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EXPERIMENTAL CONTROL OF FLUORINE REACTIONS IN HYDROTHERMAL SYSTEMS

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ABSTRACT

The solid polyphase buffer technique has been adapted to permit quantitative study of synthetic fluorine-bearing hydrothermal systems. This method involves three nested capsules; the innermost capsule contains the charge which is open to the fluorine buffer assemblage in the sealed second capsule. The outermost capsule contains an oxygen buffer; the hydrogen fugacity (f_{H_2}) in equilibrium with the fluorine buffer assemblage must be externally fixed. The buffer reactions which have been studied experimentally are:

$$\text{wollastonite} + 2HF \rightleftharpoons \text{fluorite} + \text{quartz} + H_2O \text{ (WFQ)}$$
$$\text{anorthite} + 2HF \rightleftharpoons \text{fluorite} + \text{sillimanite} + \text{quartz} + H_2O \text{ (AFSQ)}$$
$$\text{calcite} + 2HF \rightleftharpoons \text{fluorite} + \text{graphite} + H_2O + O_2 \text{ (CFG)}$$

Fugacities and compositions of the gas phase in equilibrium with the given buffer phases have been calculated from thermodynamic data and are presented as a function of temperature, total pressure, and f_{H_2}. In all cases, the concentration of HF in the gas (in wt %) never exceeds 5 percent, and is more commonly one to eight orders of magnitude smaller than that. For the WFQ and AFSQ buffers, the remainder of the gas is composed of H_2O and H_2. When graphite is present (CFG buffer), the equilibrium bulk composition of the gas phase is primarily a mixture of CO_2, H_2O, CO, CH_4, and H_2 (the exact composition depending mostly on temperature and f_{H_2}), with very minor amounts of HF.

Tests of these buffers using synthetic (F, OH) phlogopite as a charge indicate that equilibrium between buffer and charge requires less than two weeks at 775°C and 6–10 weeks at 550°C. The compositions of phlogopites in equilibrium with these 3 fluorine buffers range from F-phlogopite$_{49}$ OH-phlogopite$_{51}$ (mole %, CFG fluorine buffer with f_{H_2} specified by the nickel-nickel oxide buffer, 550°C) to F-phlogopite$_{98}$ OH phlogopite$_2$ (CFG fluorine buffer with f_{H_2} specified by the hematite-magnetite buffer, 700°C). The 700° data are most complete and demonstrate that phlogopite is extremely effective in removing fluorine from the gas phase. Extrapolating from this calibration, it appears that the most fluorine-rich natural phlogopite (75 mole % F-phlogopite) coexisted with a gas phase containing less than 0.05 mole % HF. Judging from natural biotites, a common range for igneous and metamorphic fluids would be 0.001–0.005 mole % HF. As more calibrations become available, the behavior of HF in natural environments can be established quantitatively.

INTRODUCTION

Fluorine is a common constituent of many micas and amphiboles and such accessory minerals as apatite, tourmaline, and topaz. In these minerals, fluorine freely substitutes for hydroxyl. Published data indicates that fluorine greatly enhances the thermal stability of micas and amphiboles (see, Van Valkenberg and Pike, [1952]). Hence, both the composition and the stability relations of these minerals are, in part, dependent upon the magnitudes of the H_2O and HF fugacities of their environment. In order to calibrate these effects in synthetic systems, it is necessary to develop methods which permit control of these fugacities at elevated pressures and temperatures in a predictable and quantitative manner. The most simple and direct method is to vary the bulk composition of the gas phase. This approach is unsatisfactory for fluorine-bearing systems because of the high solubility of silicates in HF at low temperatures, analytical difficulties, and inadequate knowledge of the *PVT* (and fugacity) relations in the system O-H-F under the conditions of experimental interest. Alternatively, the composition of the gas phase and its fugacities may be buffered by appropriate crystalline phases. This solid polyphase buffer approach has been widely applied to the study of redox reactions in hydrothermal systems (*e.g.*, Eugster and Wones, 1962), and has recently been expanded to include multicomponent gas systems (Eugster and Skippen, 1967). The composition of the equilibrium gases as a function of total *P* and *T* is calculated from the equilibrium constants for all the important molecular species present (JANAF tables, 1960) and from the free energy data for the solid buffer phases (Robie, 1962). The fluorine buffers have been developed in cooperation with Rieder (1968), who has used them successfully to determine the thermal stability of zinnwaldites.

FLUORINE BUFFER EQUILIBRIA

Consider a gas phase of the system O-H-F. For a given *P* and *T*, this gas phase is divariant; thus, in order to define the fugacities of all gas species present, it is necessary to specify two additional intensive parameters. One possible method is to vary independently the fugacities of O_2 and H_2 using double oxygen buffers (Munoz, 1966); this method has the severe drawback that fluorine must be initially added to the gas phase (*e.g.*, as HF). To prevent this difficulty, we have chosen to use solid fluorine-bearing buffer assemblages to control the ratio of two fugacites, while the remaining degree of freedom is removed by imposing a given hydrogen fugacity on the fluorine buffer assemblage through a Pt or Ag_7Pd_3 membrane. Figure 1 shows the experimental arrangement. The charge is contained in a gold foil and is surrounded by the fluorine buffer assemblage. This charge-buffer system is sealed in a Pt or Ag_7Pd_3 membrane. The hydrogen fugacity is fixed externally, either by using a Shaw bomb, a standard oxygen buffer, or the methane buffer (see Eugster and Skippen, 1967).

We have calculated fugacities for the following buffer reactions in the system O-H-F as a function of *P*, *T*, and f_{H_2}:

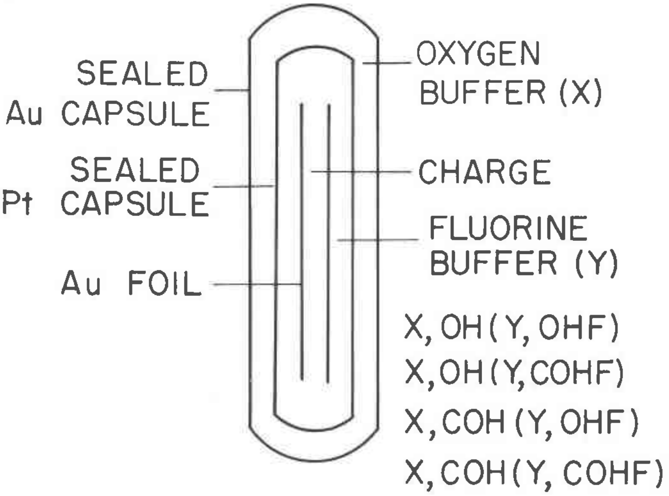

FIG. 1. Cross-sectional schematic diagram of triple capsule arrangement used for fluorine buffer experiments. The gold capsule is 1.5″ long. Notation: the fluorine buffer (Y) is enclosed by parentheses, together with the elemental composition of the gas phase. The external oxygen buffer (X) and its gas components are written to the left of the parentheses.

$$CaSiO_3 + 2HF \rightleftharpoons CaF_2 + SiO_2 + H_2O^{a} \text{ (WFQ)}$$
$$\text{wollastonite} + 2HF \rightleftharpoons \text{fluorite} + \text{quartz} + H_2O$$

$$CaAl_2Si_2O_8 + 2HF \rightleftharpoons CaF_2 + Al_2SiO_5 + SiO_2 + H_2O$$
$$\text{anorthite} + 2HF \rightleftharpoons \text{fluorite} + \text{sillimanite} + \text{quartz} + H_2O \text{ (AFSQ)}$$

These calculations require as input data: values for the equilibrium constants of H_2O and HF, free energy data for the solids taking part in the buffer reaction, fugacity coefficients (γ) for H_2O, H_2, and HF, and the f_{H_2} specified by the external buffer. All of these data are functions of temperature and most of them depend upon pressure as well.

Specifically, we have

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[a] These equations can also be written in an equivalent form:

$$CaSiO_3 + F_2 \rightleftharpoons CaF_2 + SiO_2 + 1/2\ O_2$$
$$CaAl_2Si_2O_8 + F_2 \rightleftharpoons CaF_2 + Al_2SiO_5 + SiO_2 + 1/2\ O_2$$

in which case the equilibrium constants for the reaction are $K_{Bu} = f_{O_2}{}^{1/2} f_{F_2}$. We have elected to express all buffer reactions in terms of the more abundant geologic species H_2O and HF. Needless to say, however, the fugacities of these species are no more or less meaningful than those of O_2 or F_2.

$$K_{H_2O} = \frac{f_{H_2O}}{f_{O_2}{}^{1/2} f_{H_2}} \tag{1}$$

$$K_{HF} = \frac{f_{HF}}{f_{H_2}{}^{1/2} f_{F_2}{}^{1/2}} \tag{2}$$

a) $CaSiO_3 + 2HF \rightleftharpoons CaF_2 + SiO_2 + H_2O$

b) $CaAl_2Si_2O_8 + 2HF \rightleftharpoons CaF_2 + AlSi_2O_5 + H_2O$

$$K_{B_u} = \frac{f_{H_2O}}{f_{HF}{}^2} \tag{3}$$

$$P_{TOTAL} = \frac{f_{HF}}{\gamma_{HF}} + \frac{f_{H_2O}}{\gamma_{H_2O}} + \frac{f_{H_2}}{\gamma_{H_2}} + \frac{f_{F_2}}{\gamma_{F_2}} + \frac{f_{O_2}}{\gamma_{O_2}} \tag{4}$$

Substituting (1), (2), and (3) into (4) gives

$$f_{HF}{}^2\left(\frac{K_{B_u}}{\gamma_{H_2O}}\right) + f_{HF}\left(\frac{1}{\gamma_{HF}}\right) + \left(\frac{f_{H_2}}{\gamma_{H_2}} - P_{TOTAL}\right) = 0 \tag{5}$$

f_{HF} is the only unknown in this quadratic equation; hence, it can be solved for any desired values of P and T. f_{H_2} is controlled by a specific oxygen buffer and its magnitude has been calculated previously (see Eugster and Skippen, 1967). Knowledge of f_{HF} and f_{H_2}, by proper substitution in (1), (2) and (3), yields the remaining fugacities. Fugacity coefficients for H_2O were taken from Holser (1954),[1] for H_2 from Shaw and Wones (1963) and for the remaining species from the reduced variable chart of Hougen and Watson (1946).

Note that terms involving f_{F_2} and f_{O_2} in the P_{TOTAL} equation are neglected in (5). This can be done because the magnitudes of these fugacities are so low ($<10^{-10}$ bars at all temperatures of interest) that they effectively do not add to the summation of partial pressures. For the same reason, equilibria involving other species in the system O-H-F (*e.g.*, FOH, F_2O) can be neglected.

The approach used for O-H-F gases can be extended to include C-O-H-F gases, provided that graphite is present. The assemblage graphite + C-O-H-F gas is also divariant for a given P and T. We have chosen the buffer reaction

$CaCO_3 + 2HF \rightleftharpoons CaF_2 + C + H_2O + O_2$

calcite + 2HF $\rightleftharpoons$ fluorite + graphite + H_2O + O_2 (CFG)

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[1] Using the more recent fugacity coefficients calculated by Anderson (1964) does not change the result significantly. A larger uncertainty, perhaps, is introduced by the necessary assumption of ideal mixing.

TABLE 1. EQUATIONS FOR FLUORINE BUFFERS OF THE SYSTEM C-O-H-F

$$K_w = \frac{f_{H_2O}}{f_{H_2} \times f_{O_2}^{1/2}} \quad (1) \qquad K_{HF} = \frac{f_{HF}}{f_{H_2}^{1/2} f_{F_2}^{1/2}} \quad (2) \qquad K_{CO_2} = \frac{f_{CO_2}}{f_{O_2}} \quad (3)$$

$$K_{CO} = \frac{f_{CO}}{f_{O_2}^{1/2}} \quad (4) \qquad K_{CH_4} = \frac{f_{CH_4}}{f_{H_2}^2} \quad (5)$$

$$CaCO_3 + 2HF \rightleftharpoons CaF_2 + C + H_2O + O_2 \quad (6)$$

$$K_{BU} = \frac{f_{H_2O} f_{O_2}}{f_{HF}^2}$$

$$P_{TOTAL} = \frac{f_{H_2O}}{\gamma_{H_2O}} + \frac{f_{HF}}{\gamma_{HF}} + \frac{f_{CO_2}}{\gamma_{CO_2}} + \frac{f_{CO}}{\gamma_{CO}} + \frac{f_{CH_4}}{\gamma_{CH_4}} + \frac{f_{O_2}}{\gamma_{O_2}} + \frac{f_{F_2}}{\gamma_{F_2}} + \frac{f_{H_2}}{\gamma_{H_2}} \quad (7)$$

Substituting (1)–(6) into (7) gives

$$ {}_{H_2O} \left(\frac{K_{CO}}{K_w f_{H_2} \gamma_{CO}} + \frac{1}{\gamma_{H_2O}} \right) + f_{H_2O}^{3/2} \left(\frac{1}{K_w K_{Bu}^{1/2} f_{H_2} \gamma_{HF}} \right) + f_{H_2O}^2 \left(\frac{K_{CO_2}}{K_w^2 f_{H_2} \gamma_{CO_2}} \right) + \left(\frac{f_{H_2}}{\gamma_{H_2}} + \frac{K_{CH_4} f_{H_2}^2}{\gamma_{CH_4}} - P_T \right) = 0 \quad (8)$$

The numerical value of the second term of the above equation is almost always small enough so that it can be ignored; cancelling this term leaves a simple quadratic equation to be solved for f_{H_2O}. Note that the fugacity of H_2 must be specified; also, as was true in the O-H-F system, P_{O_2} and P_{F_2} are not included in the P_{TOTAL} equation.

Depending on temperature and the imposed value of f_{H_2}, the important species may be H_2O, HF, CO_2, CO, CH_4, or H_2. The experimental arrangement is identical to the O-H-F case, and the relevant equations are presented in Table 1.

Partial results of the fugacity calculations for the systems O-H-F and C-O-H-F appear in Table 2, and the dependence of the fugacity of HF for selected fluorine buffers, temperatures, and hydrogen fugacities is shown in Figure 2.

For O-H-F buffers, the effect of changing the external oxygen fugacity on the magnitude of the internal HF fugacity is very small, and isothermal variations in f_{H_2O}/f_{HF} can be obtained only by imposing very high H_2 fugacities on the inner capsule, so that P_{H_2O} becomes much less than P_{TOTAL}. Thus, the equilibrium compositions of the two buffers HM, OH (WFQ, OHF) and NNO, OH (WFQ, OHF) are essentially identical, but they have decidedly lower f_{H_2O}/f_{HF} ratios than the buffer QFI, OH (WFQ, OHF) (Table 2). On the other hand, C-O-H-F buffers are strongly sensitive to differences in external oxygen fugacity. This difference lies in the effect the other major components have on the magnitude of f_{H_2O}.

TABLE 2. CALCULATED GAS FUGACITIES IN CHARGE FOR EIGHT TYPICAL BUFFERING SYSTEMS WHEN $P_{gas}=2$ KBAR

Temperature, °C	$-\log f_{O_2}$	$-\log f_{F_2}$	f_{H_2}	f_{H_2O}	$\log f_{HF}$
1. NNO, OH (WFQ, OHF)[a]					
327	32.088	55.227	0.603	234.0	−3.771
427	26.227	46.223	1.614	475.8	−2.437
527	21.831	39.482	3.425	809.1	−1.444
627	18.412	34.263	5.831	1142	−0.697
727	15.677	30.093	8.463	1416	−0.115
827	13.440	26.682	11.33	1650	0.356
2. QFI, OH (WFQ, OHF)					
327	41.293	59.829	3277	31.76	−4.205
427	34.321	50.270	2891	76.46	−2.834
527	29.092	43.113	2627	145.4	−1.817
627	25.026	37.570	2409	232.7	−1.042
727	21.772	33.140	2214	332.1	−0.429
827	19.110	29.517	2050	436.3	0.067
3. NNO, OH (AFSQ, OHF)					
327	32.088	51.034	0.603	233.9	−1.675
427	26.227	42.440	1.614	475.7	−0.546
527	21.832	36.021	3.425	808.7	0.287
627	18.414	31.055	5.831	1139	0.908
727	15.682	27.090	8.463	1407	1.387
827	13.452	23.834	11.33	1627	1.780
4. QFI, OH (AFSQ, OHF)					
327	41.293	55.636	3277	31.76	−2.108
427	34.321	46.487	2890	76.44	−0.943
527	29.093	39.652	2627	145.2	−0.086
627	25.030	34.362	2409	231.7	0.562
727	21.782	30.140	2214	328.1	1.071
827	19.135	26.675	2050	424.2	1.488

Temperature, °C	$-\log f_{O_2}$	$-\log f_{F_2}$	f_{H_2}	f_{H_2O}	$-\log f_{HF}$	f_{CO_2}	f_{CO}	f_{OH_4}
5. HM, OH (CFG, COHF)								
327	30.971	51.885	0.0018	2.555	3.361	3363	0.0084	0.0004
427	26.040	44.382	0.0045	1.659	2.792	3507	1.012	0.0002
527	22.351	38.765	0.0091	1.186	2.372	3530	6.419	0.0001
627	19.476	34.381	0.0149	0.860	2.051	3595	27.01	$<10^{-4}$
727	17.193	30.907	0.0210	0.614	1.824	3488	82.78	$<10^{-4}$
827	15.331	28.065	0.0274	0.452	1.643	3351	204.5	$<10^{-4}$
6. NNO, OH (CFG, COHF)								
327	32.154	53.660	0.603	216.9	2.988	220.4	0.0215	45.07
427	26.552	45.150	1.614	327.3	1.901	1078	0.5610	27.93
527	22.589	39.122	3.425	338.1	1.264	2041	4.881	19.25
627	19.605	34.575	5.831	289.2	0.852	2669	23.28	12.59
727	17.271	31.025	8.463	225.9	0.580	2912	75.64	7.932
827	15.384	28.144	11.334	176.0	0.375	2969	192.5	5.236

Temperature, °C	$-\log f_{O_2}$	$-\log f_{F_2}$	f_{H_2}	f_{H_2O}	$-\log f_{HF}$	f_{CO_2}	f_{CO}	f_{CH_4}
7. WMC, COH (CFG, COHF)								
327	41.101	67.080	6.77	0.0819	9.173	$<10^{-4}$	$<10^{-4}$	5688
427	33.391	55.409	22.04	1.700	6.463	0.0001	0.0002	5207
527	27.583	46.613	53.60	16.84	4.412	0.0207	0.0016	4716
627	23.062	39.760	104.6	96.96	2.818	0.9327	0.4351	4049
727	19.444	34.284	164.0	358.9	1.566	1.956	6.200	2980
827	16.483	29.794	189.6	829.9	0.588	23.58	54.26	1466

TABLE 2. (*Continued*)

Temperature, °C	$-\log f_{O_2}$	$-\log f_{F_2}$	f_{H_2}	f_{H_2O}	$-\log f_{HF}$	f_{CO_2}	f_{CO}	f_{CH_4}
		8. C, CH (CFG, COHF)						
327	43.453	70.609	6.78	0.0055	10.937	$<10^{-4}$	$<10^{-4}$	5690
427	37.232	61.170	22.08	0.0205	9.342	$<10^{-4}$	$<10^{-4}$	5226
527	32.519	54.016	54.17	0.0580	8.111	$<10^{-4}$	$<10^{-4}$	4817
627	29.626	49.606	109.4	0.0530	7.732	$<10^{-4}$	0.0002	4433
727	26.679	45.137	191.7	0.101	6.960	$<10^{-4}$	0.0014	4070
827	24.470	41.773	302.3	0.134	6.476	$<10^{-4}$	0.0055	3726

[a] For buffer notation see Figures 1 and 2. More complete results and computer program available upon request (HPE).

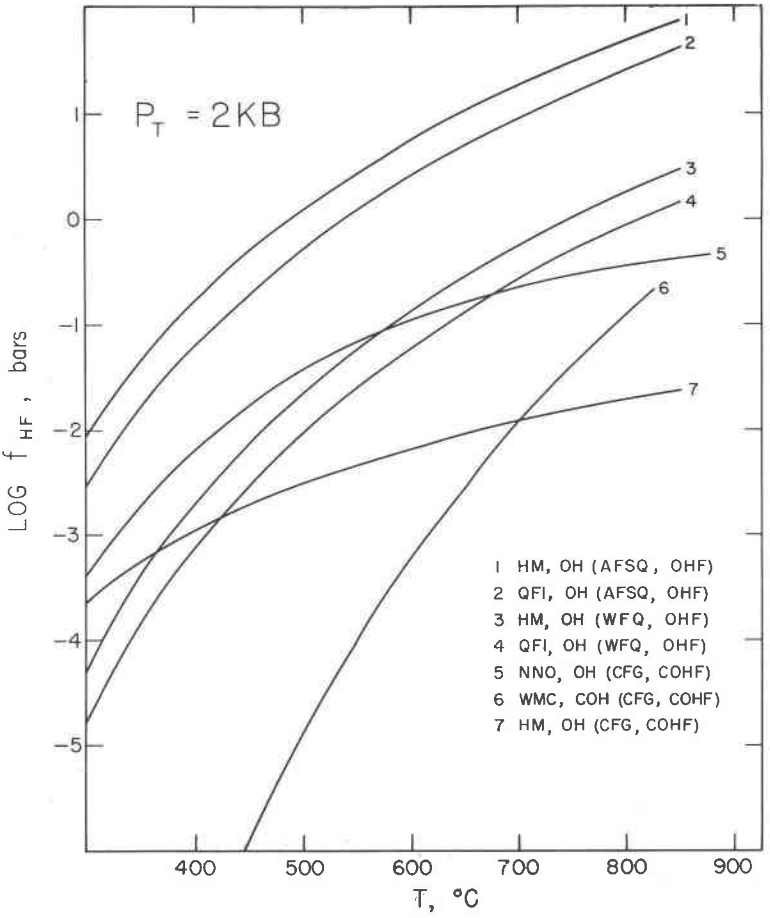

FIG. 2. Variation of HF fugacity with temperature calculated for a number of fluorine buffers at a total pressure of 2 kbar. Buffer assemblages (neglecting gas) are: HM, hematite +magnetite; NNO, nickel+nickel oxide, QFI, quartz+fayalite+iron; WMC, wustite +magnetite+graphite; AFSQ, anorthite+fluorite+sillimanite+quartz; WFQ, wollastonite+fluorite+quartz; CFG, calcite+fluorite+graphite.

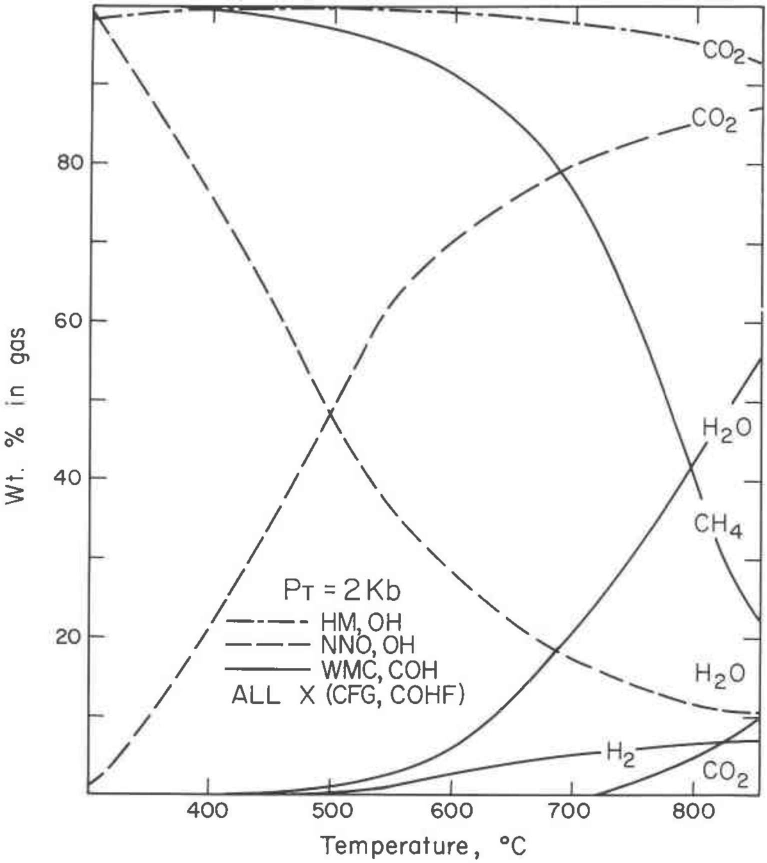

FIG. 3. Bulk composition of gas phase (major components only) in equilibrium with the CFG buffer at 2kbar plotted as a function of temperature and hydrogen fugacity. Dash-dot curve: HM, OH (CFG, COHF); dashed curve: NNO, OH (CFG, COHF); solid curve: WMC, COH (CFG, COHF). HF is too minor a component to show up on this type of plot.

At 2 kbar gas pressure the partial pressure of HF never exceeds 50 bars, and is usually reckoned in tenths or hundredths of a bar. Hence, the bulk chemistry of the C-O-H-F system is very similar to that of the C-O-H system (French, 1966). Thus, for high oxygen fugacities (*e.g.*, HM buffer), the gas phase is predominantly CO_2; for intermediate oxygen fugacities (*e.g.*, NNO buffer), H_2O is dominant at low temperatures, but is rapidly replaced by CO_2 at higher temperatures; for very low oxygen fugacities (*e.g.*, QFI buffer), $H_2+CO+CH_4$ become the dominant species (Fig. 3).

It is important to consider the effect of these buffers on an experimental system. Consider a schematic fluorination reaction

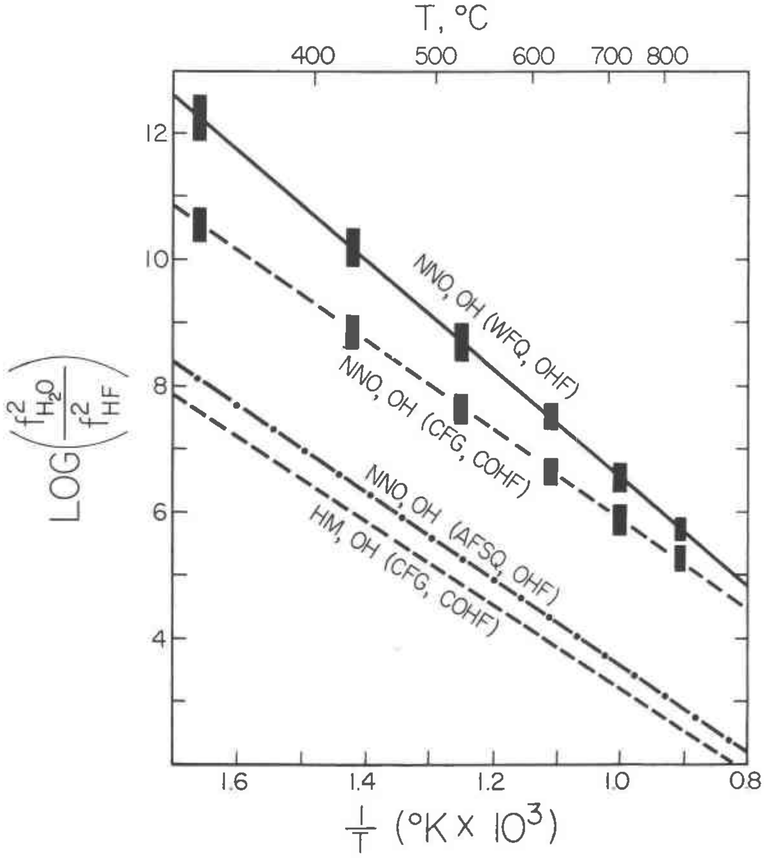

FIG. 4. Log ($f_{H_2O}{}^2/f_{HF}{}^2$) versus reciprocal temperature for four fluorine buffers. The height of the solid bars placed on the upper two curves represents the extent of uncertainty in the equilibrium constant which can be solely attributed to uncertainties in $\Delta G°$ values for the solid buffer phases. For symbols, see Fig. 2.

$$A(OH)_2 + 2HF \rightleftharpoons AF_2 + 2H_2O$$

Each buffer curve is plotted on a log *K vs* 1/T grid, with *K*'s obtained from the calculated fugacities of H_2O and HF for each buffer (Fig. 4).[1] The plot reveals a number of interesting facts pertinent to fluorine-OH reactions controlled by fluorine buffers: 1. Fluorination is favored by increasing temperature and, conversely, hydroxylation is favored with decreasing temperature; 2. The slopes of the buffer curves are nearly parallel; 3. The effect of external oxygen fugacity on fluorination is opposite

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[1] Assuming no solid solution.

TABLE 3. MOLECULAR AND IONIZED SPECIES CALCULATED FOR THE BUFFER NNO (OH), WFQ (OHF) AT 2 KBAR[a]

T, °C	log f_{H_2O}	log f_{H_2}	log f_{HF}	log a_{F^-}	log a_{H^+}
450°	2.735	0.289	−2.189	−3.49	−3.50
550°	2.945	0.592	−1.256	−3.55	−3.53
650°	3.080	0.806	−0.552	−3.74	−3.68

[a] Data for HF: Barnes, Hegelson & Ellis (1966), Table 18-4 C (p. 407). Data for H_2O: ibid, Table 18-1 C (p. 404); density of supercritical H_2O from Kennedy & Holser (1966), Table 16-1 (p. 378).

for O-H-F and C-O-H-F buffers; for C-O-H-F buffers decreasing f_{O2} favors hydroxylation, whereas for O-H-F buffers decreasing f_{O_2} favors fluorination, although in the latter case the effect is not detectable over ranges where P_{H_2} is low compared to P_{TOTAL}. (Table 2).

EFFECT OF IONIZATION

In addition to the molecular dissociation of H_2O and HF, some degree of ionization will occur, as governed by the ionization constants

$$K_{HF} = \frac{a_{H^+}a_{F^-}}{a_{HF}} \quad \text{and} \quad K_{H_2O} = \frac{a_{H^+}a_{OH^-}}{a_{H_2O}}$$

Ionization will, of course, have no effect on the fugacity *ratios* defined by the fluorine buffer equations. Moreover, these ionization equilibria will not effect the magnitudes of the *individual* calculated fugacities (*i.e.*, will not effect the P_{TOTAL} equation) providing that the population of ionized species is always much less than the population of molecular species. From the values for the ionization constants for H_2O and HF and 2kbar and temperatures of 450°, 550°, and 650°C (Barnes, *et al.*, 1966, p. 404 and 407), values for a_{H^+} and a_{F^-} have been calculated for the NNO, OH (WFQ, OHF) buffer, assuming that H^+, F^- and OH^- are the only ionized species present. The results (Table 3) predict that fluorine is present dominantly in the molecular state (as HF), and that the sum of the ionized components is sufficiently small relative to P_{TOTAL} so that they may be safely ignored. It is probably worth noting, however, that although the molecular versus the ionic approaches to fluorine (or fluoride) equilibria are very different, the results of the separate approaches must be identical. This point is emphasized by combining the equations for the ionic dissociation of H_2O and HF with the restriction of electrostatic neutrality, *i.e.*, that the sum of the number of moles of positive ions must equal the sum of the number of moles of negative ions, to form the single equation

$$a_{H^+} = \gamma_{H^+}\left[\left(\frac{K_{HF}a_{HF}}{\gamma F^-}\right) + \left(\frac{K_{H_2O}a_{H_2O}}{\gamma OH^-}\right)\right]$$

where γ_{H^+}, γ_{F^-}, and γ_{OH^-} represent the activity coefficients for the respective ions. The equation shows that once the activities of the molecular species are independently defined, the pH and hence the activities of all the ions in the gas phase are fixed.

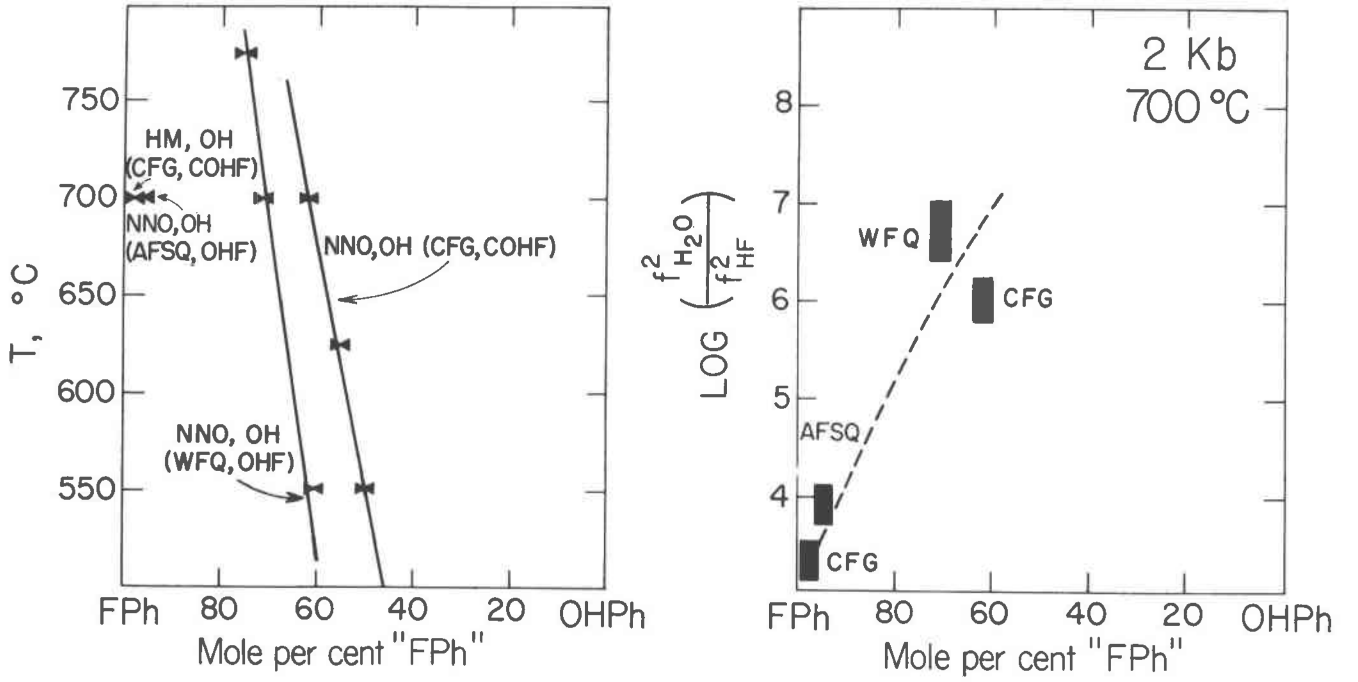
DEMONSTRATION OF EQUILIBRIUM

Equilibrium between fluorine buffer and charge was investigated using both crystalline hydroxyphlogopite and fluorophlogopite as starting materials. Phlogopite was chosen because it is one of the few phases showing (OH, F) solid solution for which both end members can be readily obtained in a pure state. By using both end members, the composition of the (F, OH) phlogopite solid solution in equilibrium with a given fluorine buffer at a fixed temperature can be approached from both sides. The composition of the intermediate phlogopites was determined by X rays on the basis of the d(005) assuming that a linear correlation can be made be-

TABLE 4. RUN TABLE FOR PHLOGOPITE EQUILIBRATED WITH CFG, WFQ, AND AFSQ FLUORINE BUFFERS AT 2 KBAR

Starting Material	Temperature °C[a]	Time, days	Final Composition[a]
A. NNO, OH (CFG, COHF)			
gel	700	24	$F_{61}OH_{39}$
F-phlog	700	24	$F_{60}OH_{40}$
OH-phlog	700	24	$F_{64}OH_{36}$
OH+F-phlog	625	74	$F_{55}OH_{45}$
OH+F-phlog	550	108	$F_{49}OH_{51}$
B. HM, OH (CFG, COHF)			
OH-phlog	700	10	$F_{39}OH_{61}$
OH+F-phlog	700	21	$F_{61}OH_{39}+F_{95}OH_5$
$F_{61}OH_{39}+F_{95}OH_5$	700	12	$F_{96}OH_4$
C. NNO, OH (WFQ, OHF)			
OH+F-phlog	775	10	$F_{75}OH_{25}$
OH+F-phlog	700	54	$F_{71}OH_{29}$
OH+F-phlog	550	108	$F_{60}OH_{40}$
D. NNO, OH (AFSQ, OHF)			
OH-phlog	700	68	$F_{95}OH_5$

[a] Temperatures are ±5°C; Compositions are precise to ±2 mole %, but accuracy may be considerably less due to the linear extrapolation of the X-ray determination curve.



(a) (b)

FIG. 5. a. Compositions of phlogopite in equilibrium with four fluorine buffers at 2kbar plotted as a function of temperature. Arrows show direction of movement towards the equilibrium value. FPh: fluorophlogopite; OHPh: hydroxyphlogopite.

b. Compositions of phlogopite equilibrated with four fluorine buffers at 2kbar, 700°C (see 5a) plotted as a function of the log of the squared fugacity ratio. The relative compositions of micas equilibrated with the NNO, OH (CFG, COHF) and NNO, OH (WFQ, OHF) buffers are in the opposite direction from that predicted by the fugacity ratio.

tween the basal spacings of the end members and composition in mole percent. Compositions can be determined to a precision of better than ±2 percent. Experiments were performed in standard externally heated furnaces using cold seal rod bombs at a total pressure of 2 kbar.

In most cases, a mechanical mixture of OH-phlogopite + F-phlogopite was used as a starting material once it had been established that reaction could be obtained using each phase separately; in these cases, the two-phase mixture was run under the desired conditions until a single, sharp (005) reflection was obtained from the quenched sample. The results are shown in Table 4 and Fig. 5. The AFSQ buffer equilibria were calculated using sillimanite as the aluminosilicate phase even though andalusite may be the stable polymorph at 2 kbar, 700°C (Gilbert *et al.* 1968). The small difference in the heats of formation of andalusite and sillimanite (0.48 kcal/mole at 968° K, Holm and Kleppa, 1966) results in a very small shift in the position of the buffer curve.

A number of facts emerge from the data. First, because the reaction can be approached from both sides, equilibrium between buffer and charge is demonstrated. Second, the run times needed to homogenize the two-phase phlogopite mixtures are considerably longer than equivalent run times needed to demonstrate the direction of a redox reaction at the same temperature. This could be either because the exchange of fluorine with hydroxyl is a slow process or because of the time required for the gas phase to equilibrate with the buffer. Third, a calibration problem is apparent. The phlogopites equilibrated with the WFQ (OHF) buffer are more fluorine-rich than those equilibrated with the CFG (COHF) buffer at the same temperature; the calculated $f_{H_2O}{}^2/f_{HF}{}^2$ values (Fig. 4) predict the opposite result. This difficulty could arise from inadequately known $\Delta G°$ for the various buffer phases, or from nonideal mixing in the gas phase. Taking these possibilities in turn, the maximum errors in $\Delta G°$ for the various buffer phases as reported by Robie (1962) have been compiled and used to calculate maximum and minimum limits for log K as shown by the size of the error flags in Figure 4. Although this represents a fair-sized source of error, it alone cannot explain the discrepancy. With regard to the second possibility, the method of reduced variables was used to determine fugacity coefficients for CO, CH_4, and HF; as these are fairly crude approximations at best, the values must be viewed with reservation as possible error sources. More serious, however, these fugacity coefficients relate to pure homogeneous systems in which there are no interactions between *different* molecules; extrapolation of these compounding approximations to complex fluorine-bearing gases containing a large number of molecular species may prove to be unwarranted. To evaluate the problem, more data is needed using different buffers. Ultimately, the system O-H-F should be investigated systematically. Nonetheless, the phlogopite experiments are very promising. Once calibration difficulties can be resolved, phlogopite itself will provide a very useful sliding scale which can be used to record the f_{H_2O}/f_{HF} ratios in future experiments which involve complex fluorine-bearing hydrothermal gases.

GEOLOGIC APPLICATIONS

The data obtained for the (OH, F)-phlogopites are much too incomplete to warrant any definite conclusions. However, the 700°C isotherm of (Fig. 5b) illustrates a very significant point. Consider the exchange reaction

$$\underset{\text{OH-phlogopite}}{KMg_3AlSi_3O_{10}(OH)_2} + 2HF \rightleftharpoons \underset{\text{F-phlogopite}}{KMg_3AlSi_3O_{10}F_2} + 2H_2O$$

Assuming that the dashed curve in Figure 5b represents the equilibrium position of this reaction at 700°C and 2 kbar pressure, we can calculate the composition of the gas phase in equilibrium with an (OH, F)-phlogopite, using the relation

$$f_i = f_i^\circ \times X_i$$

where f_i is the fugacity of i in the gas mixture, f_i° is the fugacity of pure i at the same P and T, and X_i is the mole fraction of i in the mixture. At 700°C, 2 kbar, $f_{H_2O}^\circ = 1360$ bars, $f_{HF}^\circ = 4020$ bars. The correlation between gas and phlogopite composition was calculated from Figure 5b and is plotted in Figure 6. The distribution of fluorine between mica and gas is obviously very asymmetric, with the mica removing the fluourine nearly quantitatively from the gas.[1] In other words, during crystallization phlogopite acts as a very efficient trap even for small traces of HF.

The effect of changes in P, T and biotite composition on the curve in Figure 6 is not known, but it is probable that a similar relationship exists for most igneous and metamorphic phlogopites and biotites.[2] If this is true, the gas phase in equilibrium with the most fluorine-rich phlogopite (75 mole % F-phlogopite, see Deer, *et al.*, 1962) would have contained no more than 0.05 mole percent HF. According to the biotite analyses

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[1] This conclusion seems to be at variance with the results of Noda and Ushio (1964), who were unable to grow very fluorine-rich phlogopite from an aqueous phase even with large fluorine excess in the starting material. In their experiments, however, solid $KMgF_3$ was also present and they did not determine the composition of the gas phase.

[2] According to preliminary data of Rieder (1968), this extrapolation may not be valid for annite. It may also be questionable for the case of lepidolites, as indicated by the good correlation between lithium and fluorine contents (Munoz, 1966; Rieder, 1968).

tabulation of Foster (1960), a more common range would be 0.001–0.005 mole percent HF. At a gas pressure of 2000 bars, this would correspond to a HF fugacity of 0.04–0.2 bars. According to data of Wyllie and Tuttle (1961), this amount of HF does not affect the melting temperatures of albite and granite and probably other fluorine-free silicate assemblages; but it will strongly influence the thermal stability of (OH, F) solid solutions. Hence, mica-amphibole equilibria will also be affected by it.

Perhaps even more interesting than the low values of f_{HF} and X_{HF} in igneous and metamorphic gases is the ubiquitous *presence* of HF, as reflected by the mica compositions. As more calibrations become available, it will be possible to obtain a quantitative picture of the behavior of HF and hence F_2 in igneous and metamorphic processes.

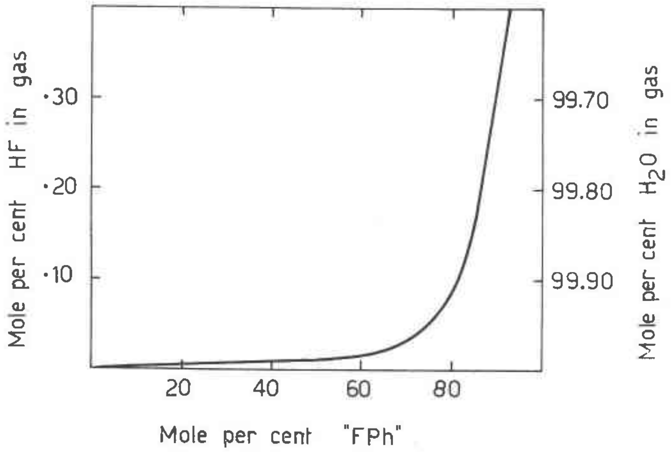

FIG .6. Distribution of fluorine between phlogopite and gas at 700°C, 2 kbar, calculated from Figure 5b. The vertical scale is 200 times the horizontal scale FPh: fluorophlogopite. Right-hand ordinate valid only for an H–O–F gas.

PRACTICAL CONSIDERATIONS: CHOICE OF FLUORINE BUFFER

An oxygen buffer is separated from the charge by a metallic membrane permeable only to hydrogen; thus, contamination of the charge by metallic ions is avoided. However, lacking a fluoride-specific membrane, the fluorine buffer gas is in direct contact with the charge and is only mechanically separated from the buffer phases by a crimped foil packet or tube. Thus, by means of exchange with the vapor phase, some transfer of material from the buffer to the charge can occur. This problem can be avoided by choosing a buffer whose components will be inert to the charge under the desired experimental conditions. For example, for the phlogopite case described in this report, the only possible buffer contaminant is Ca, by means of the substitution of Ca for K in the interlayer site of the mica. However, in order to form Ca-phlogopite (clintonite or xanthophyllite, Deer *et al.*, **3**, p. 99) from phlogopite, alumina must be added to and silica expelled from the tetrahedral layer in order to maintain electrical neutrality; inasmuch as there is no source of additional alumina in the buffer and no excess quartz was observed in the quenched charges, it appears that contamination did not occur. Nonetheless, contamination of this type is a problem to which future users of the buffer method should be alerted.

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