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APATITE CHEMISTRY AND PHOSPHORUS FUGACITY IN A DIFFERENTIATED IGNEOUS INTRUSION

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ABSTRACT

The trace element chemistry of apatite [$Ca_5(PO_4)_3(OH, Cl, F)$] from Shonkin Sag laccolith exhibits systematic changes during differentiation. With increasing differentiation apatite becomes enriched in Si, Na, K, Sr, and rare earth elements, while becoming depleted in Fe and Mg. Extreme differentiation has produced the rare earth mineral britholite ($\Sigma\ RE = 55.7\%$) in the most highly evolved rock type, a soda syenite. Calculated phosphorus fugacities range from 10^{-25} to 10^{-30} bars over the crystallization interval of the laccolith (985–700°C). These values are intermediate to those of olivine-magnetite bearing basalts and feldspar-free lavas, and are slightly less than fugacities calculated for basalts containing metallic iron, representing possible lunar basalt analogs.

INTRODUCTION

Apatite [$Ca_5(PO_4)_3(OH, F, Cl)$] is ubiquitous in igneous rocks and is generally the sole locus of phosphorus. Although apatites consist almost entirely of Ca, P, O, and a hydroxyl-halogen member, they contain significant trace amounts of numerous elements. This paper describes the changing chemistry of apatite during crystallization of the Shonkin Sag laccolith, a strongly differentiated alkaline intrusion ranging in rock types from a mafic shonkinite chilled margin to a soda syenite final residuum (Nash and Wilkinson, 1970; 1971).

PETROGRAPHY

Apatites are present in all rocks of Shonkin Sag except the most highly differentiated variety where a rare earth mineral, britholite, is present instead. Apatites change radically in their morphology from stubby prisms in the chilled margin to extremely elongate needles in the salic differentiates. In the chilled margin (samples 2 and 7) apatite is present as microphenocrysts and as inclusions in olivine, clinopyroxene, and pseudoleucite phenocrysts. The rare, partially resorbed, phlogopite phenocrysts are apatite free. The stubby microphenocrysts average about 0.15 mm in diameter (⊥ to the *c*-axis) with a length/breadth ratio of approximately 3:1. Smaller apatites of similar length/breadth ratios occur in the groundmass. Apatites of similar size are found in the coarser shonkinite as well (3,6,33,11 in Table 1). In the syenite pegmatite (29) most apatites are still stubby, but a few show a tendency toward elongation (length/breadth = 6:1). In the syenite

Table 1. Microprobe analyses of apatite from Shonkin Sag laccolith.

	chilled margin	shonkinite		chilled margin	shonkinite		syenite pegmatite	syenite		soda syenite	
Sample Number	7	33	3	2	6	11	29	30	18	31	10
SiO_2	0.45	0.50	0.65	0.48	0.50	0.63	0.57	0.81	0.56	0.81	0.78
Al_2O_3	0.03	0.04	0.04	0.07	0.08	0.06	0.06	0.06	0.06	0.08	0.05
FeO*	0.31	0.31	0.29	0.34	0.24	0.29	0.18	0.20	0.27	0.16	0.17
MnO	0.07	0.07	0.07	0.08	0.09	0.08	0.07	0.08	0.08	0.09	0.09
MgO	0.33	0.15	0.19	0.23	0.12	0.20	0.13	0.13	0.13	0.09	0.11
CaO	54.4	54.4	54.0	54.3	54.5	54.6	54.5	54.1	54.0	53.6	53.2
BaO	0.07	0.04	0.05	0.08	0.06	0.06	0.06	0.06	0.06	0.06	0.07
SrO	0.90	1.01	0.97	1.01	1.48	1.19	0.99	1.40	1.10	1.55	1.60
PbO	0.09	0.06	0.06	0.06	0.04	0.08	0.05	0.08	0.06	0.08	0.04
Na_2O	0.15	0.29	0.35	0.25	0.28	0.28	0.14	0.22	0.28	0.31	0.34
K_2O	0.09	0.04	0.06	0.16	0.06	0.09	0.07	0.19	0.05	0.25	0.23
P_2O_5	40.9	40.9	40.6	41.1	40.9	40.7	40.9	40.5	40.6	40.2	39.8
Nb_2O_5	0.08	0.08	0.09	0.07	0.08	0.09	0.07	0.07	0.09	0.08	0.08
Ce_2O_3	0.21	0.25	0.25	0.20	0.36	0.31	0.35	0.41	0.44	0.54	0.50
La_2O_3	0.12	0.16	0.16	0.12	0.22	0.20	0.20	0.25	0.27	0.33	0.27
Nd_2O_3	0.17	0.12	0.22	0.17	0.24	0.23	0.25	0.21	0.24	0.33	0.33
SO_3	0.15	0.22	0.30	0.15	0.22	0.22	0.22	0.22	0.17	0.15	0.17
Cl	0.34	0.34	0.18	0.32	0.16	0.12	0.23	0.11	0.23	0.12	0.19
F	2.6	2.1	2.4	2.7	2.5	2.5	3.3	3.3	3.1	3.3	3.2
Sum	101.5	101.1	100.9	101.9	102.1	101.9	102.3	102.1	101.8	102.1	101.2
$-O \equiv Cl,F$	1.1	0.9	1.0	1.1	1.1	1.1	1.4	1.4	1.3	1.4	1.3
Total	100.4	100.2	99.9	100.8	101.0	100.8	100.9	100.7	100.5	100.7	99.9
Host rock diff. index[1]	30.5	33.7	42.3	44.0	44.1	46.8	53.6	64.1	64.0	68.8	69.1

*Total Fe reported as FeO.

1. Differentiation index (Thornton and Tuttle, 1960).

(18, 30) elongate apatites predominate, averaging 0.04 mm in diameter, with lengths up to 60 times the breadth. Soda syenite apatites (10, 31) have length/breadth ratios up to an extreme of 300:1 (*e.g.*, 0.05 × 15.0 mm); most ratios are of the order of 40 to 100. The most evolved rock of the sequence (34) does not contain apatite as I erroneously reported previously (Nash and Wilkinson, 1970, Table 1).

Although superficially resembling apatite, the mineral, britholite, was discovered with the microprobe by being extraordinarily enriched in rare earth elements.

CHEMISTRY

Microprobe analyses of apatite from Shonkin Sag laccolith are given in Table 1. To a first approximation apatites are simply calcium phosphate with an hydroxyl-halogen appendage. Of interest are the subtle variations of trace element concentrations in apatite during igneous differentiation. The apatites in Table 1 are arranged in increasing order of the differentiation index of their host rocks (Nash and Wilkinson, 1970, Table 2). From this arrangement several systematic elemental variations are evident (Table 1). Si, Na, K, Sr, Ce, La, and Nd increase in abundance in apatite with differentiation. Those that decrease include Fe and Mg, while Al, Mn, Pb, Nb, and S levels, which are low throughout, exhibit no measurable trend. Of the major constituents, CaO and P_2O_5, both decrease slightly with differentiation. With respect to halogen content, the apatites are essentially fluorapatites, with fluorine content increasing with differentiation, while Cl decreases.

In general, the trace-element variation within apatites reflects the variation found for host rocks as a whole (Nash and Wilkinson, 1971). That is, those elements normally concentrated in differentiated residua, such as the rare earths, are highest in the apatites in these rocks, while those elements normally depleted during differentiation such as Fe and Mg decrease as well in apatite. Accordingly, it can be concluded that the relative enrichment or depletion of such elements in apatites can serve as indicators of relative degree of differentiation of cogenetic igneous rocks.

Apatite is absent in the most highly evolved rock of the Shonkin Sag differentiation sequence, a soda syenite (sample 34). In its place occurs the rare earth mineral, britholite, identified primarily on chemical grounds (Table 2). The ideal britholite formula is $Ce_3Ca_2(SiO_4)_3OH$, however in nature there is considerable substitution of rare earths for Ce, together with phosphorus substituting for Si, and F for OH (Vlasov, 1966). Although the britholite formula is readily obtained from apatite by the simple substitution of $RE^{3+} + Si^{4+}$ for $Ca^{2+} + P^{5+}$, whether or not britholite crystallized directly from the rare earth enriched magmatic residuum supplanting apatite, or a postmagmatic hydrothermal recrystallization of pre-existing apatite is unresolved.

The britholite occurs in a frequency of one to two grains per thin section; the grains are approximately 0.05 mm in diameter, colorless,

Table 2. Britholite analyses

	Soda Syenite	
Sample	1	2
Ce_2O_3	22.5	60.54
La_2O_3	16.3	
Pr_6O_{11}	2.79	
Nd_2O_3	6.92	
Sm_2O_3	1.66	
Eu_2O_3	0.61	
Gd_2O_3	2.85	
Dy_2O_3	0.29	
Ho_2O_3	0.98	
Er_2O_3	0.26	
Yb_2O_3	0.18	
Y_2O_3	0.40	
SiO_2	16.2	16.77
ZrO_2	0.06	--
(continued)		
TiO_2	0.02	--
Al_2O_3	0.09	--
FeO*	0.08	0.39
MgO	0.02	0.13
CaO	16.6	11.28
BaO	0.07	--
SrO	0.46	--
PbO	0.24	--
Nb_2O_5	0.13	--
Na_2O	1.00	1.85
K_2O	0.07	--
P_2O_5	7.03	6.48
S	0.07	--
Cl	0.28	--
F	3.8	1.33
Sum	102.0	100.08
less O = F,Cl	1.6	0.56
TOTAL	100.4	99.52

* Total Fe reported as FeO

1. Shonkin Sag soda syenite (Sample 34).

2. Greenland (Bröggild, 1905) (includes 1.27% H_2O).

and have straight extinction. Britholite, not before reported in the United States, occurs in the nepheline-sodalite syenite pegmatite of Julianehaab, Greenland (Böggild, 1905, 1953), a vein at Oka, Quebec (Hughson and Sen Gupta, 1964; Gold, 1966), and has been described from a number of alkaline igneous rocks (alkali syenite and granite) in the Soviet Union and China (Vlasov, 1966).

PHOSPHORUS FUGACITY

The fugacity of phosphorus as a function of temperature has been calculated for several theoretical igneous assemblages by Stormer and Carmichael (1971). Similarly, it is possible to calculate the fugacity of phosphorus during the crystallization of the Shonkin Sag laccolith by constructing a general equation for its mineral assemblage. For Shonkin Sag the following mineral relationship is appropriate:

$$\underset{\text{apatite}}{Ca_5(PO_4)_3OH} + 5/2\ \underset{\text{forsterite}}{Mg_2SiO_4} + \underset{\text{annite}}{KFe_3AlSi_3O_{10}(OH)_2}$$

$$+ 1/2\ \underset{\text{sanidine}}{KAlSi_3O_8} + 15/2\ \underset{SiO_2\text{(liquid)}}{SiO_2} = 5\ \underset{\text{diopside}}{CaMgSi_2O_6} + 3/2\ \underset{\text{fayalite}}{Fe_2SiO_4}$$

$$+ 3/2\ \underset{\text{leucite}}{KAlSi_2O_6} + 15/4\ O_2 + 3/2\ H_2O + 3P.$$

For which, with all phases at unit activity[1],

$$\frac{\Delta G_r^\circ}{2.303RT} = \frac{184{,}943}{T} - 42.09.$$

Accounting for impure phases, phosphorus fugacities at Shonkin Sag may be calculated as follows:

$$\log f_P = -1/3\Big[\frac{185{,}943}{T} - 42.09 + 5 \log a_{di} + 3/2 \log a_{1c}$$

$$+ 3/2 \log a_{fa} + 3/2 \log f_{H_2O} + 15/4 \log f_{O_2} - \log a_{ap}$$

$$- 5/2 \log a_{fo} - 15/2 \log a_{SiO_2} - \log a_{ann} - 1/2 \log a_{san}\Big].$$

In the case of Shonkin Sag, a number of thermodynamic assumptions must be made. No high temperature free energy data are available for fluorapatite, therefore the data for hydroxyapatite have been used. It is assumed that apatite, diopside and leucite are at unit activity.

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[1] Thermodynamic data are taken from Robie and Waldbaum (1968), Stull *et al.* (1966), and Kelly (1962). As noted by Stromer and Carmichael (1971), $\Delta G^\circ_{f,T}$ values for hydroxyapatite given by Robie and Waldbaum (1968) are erroneous since the value for $\Delta H^\circ_{f,298}$ as given is twice the correct value (double formula unit).

Sanidine mole percent has been taken to be 0.8 throughout, and its activity has been calculated from the excess free energy data of Waldbaum and Thompson (1968) and Thompson and Waldbaum (1968). Olivine and biotite compositions are given by Nash and Wilkinson (1970, Table 8); the olivine series is assumed to be ideal, while annite activities have been calculated from the activity coefficient of Wones and Eugster (1965). Silica activities, and water and oxygen fugacities are those given by Nash and Wilkinson (1970).

The variation of phosphorus fugacity as a function of decreasing temperature and changing composition of mineral phases during differentiation is shown in Figure 1. Phosphorus fugacities for the rocks of Shonkin Sag, which contain sanidine, leucite, and originally nepheline (now replaced by zeolites), lie intermediate between values for

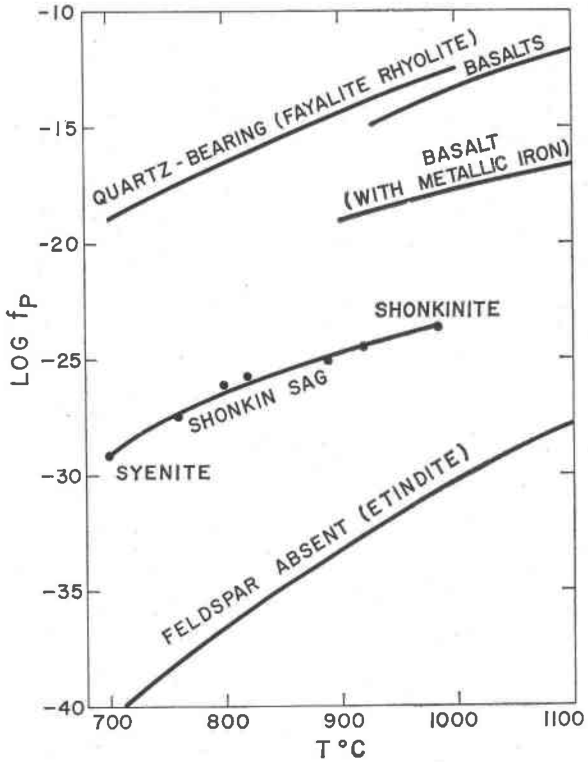

Fig. 1. Phosphorous fugacities [$\Delta G^\circ/(3)(2.303\ RT)$] as functions of temperature. Values for fayalite rhyolite, basalt, and etindite are from Stormer and Carmichael (1971). Solid circles represent data points calculated from specific mineral compositions at Shonkin Sag.

silica oversaturated rocks such as rhyolites and values for strongly undersaturated, feldspar-free assemblages such as etindites (Stormer and Carmichael, 1971). These two diverse types of rocks are distinct in terms of silica activity and oxygen fugacity which, as calculated, is in itself sensitive to silica activity (*cf.* Nash *et al.*, 1969; Nash and Wilkinson, 1970). Accordingly it is not surprising that the rocks of Shonkin Sag laccolith, undersaturated with respect to silica but containing feldspar, possess phosphorus fugacities intermediate to quartz-bearing and feldspar-free igneous rocks.

The effect of decreased oxygen fugacity on phosphorus fugacity can be demonstrated by considering a theoretical basalt assemblage which, containing a silica-rich residuum, is tholeiitic in affiinity yet contains metallic iron indicative of crystallization under relatively low oxygen fugacities. Stromer and Carmichael offer the following equation as representative of a basaltic assemblage:

$$\begin{aligned} Ca_5(PO_4)_3\,OH + 3\ MgAl_2O_4 + 45/4\ Fe_2SiO_4 & \\ &= 15/2\ Fe_3O_4 + 1/2\ Mg_2SiO_4 \\ &\quad + 2\ CaMgSi_2O_6 + 3\ CaAl_2Si_2O_6 \\ &\quad + 3/4\ SiO_2 + 1/2\ H_2O + 3\ P. \end{aligned}$$

The effective oxygen fugacity (buffered by quartz, magnetite, and silica) may be reduced through the elimination of magnetite as follows:

$$15\ SiO_2 + 15/2\ Fe + 15/2\ Fe_3O_4 = 15\ Fe_2SiO_4$$

The sum of the two above reactions gives

$$\begin{aligned} Ca_5\,(PO_4)_3\,OH + 3\ MgAl_2O_4 + 57/4\ SiO_2 + 15/2\ Fe & \\ &= 15/4\ Fe_2SiO_4 + 1/2\ Mg_2SiO_4 + 2\ CaMgSi_2O_6 \\ &\quad + 3\ CaAl_2Si_2O_8 + 1/2\ H_2O + 3\ P. \end{aligned}$$

For this reaction,

$$\begin{aligned} \frac{\Delta G_r{}^\circ}{2.303RT} = \frac{59{,}721}{T} &+ 3.15 + 15/4 \log a_{fa} + 1/2 \log a_{fo} + 2 \log a_{di} \\ &+ 3 \log a_{an} + 1/2 \log f_{H_2O} + 3 \log f_P - \log a_{ap} - 3 \log a_{sp} \\ &- 57/4 \log a_{SiO_2} - 15/2 \log a_{Fe}. \end{aligned}$$

It is assumed that ideal solid solution takes place; the substitution of appropriate values for a basaltic mineralogy, together with a water fugacity of 500 bars, and silica activities taken from Carmichael *et al.* (1970), provide for the calculation of phosphorus fugacity as a function of temperature (Fig. 1). The calculated fugacities of phosphorus for low oxygen fugacity basalts are approximately four orders of magnitude less than those calculated for magnetite-olivine basalts, which crystallize at higher oxygen fugacities.

A natural analog to low oxygen fugacity lavas are those lunar basalts which contain metallic iron. It should be emphasized that the applicability of this model to lunar lavas is critically dependent upon the assumption of a finite water fugacity. Since the lifetime of an H_2O molecule in the lunar atmosphere is about 3×10^4 sec (about nine hours) (Johnson, 1971), any H_2O which may have been released from the lunar interior by ancient magmatic activity has obviously been long since lost. There is no question of the presence of volatiles such as fluorine and chlorine in lunar magmas, as indicated by apatite and whitlockite which contain both halogens (Haines *et al.*, 1971). Although degassing of the earth's interior has provided abundant water vapor, the apparent lack of hydroxyl-bearing minerals in lunar igneous rocks leaves the presence of magmatic water in doubt. However, if a finite water fugacity was present, the lunar magmatic phosphorus fugacities would be of the order of the values shown in Figure 1 for metallic iron-bearing basalts. A reduction of the f_{H_2O} from 500 to one bar will increase the phosphorus fugacity by only about 1.3 orders of magnitude.

The calculated fugacity values are subject to considerable error. Hydroxyapatite free energy values have been used although fluorapatite is the actual phase present; moreover, it is certain that diopside activities are not unity throughout the Shonkin Sag differentiation sequence. However, in the absence of reliable activity coefficients for clinopyroxene the assumption has been made. Changes in the data input will serve to shift the f_p/T curves up or down, while the geometry will remain essentially the same, indicating a decrease in phosphorus fugacity with decreasing temperature. Moreover, the trend for the natural assemblage, which takes into account the changing chemistry of the mineral phases and volatile constituents, is consistent with those trends calculated for several diverse theoretical igneous assemblages.

BIOTITE-APATITE GEOTHERMOMETRY

Stormer and Carmichael (1971) have explored the use of coexisting biotite and apatite fluorine/hydroxyl contents as an igneous geothermometer. Using the fluorine/hydroxyl distribution curves for apatite-biotite pairs calculated by Stormer and Carmichael (1971, Fig. 2) equilibration temperatures for samples 3, 11, and 29 range from 100° to 250°C, far below crystallization temperatures calculated for samples 3 and 11 (985°–760°C, Nash and Wilkinson, 1970) and sample 29 (770°C calculated from the oxygen isotope data of Taylor, 1968). Stormer and Carmichael (1971) attribute such abnormally low temperatures at Shonkin Sag and elsewhere to the preferential subsolidus loss of fluorine in biotite as compared to apatite. The isotope data of Taylor and Epstein (1969) indicate substantial post-magmatic reequilibration of the rocks of Shonkin Sag laccolith with meteoric ground water.

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