Francolite in a concretion from argillaceous sediments in the Westphalian of Yorkshire

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PHOSPHATES are not uncommon in Coal Measures' sediments and collophane, a colloform variety of apatite, is frequently encountered. Their chemistry and origin are, however, not well documented partly because of analytical difficulties associated with mixtures of microcrystalline minerals. In a chemical study of sideritic concretions from a clay-rich sediment sequence in a quarry of the Hepworth Iron Co., Penistone, Yorkshire, (Pearson, 1973; 1974a), the phosphate contents of concretions were found to be enriched relative to the host sediments by factors of ten to a hundred. Deans (1938) interpreted macrosegregations of francolite (carbonate fluorapatite) in an oolitic ironstone as being of late diagenetic origin from textural evidence. In the present case initial transmitted-light microscopy had suggested phosphate was present as a cryptocrystalline groundmass and probably of early diagenetic origin. Detailed chemical, XRD, and microprobe work has been carried out in order to characterize the phosphate and provide a clue to its origin.

Petrography and mineralogy. Concretion 33 was chosen for the present study since acid soluble analysis of the whole concretion had shown the highest phosphate content and its petrography appeared to be unique amongst the concretions in this sequence.

The transmitted-light photomicrographs in fig.1 show relatively large (30-100μm) high-birefringence spherulites set in an apparently isotropic light brown groundmass in which occasional subhedral quartz (5-40μm) and flakes of illite or mica (retaining the original bedding fabric) are visible. Small opaque grains (1-10μm) can be readily identified as pyrite in the reflected light image and are seen to be present with subhedral quartz within both spherulites and groundmass. The spherulites alone show birefringence and Fe and Mg X-ray distribution images indicate they are magnesian siderites (? pistomesite).

The P image confirms the matrix as dominantly phosphatic but the Si and Al images show intimate mixing with an aluminosilicate phase, presumably a clay mineral. A single large patch of Al-rich (? kaolinitic) clay can be seen top centre. Quartz is highlighted well in the Si image and is more prominent than at first suspected. The two bright streaks on the Mg image possibly represent chlorite flakes in cross section as they are not shadowed on the Si, Al images.
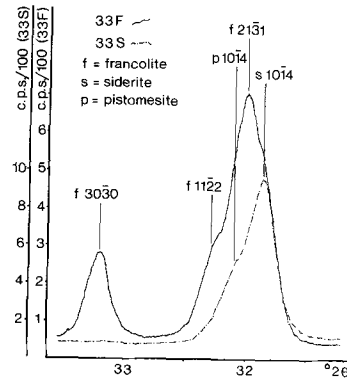

Fig.2. Cu-Kα diffractometer traces (1°/min.) for the separated fractions.

XRD shows the approximate mineralogical composition of the concretion to be siderite 50%, apatite 25%, clay minerals 14%, and quartz 7%. Clay minerals present include kaolinite, illite, and chlorite with traces of a mixed layer mineral.

Preparation of material for chemical analyses. 50g of crushed sample was sedimented in water in batches to remove fines (<30μm) and the remaining (<30μm) material split into four fractions (30-50μm, 125-212μm and 212μm) by wet sieving. The three coarser fractions were separated by density in methylene iodine (S.G. 3.4) and examined optically and by XRD. On the basis of this the three 'float' fractions were combined to give a phosphate-rich fraction (33F) and the 50-125μm 'sink' fraction selected as the purest siderite specimen (33S). Diffractometer traces in fig.2 show that a good, if incomplete separation is achieved. Note that magnesian siderite (pistomesite) is present in 33S, indicating a clear affinity to other sideritic concretions in the sequence. The 30-50μm fraction (not MeI$_2$ separated) was also nearly pure siderite whilst the <30μm fraction showed no appreciable change from the bulk sample.

After agate grinding and homogenizing, the two selected fractions were analysed for acid-soluble cations and CO_2 following the procedure in Pearson (1974a) and for H_2O^- and H_2O^+ by ignition under N_2. Fluorine was determined by a pyrohydrolytic method after Clements et al. (1971). The data shown in table I are averages of duplicates in each case.

Calculation of phase compositions. The acid-soluble analyses of both fractions comprise carbonate, phosphate, and a small silicate contribution. If it is assumed that these phases have the same composition in each fraction then the phase compositions may be evaluated. As two siderites are present some separation will occur (Pearson, 1974b) but may be reasonably ignored here. Corrections are made for cations leached from silicates by reference to Al in the leachate (Pearson, 1974a) and for H_2O^+ present in clay minerals assuming an average shale value of 8% H_2O^+ for the insoluble residue.

An initial estimate of the apatite composition is obtained from 33F by assuming all the Ca is in apatite. This is used to obtain a
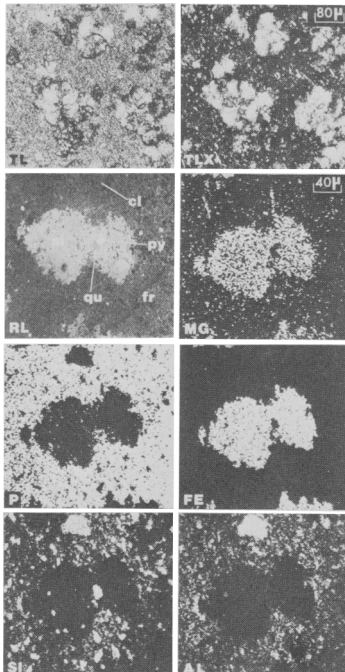

Fig.1 Siderite, francolite, pyrite, quartz, and a clay mineral in concretion 33; TL, TLX, transmitted light (plane and crossed polars); RL, reflected light and Mg, P, Fe, Si, Al X-ray distribution photographs for these elements. The lower six photographs are of the same area.

TABLE I.

	Acid Soluble		Corrected	
	33F	33S	33F	33S
Al_2O_3	1.02 ± 0.03	0.46 ± 0.03	-	-
P_2O_5	20.91 ± 0.30	4.37 ± 0.10	20.91	4.37
CaO	30.50 ± 0.10	9.16 ± 0.05	30.19	9.02
MgO	1.23 ± 0.02	4.42 ± 0.04	0.80	4.20
FeO	10.54 ± 0.10	40.57 ± 0.35	8.72	39.73
MnO	0.11 ± 0.01	0.41 ± 0.01	0.08	0.40
CO_2	9.06 ± 0.30	31.10 ± 0.50	9.06	31.10
F	2.10 ± 0.02	0.42 ± 0.02	2.10	0.42
H_2O^+	*2.81 ± 0.30	*1.10 ± 0.20	0.71	0.32
H_2O^-	0.75 ± 0.02	0.48 ± 0.02	0.75	0.48
	79.03 ± 1.20	92.49 ± 1.32	73.32	90.04
Insoluble Residue	20.2	8.1		

All values % whole rock

* bulk sample: includes clay mineral OH

TABLE III.

Reflection	I/I_1	$°2\theta$ Cu Kα	d (Å)	d (Å)†	I/I_1†
10$\bar{1}$0	4	10.95	8.08	8.04	18
20$\bar{2}$0	4	22.00	4.04	4.04	16
11$\bar{2}$1	4	23.04	3.86	3.86	2
0002	20	25.87	3.444	3.43	20
10$\bar{1}$2	8	28.15	3.170	3.16	6
21$\bar{3}$0	12	29.20	3.052	3.05	35
21$\bar{3}$1	100	31.98	2.799	2.790	55
11$\bar{2}$2	16	32.29	2.773	2.769	16
30$\bar{3}$0	36	33.20	2.698	2.692	100
20$\bar{2}$0	16	34.20	2.622	2.619	8
30$\bar{3}$1	4	35.80	2.508	2.506	4
31$\bar{4}$1	8	42.20	2.142	2.134	4
30$\bar{3}$2	8	42.50	2.128		
11$\bar{2}$3	4	43.94	2.061		
20$\bar{2}$3	4	45.45	1.996		
22$\bar{4}$2	16	47.02	1.933	1.931	12
31$\bar{4}$2	8	48.35	1.882		
21$\bar{3}$3	12	49.65	1.836	1.834	10

† Francolite from Staffel, Germany. Brophy and Nash (1968). XPDF card no. 21-141.

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siderite Ca content from 33S and the process repeated to self-consistency. All Fe, Mn and Mg is assumed to be in siderite and CO_2 equivalent to carbonate cations calculated (table II). The excess of determined over equivalent CO_2 is not experimental error and must be attributed to the phosphate phase which is thus a carbonate fluorapatite and will be referred to as francolite. Its oxide composition is calculated in table II together with the number of atoms per formula unit on the basis Ca = 10. Thus the formula may as a first approximation be expressed:

$$Ca_{10}(PO_4)_{5.59}\ (CO_2)_{1.00}\ (OH_{1.49}F_{2.10}).$$
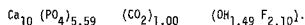
The carbonate phase composition (an average for siderite and pistomesite) is also calculated in table II. It is very comparable with that in other concretions in the sequence (Pearson, 1974a).

TABLE II

	Siderite phase †						Francolite phase †				
	FeO	MnO	CaO	MgO	CO_2(cal.)	CO_2(det.)	CaO	P_2O_5	F	H_2O	CO_2
33 F	8.72	0.08	0.62	0.80	6.75	9.06	29.57	20.91	2.10	0.71	2.31
33 S	39.73	0.40	2.83	4.20	31.39	31.10	6.79	4.37	0.42	(0.32)	0.34

† values % whole rock

Siderite composition (33 S) mole % carbonate phase

$Fe CO_3$	$Mn CO_3$	$Ca CO_3$	$Mg CO_3$
81.55	0.83	6.44	11.18

Francolite composition (from 33 F)

	wt.% phosphate phase	No. of atoms	(1)	(2)
P_2O_5	38.22	P	5.588 }16.583	5.281
CO_2	4.222	C	0.995	0.940
CaO	54.04	Ca	10	9.451
F	3.838	F	2.096 }13.590	1.980
H_2O^+	1.298	OH	1.494	1.412
	101.62	O,OH,F	27.758	26.234
O ≡ F	1.62	O	24.168	22.841
	100.00	*charges	53.41	50.48

(1) on basis Ca = 10. Equivalent density calculated from cell dimensions is 3.333.

(2) Assuming a density of 3.15.

* Total cation charges assuming conventional charges of 5, 4, 2 and 1 for P, C, Ca and H.

Measurement of unit cell parameters. A $\frac{1}{2}°$/min Cu Kα diffractometer trace was indexed as far as possible by comparison with powder data for hydroxyapatite (from Brown, 1961). 2θ angles for 18 lines between 10° and 50°, corrected for angular shift by reference to adjacent quartz lines, are indexed and d values recorded in table III.

A least squares calculation gives the lattice parameters as $\underline{a}$ = 9.349Å, $\underline{c}$ = 6.887Å with $\underline{c}/\underline{a}$ = 0.737. These dimensions are very similar to those given for a francolite from Staffel, Germany (Brophy and Nash, 1968): $\underline{a}$ = 9.346Å, $\underline{c}$ = 6.887Å, $\underline{c}/\underline{a}$ = 0.737. The relative X-ray intensities for their reflections are however considerably different from those recorded for the present mineral, thus the two specimens are unlikely to be structurally identical.

The structure of francolite. Deer, Howie and Zussman (1962) have summarized the problems arising from accomodation of C in the apatite structure. Early suggestions that X-ray amorphous $CaCO_3$ is absorbed on the apatite surface (Thewlis et al., 1939) or that CO_3^{2-} replaces PO_4^{3-} by surface ion exchange (Neuman and Neuman, 1953) have been discredited by more recent work showing that carbonate fluorapatites have distinctive refractive indices (McConnell, 1952), XRD patterns (Altschuler et al., 1953), and infra-red spectra (Brophy and Nash, 1968) that can be simulated neither by mixtures of calcite and fluorapatite nor by surface exchange.

Structural substitution by C at both P and Ca positions has been proposed by several authors (e.g. McConnell, 1960) though the latter rules out any possibility of CO_3^{2-} replacing OH^-, F^- ions. Recalculation of the present analysis (following Sandell et al., 1939) from an equivalent density of 3.333 to an assumed more realistic one of 3.15 (table II) reduces the anion total to an acceptable figure. All H and C atoms can now be assigned to F, P and Ca sites if the method of Brophy and Nash (1968) is followed to give:

$$(Ca_{9.45}C_{0.57})\ (P_{5.28}[H_4]_{0.35}C_{0.37}O_{24})\ (OH_{0.02}F_{1.98})$$
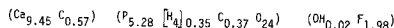
This must be regarded with some caution in view of the uncertainty in the H_2O^+ figure.

A geological interpretation. Several possible origins have been suggested for phosphatic nodules.

Such nodules may represent fossil coprolites in which the phosphate is derived from organic residues. Zangerl and Richardson (1963) described apatite-bearing coprolites with a light to dark brown structureless groundmass, which they assumed to be collophane. A non-concretionary origin is implicit.

Ames (1959) synthesized apatite by replacement of calcite in $0.3\underline{M}$ Na_3PO_4 and analysed samples at intervals. Material approximating to francolite could be obtained by this method but he found no evidence for the inclusion of CO_3^{2-} into the apatite lattice when it was crystallized from solution. He concluded that the formation of marine phosphorites by diagenetic replacement of Ca CO_3 was feasible in Ca-saturated water with PO_4^{3-} > $0.1\mu g/ml$ and pH > 7.0.

Gluskoter et al. (1970) demonstrated early replacement of cellulose by carbonate fluorapatite in a petrified log in black shales but there are no recorded instances where direct precipitation of francolite from solution under geological conditions has been proved.

In the present case the petrographic and microprobe evidence shows that francolite is present as cryptocrystalline matrix material in which detrital micas and other layer silicate grains are partly orientated. The siderite spherulites do not appear to be replacive and probably formed very early in the diagenetic history of these clay-rich sediments. A kaolinite X-ray study on a sideritic concretion from the same sequence (Oertel and Curtis, 1972) showed near-random orientation at the concretion centre indicating that siderite growth began in uncompacted sediment. It may be therefore that in concretion 33 the matrix crystallized slightly later but still in relatively watery sediment since the acid insoluble residue is no higher than average and no obvious distortion or oriented flakes around the siderites can be seen.

A coprolite origin is improbable. Whilst the absence of any gastric charactersitics may be explained by destructive phosphate replacement, the similarity of the quartz : kaolinite : mica of the residue with that of the host shale suggests a common origin. All concretions in the sequence show phosphate enrichment relative to the shale, yet, with the exception of a cone-in-cone concretion, calcite is absent. The latter concretion is of undoubted late diagenetic (post-compactional) origin and thus a replacement mechanism seems not unreasonable. Early concretional and perhaps also some detrital calcite was probably replaced as PO_4^{3-} concentration increased in the pore water with degradation of basic proteins in the organic rich sediment. Such putrefaction would tend to maintain the high pH necessary for francolite formation.

Knowles (1963) in an investigation of phosphatic nodules of the same age fdom nearby exposure proposed on the basis of Uranium enrichment that the phosphate was syngenetic with the sediment : ion exchange took

place while the collophane pellets rolled to and fro on the sea bed. This can almost certainly be discounted in the present case as concretion 33 was taken from immediately below the seat earth in the probable non-marine 'blue clays'.

Microprobe X-ray scanning photographs clearly have great potential in textural studies on fine grained sediments and it is anticipated that work currently in progress on other concretionary minerals and host sediments will provide valuable information on diagenetic reactions.

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F.Scordari : Ferrinatrite (Appendix – H-bonding)

The crystal structure of ferrinatrite and its relationships to Maus' salt, by F.Scordari (this vol., pp. 375-83)

Appendix: Hydrogen bonds. The six hydrogen atoms belong to three independent water molecules, shared among Na polyhedra. They could not be located from a difference Fourier synthesis. Positions assigned on purely geometric criteria and on a combination of geometric and valency-balance criteria are not incomplete agreement in respect of the hydrogen bonds to one of the three water molecules: purely geometric criteria suggest that Aq(3) is hydrogen-bonded to O(7,3) and O(5) or O(5,4), while when valency-balance is taken into account bonds to O(6) and O(11) or O(2,3) seem more probable.

From geometric considerations of the interatomic distances and angles (Table II, p.   ) Aq(2) has three distances less than 3.2Å, corresponding to possible hydrogen bonds, but of the three angles between these vectors, two are outside the acceptor – donor – acceptor range suggested by Ferraris and Franchini-Angela (1972) the most probable bonding is therefore O(7,4) – Aq(2) – O(5,3). For Aq(1), which has several suitable distances and acceptor – donor – acceptor angles, hydrogen bonds to O(12) and O(12,4) are the most likely, since O(12) is only shared by S(3) tetrahedra. For Aq(3) the most probable configurations from purely geometrical considerations are O(7,3) – Aq(3) – O(5,4) and O(7,3) – Aq(3) – O(5).

Electrostatic valency-balance calculations were carried out using the bond:strength:bond-length relation given by Brown and Shannon (1973) and the curve of bond-valencies reported by Donnay and Donnay (1973). Taken together with the geometrical considerations, they support the above conclusions concerning the bonding of Aq(1) and Aq(2), but for Aq(3) either O(6) – Aq(3) – O(11) or O(6) – Aq(3) – O(2,3) leads to a better balance.

All other possible configurations have been examined, but neither the purely geometric nor the geometric plus valency-balance considerations are in full agreement with the total electrostatic valency balance on the oxygen atoms. The geometrical criterion leads to O(7) and O(5) being much overbonded and O(6) much underbonded for O(7,3) – Aq(3) – O(5,4). On the other hand application of both geometric and valency-balance criteria leads to O(8) being underbonded and Aq(1), Aq(2), and Aq(3) overbonded for O(6) – Aq(3) – O(11). Similar arguments may be brought forward for O(7,3) – Aq(3) – O(5) and O(6) – Aq(3) – O(2,3).

Thirdly, if we consider the electrostatic valency balance alone, the best balance is given by bonds from Aq(1) to O(8,2) and O(12,4), from Aq(2) to O(12) and O(7), and from Aq(3) to O(6) and O(5,4).

In Table IV the valency balance is summarized on all three criteria; the differences do not seem sufficient to make a definite decision.

Table IV. Electrostatic valence balance; E, on valence-balance criteria only, assuming Aq(1) bonded to O(8,2) and O(12,4), Aq(2) to O(12) and O(7), and Aq(3) to O(6) and O(5,4); G, on geometric criteria alone, assuming Aq(1) bonded to O(12) and O(12,4), Aq(3) to O(7,3) and O(5,3), and Aq(3) to O(7,3) and O(5,4); GE, and valence-balance and geometric criteria jointly, assuming Aq(1) and Aq(2) bonded as under G, but Aq(3) bonded to O(6) and O(11).

Atom	Fe	S	Na(1)	Na(2)	Na(3)	E H‖‖	E Sum	G H‖‖	G Sum	GE H‖‖	GE Sum
O(1)	0.50†	1.42††	–	–	–	–	1.92	–	1.92	–	1.92
O(2)	0.50†	1.42**	–	–	–	–	1.92	–	1.92	–	1.92
O(3)	0.49*	1.38**	–	0.17	–	–	2.04	–	2.04	–	2.04
O(4)	0.51*	1.36††	0.17	–	–	–	2.04	–	2.04	–	2.04
O(5)	–	1.65**	–	0.06	0.18	0.17	2.06	{0.11, 0.17}	2.17	0.11	2.00
O(6)	–	1.55**	0.10	0.11	–	0.14	1.90	–	1.76	0.13	1.89
O(7)	–	1.61††	{0.06, 0.20}	–	–	0.17	2.04	{0.16, 0.13}	2.16	0.16	2.03
O 8)	–	1.61††	0.09	0.11	–	0.13	1.94	–	1.81	–	1.81
O(9)	0.50‡	1.43‡‡	–	–	–	–	1.93	–	1.93	–	1.93
O(10)	0.50‖	1.39‡‡	–	–	{0.14, 0.05}	–	2.08	–	2.08	–	2.08
O(11)	–	1.52‡‡	–	0.14	{0.11, 0.14}	–	1.91	–	1.91	0.12	2.03
O(12)	–	1.66‡‡	–	–	–	{0.17, 0.17}	2.00	{0.17, 0.17}	1.95	{0.12, 0.17}	1.95
Aq(1)	–	–	0.21	–	0.18	{0.17, 0.83}	2.09	{0.88, 0.83}	2.10	{0.88, 0.83}	2.10
Aq(2)	–	–	0.17	0.22	–	{0.83, 0.83}	2.05	{0.89, 0.84}	2.12	{0.89, 0.84}	2.12
Aq(3)	–	–	–	0.19	0.20	{0.86, 0.83}	2.08	{0.87, 0.83}	2.09	{0.87, 0.88}	2.14
Sum	3.00	18.00	1.00	1.00	1.00	6.00	30.00	6.00	30.00	6.00	30.00

* Fe(1); † Fe(2); ‡ Fe(3); ‖ Fe(4); ** S(1); †† S(2); ‡‡S(3);
‖‖ The hydrogen atoms are, of course, members of Aq(1), Aq(2), and Aq(3), and linked by "hydrogen bonds" to O(5) to O(12)

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