of ±10 percent (relative) in fluorine and hydroxyl occupancies translates to approximately 0.2 log units of uncertainty in log K. However, when the absolute amount of fluorine in the mica approaches small values (less than 0.5 weight percent), the relative error will commonly be significantly larger.

Postcrystallization leaching of fluorine from micas has been suggested to be a common phenomenon (Carmichael et al. 1974). Figure 3 shows the effect of preferential fluorine loss by biotite or muscovite; loss

from biotite will lower log K, whereas loss from muscovite will have the opposite effect.

Example

Complete published analyses of coexisting biotites and muscovites are rare. As an example of the use of the equilibrometer, we have chosen a set of analyses given by Müller (1966) for micas from a series of biotite–muscovite granites. The equilibrium constants and the data from which they were calculated are given in Table 2, and illustrated in Figure 4. When one considers analytical uncertainties, the
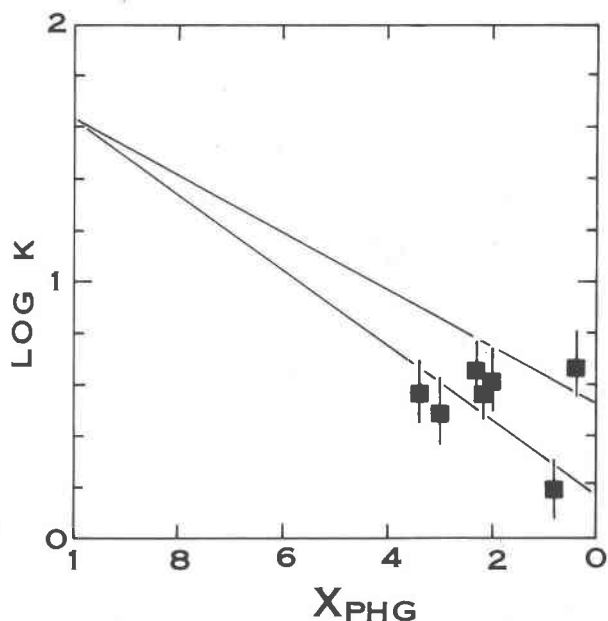

Fig. 4. Muscovite–biotite pairs from European granites (Müller, 1966) plotted on the equilibrometer. Error bars represent ± 10 percent uncertainty in fluorine and hydroxyl site occupancies.

micas appear to be in equilibrium with respect to F $\rightleftharpoons$ OH exchange. The result is not unexpected, if the dynamics of a cooling intrusion are considered. Fractionation of fluorine into the micas is so strong that an overwhelming proportion of the fluorine in the system is in the hydrous phases, even during exsolution of an aqueous fluid. Without a later influx of unrelated fluids, no conceivable way exists to transport enough fluorine to generate recognizable disequilibrium.

Acknowledgments

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