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Apatite composition and the fugacities of HF and HCl in metamorphic fluids

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ABSTRACT. Microprobe analyses of the halogen contents of apatites from two samples of amphibolite-facies schist from Connemara, Ireland, have been used to calculate the fugacity ratios f_{HCl}/f_{H_2O} and f_{HF}/f_{H_2O} using the experimental data of Korzhinskiy. The results imply fugacities for both acids in the range 0.03 to 0.1 bars, but whereas for the lower grade rock $f_{HF} > f_{HCl}$, the migmatitic sample gives $f_{HF} \simeq f_{HCl}$. An independent estimate of f_{HF}/f_{H_2O} from the biotite composition in one sample is in acceptable agreement with the result obtained from apatite.

KEYWORDS: apatite, halogens, metamorphic fluid, schist, Connemara, Ireland.

MOST studies of metamorphic fluid composition are concerned only with the principal gas species present, but aqueous fluids in particular can also carry significant quantities of dissolved material, predominantly in the form of chloride complexes at moderate to high grades but with significant dissociation of the dominant species (normally NaCl) in the greenschist facies or at lower temperatures (Poty *et al.*, 1974; Eugster, 1977; Eugster and Gunter, 1981). It is possible to calculate the content of the major species in aqueous solution in equilibrium with a range of common mineral species from thermodynamic data compilations or directly from the original experiments, provided that a reasonable estimate can be made of the total chloride content of the fluid phase, e.g. from fluid inclusion studies, and provided that chloride is indeed the dominant anion. It is of particular interest to know the content of acid species in the fluid phase under different conditions, because migration of fluids of different acidities has the potential for metal transport and ore formation. This paper describes a means of estimating HF and HCl fugacities in metamorphic fluids.

One way to measure the halogen-acid contents of metamorphic fluids is to determine the halogen concentrations in coexisting hydrous minerals in which OH can be replaced by F or Cl because the extent of such substitution depends directly on the relative fugacities of H_2O, HF and HCl in the fluid. This can be most readily done for substitution of F for OH because F is often present in hydrous minerals in detectable quantities. Stormer and Carmichael (1971) considered $F \rightleftharpoons OH$ exchange between biotite and apatite in igneous systems and Munoz and Luddington (1974) have calibrated the same exchange between biotite and fluid over a range of metamorphic temperatures as a function of T and biotite composition using a fluorine buffer technique, thereby providing a means of calculating f_{HF} directly from biotite analyses. Cl is, however, strongly partitioned into the fluid phase and in metamorphic rocks it is seldom present in any mineral in quantities that can be readily determined. Apatite is, however, widespread in metasediments and may contain sufficient chlorine for quantitative analysis. Furthermore, since fluorine is usually the dominant anion in metamorphic apatites, their compositions reflect the fugacities of both HF and HCl. Korzhinskiy (1981) has carried out a series of experiments with halogen buffers on the HF-H_2O-apatite and HCl-H_2O-apatite systems at 1-4 kbar and 500-700 °C, and has calculated the behaviour in the HCl-HF-apatite system assuming ideal solution between the fluor-, chlor- and hydroxyapatite end members. These results have been used here to calculate f_{HCl} and f_{HF} in the metamorphic fluid in equilibrium with two samples of metapelite from Connemara, Ireland.

Sampling and analysis. Both samples come from eastern Connemara and were included in the study of regional metamorphism by Yardley *et al.* (1980) from which temperature estimates are taken. The geology of the region is shown in Leake (1981). Sample BY 111 (Irish National Grid Ref. L 931 526) is a staurolite-sillimanite schist, lacking muscovite, from the upper staurolite-sillimanite transition zone, for which a temperature of around 620 °C has been estimated, while BY 244 (Grid Ref. L 934 463) is a migmatized two-feldspar biotite-sillimanite-cordierite schist with coexisting magnetite and ilmenohematite for which a temperature of 700 °C is taken. This last figure is supported by recent work

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by Barber and Yardley (in press), who also estimate a pressure around 5 kbar for both zones, a result that is not surprising in view of the earlier conclusion (Yardley *et al.*, 1980) that heating by synorogenic intrusives was a major heat source for the high-temperature phase of metamorphism in the region.

Microprobe analyses of apatite were performed using the ARL EMX-SM wavelength dispersive microprobe at the University of Washington, Seattle. Each analysis given in Table I is the mean obtained from 25-second counts on each of approximately 8 points from 2 to 4 adjacent grains, and results from different parts of the same probe slide are presented separately. A large spot size (*c.* 10 microns) was used throughout to avoid beam damage. The principal analytical problem was the determination of Cl, and for this a range of well-analysed natural apatites were used as standards. Because of the very low levels of Cl, accurate determination of the background is of paramount importance, and this was done by counting at both sides of the peak position on one of the apatites analysed. Mean peak and background counts are included in Table I and demonstrate that, although the peak : background ratio is small, the peak counts are significantly above background and the difference between samples is real. In other respects the apatite compositions are straightforward; they are fluorapatites with no significant substitution for phosphate. Hydroxyl contents in the formula have been estimated assuming F + Cl + OH = 1.

TABLE I. *Microprobe analyses of apatites*

	BY 111*a*	BY 111*b*	BY 244*a*	BY 244*b*
CaO	55.06	56.03	54.89	54.62
SrO	0.01	0.01	0.01	0.02
Y_2O_3	0.14	0.18	0.16	0.19
F	3.33	3.41	3.25	3.11
Cl	0.01	0.01	0.03	0.04
P_2O_5	41.81	42.18	42.02	41.86
Total	98.96	100.38	98.98	98.52
No. of ions on the basis of 13 (O, OH, F, Cl)				
Ca	5.017	5.040	4.996	4.997
Sr	0.0005	0.0005	0.0005	0.001
Y	0.006	0.008	0.007	0.009
F	0.896	0.905	0.873	0.840
Cl	0.001	0.001	0.004	0.006
P	3.010	2.998	3.022	3.026
OH*	0.103	0.093	0.123	0.154
Raw count data for Cl, mean of 25-second counts, 1σ errors				
Peak	436 ± 18	400 ± 4	520 ± 25	567 ± 19
Backgr. 1	—	—	349 ± 10	—
Backgr. 2	—	—	358 ± 15	—

Notes: BY 111*a* and *b* come from different areas of the same slide. BY 244 is migmatized and analysis *a* is from restite, *b* from leucosome vein.

* OH estimated by difference.

Calculation of HF and HCl fugacities in the metamorphic fluid. Korzhinskiy (1981) obtained linear relationships between the log fugacity ratio in the fluid phase, log (f_{HCl}/f_{H_2O}) or log (f_{HF}/f_{H_2O}), and the log ratio of the mole fractions of the appropriate apatite end members, i.e. log $(X_{Cl\text{-}ap}/X_{OH\text{-}ap})$ or log $(X_{F\text{-}ap}/X_{OH\text{-}ap})$. Equilibrium constants, K_e, can be defined for both the Cl–OH and the F–OH system, with the form:

$$K_e^{Cl/OH} = \frac{f_{HCl} \cdot a_{OH\text{-}ap}}{f_{H_2O} \cdot a_{Cl\text{-}ap}}.$$

Korzhinskiy (1981) provides expressions for $K_e^{Cl/OH}$ and $K_e^{F/OH}$ as a function of P and T that were obtained directly from the experimental data and are not necessarily thermodynamically consistent. However, they appear to fit the data well and since inconsistencies are less than experimental uncertainty and the experiments were performed over a similar range of temperatures to those for the formation of the Connemara rocks, Korzhinskiy's expressions have been used directly in this study to obtain the values of K_e given in Table II.

Combining values for K_e at appropriate P and T with mineral compositions from Table I, and assuming ideal solid solution between chlor-, hydroxy-, and fluorapatite end members, yields values for log (f_{HCl}/f_{H_2O}) and log (f_{HF}/f_{H_2O}); f_{HCl} and f_{HF} have been obtained from these using water fugacities from Burnham *et al.* (1969) for the appropriate P–T conditions assuming that the fluid is sufficiently dilute that $f_{H_2O}^{fluid} = f_{H_2O}^{\circ}$ where $f_{H_2O}^{\circ}$ is the fugacity of pure water at the P and T of interest. This calculation is not at all sensitive to uncertainties of a few hundred bars in f_{H_2O}. Full results are given in Table II.

TABLE II. *Calculations of gas fugacities from the analyses of Table I*

Sample	BY 111*a*	BY 111*b*	BY 244*a*	BY 244*b*
P (bars)	5000	5000	5000	5000
T (°C)	620	620	700	700
f_{H_2O} (bars)	3143	3143	3810	3810
$\log K_e^{Cl/OH}$	−3.1933	−3.1933	−3.1105	−3.1105
$X_{Cl\text{-}ap}/X_{OH\text{-}ap}$	0.0140	0.0153	0.0352	0.0375
$\log(f_{HCl}/f_{H_2O})$	−5.047	−5.009	−4.564	−4.536
f_{HCl} (bars)	2.82×10^{-2}	3.08×10^{-2}	1.1040	0.1108
$\log K_e^{F/OH}$	−5.6595	−5.6595	−5.4045	−5.4045
$X_{F\text{-}ap}/X_{OH\text{-}ap}$	8.695	9.712	7.122	5.444
$\log(f_{HF}/f_{H_2O})$	−4.720	−4.672	−4.552	−4.669
f_{HF} (bars)	6.69×10^{-2}	6.69×10^{-2}	0.1069	8.16×10^{-2}

It is apparent that the between-sample variations in f_{HF} and f_{HCl} are much greater than the variation within samples, and that the fugacity of both acids is greater in the higher-grade rock. This is precisely what would be expected in the case of chloride solutions, for which a considerable body of experimental and theoretical literature exists, but it is interesting to note that the variation in HF fugacity is apparently smaller.

An independent estimate of f_{HF}. An estimate of f_{HF} can also be made from the composition of biotite mica using the experimental study by Munoz and Luddington (1974) of fluoride-hydroxyl exchange between fluid and biotite. Microprobe analyses of biotites, including fluoride determinations for a number of samples, are given by Yardley *et al.* (1980), and the mean fluorine content of 0.27% for BY 111 given there appears to be typical for the region. The uncertainty in estimating the OH content of the mica is much greater than for apatite because of the presence of an unknown amount of Fe^{3+}, but the assumption that $F + OH = 2$ gives $X_{F\text{-bio}}/X_{OH\text{-bio}} = 0.0336$. Munoz and Luddington (1974) found that fluoride-hydroxyl exchange depends on the Mg/Fe ratio of biotite, but not appreciably on its Al content, so taking $X_{Mg} = 0.42$ for biotite in BY 111 and $T = 620\,°C$ gives:

$$\log K = \log (X_{F\text{-bio}}/X_{OH\text{-bio}}) + \log (f_{H_2O}/f_{HF}) = 2.9071.$$

From this, $\log (f_{HF}/f_{H_2O}) = 4.381$, which is in good agreement with the values tabulated for this sample in Table II, deviating by a factor of 2, or little more than the margin of uncertainty in the experimental determinations on apatite-fluid equilibria.

Conclusions. With careful analysis, apatite appears to act as a useful sensor of the fugacities of HF and HCl in metamorphic fluids, and indeed in the case of HF, apatite may in fact buffer the fluid composition in many rocks. For HCl, the amount of chlorine present in the fluid phase is probably so large relative to that in apatite or other minerals that buffering of fluid composition by the solid phases is less likely.

Apatite is stable over the entire range of metamorphic conditions, and so it could be argued that its composition now may not represent that at the peak of metamorphism. However, the grains do not exhibit zoning and the samples analysed show no evidence for late-stage recrystallization; in view of this and the agreement with results from biotite, the values given here are believed to represent peak metamorphic conditions.

Estimates of f_{HCl} in the fluid phase are of considerable significance for studies of metasomatism and ore-formation during metamorphism, because reaction between HCl and solid phases provides a means of taking up metals into solution, and hence fluids with high f_{HCl} will have the greatest potential for mass transfer. The role of HF is less clear but there is here evidence to indicate that fluoride species might be important in metamorphic fluids. Systematic analysis of apatites within a metamorphic terrane may provide an interesting indicator of fluid movement pathways.

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