Fluorine-deficient apatite

PURE, end-member fluorapatite has the formula $Ca_{10}(PO_4)_6F_2$. Natural apatite does not have this composition because extensive substitutions occur for both Ca and PO_4 (Lehr et al., 1967; McClellan and Lehr, 1969; McClellan, 1980; McArthur, 1978, 1985). In sedimentary apatite concentrations of F and CO_2 are usually greater than 1% and the mineral is termed francolite* (Sandell et al., 1939; McConnell, 1973). The CO_3^{2-} ion substitutes for PO_4^{3-} and may occupy 30% of the PO_4^{3-} sites in the mineral structure (McClellan, 1980). Such highly-substituted apatite also contains F in excess of the 2 moles per formula weight that is present in fluorapatite. This 'excess F' is commonly assumed to balance the loss of negative charge that results when CO_3^{2-} substitutes for PO_4^{3-}. The proposal that PO_4 is replaced by $(CO_3 + F)$ appears to have first been made by Bornemann-Starinkevitch (1938) disguised in confusing proposals that francolite could be represented as a mixed oxide. Support and clarification soon came in Bornemann-Starinkevitch (1939) and from Belov (1939). Objections to this substitution have been made on the grounds (1) that the electrostatic repulsion between F^- and CO_3^{2-} would be too high for this species to exist (Carlstrom and Glass, 1963) and (2) that no relation exists between CO_2 and (F + OH) in natural francolites (McConnell, 1970). Although the substitution has been widely cited no compelling evidence has been presented to confirm it. Indeed, McClellan (1980) suggests that only 40 mole% of structural CO_2 is accompanied by additional F and he gives the general formula of francolite as:

$$Ca_{10-x-y}Na_xMg_y(PO_4)_{6-z}(CO_3)_zF_{0.4z}F_2$$

The evidence exists, nevertheless, for the substitution of CO_3^{2-} and F^-, on a numerical basis of 1:1, in unaltered francolite. Such francolite is rare on land but common in phosphorites on the sea-floor. In order to avoid inter-laboratory bias only data obtained in the author's laboratory are considered. Data on structural CO_2 and F/P_2O_5 ratios in unaltered francolite are given by Benmore (1984), McArthur (1985), McArthur et al.

* The term carbonate fluorapatite is preferred to francolite in some countries.

(1988, Cape Province Margin), and Table 1. A plot of these data—F/P_2O_5 weight % ratio versus% structural CO_2—is shown in Fig. 1. The use of the F/P_2O_5 ratio circumvents the need to recalculate the data to a pure-francolite basis. Measurement of CO_2 was by the peak-pair method of Gulbrandsen (1970) which gives the % CO_2 in pure francolite. Bremner (1978) and Glenn et al. (1988) have shown that chemical and X-ray determinations of structural CO_2 in sea-floor francolite are indistinguishable, within error.

A least-squares regression of F/P_2O_5 on CO_2 is shown on Fig. 1. The slope of the line is 1.54 ± 0.12 and its intercept on the F/P_2O_5 axis is 5.1 ± 0.61. The data are somewhat skewed toward high values. This distorting effect can be partially removed by regressing means of each data set. Similar results are obtained: the slope is 1.58 ± 0.11 and the intercept is 4.9 ± 0.52. Also drawn on Fig. 1 is the line for replacement of PO_4^{3-} by $(CO_3^{2-} + F^-)$ on a 1:1 mole basis. It is defined at the upper end by the end-member composition given by McClellan (1980) for highly substituted francolite (point A on Fig. 1; 34% P_2O_5, 6.3% CO_2 and 5.04% F). The lower end of the line is defined by subtracting CO_2 and F from McClellan's end-member, in a mole ratio of 1:1, to give 0% CO_2. The F remaining is used to calculate a F/P_2O_5 value for the 'unsubstituted' end-member (point B on Fig. 1). The regression line and the theoretical line are within error of each other. The data on samples from many locations conform well to the theoretical line. It is interesting to see that the two analyses of francolite quoted by Sandell et al. (1939) also fall very close to the line (see key to Fig. 1).

Fig. 1 shows conclusively that CO_3^{2-} and F^- are coupled numerically on a mole basis of 1:1 as a joint substitution for PO_4^{3-}. It does not prove that PO_4^{3-} is actually replaced by the species $(CO_3.F)^{3-}$. The problem of where the 'excess F' resides in the structure cannot be resolved by chemistry alone and awaits further crystallographic work.

Fluorine-deficiency in apatite has been noted by McClellan and Lehr (1969), principally in insular and igneous apatites. In such samples they note that 'infrared examination showed all these apatites contained hydroxyl which apparently had
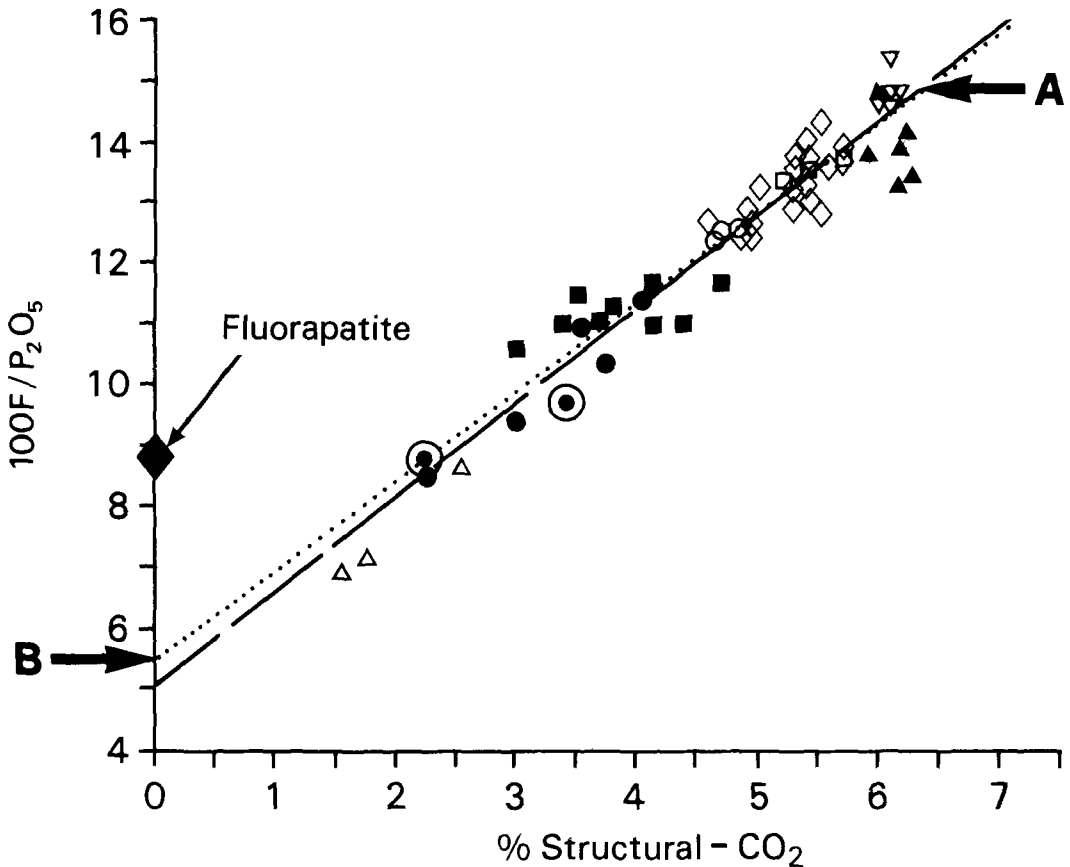
FIG. 1. Structural CO_2 vs. $100F/P_2O_5$ wt.% ratio for unaltered francolite. Data sources listed in text and Table 1. Solid circle; Peru, Sechura: Open triangle; Peru, Ocucaje: Solid square; Peru/Chile margin: Solid triangle; Moroccan margin: Diamond; Cape Province margin: Open square; Chatham Rise: Open triangle, inverted; Blake Plateau: Open circle; Californian Margin. A = highly substituted end-member francolite (McClellan, 1980). B = A minus $(CO_2 + F)$. Dotted circle = analyses of Sandell et al. (1939).

substituted for part of the fluorine'. In Recent francolite from the continental margins of Namibia and Peru/Chile McClellan (1980) notes 'the F/P_2O_5 ratio is so low that some OH for F substitution may be taking place'. The intercept of the regression line in Fig. 1 shows that this is almost certainly the case in all unaltered francolite, and not only for the francolite in Recent phosphorites. The F deficiency noted by McClellan (1980) cannot be a shortfall of 'excess F' (i.e. that accompanying CO_2) or the 1:1 relationship seen in Fig. 1 would not exist. The deficiency is in F that is structurally incorporated in the normal crystallographic positions.

The regression line for the mean data has an intercept on the F/P_2O_5 axis of 4.9 ± 0.52. This represents a F content in the apatite of $2.07 \pm 0.22\%$ or, in molar terms 1.10 ± 0.12 atoms of F^-. The remaining 0.90 ± 0.12 atoms of F^- in

the structural sites has been replaced, presumably by OH^-. If so, the F/OH ratio is within error of unity. For unaltered francolite the generalized francolite formula of McClellan (1980) can therefore be rewritten

from $Ca_{10-x-y}Na_xMg_y(PO_4)_{6-z}(CO_3)_zF_{0.4z}F_2$

to

$Ca_{10-x-y}Na_x Mg_y (PO_4)_{6-z} (CO_3)_z F_z . F. OH.$
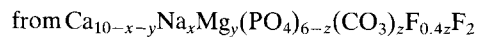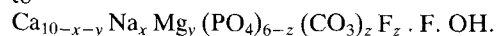
McClellan's end-member francolite contains 0.45 moles per formula weight of Na. This value is suspiciously close to $\frac{1}{2}$. All unaltered marine francolite contains similar amounts and the concentrations are not related to substitution of CO_2 or F (McArthur, 1985). There are many ways to balance the deficiency of positive charge. One interesting speculation is that francolite may form with a Na/OH of 1 with $\frac{1}{2}$ of the OH replaced

Table 1.

SAMPLE	CO_2	$100F/P_2O_5$	SAMPLE	CO_2	$100F/P_2O_5$
BLAKE PLATEAU			**MOROCCAN MARGIN**		
BP1	5.9	14.2	135	6.2	14.0
BP2	6.0	14.7	136(1)	6.2	14.2
BP3	6.1	15.4	1022(1)	6.3	13.6
BP4	6.1	14.6	1022(2)	6.0	14.8
BP5	6.2	14.9	139(1)	5.9	13.8
BP6	6.1	14.9	966(2)	6.2	13.3
CHATHAM RISE			**PERU/CHILE MARGIN**		
CMI-CX-45	5.4	13.6	PD-1205(B1)	4.1	11.7
CMI-C-46B	5.2	13.4	-1205(B2)	3.8	11.3
CMI-C-C70	5.7	13.8	-15-13	3.5	11.5
			-15-17(B2)	3.7	11.1
CALIFORNIAN MARGIN			-15-17(B3)	4.3	11.0
			-18-30(B1)	3.4	11.0
AHF 7406	4.7	12.6	-19-33(L)	3.0	10.6
AHF 14399	4.8	12.4	-19-37(A)	4.4	11.0
AHF 14414	4.8	12.6	-2408-1212	4.7	11.7
PERU, SECHURA			**PERU, OCUCAJE**		
P81/SM-1P(C)	3.0	9.4	P81-OC-A(1)	1.59	6.9
-2P	2.3	8.5	-A(2)	1.79	7.2
-4P	3.7	10.4	-A(9)	2.55	8.7
-6P	4.0	11.4			
-MP(A)	3.6	11.0			

by H_2O. Many analyses of sea-floor *phosphorite* show the presence of combined water (e.g. Baturin, 1982; McArthur *et al.*, 1988). Unfortunately, there are no reliable determinations of structural H_2O in sea-floor *francolite* with which to test this suggestion.

References

Baturin, G. N. (1982) *Phosphorites on the sea-floor. Origin, composition, distribution.* Elsevier, 343 pp.

Benmore, R. A. (1984) *Stable isotopic and geochemical evidence for the origin of phosphates.* Ph.D. thesis, Univ. London, unpub., 242 pp.

Belov, I. D. (1939) On some isomorphic substitutions in the apatite group. *Dokl. Acad. Nauk SSSR*, **22**, 89–92.

Bornemann-Starinkevitch, I. D. (1938) On some isomorphic substitutions in apatite. Ibid. **19**, 253–9.

—— (1939) On isomorphic substitutions in apatite. Ibid. **22**, 113–5.

Bremner, J. M. (1978) *Sediments on the continental margin off South West Africa between latitudes 17° and 25°S.* Ph.D. thesis, Univ. Capetown, 300 pp.

Carlstrom, M. D. and Glass, J. E. (1963) Ultrastructure of dental enamel: V. The state of water in human enamel. *J. Ultrastructure Res.* **8**, 24–9.

Glenn, C. R., Aurther, M. A., Yeh, H.-W. and Burnett, W. C. (1988) Carbon isotopic composition and lattice-bound carbonate of Peru–Chile margin phosphorites. *Mar. Geol.* **80**, 287–307.

Gulbrandsen, R. A. (1970) Relation of carbon dioxide

content of apatite of the Phosphoria Formation to regional facies. *U.S. Geol. Survey Prof. Paper*, **700B**, 9–13.

Lehr, J. R., McClellan, G. H., Smith, J. P. and Frazier, A. W. (1967) Characterisation of apatites in commercial phosphate rocks. *Coll. int. sur les phosphates mineraux solides*, Toulouse, p. 29.

McArthur, J. M. (1978) Systematic variations in the contents of Na, Sr, CO_3 and SO_4 in marine carbonate-fluorapatite and their relation to weathering. *Chem. Geol.* **21**, 89–112.

—— (1985) Francolite geochemistry compositional controls during formation, diagenesis, metamorphism and weathering. *Geochim. Cosmochim. Acta*, **49**, 23–35.

—— Thomson, J., Jarvis, I. A., Fallick, A. E. and Birch, G. F. (1988) Eocene to Pleistocene phosphogenesis off western South Africa. *Mar. Geol.* **85**, 41–63.

McClellan, G. H. (1980) Mineralogy of carbonate-fluorapatite. *J. Geol. Soc. London*, **137**, 675–81.

—— and Lehr, J. R. (1969) Crystal chemical investigations of natural apatites. *Am. Mineral.* **54**, 1379–91.

McConnell, D. (1970) Crystal chemistry of bone material. Hydrated carbonate apatites. Ibid. **55**, 1659–69.

—— (1973) *Apatite.* 111 pp. Springer-Verlag.

Sandell, E. B., Hey, M. H. and McConnell, D. (1939) The composition of francolite. *Mineral. Mag.* **25**, 395–401.

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