Read at the Annual Conference of the Ussher Society, January 1989

The distribution and significance of sedimentary apatite in Lower to Middle Devonian sediments east of Plymouth Sound

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Humphreys, B. and Smith, S.A. 1989. The distribution and significance of sedimentary apatite in Lower to Middle Devonian sediments east of Plymouth Sound. *Proceedings of the Ussher Society, 7, 118-124.*

Carbonate-fluorapatite (francolite) in the form of concretions, both *in situ* and locally reworked, bone fragments (biogenic apatite), a replacement of precursor carbonate in intraskeletal voids, and a direct pore-filling cement, is found at distinct horizons within the Lower and Middle Devonian succession of south Devon. The francolite cements are characterised by distinct cathodoluminescence colours of either bright pink or deep blue. The principal occurrences of apatite, within the Bovisand Formation and at the base of the Jennycliff Slate Formation, correspond to major transgressive events. Phosphatic concretions within the Dartmouth Group may relate to marine incursions in a predominantly alluvial environment.

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Introduction

Phosphorites of Devonian age are comparatively rare (Bentor 1980). Unlike the extensive and economic phosphorite deposits that formed during the early Cambrian, Ordovician, Permian, late Cretaceous to Eocene, and Miocene, the reported occurrences of apatite in the Devonian consist of thin pebbly horizons, often associated with disconformity surfaces, and sometimes of phosphatised shell debris or sporadic bone beds (e.g. Aval et al. 1968; Baird 1978; Cathcart and Schmidt 1977; Coles and Varga 1988; Derré and Krylatov 1976; Paproth and Zimmerle 1980). Such thin 'horizons may assist with stratigraphical correlation as well as having implications for the nature of the depositional and early diagenetic environments.

During a study of the sedimentology of the Lower to Middle Devonian sequence on the east side of Plymouth Sound, grey to black, sometimes reddened concretions, either in situ or reworked into thin lags, sometimes with skeletal debris, were observed in silty mudstones at various stratigraphic intervals. X-ray diffraction was used to confirm that the concretions were indeed composed of apatite rather than siderite, which can have a similar appearance in the field. Biogenic apatite in the form of fish bones and scales, possible phosphatic conodonts, and a cryptocrystalline apatite cement which fills the internal cavities of shells have also been encountered. Apatite is most abundant in the Bovisand Formation (Meadfoot Group), with small but nevertheless significant occurrences at the base of the Jennycliff Slate Formation (Plymouth Group) and within the Dartmouth Group. Apatite-bearing strata might be present in up to 10% of the total Lower and Middle Devonian succession.

This brief account summarises the modes of occurrence of the apatite, relates them to the depositional and early diagenetic environments of the host mudstones, and suggests how these occurrences may usefully be integrated into stratigraphical studies.

Stratigraphical and structural setting

Devonian sedimentary rocks of Pragian (Lower Devonian) to Fammenian (Upper Devonian) age are exposed in the vicinity of Plymouth (Fig. 1). The stratigraphy of the Lower and Middle Devonian in this area has been subject to recent revision (Chandler and McCall 1985; Seago and Chapman 1988). The oldest rocks in the Plymouth area belong to the Dartmouth Group, a c.4km thick package of silty mudstones with subordinate siltstones, sandstones, pebbly mudstones and intercalated volcanics. The base of this group is not seen at outcrop. The succeeding Meadfoot Group consists of the Bovisand Formation, a sequence of silty mudstones with thinly bedded sandstones and limestones, and the Staddon Grits Formation comprising sandstones and siltstones. The Staddon Grits Formation is at its thickest around Plymouth Sound. Estimates of its maximum thickness range from 400m (Pound 1983) to over 600m (Harwood 1976), giving the Meadfoot Group a total thickness of at least 500m, and perhaps up to 700m (Harwood 1976). The Jennycliff Slate Formation, c.500m thick, is the lowermost division of the Plymouth Group, a heterogeneous succession of limestones, shales and volcanics which, as a result of tectonic thickening, forms a sedimentary pile in the Plymouth area which may measure several kilometres (Chandler and McCall 1985). The Jennycliff Slate Formation passes conformably up into the Plymouth Limestone Formation, a locally developed carbonate facies with stromatoporoids, which shows a diachronous upward passage into shales.

The main structural event affecting the study area, D1, produced a series of asymmetric Fl folds that are overturned towards the north-west, and an associated slaty cleavage dipping to the south-east (Seago and Chapman 1988). Locally, thrusts and crenulation cleavage are observed within the Meadfoot Group (Seago and Chapman 1988 p. 794). On the east side of Plymouth Sound the rocks generally young northwards on the overturned limb of a major fold within the Meadfoot Group. From their contact with the Meadfoot Group at the southern end of Crownhill Bay (SX 493 499), rocks of the Dartmouth Group young south-eastwards.

Depositional environments

Despite intense tectonic disruption of bedding and the development of cleavage, sedimentary features are sufficiently numerous to allow reconstruction of the environments of deposition for the various lithologies. For brevity, environmental interpretations are only summarised here, but more comprehensive accounts are presented by Humphreys and Smith (in press) and Smith and Humphreys (this volume).

The Dartmouth Group includes a substantial thickness of lacustrine deposits, probably deposited in large perennial lakes, underlying an extensive distal fluvial and playa sequence. Subaqueous deposition in lakes is supported by an association of wave ripples, lenticular bedding, bioturbation, fish remains and the general heterolithic character of the beds. Access by marine waters to the lakes may have occurred periodically, perhaps as a result of local tectonic movements, causing the salinity to change from freshwater to brackish or even marine.

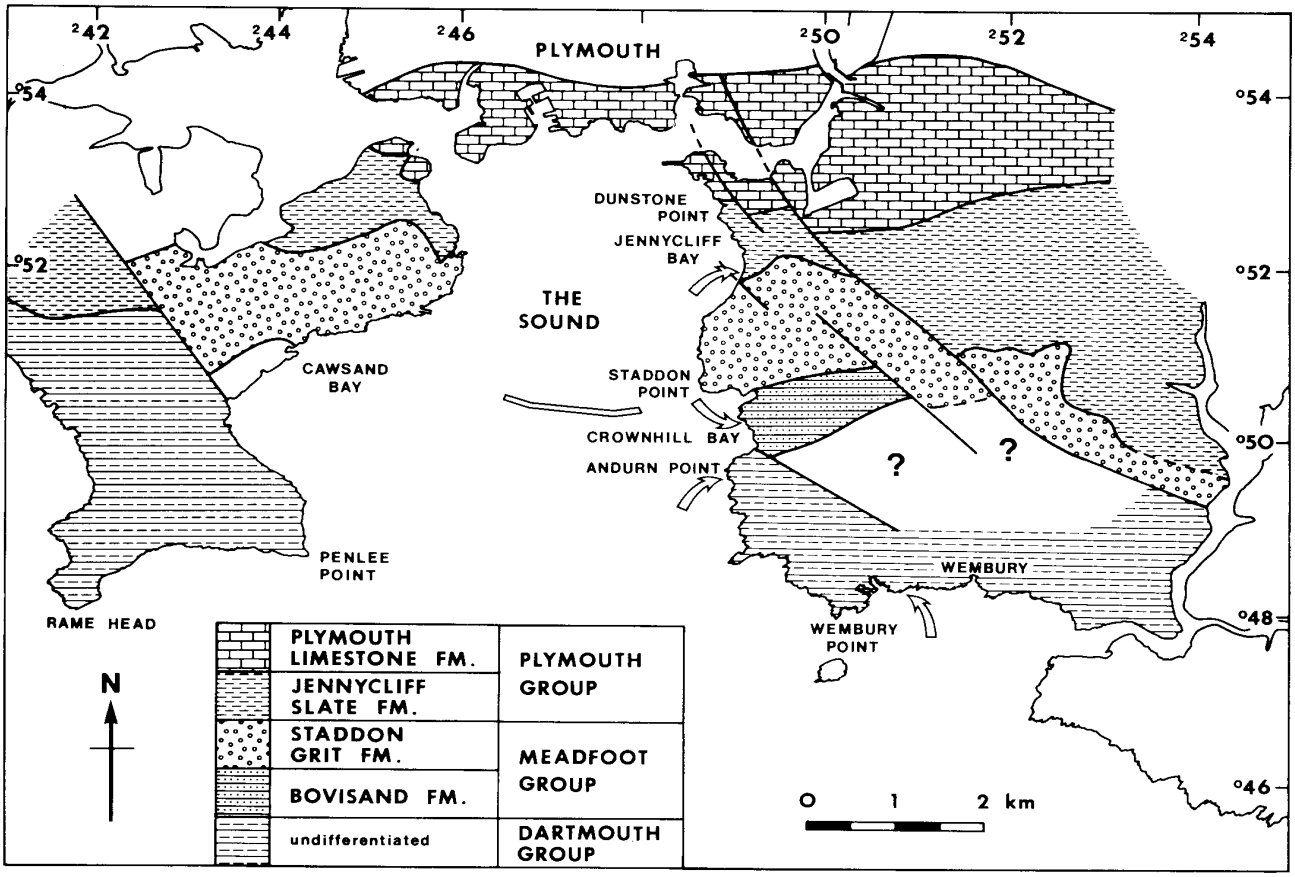

Figure 1. Geological sketch map of the coastal sections around Plymouth Sound with major apatite occurrences arrowed. The geology and fault patterns largely follow the most recent map presented by Seago and Chapman (1988, p.792). Relative thickness of the Formations are shown in Fig. 4. The question marks indicate areas of geological uncertainty which are currently being remapped by the British Geological Survey.

The Bovisand Formation represents a change to fully marine deposition, with basal beds of reddened silty mudstones with thin sandstones and limestones, probably deposited under storm influences, passing up into predominantly dark grey mudstones in the centre of Crownhill Bay. These mudstones were deposited on an outer shelf, below wave base, under conditions of relatively low rates of deposition. Some fine sand and silt layers were periodically deposited by waning energy storm currents. The environment supported a rich fauna as shown by laterally impersistent shell accumulations or isolated shells comprising solitary corals, disarticulated brachiopods valves, crinoid columnals, bryozoans and rare fragments of orthocone nautiloids. Some of these shells show excellent preservation and appear to be close to their life position. Bioturbation shows that bottom waters and, locally, the uppermost sediment layers were oxic, but the presence of pyrite throughout the sediments indicates the widespread development of anoxic conditions below the sediment-water interface. The upper levels of the Bovisand Formation are characterised by more silty mudstones with numerous sandstone partings separated by silty mudstones. The sandstone beds, usually less than 20cm thick, show a number of recurring features, including sharp scoured bases, tops and bases that show reciprocal thickening and thinning and lateral impersistence, pinching and swelling of individual laminae, and low-angle and undulatory lamination. These features, when considered collectively, indicate deposition by storm-induced processes. The lowermost beds of the overlying Staddon Grits Formation, on the northern flank of Crownhill Bay, record a shoaling sequence with coastal plain sediments heralding the onset of alluvial deposition. In the vicinity of Staddon Point, erosive-based, parallel-laminated and trough cross-bedded sandstones, sometimes with conglomerate lags are interpreted as the deposits of relatively shallow, sand-dominated ephemeral streams.

The base of the Jennycliff Slate Formation is seen in the vicinity of the waterfall in Jennycliff Bay (SX 490 518), where complex recumbent folding and poorly exposed thrusts obscure the contact with the underlying Staddon Grit Formation. The contact is conformable according to Chandler and McCall (1985). The basal beds were deposited in shallow water, as a muddy nearshore facies (restricted bay, lagoonal and estuarine environments) which developed as the sea encroached over the drowned alluvial landscape. The sediments were rapidly colonised by deposit-feeding organisms and are characterised by a profusion of *Spirophyton minusculum* burrows at some levels. Succeeding levels in the sequence remain mudstonedominated, but show an influx of thin beds of storm-deposited fine-grained sandstones with gutter casts and laterally persistent limestone beds towards the junction with the overlying Plymouth Limestone Formation.

Stratigraphical distribution of apatite

Dartmouth Group

Concretions of calcite and iron minerals have been previously reported from the Dartmouth Group by Dineley (1966), but not of apatite. In this survey, phosphatic concretions have been found in the oldest two divisions of the Dartmouth Group, the Renney Rocks Formation and the Wembury Formation of Seago and Chapman (1988). The apatite is restricted to

lacustrine deposits with mudstones showing bioturbation, fish remains, and sometimes wave ripples. It is found at two localities, one south of Andurn Point (SX 490 498), and one between Wembury and Wembury Point (SX 511 484). At the latter site at least three layers of concretions are exposed on a c.10m section within the wave cut platform representing a stratigraphic interval of c.8m. Preliminary surveys have not detected phosphatic nodules within the younger Yealm and Warren Formations.

The concretions are small (generally less than 3 to 4cm in diameter) and rounded. They are always concentrated in laterally extensive, but intermittent thin layers (generally one concretion thick) which follow bedding. Although it may appear that they are *in situ,* perhaps representing an ancient geochemical boundary such as an oxic-anoxic boundary (see later discussion), it is more likely that the concretions have been locally reworked and therefore represent condensed horizons. This interpretation is supported by the irregular lateral spacing and local bunching of the concretions, their fairly uniform size, and their sharply defined outlines. These characteristics contrast with the *in situ* concretions in the Bovisand Formation. Closely associated bioturbated horizons also suggest pauses in sedimentation.

Meadfoot Group

The existence of concretionary apatite and phosphatic replacements of shells in the Bovisand Formation has been previously reported by Harwood (1976). The most abundant phosphatic concretions noted in our survey occur within an approximately 50m thick interval of medium to dark grey silty mudstones forming the central portion of the Bovisand Formation exposed in Crownhill Bay. Apatite is absent from overlying silty mudstones Within the Bovisand Formation where storm deposits are present. In contrast with the Dartmouth Group, concretions are not concentrated along particular bedding planes but are distributed randomly through the mudstones. Small red nodules, which include pyrite as well as iron oxides (hematite and limonite), are also numerous. The phosphatic concretions show several forms, from a preponderance of small concretions (1 to 5cm diameter), usually with smooth margins, to larger ellipsoidal forms with margins that vary from sharp to diffuse. Elongate concretions, up to 8cm long, sometimes nucleated around skeletal debris such as orthocone nautiloids, are also numerous. Harwood (1976 p.335) reported phosphatic replacements of bryozoan and coral skeletons and haematite nodules. Present observations suggest that a finely crystalline apatite cement may occlude intraparticle voids, particularly of bryozoan fragments (Fig. 3C), but phosphatisation of the shell walls is uncommon. We have not found evidence that apatite replaces haematite nodules. It appears that haematite is a weathering product of nodular pyrite and that the distribution of pyrite and apatite were similar.

Harwood (1976 p. 336) also alluded to the occurrence of phosphatic debris within what is now classified as the basal Staddon Grits Formation, north of Bovisand Beach. The authors have seen no phosphatic material here, but there are several fault slices of Bovisand Formation rocks, juxtaposed against fluvial sandstones, which may contain some phosphatic material.

Plymouth Group

Field observations have been limited to the Jennycliff Slate Formation and parts of the Plymouth Limestone Formation. In the intervals investigated, apatite is very restricted, being concentrated at the base of the group. Small, reworked black phosphatic pebbles, bone fragments and an intraskeletal apatite cement occur at the base of the Jennycliff Slate Formation, particularly within a crinoidal limestone horizon, but also in other thin shell lags. Elsewhere in the Jennycliff Slate Formation, the black and grey nodules found are either calcite, dolomite, siderite, pyrite or, more often, combinations of these minerals.

The large parts of the Lower and Middle Devonian succession from which apatite-bearing strata are absent were deposited in fluviatile and associated non-marine environments (the bulk of the Staddon Grits Formation and the Dartmouth Group).

Petrography

In all samples analysed by X-ray diffraction, the phosphorusbearing mineral showed diagnostic reflections for francolite (McConnell 1973 p.88-89), a fluorine-enriched (>1%F) carbonate-apatite with a variable composition that can be represented by (Ca, Mg, Sr, $Na)_{10}$ (PO_4, SO_4, $CO_3)_6F_{2-3}$. In addition to francolite, concretions usually include clay minerals, typically iron-rich chlorite and white mica, silt-size quartz and feldspar (albite) and sometimes pyrite (Fig. 2). X-ray fluorescence analyses on some nodules show that the P_2O_5 content reaches 20%.

In thin section the francolite is typically brown (of various hues) and virtually isotropic; internal textures are often difficult to discern. Study of the detailed distribution of disseminated

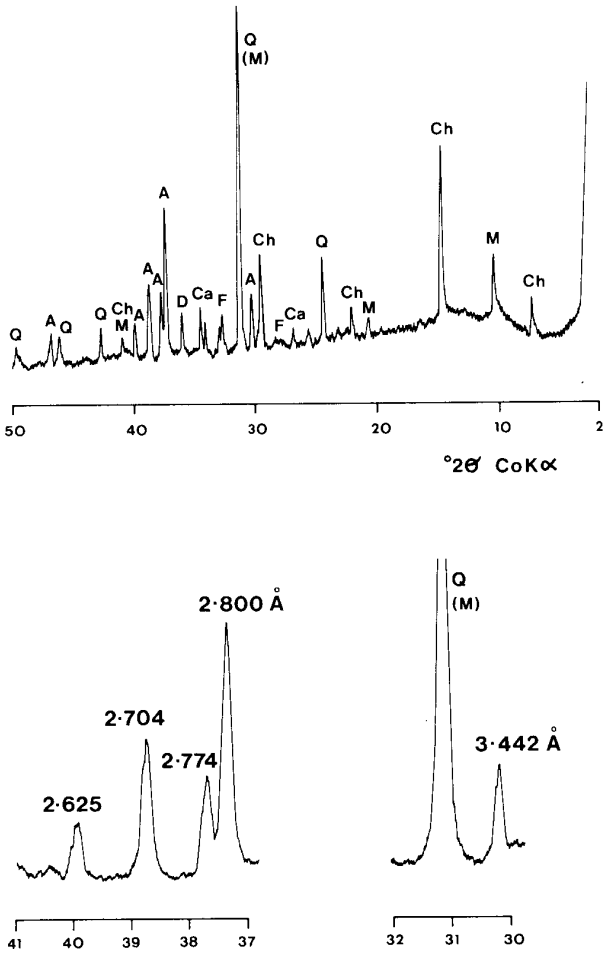

Figure 2. X-ray diffraction pattern of a phosphatic nodule from the Dartmouth Group, with enlargement of the major apatite reflections. The basal spacings, shown in Angstroms (A), and relative intensities of the apatite peaks are characteristic of a well crystallised francolite. Slight variations in the basal spacings occur between samples; the prominent 211 reflection varies between 2.799 and 2.801 Å. The nodule also includes clay minerals, chlorite (Ch) and mica (M), quartz (Qu), feldspar (F) and calcite (Ca). Quartz and mica reflections are coincident at 31°.

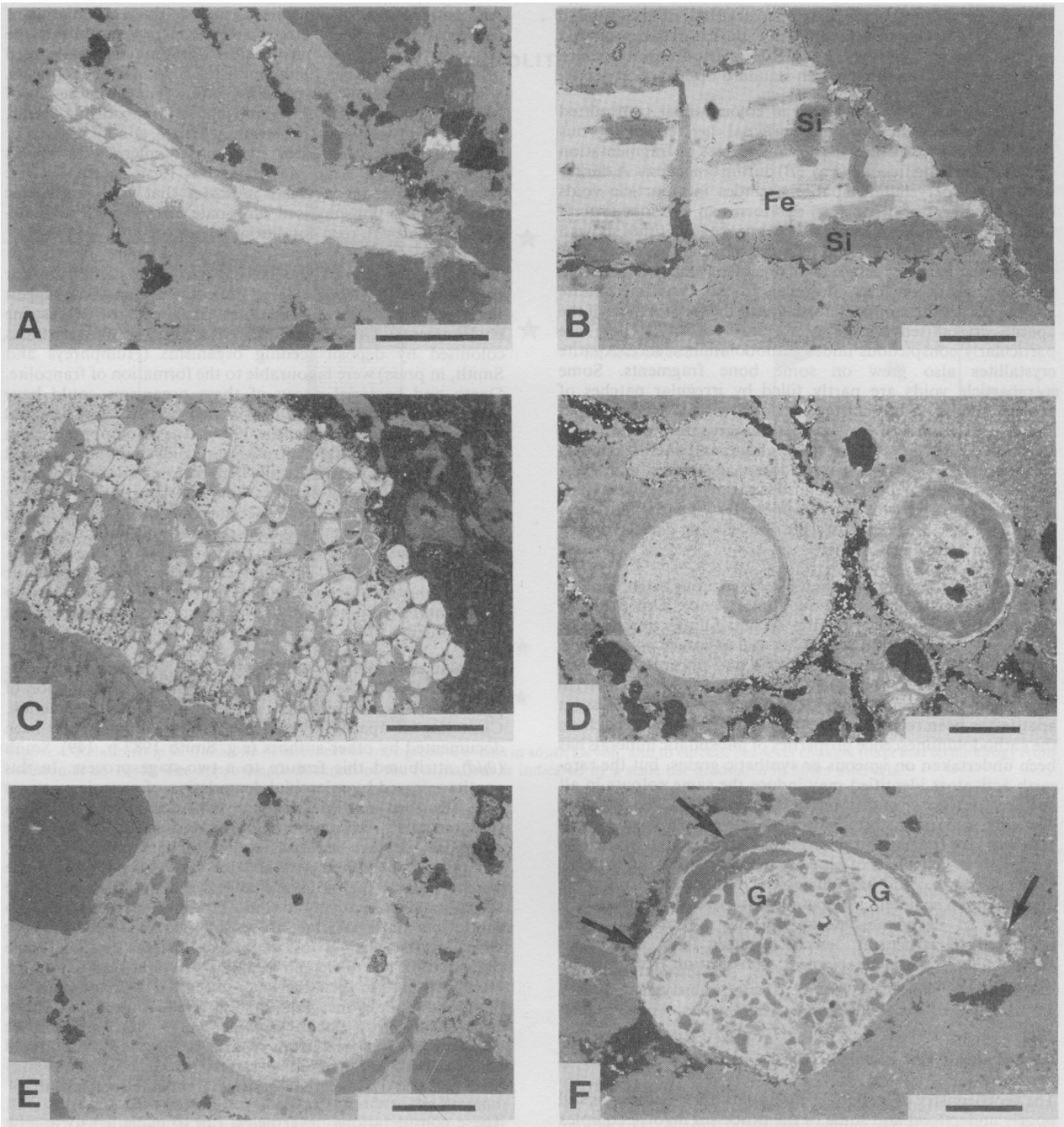

Figure 3. BSEM images illustrating the occurrence of carbonate-fluorapatite (francolite) in thin sections. The apatite is pale grey, ferroan calcite medium grey, quartz dark grey and porosity (araldite-impregnated) black. Identification of shell material is tentative because diagnostic microstructures have been lost through fragmentation and recrystallisation. C is from the Bovisand Formation in Crownhill Bay. All other illustrations are from a calcite-cemented shell and phosphatic layer at the base of the Jennycliff Slate Formation in Jennycliff Bay.

A. Bone fragment showing numerous fractures due to compaction, and traces of original layered structure. Scale bar = 400µm.

B. Bone fragment showing partial silicification (Si) through replacement and filling of borings. Finely crystalline iron oxides (Fe) are present along one lamina. The quartz grain (top right) shows a slightly sutured surface where it impinges on the bone fragment. Scale bar = 100µm.

C. Transverse section through a large bryozoan frond showing zooecia filled or lined with a finely crystalline apatite. The apatite may have replaced a carbonate mud fill. Scale bar = 1 mm.

D. On the left, a transverse section through a juvenile goniatite or gastropod shows a carbonate fill with a speckly appearance due to finely disseminated apatite. Phosphatisation of the fill is incomplete in this case. On the right, a nearly circular shell fragment of uncertain affinity (tranverse cross-section through a tentaculitid or a hollow brachiopod spine are the likely possibilities) shows a peripheral rim of partly phosphatised calcite, and an internal void partly filled by phosphatised micrite. Scale bar = 400µm.

E. Geopetal fabric within a circular shell fragment, made conspicuous by the partial replacement of the internal micritic matrix by apatite. The distinction between the shell outline and surrounding calcite cement is lost under this BSEM image. Scale bar = 200µm.

F. Phosphatic concretion including quartz and feldspar grains which formed within what appears to be the shattered remains of a trilobite carapace (see arrows), now recrystallised and partly silicified. Note the distinct convoluted shape of the shell fragments and the turned-under end. Some very small crystals of galena (G) occur within the concretion (these appear white, and can just be discerned in small black voids). Scale bar = 200µm.

apatite crystallites and the microtexture of phosphatic replacements is therefore facilitated by the use of backscattered electron microscopy (Fig. 3) or cathodoluminescence petrography in conjunction with standard optical microscopy.

Bone fragments are pale brown in colour under transmitted light, showing relics of their original layered or porous structure, and have suffered varying degrees of fragmentation (Fig. 3A) and silicification (Fig. 3B) during diagenesis. A darker brown cryptocrystalline apatite occludes intraparticle voids (body chambers of organisms) and forms an envelope around shell fragments (Fig. 3C and D). The apatite sometimes shows a geopetal fabric (Fig. 3E) and includes relic patches of micrite, suggesting that it replaced a precursor micritic internal sediment. In other cases, however, finely crystalline apatite crystallites are disseminated throughout the micrite fill as if the apatite crystallised within intercrystal porosity. These are particularly conspicuous under cathodoluminescence. Apatite crystallites also grew on some bone fragments. Some intraparticle voids are partly filled by irregular patches of apatite, similar to the cluster cement described by Krajewski (1984). Accretionary pebbles or aggregates of apatite cemented, silt-sized silicate grains, bone and shell fragments also occur (Fig. 3F). Some of these aggregates may have originated as sediment accumulations within intraskeletal voids or shelter porosity which were cemented by apatite, and later liberated by breakage of the enveloping shell during contemporaneous reworking.

The carbonate-fluorapatite shows a conspicuous bright pink or deep blue colour under cathodoluminescence. This property enables small patches of apatite cement filling cavities to be readily identified in thin section as well as larger nodules and replacements. Pink-luminescent bone and phosphatised shell fragments have been previously observed by one of us (B.H.) in Palaeozoic sediments from Jordan, and pink-luminescent apatite has been recorded by Dudley (1976). Most research on the cathodoluminescence properties of phosphatic minerals has been undertaken on igneous or synthetic grains, but the rare-earth activators identified may induce the same colours in all apatites, irrespective of their origin (Mariano 1988). The rare earth elements samarium and dysprosium have been suggested as activators for the pink luminescence of apatite, and cerium and europium as activators of blue luminescence (Marfunin 1979). These elements could be inducing the luminescence colours in the Devonian sedimentary apatites. However, the strong blue emission of carbonate-fluorapatite has alternatively been attributed to structural defects resulting from anomalous amounts of rare-earth element substitution for calcium (Mariano 1988 p.101).

Discussion

Environmental and chemical constraints on the formation of francolite

The geochemistry of carbonate-fluorapatite precipitation is still poorly understood and some of the processes involve complex biochemistry. Nevertheless, a few general statements can be made on the likely early diagenetic environment in which the apatite crystallised. Because of the chemical constraints on the formation of francolite (i.e. the availability of Ca, Mg, Sr, SO_4, as well as PO_4, and Eh-pH conditions - see Coleman 1985), it can be concluded that a marine environment is more conducive to the formation of phosphatic concretions than a non-marine subaqueous environment. Indeed, most phosphatic concretions are reported to be of marine origin (Bentor 1980; Kolodny 1981). Most ocean water at the present day is near saturation relative to carbonate fluorapatite (Kolodny 1981), and the availability of phosphorus was probably not the most important limiting factor in the formation of francolite in the Devonian sediments.

Organisms play a crucial role in the extraction of phosphorus from seawater and its subsequent concentration in sediments. Alternative sinks for phosphorus include the accumulation of fish remains on the substrate, and the incorporation into the sediment of clay plates or iron oxides which may carry adsorbed phosphorus (Bremner 1980; Smith 1987). In marine sediments, where dissolved ions are plentiful, subtle changes in the rate of burial, the availability of organic matter and oxidising agents, and Eh and pH may constrain whether apatite, pyrite or glauconite are precipitated in localised microenvironments (Coleman 1985). Francolite does not form in totally oxic conditions; isotope analysis indicates that both authigenic francolite and phosphatised carbonate form in both sulphatereducing and sub-oxic conditions (Benmore *et al.* 1983).

The marine origin of francolite has particular significance for the Dartmouth Group. Here, francolite concretions suggest that marine waters sometimes invaded the lacustrine environment. Throughout the succession only substrates colonised by deposit feeding organisms (Humphreys and Smith, in press) were favourable to the formation of francolite. Death and bacterial decay of these organisms could have released significant amounts of phosphorus to interstitial waters (Baturin and Bezrukov 1979). It is also apparent from the apatite cement filling intraskeletal voids that semi-enclosed microenvironments with locally high concentrations of organic matter were favourable sites for phosphatisation. In the Dartmouth Group, where francolite concretions are restricted to horizons with numerous fish remains and burrows (Smith and Humphreys, this volume), local dissolution of bone may have been significant. The association between phosphatic nodules and fish remains has been noted on the SW African continental shelf, an active site of apatite formation at present (e.g. Baturin 1974 p.82; Bremner 1980).

The centres of some concretions from the Bovisand Formation contain numerous small cubic pores, formed by oxidation of pyrite, and pyrite is often detected by X-ray diffraction. Clustering of apatite crystals around pyritic nuclei has been documented by other authors (e.g. Smith 1987 p. 149). Smith *(ibid)* attributed this feature to a two-stage process. In this apatite released by microbial degradation of organic matter is first adsorbed onto ferric oxyhydroxides. There is then a simultaneous precipitation of pyrite and apatite as the ferric oxyhydroxides are reduced in the sulphate reduction zone. Exhaustion of sulphate available for pyrite formation could be another causal factor in a change from pyrite to francolite formation. Alternatively it could be viewed as the result of a subtle chemical change from an anoxic to a sub-oxic environment which would favour apatite rather than pyrite precipitation (see Coleman 1985). This could result from the introduction of oxygenated water to the site of precipitation by bioturbation, or by the agitation of surface sediment layers due to storm wave disturbance. However, since phosphatic concretions are absent from storm beds in the Bovisand and Jennycliff Slate Formations, rapid episodic deposition may have prevented rather than assisted francolite formation.

These considerations nevertheless fail to explain why apatite did not precipitate throughout the marine Devonian in the study area, particularly in bioturbated mudstones forming large parts of the Jennycliff Slate Formation and the basal, marine-influenced, Staddon Grits Formation. A further, perhaps catalytic factor may have been eustatic sea-level changes.

Relationship to transgressions

It has been found elsewhere that the formation of *in situ* phosphatic concretions is associated with peaks of basin-wide transgressive events (e.g. Balson 1987; Burnett and Veeh 1977). Transgressions bring a fresh supply of phosphorus which can be subsequently utilised by organisms. Basal lag phosphorites are also associated with the start of major transgressive events. These are periods of erosion and winnowing with negligible sedimentation, e.g. the basal "Coprolite Bed" of the Lower Cretaceous Speeton Clay in Yorkshire (Scott *et al.* 1987), and the nodular phosphorite deposits at the base of the Pliocene

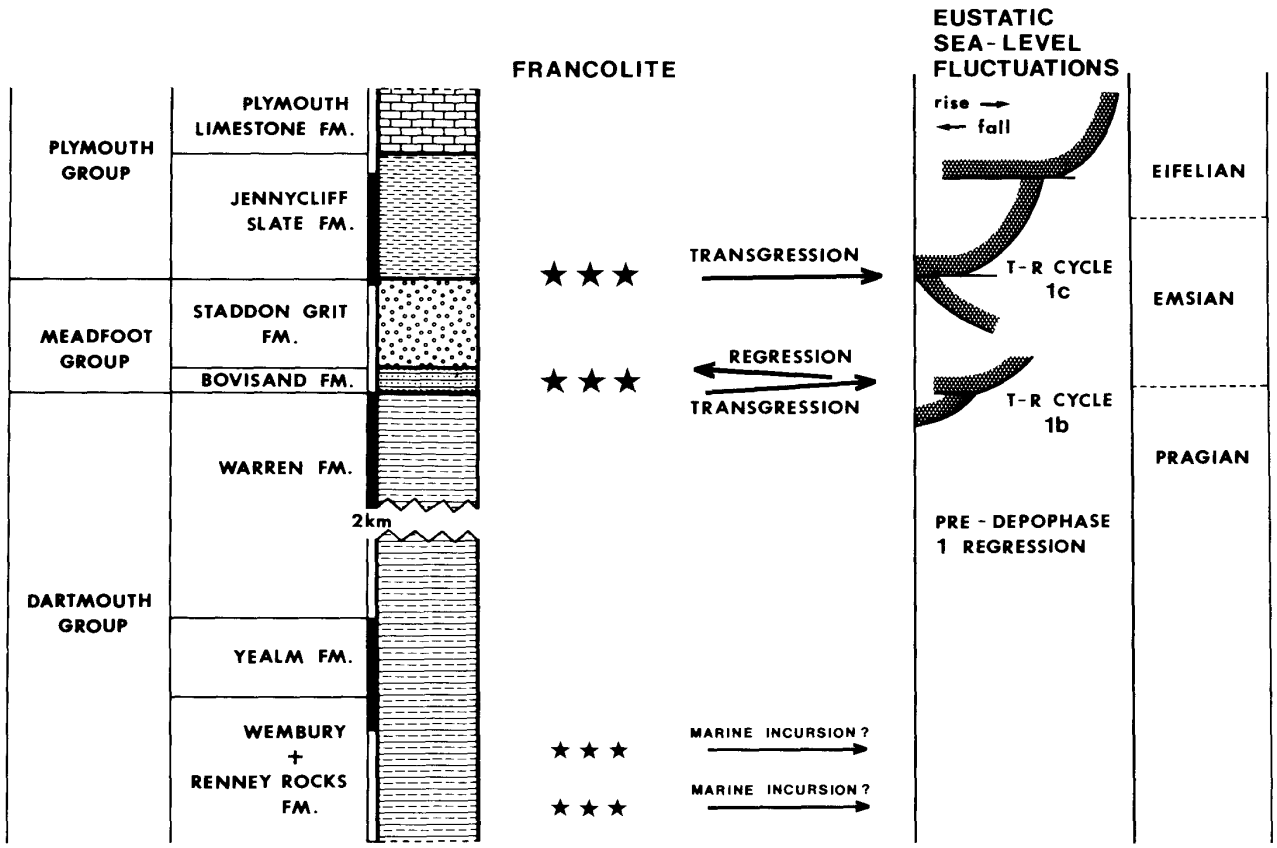

Figure 4. Relationship of francolite occurrences to transgressive events in south Devon, and to eustatic sea-level changes (data and terminology from Johnson *et al.* 1985). The approximate thickness of the Formations is indicated by a scale bar graduated in 500m intervals.

Coralline Crag and Plio-Pleistocene Red Crag in East Anglia (Balson 1980).

In south Devon phosphorite concretions occur in beds deposited during transgressive phases when rates of sediment supply to the basin were relatively low. The range of water depths in which it formed was, however, quite variable. In the largely non-marine Dartmouth Group, thin phosphatic pebble beds occur in the parts of the sequence which show structures suggestive of marine influences (Smith and Humphreys, this volume). In the Bovisand Formation *in situ* concretions are particularly abundant in mudstones deposited at the peak of a transgressive phase. Within the constraints of present biostratigraphical resolution, this transgressive event appears to correlate with a major Devonian eustatic cycle (T-R cycle 1b of Johnson *et al.* 1985) which broadly corresponds to the Pragian-Emsian stage boundary (Fig. 4). The marine incursion may have just preceeded the base of the Emsian. Evidence for this is provided by a marine fauna from the upper parts of the Dartmouth Group in Cornwall (Evans 1981). In the Jennycliff Slate Formation pebble and shell lags mark the onset of a major transgression which may relate to the onset of the eustatic T-R cycle lc of Johnson *et al.* (1985). This transgression does not correspond to the Emsian-Eifelian stage boundary (Lower-Middle Devonian Series boundary) as currently accepted (Chandler and McCall 1985). However, palynological work currently being undertaken on the south Devon sequence suggests that a downward shift of the stage boundaries is required (A. Dean, pers. comm.).

Potential for lithostratigraphical correlation

This survey has shown that phosphorite concretions are restricted to distinct stratigraphical intervals, and, because these correspond to transgressive phases of sedimentation, francolite-bearing beds are likely to be laterally continuous. Phosphatic nodules are conspicuous in the field because they are generally darker than the host mudstones. Because francolites generally survive the effects of low-grade metamorphism (although elemental concentrations are altered, McClellan 1980; Smith 1987), phosphatic horizons may have potential for lithostratigraphical correlation. This could be especially important in south Devon where the possibility of correlation using clay mineral assemblages, a technique that can be successfully applied in younger mudstone sequences (e.g. Fisher and Jeans 1982), is precluded by metamorphic alteration.

Conclusions

1. Carbonate- fluorapatite (francolite) occurs in Devonian mudstones or silty mudstones deposited in a wide range of water depths from a distal shelf to nearshore shallow embayments to lacustrine settings. These occurrences correspond to periods of relatively low rates of deposition, sometimes with reworking and bioturbation of the substrates. Lags of locally reworked phosphatic nodules represent condensed horizons.

2. Biological concentration of phosphorus occurred, either through deposit-feeding organisms which extracted phosphorus from seawater, or through the accumulation of fish remains on the muddy substrates.

3. Episodes of francolite precipitation followed periods of sea-level rise which replenished supplies of nutrients in shelf areas. In the Jennycliff Slate Formation, phosphorites formed following a major marine incursion over the alluvial sediments of the Staddon Grits Formation. In the Bovisand Formation,

the authigenesis of francolite followed a marked deepening of the sea, with the consequent diminution of storm-fed clastics. Francolite in the Dartmouth Group indicates early marine incursions into a predominantly alluvial setting at the margins of a continental area.

4. If work in adjacent areas confirms that the phosphorite concretions are restricted to a few stratigraphic horizons as reported here, the phosphatic pebbles and concretions could provide immediately recognisable lithostratigraphical markers.

Acknowledgements. This study was undertaken as part of the BGS Cornwall and South Devon Project directed by Dr Brian Leveridge. The manuscript was improved by the critical reading of Dr R.W.O'B Knox and an anonymous referee whose many comments are gratefully acknowledged. The authors would like to thank Dr Peter Balson for early discussion on the topic of sedimentary apatites and also for constructive comments on the manuscript. This paper is published with the approval of the Director, British Geological Survey (N.E.R.C.).

References

Aval, M.M., Namin, M.S., Ghasemipur, R., Altschuler, Z.S. and Hignett, T.P. 1968. Recent phosphate discoveries in Iran. Part II. Upper Devonian phosphate. *Reports of the Geological Survey of Iran, 10,* 14-55.

Baird, G.C. 1978. Pebbly phosphorites in shale: a key to recognition of a widespread submarine discontinuity in the Middle Devonian of New York. *Journal of Sedimentary Petrology, 48,* 545-555.

Balson, P.S. 1980. The origin and evolution of Tertiary phosphorites from eastern England. *Journal of the Geological Society, 137,* 723-729.

Balson, P.S. 1987. Authigenic phosphorite concretions in the Tertiary of the southern North Sea Basin: an event stratigraphy. *Mededelingen van der Werkgroep voor Tertiaire en Kwartaire Geologie, 24,* 79-94.

Baturin, G.N. 1974. On the geologic consequences of mass mortality of ichthyo-fauna in the ocean. *Oceanology, 14,* 80-84.

Baturin, G.N. and Bezrukov, P.L. 1979. Phosphorites on the sea floor and their origin. *Marine Geology, 31,* 317-332.

Benmore, R.A., Coleman, M.L. and McArthur, J.M. 1983. Origin of sedimentary francolite from its sulphur and carbon isotope composition. *Nature, 302,* 516-518.

Bentor, Y.K. 1980. Phosphorites - the unsolved problems. *In:* Bentor, Y.K. (ed) Marine phosphorites - geochemistry, occurrence, genesis. *Society of Economic Paleontologists and Mineralogists Special Publication, 29,* 3-18.

Bremner, ,LM. 1980. Concretionary phosphorite from SW Africa. *Journal of the Geological Society, London, 137,* 773-786.

Burnett, W.C. and Veeh, H.H. 1977. Uranium-series disequilibrium studies in phosphorite nodules from the west coast of South America. *Geochimica et Cosmochimica Acta, 41,* 755-764.

Cathcart, J.B. and Schmidt, D.L. 1977. Middle Paleozoic sedimentary phosphate in the Pensacola Mountains, Antarctica. *United States Geological Survey Professional Paper, 456-E,* E1-18.

Chandler, P. and McCall, G.J.H. 1985. Stratigraphy and structure of the Plymouth - Plymstock area: a preliminary revision. *Proceedings of the Ussher Society, 6,* 253-257.

Coleman, M.L. 1985. Geochemistry of diagenetic non-silicate minerals: kinetic considerations. *Philosophical Transactions of the Royal Society, London, A 315,* 39-56.

Coles, K.S. and Varga, R.J. 1988. Early to middle Paleozoic phosphogenic province in terranes of the southern Cordillera, western United States. *American Journal of Science, 288,* 891-924.

Derré, C. and Krylatov, M.S. 1976. Comparaison entre la série de Salau (Ariège) et d'autres séries du Dévonien de la partie centrale des Pyrenees. Un caractère original de la partie inférieure du Dévonien: presence de phosphates. (Comparison between the Salau Series, Ariege, and another series from the Devonian of the central region of the Pyrenees; an original characteristic of the Lower Devonian; occurrence of phosphates. *Compte Rendu de 1'Académie des Sciences, Serie D, 282,* 2051-2054.

Dineley, D.L. 1966. The Dartmouth Beds of Bigbury Bay, south Devon. *Quarterly Journal of the Geological Society, London, 122,* 187-217.

Dudley, R.J. 1976. The use of cathodoluminescence in the identification of soil minerals. *Journal of Soil Science, 27,* 487-494.

Evans, K.M. 1981. A marine fauna from the Dartmouth Beds (Lower Devonian) of Cornwall. *Geological Magazine, 118,* 517-523.

Fisher, M.J. and Jeans, C.V. 1982. Clay mineral stratigraphy in the Permo-Triassic red bed sequences of BNOC 72/10-IA, Western Approaches, and the south Devon coast. *Clay Minerals, 17,* 79-89.

Harwood, G.M. 1976. The Staddon Grits - or Meadfoot Beds? *Proceedings of the Ussher Society, 3.* 333-338.

Humphreys, B. and Smith, S.A. (in press). The sedimentology of a Lower to Middle Devonian regressive-transgressive sequence, Plymouth Sound, SW England. *Proceedings of the Geologists' Association.*

Johnson, J.G., Klapper, G. and Sandberg, C.A. 1985. Devonian eustatic fluctuations in Euramerica. *Geological Society of America Bulletin, 96,* 567-587.

Kolodny, Y. 1981. Phosphorites. *In:* Emiliani, C. (ed) *The Sea. Vol. 7. The Oceanic Lithosphere.* Wiley, New York, 981-1023.

Krajewski, K.P. 1984. Early diagenetic phosphate cements in the Albian condensed glauconitic limestone of the Tatra Mountains, Western Carpathians. *Sedimentology, 31,* 443-470.

Marfunin, A.S. 1979. *Spectroscopy, luminescence and radiation centers in minerals.* Springer-Verlag, Berlin.

Mariano, A.N. 1988. Some further geological applications of cathodoluminescence. *In:* Marshall, D.J. *Cathodoluminescence of Geological Materials.* Unwin Hyman, London, 94-123.

McClellan, G.H. 1980. Mineralogy of carbonate fluorapatites *Journal o.1 the Geological Society, London, 137,* 675-681.

McConnell, D. 1973. *Apatite. Its crystal chemistry, mineralogy, utilization, and geologic and biologic occurrences.* Springer-Verlag, Wien-New York.

Paproth, E. and Zimmerle, W. 1980. Stratigraphic position, petrography, and depositional environment of phosphorites from the Federal Republic of Germany. *Mededelingen Rijks Geologische Dienst, 32-11,* 81-95.

Pound, C.J. 1983. The sedimentology of the Lower-Middle Devonian Staddon Grits and Jennycliff Slates on the east side of Plymouth Sound, Devon. *Proceedings of the Ussher Society, 5,* 465-472.

Scott, P.W., Kimyongur, N. and Middleton, R. 1987. The mineralogy and petrology of the "Coprolite Bed" phosphorite deposit (Lower Cretaceous) at Speeton, North Yorkshire. *Proceedings of the Yorkshire Geological Society, 46,* 123-131.

Seago, R.D. and Chapman, T.J. 1988. The confrontation of structural styles and the evolution of a foreland basin in central SW England. *Journal of the Geological Society, London, 145,* 789-800.

Smith, R.D.A. 1987. Early diagenetic phosphate cements in a turbidite basin. *In:* Marshall, J.D. (ed) Diagenesis of Sedimentary Sequences. *Geological Society Special Publication, 36,* 141-156.

Smith, S.A. and Humphreys, B. 1989. Lakes and alluvial sandflat - playas in the Dartmouth Group, southwestern England. *Proceedings of the Ussher Society, 7,* 112-117.