

Fluorine-Hydroxyl Exchange in Apatite and Biotite: A Potential Igneous Geothermometer

J. C. STORMER and I. S. E. CARMICHAEL

Department of Geology and Geophysics, University of California, Berkeley 94720

Received February 12, 1971

Abstract. The free energy data for the simple fluorides, chlorides and hydroxides have been used to predict the distribution of these anions in hydrous minerals. The calculated partition of fluorine in phlogopite agrees well with published results; the distribution of fluorine and hydroxyl between apatite and phlogopite is temperature dependent and has been calculated. The temperatures deduced from analyses of natural apatite-biotite pairs frequently show discrepancies as compared with independent temperature estimates; these probably arise from late-stage exchange of the fluorine in phlogopite with an aqueous fluid, for which independent evidence is available.

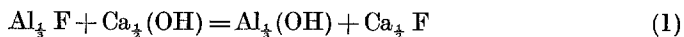
The fugacity of phosphorus in equilibrium with apatite, a ubiquitous hydrous mineral, has been calculated for various mineral assemblages. The estimates, which are subject to considerable error, are lower for basanites and alkali-basalts than for tholeiites and range from approximately 10^{-14} at 1000°C to 10^{-16} bars at 750°C for fayalitic rhyolites.

Introduction

Apatite, $\text{Ca}_5(\text{PO}_4)_3(\text{OH}, \text{F})$ is the commonest of all the hydrous minerals in igneous rocks, and together with coexisting micas and amphiboles may contain significant amounts of a halogen substituting for the hydroxyl group. However little seems to be known of the partition of F, Cl and (OH) between these phases in igneous rocks, or how their distribution could vary with temperature. As thermodynamic data for the chlorine, fluorine and hydroxyl end-members of these mineral groups are usually not known, it seems worthwhile to estimate the distribution of Cl, F and (OH) by using thermodynamic data on their simple compounds. The conclusions may only be roughly applicable to the complex minerals of igneous rocks but, as will be seen in the sequel, prediction from an admittedly crude model in some cases agrees well with experiment.

Free Energy of F, Cl and (OH) Exchange

The differences in free energies between the hydroxides, fluorides and chlorides of most of the common cations are shown in Table 1, where they are arranged in accordance with the periodic table. Values for iron compounds are not available but the trends shown in the table indicate that the values for ferrous iron should be similar to those for magnesium. To facilitate comparison of data for cations of different valency, the free energy values in the table have been normalized to the free energy of the compound containing one mole of the anion. The free energy of an exchange between two of these compounds, for example:



is then the difference between the values listed for the cations (Al and Ca) in Table 1.

$$\Delta G_1 = (-31.7) - (-21.9) = -9.8 \text{ K.cals.} \quad (1a)$$

The free energy of a reaction, ΔG , varies with temperature and pressure as follows:

$$\left(\frac{\partial \Delta G}{\partial T}\right)_P = -\Delta S \quad \text{and} \quad \left(\frac{\partial \Delta G}{\partial P}\right)_T = \Delta V.$$

Since equal amounts of similar phases are present as both products and reactants, the entropy, ΔS , of these reactions will be relatively small (cf. Searcy, 1970) and the free energy of the reaction ΔG will not change greatly with temperature. The same is true of the volume of reaction ΔV which controls the change in free energy with pressure. In the discussion which follows we have assumed that the free energies of the exchange reactions change negligibly with temperature and pressure.

By writing exchange reactions for these compounds it becomes apparent that the more negative the value for the cation in Table 1A the greater is its tendency to associate with fluorine rather than a hydroxyl group (or in Table 1B with chlorine rather than a hydroxyl group; or in Table 1C with fluorine rather than chlorine). Several interesting features are then immediately apparent in these tables.

Table 1. Free energy differences—fluorides, chlorides, and hydroxides (Kcal/mole anion, 298° C, 1 bar)

A			B			C		
$\Delta G_f(\text{MF}) - G_f(\text{MOH})$			$\Delta G_f(\text{MCl}) - G_f(\text{MOH})$			$\Delta G_f(\text{MF}) - G_f(\text{MCl})$		
H			H			H		
-10.7			+31.9			-42.5		
Li			Li			Li		
-34.1			—			—		
Na	Mg	Al	Na	Mg	Al	Na	Mg	Al
-38.6	-28.3	-21.9	-0.6	+28.9	+40.9	-38.0	-57.2	-62.8
K	Ca		K	Ca		K	Ca	
-37.6	-31.7		-6.8	+17.7		-30.8	-49.3	

Table 1A shows that compared with hydroxyl ion the fluoride ion should have a strong preference for cations other than hydrogen, especially calcium, magnesium and the alkalis. Table 1C shows the fluoride ion's preference for magnesium, calcium and aluminium when compared with chloride ion. Therefore, when it is competing with hydroxyl and chloride in a geological environment, fluoride should be preferentially incorporated in minerals where it is associated with magnesium (probably also Fe^{++}) and calcium. Likewise, chloride should be preferentially incorporated in alkali chloride compounds. In igneous rocks these relationships are seen in the typical predominance of fluoride over chloride and often hydroxyl in micas, amphiboles, and apatites (Table 2) (Correns, 1956) while H_2O and alkali chlorides predominate in volcanic emanations and hydrothermal

Table 2. Analyses and temperature data for biotite-apatite pairs

Sample Number	Apatite			Biotite			Temperature Estimates		% H ₂ O in rock
	% Cl	% F	F/F + OH	% Cl	% F	F/F + OH	F—OH	Other data	
<i>Italian volcanics (biotite and apatite in groundmass)</i>									
Leucite trachytes									
A 88-17	0.04	3.5	92	0.04	6.2	73	1027	1274 (1)	1.91 ^a
B 89-21	0.04	3.4	89	0.04	5.8	68	997	1310 (1)	0.72 ^a
Leucite basanites									
C 94-14	0.75	3.3	86	0.10	5.7	69	1350	1290	0.45 ^a
D 96-6	0.06	3.27	86	0.02	5.8	68	1330	—	1.78 ^a
<i>Lavas with biotite and apatite phenocrysts</i>									
Lassen Dacites									
E L 118	1.33	1.55	50	0.12	0.28	3	300	880 (1) 880 (2)	0.82 ^b
F Cal 13	0.96	1.90	58	0.09	0.38	4	320	982 (1) 980 (2)	1.30 ^b
G Cal 19	1.16	1.70	52	0.10	0.28	3	280	935 (1) 865 (2)	1.24 ^b
Trachytes									
H 3811	0.94	1.94	59	0.11	0.68	8	340	1000 (1) 1010 (2)	2.00 ^c
I 1909-261	0.65	3.18	93	0.17	2.16-1.50	24-16	180-140	1004 (1)	1.14 ^c
J G-24	0.31	2.70	75	0.04	0.53	6	170	—	0.41 ^c
Leucite Hills									
K A-1805	0.04	3.46	90	—	3.46-3.06	41-34	400-330	1245 (3)	4.98 ^d
L J-14	0.26	3.22	88	—	2.61-1.80	29-20	320-230	—	4.21 ^d
M A-128	0.05	3.50	93	0.02	4.75-1.98	53-22	430-170	1165 (3)	2.68 ^d
N A-1741	0.11	3.16	82	—	3.71-1.76	41-20	620-320	1200 (3)	3.43 ^d
O A-1770	0.11	3.45	90	—	3.50-1.88	38-21	3360-220	1215 (3)	1.84 ^d

^a Carmichael (unpublished data). ^b Carmichael (1967b). ^c Carmichael (1965). ^d Carmichael (1967a).

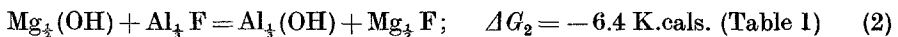
(1) Plagioclase geothermometer (Kudo and Weill, 1970); most calcic composition at 0.5 Kbar H₂O.

(2) Iron-titanium oxide geothermometer (Buddington and Lindsley, 1964).

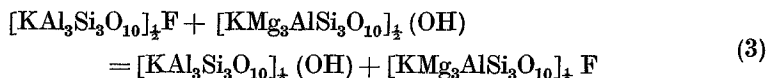
(3) Melting data, liquidus at 1 atm.

solutions. Coexisting minerals may also strongly partition the halogens, as in the leucite-basanite lavas of Vesuvius, where sodalite (NaCl.Na₃Al₃Si₃O₁₂) without detectable F, coexists with fluorine-rich (Cl-poor) phlogopite and apatite (Table 2) (Stormer and Carmichael 1971).

The distribution of the halogens and hydroxyl in the mica group of minerals also corresponds with predictions based on the values given in Table 1. In the mica structure, F⁻ or (OH)⁻ is associated with the octahedral cations Mg or Al, and the structure of phlogopite or muscovite can be represented by a central layer of brucite [Mg₃(OH)₆] or gibbsite [Al₂(OH)₆] respectively, where four of the six (OH) ions are replaced by oxygens of the tetrahedral layer. Thus the exchange reaction:



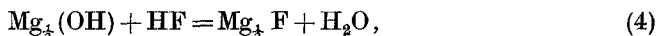
can be used to model the mica exchange reaction¹:



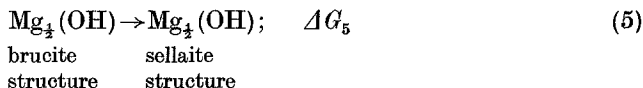
which from the evidence of Eq. (2) ($\Delta G_2 = -6.4$ K.cal.) should proceed to the right. Published analyses of muscovites and biotites show that biotites, with octahedral Mg and Fe^{++} , always contain more fluorine than the coexisting muscovite, with octahedral Al (Correns, 1956; Evans, 1969; Gillberg, 1964).

Lepidolite and zinnwaldite, which both have Li in octahedral sites, show a strong preference for fluorine which is to be expected considering the large negative $\text{LiF} - \text{LiOH}$ free-energy difference (Table 1A) (Munoz and Eugster, 1969, p. 956).

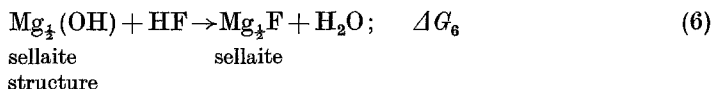
It should be emphasised that the hydroxide and fluoride compounds listed in Table 1 have different structures. Thus $\text{Mg}(\text{OH})_2$ has the hexagonal CdI_2 structure, whereas sellaite, MgF_2 , has the tetragonal rutile structure, so that the exchange reaction:



can be visualised as having two free-energy increments. One will be represented by the structural transformation



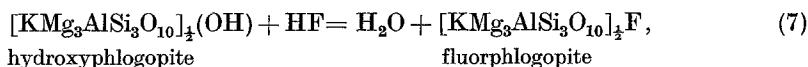
and the other, the exchange reaction, can be represented as



The free-energy of any structural transformation (ΔG_5) will be absent in solid solutions, but the experimental results on phlogopite-gas equilibria suggest that ΔG_5 is small relative to the exchange energy ΔG_6 .

Phlogopite-Gas Equilibrium

A more quantitative test of the assumptions we have made is available. Muñoz and Eugster (1969) have published an experimentally determined curve showing the distribution of fluorine between phlogopite and a water-hydrogen fluoride gas at 700°C and 2 Kilobars pressure. This has been reproduced in Fig. 1. A hypothetical curve for the same distribution can be calculated from the following reaction:



1 If the mineral formula unit contained more than one F, Cl or (OH), the exchange reaction would imply that two or four F would exchange as a single unit for the corresponding unit of (OH). Moreover writing the exchange formulae with a single exchangeable anion also simplifies any activity term (cf. Darken and Schwertfeger, 1966).

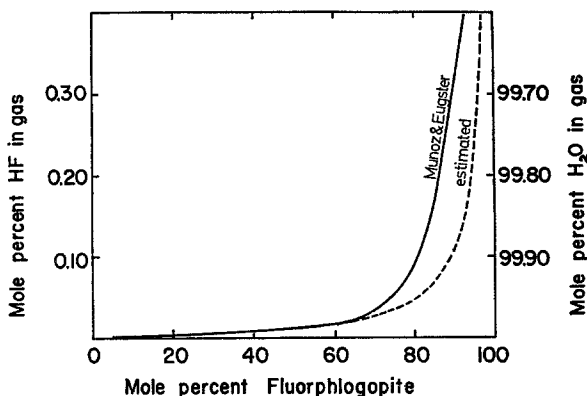


Fig. 1. Distribution of fluorine between phlogopite and gas at 700°C and 2 kbar from Muñoz and Eugster (1969). Dashed curve calculated for reaction at 298°K and 1 bar. The vertical scale is 200 times the horizontal scale. Mole percent H₂O in gas valid only for H—O—F gas

and at equilibrium:

$$-\Delta G_7^\circ = RT \ln \left[\frac{\alpha_{\text{H}_2\text{O}} \cdot \alpha_{\text{F-phlogopite}}}{\alpha_{\text{HF}} \cdot \alpha_{(\text{OH})\text{-phlogopite}}} \right]. \quad (7a)$$

By assuming ideal mixing in both gas and phlogopite this becomes with rearrangement of terms:

$$\log \frac{X_{\text{HF}}}{X_{\text{H}_2\text{O}}} = \frac{\Delta G_7^\circ}{2 \cdot 303 RT} + \log \left[\frac{X_{\text{F-phlog.}}}{X_{(\text{OH})\text{-phlog.}}} \right]. \quad (7b)$$

By using our assumption that the phlogopite exchange free energy is equal to the differences in the fluorine-hydroxide free energies of magnesium and hydrogen, then from Table 1A

$$\Delta G_7^\circ = (-28.3) - (-10.7) = -17.6 \text{ K.cals}, \quad (7c)$$

from which the estimated curve in Fig. 1 has been calculated.

The results are remarkably close to the experimentally determined values, if the greatly expanded vertical scale of the figure is taken into account. Unfortunately there is no other direct experimental evidence, but it appears that interaction between the octahedral cation and fluoride or hydroxyl is the most significant factor controlling their distribution. Factors such as interaction with other ions in the mica, and the energy of the structural transition of Mg(OH)₂ (cadmium iodide) to MgF₂ (rutile), as well as temperature² and pressure dependence of the free energy of exchange appear to be small in comparison.

An Apatite-Biotite Geothermometer

Apatite and phlogopite (or biotite) are found together in a wide variety of igneous and metamorphic rocks, and both show a range of fluorine-hydroxyl substitution, so that a geothermometer based on F—(OH) exchange could apply to a considerable range of rock types. It seems reasonable to assume from the structure of apatite that the free energy of fluorine-hydroxyl exchange in apatite can be modelled by calcium fluoride and calcium hydroxide, as in the normal apatite structure the fluorine or hydroxyl is surrounded by three calcium ions (see

² Free-energy data at 973°K are known for Mg(OH)₂, MgF₂, H₂O and HF and do not give any significantly better correspondence with the experimental curve in Fig. 1.

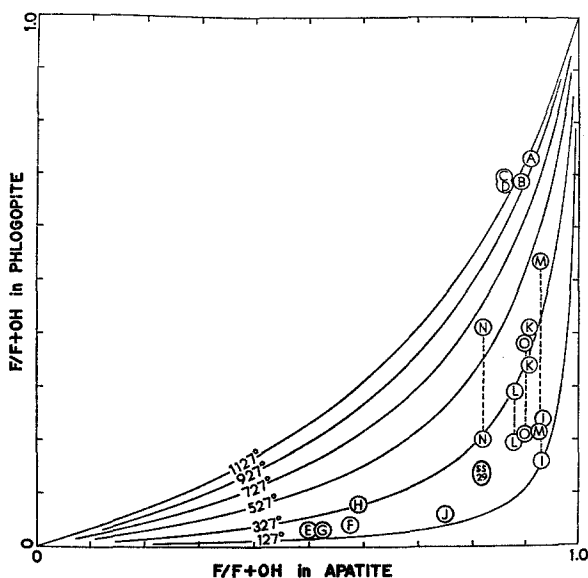
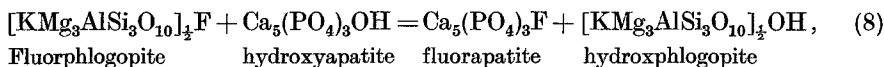


Fig. 2. Hypothetical distribution of fluorine and hydroxyl between phlogopite (biotite) and apatite for temperatures from 127°C (400°K) to 1127°C (1400°K). The fluorine-hydroxyl ratios of coexisting biotites and apatite from some volcanic rocks are plotted as labeled in Table 2. *A* to *D*, leucite trachytes and basanites from Italian province. *E* to *G*, Lassen dacites. *H* to *J*, various trachytes. *K* to *O*, Leucite Hills volcanics. *SS.29* from Shonkin Sag Laccolith (Nash and Wilkinson, 1970)

Deer *et al.*, 1962). The role of fluorine in carbonate apatites is more complex (McClellan and Lehr, 1969) and such apatites are excluded from this discussion.

The equilibrium distribution of fluorine and hydroxyl with respect to temperature can be calculated from the following relationship:



and

$$\frac{-\Delta G_8^\circ}{2 \cdot 303 RT} = \log \left[\frac{X_{(\text{OH})-\text{phlog.}}}{X_{\text{F-phlog.}}} \right] + \log \left[\frac{X_{\text{F-ap.}}}{X_{(\text{OH})-\text{ap.}}} \right]. \quad (8a)$$

Using a value derived from Table 1 for free energy, and assuming ideal mixing, isothermal curves of the equilibrium distribution were calculated and have been plotted in Fig. 2. This estimate of free energy for the fluorine-hydroxyl exchange reaction between phlogopite and apatite may, in fact, be more nearly correct than that for the phlogopite-gas reaction (above), since in this case the structural transition energies contained in Table 1 for the calcium and magnesium compounds will tend to cancel.

In order to test the validity of this geothermometer, electron microprobe analyses of a variety of igneous apatite-biotite (phlogopite) pairs were made from rocks for which some sort of independent temperature data are available. The microprobe determinations of Cl and F in coexisting phlogopitic-mica and apatite are given in Table 2. As complete analyses of all the minerals were not available, the F/F + (OH) ratio was calculated assuming that each mineral has completely filled (OH, F, Cl) group, as (OH) cannot be determined on the microprobe. The values of F/F + (OH) for the mineral pairs are plotted in Fig. 2.

Temperatures indicated by the hypothetical distribution model and the analyses correspond poorly with probable crystallisation temperatures for most of

these rocks (Table 2); there are several factors which could contribute to any discrepancy. Undoubtedly the assumptions of ideal mixing behavior and of the free-energy values only approximate the real relationships. Also the analyses of the mineral pairs could contain systematic errors due to uncertainty of the fluorine contents of the microprobe mineral standards.

However, post-crystallisation exchange of hydroxyl for fluorine in the biotites seems to be a major source of error for most of the biotite-apatite pairs. This is particularly evident when comparing the data for the Leucite Hills volcanics with those for the leucite-bearing Italian lavas. In the Italian lavas (*A-D*, Fig. 2) phlogopite and apatite are homogeneous and occur as groundmass phases. Their hydroxyl-fluorine ratios also indicate reasonable magmatic temperatures of equilibration, considering other uncertainties involved. In contrast, phlogopite and apatite in the lavas of the Leucite Hills crystallised early (*K-O*, Fig. 2). Although the apatite crystals are homogeneous with respect to F, phlogopite often has a very variable F distribution (Table 2) which decreases towards the crystal margins. Analyses of the Leucite Hills lavas also show very high water contents (Table 2) whereas those of the Italian lavas are generally lower. This evidence suggests to us that phlogopite has exchanged its fluorine at low temperatures with a pervasive aqueous fluid. Apatite seems relatively unaffected by this process; the difficulty of removing fluorine from apatite in chemical analysis is well known (Huang and Jackson, 1967).

One example of late magmatic interaction with meteoric water is a biotite in the Shonkin Sag laccolith whose deuterium/hydrogen ratio (Taylor and Epstein, 1968) showed that it had exchanged extensively. Phlogopite from the same sample (SS.29) was found to be deficient in fluorine by Nash and Wilkinson (1970) in relation to the accompanying amphibole. Analysis of the coexisting apatite from SS.29 (Nash pers. comm.) shows that the distribution of F and (OH) between apatite and the exchanged biotite is similar to the distribution in the Leucite Hills assemblages; in Fig. 2, SS.29 plots well below the temperature indicated by oxygen isotopes (770°C). This data on water-exchanged biotite confirms the suggestion that post magmatic alteration is a major source of discrepancy between the apatite-biotite geothermometer and the independent temperature estimates (Table 2). It appears that the fluorine content of biotite may provide a sensitive indication of late stage aqueous exchange alteration, which from Taylor's (1968) data, may be rather a common phenomenon in cooling igneous rocks.

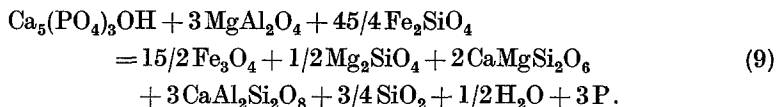
The pattern of chlorine distribution between mica and apatite (Table 2) shows that apatite is invariably enriched (up to 1.3%) with respect to the coexisting mica. This follows the general prediction from the data of Table 1C, where the fluoride-chloride exchange for Ca is less negative than for Mg, and hence Ca would be expected to combine more readily with Cl than either Mg or Al.

Phosphorus Fugacity

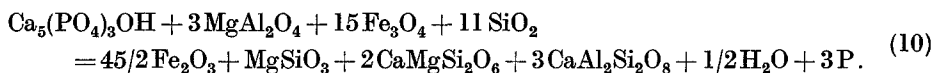
Apatite is found in almost every igneous rock, although often as a minor accessory, so that if the relevant thermodynamic data are known, it is then possible to calculate the fugacity of phosphorus from equations which are plausible represen-

tations of apatite parageneses. The thermodynamic data for the various components are taken from Robie and Waldbaum (1968) and the Janaf tables. It has been assumed, despite the evidence of Table 2, that igneous apatite is entirely the hydroxyl-variety, for which data exist³.

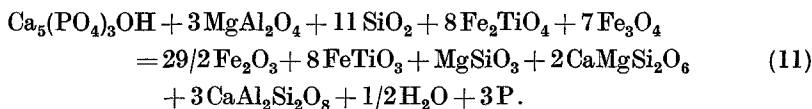
For olivine-magnetite assemblages, such as basalts or fayalite-bearing obsidians, the following reaction is fitting:



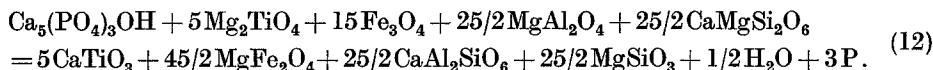
If the oxidation state is higher, or the pair olivine-magnetite is replaced by magnetite-haematite, then the following reaction serves for these more oxidised assemblages:



For igneous assemblages without olivine, but with two iron-titanium oxide phases, the following reaction, typical of andesite and olivine-free tholeiitic assemblages is plausible.



Lastly for the unusual feldspar-free but nepheline rich lavas called etindites, the equation below is cumbersome



The calculated variation of phosphorus fugacity (f_P) (or more correctly $\Delta G^\circ/(3)(2.303 RT)$) with temperature has been plotted for these four reactions in Fig. 3; each component is present in its standard state, namely as an independent phase with unit activity. In the case of H_2O the standard state is unit fugacity; the effect of 5000 bars H_2O fugacity on the equilibrium displacing the standard state curve of Eq. (12) is shown in Fig. 3.

In order to calculate the values of f_P for an actual igneous assemblage, it is necessary to assume that the various components mix ideally, so that their activities can be set equal to their mole fractions. Eq. (9) is re-written to take account of the reduced activity of those components which form solid solutions, in this way:

$$\begin{aligned} \log f_P = \frac{1}{3} \left[\frac{\Delta G^\circ}{2.303 RT} + 3 \log a_{\text{MgAl}_2\text{O}_4}^{\text{spinel}} + \frac{45}{4} \log a_{\text{Fe}_2\text{SiO}_4}^{\text{olivine}} - \frac{15}{2} \log a_{\text{Fe}_3\text{O}_4}^{\text{spinel}} - \frac{1}{2} \log a_{\text{Mg}_2\text{SiO}_4}^{\text{olivine}} \right. \\ \left. - 2 \log a_{\text{CaMgSi}_2\text{O}_6}^{\text{pyroxene}} - 3 \log a_{\text{CaAl}_2\text{Si}_2\text{O}_8}^{\text{plagioclase}} - \frac{3}{4} \log a_{\text{SiO}_2}^{\text{liquid}} - \frac{1}{2} \log f_{\text{H}_2\text{O}} \right] \end{aligned}$$

³ The values given by Robie and Waldbaum (1968) for the free-energy of formation of apatite are in error as the correct value for the enthalpy of the given formula unit at 298 (ΔH_f°) is half the stated value.

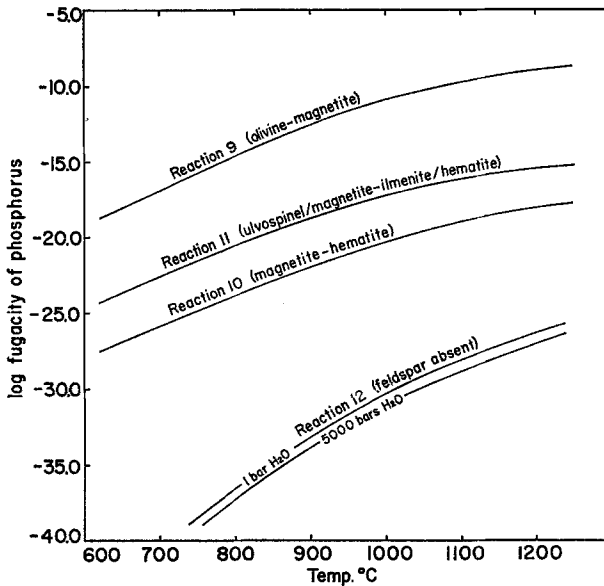


Fig. 3. Variation of $\Delta G^\circ/(3) 2.303 RT (= \log f_P)$ with temperature for the four apatite reactions discussed in the text. All the components are in their standard states. Note the effect of 5000 bars f_{H_2O} in displacing the equilibrium curve of Eq. (12)

Although it may reasonably be assumed (for our purposes) that hydroxyl apatite has unit activity, and that the olivine, pyroxene ($CaMgSi_2O_6$) and feldspar ($CaAl_2Si_2O_8$) components mix ideally in their respective phases, the two spinel components (Fe_3O_4 and $MgAl_2O_4$) unmix at low temperature. This indicates that their solid solutions are nonideal and that their activities are not equal to their mole fractions. It is also difficult to evaluate the amount of the $MgAl_2O_4$ component in any analysis of a spinel phase; certainly the amount is always small, particularly in tholeiitic lavas (ca. 0.005) but it increases in alkali basalts and basanites (ca. 0.03).

A value for silica activity can be estimated from Carmichael *et al.* (1970) and f_{H_2O} can be arbitrarily assumed to be 500 bars as seems to be the case in many acid lavas (Stormer and Carmichael, 1970); if f_{H_2O} is less than 500 bars, the curve of f_P will be displaced by less than one orders of magnitude (Fig. 3).

Using typical mineral data, and assuming ideal mixing, the sum of the logarithmic terms for Eq. (9) has been determined for a typical tholeiite, alkali-basalt, basanite and rhyolite. In Fig. 4 curves delineating the likely limits of f_P for these four rock types are shown; as Peck *et al.* (1966) have shown that apatite precipitates at $1000^\circ C$ in the Alae (Hawaii) tholeiitic lava lake, the basaltic curves in Fig. 4 should not be extended to liquidus temperatures. The lower temperature limits of basalt are taken as $900^\circ C$ and the range for fayalitic-rhyolites as $925-750^\circ C$.

Phosphorus has been determined in the fumarolic gas of the Showa-shinzan hypersthene-dacite (White and Waring, 1963) which at $750^\circ C$ (the gas collection temperature) was presumably present as P_4O_{10} . An approximate calculation of f_P in equilibrium with this P_4O_{10} at $750^\circ C$ has been made and is plotted in Fig. 4; considering the numerous approximations and uncertainties, the agreement

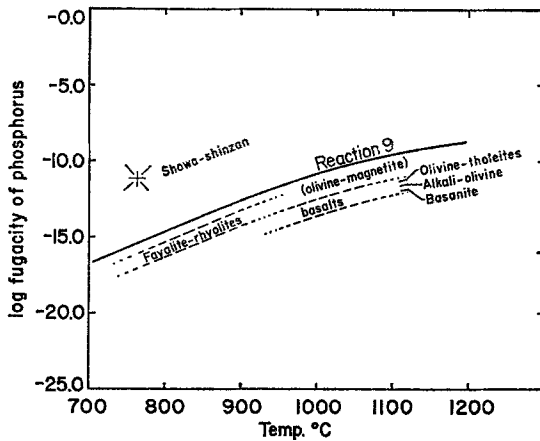


Fig. 4. Estimated limits of phosphorus fugacity for olivine-bearing basalts and rhyolites using typical mineral data substituted in Eq. (13) (see text). Upper temperature limit of apatite in basalts is assumed to be near 1000°C (Peck *et al.*, 1966). The calculated f_P of an analysed fumarolic gas (750°) of the Showa-shinzo hypersthene-dacite is also plotted (White and Waring, 1963).

between the gas and the calculated fugacity of phosphorus for fayalitic-rhyolites is not unreasonable.

Substitution of mineral data into the three other apatite equations would require additional assumptions of ideal mixing of components which are frequently found in small concentration in nature; this compounds the errors especially as the stoichiometric coefficients are often large. Accordingly the other equations have been ignored, as, for example, the sum of the relevant logarithmic terms for Eq. (12) for the typical etindite is +8.9, which leads to $\log f_P$ ranging from -19 to -35 bars.

Conclusions

For apatite and phlogopite to be in exchange equilibrium with fluorine and hydroxyl at magmatic temperatures, we should expect F to occupy approximately 75% of the (OH) sites in apatite and between 60 and 75% in the coexisting biotite (Fig. 2). As many natural assemblages do not show this, either F was originally absent from the fluid component, or there has been extensive late-stage exchange at low temperatures with an aqueous fluid, mainly affecting the mica. Isotopic evidence on the Shonkin Sag laccolith supports this view. This exchange is apparently very common in igneous rocks, and a low content of F in phlogopite may serve to indicate it as well as isotopic evidence. As both apatite and phlogopite preferentially combine with F, the fluorine content of a fresh rock should closely represent its original concentration.

The estimates of f_P in various rock types (Fig. 4) are subject to considerable error due mainly to the unknown mixing properties of components in the iron-titanium oxide group of minerals, which also only occur in small amounts.

Acknowledgments. This research has been generously supported by the U.S. National Science Foundation with a Graduate Fellowship (1970-71) to Stormer and a research grant (GA 11735) to Carmichael. Mr. Robert Heming assisted with some of the microprobe analyses.

References

- Buddington, A. F., Lindsley, D. H.: Iron-titanium oxide minerals and synthetic equivalents. *J. Petrol.* **5**, 310–357 (1964).
- Carmichael, I. S. E.: Trachytes and their feldspar phenocrysts. *Mineral. Mag.* **34**, 107–125 (1965).
- The iron-titanium oxides of salic volcanic rocks and their associated ferromagnesian silicates. *Contr. Mineral. and Petrol.* **13**, 36–64 (1967a).
- The mineralogy and petrology of the volcanic rocks from the Leucite Hills, Wyoming. *Contr. Mineral. and Petrol.* **15**, 24–66 (1967b).
- Nicholls, J., Smith, A. L.: Silica activity in igneous rocks. *Am. Mineralogist* **55**, 246–263 (1970).
- Correns, C. W.: The geochemistry of the halogens. *Phys. Chem. Earth* **1**, 181–234 (1956).
- Darken, L. S., Schwerdtfeger, K.: Appendices in Schwerdtfeger, K., and A. Muan: Activities in olivine and pyroxenoid solid solutions of the system Fe—Mg—SiO₂ at 1150°C. *Trans. Aime* **236**, 201–211 (1966).
- Deer, W. A., Howie, R. A., Zussman, J.: *Rock forming minerals*. 5, New York: Wiley 1962.
- Evans, B. W.: Chlorine and fluorine in micas of pelitic schists from the sillimanite-orthoclase isograd, Maine. *Am. Mineralogist* **54**, 1209–1210 (1969).
- Gillberg, M.: Halogens and hydroxyl contents of micas and amphiboles in Swedish granitic rocks. *Geochim. Cosmochim. Acta* **28**, 594–516 (1964).
- Huang, P. M., Jackson, M. L.: Fluorine determination in rocks and minerals. *Am. Mineralogist* **52**, 1503–1514 (1967).
- Kudo, A. M., Weill, D.: An igneous plagioclase thermometer. *Contr. Mineral. and Petrol.* **25**, 5–65 (1970).
- Janaf, Thermochemical Tables. Midland, Michigan: The Dow Chemical Co. 1960–1962.
- McClellan, G. H., Lehr, J. R.: Crystal chemical investigation of natural apatites. *Am. Mineralogist* **54**, 1374–1391 (1969).
- Muñoz, J. L., Eugster, H. P.: Experimental control of fluorine reactions in hydrothermal systems. *Am. Mineralogist* **54**, 943–959 (1969).
- Nash, W. P., Wilkinson, J. F. G.: Shonkin Sag Laccolith, Montana. I. Mafic minerals and estimates of temperature, pressure, oxygen fugacity and silica activity. *Contr. Mineral. and Petrol.* **25**, 241–269 (1970).
- Peck, D. L., Wright, T. L., Moore, J. G.: Crystallization of tholeiitic basalt in Alae lava lake, Hawaii. *Bull. Volcanol.* **29**, 629–656 (1966).
- Robie, R. A., Waldbaum, D. R.: Thermodynamic properties of minerals and related substances at 298°K (25°C) and one atmosphere (1.013 bars) pressure and at higher temperatures. *U.S. Geol. Surv. Bull.* 1259 (1968).
- Searcy, A. W.: Entropy and high temperature physical and chemical processes. Chemical and mechanical behavior of inorganic materials, chapt. 2, p. 15. New York: Wiley 1970.
- Stormer, J. C., Carmichael, I. S. E.: The Kudo-Weill geothermometer and porphyritic acid glasses. *Contr. Mineral. and Petrol.* **28**, 306–309 (1970).
- The free energy of sodalite and the behavior of chloride, fluoride and sulphate in silicate magmas. *Am. Mineralogist* **56**, 292–306 (1971).
- Taylor, H. P.: Oxygen isotope geochemistry of igneous rocks. *Contr. Mineral. and Petrol.* **19**, 1–71 (1968).
- Epstein, S.: Hydrogen-isotope evidence for influx of meteoric groundwater into shallow igneous intrusions. (abs.) *Geol. Soc. Am. Spec. Papers* **121**, 294 (1968).
- White, D. E., Waring, G. A.: Volcanic emanations. *U.S. Geol. Surv. Prof. Pap.* 440-K (1963).

Dr. J. C. Stormer
Department of Geology and Geophysics
University of California
Berkeley, California 94720, U.S.A.