Composition and origin of phosphate nodules from the Dogger Formation, Yorkshire Coast, Northeast England

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Phosphate nodules (1–5 cm, in diameter) are concentrated in some of the foresets of the higher crossbedded part of the Dogger Formation, Yorkshire Coast. The nodules are composed of fine-grained impure phosphatic mudstone, without clear structure. They are usually admixed with coprolites, skeletal apatite and glauconite pellets in a feldspathic sandstone matrix. The phosphatic materials are found to be composed of carbonate-fluorapatite. The chemical formula both of nodules and bones are rather similar. The phosphatic materials are believed to be clasts of a micritic phosphate bed broken during a period of regression.

Introduction

Phosphate nodules are conspicuous component of the Dogger Formation which unconformably overlies the Liassic sequence along the Yorkshire Coast between Scarborough and Whitby (Fig. 1). For summary of the stratigraphy of the Yorkshire Coast (Hemingway, 1974; Hancock and Fisher, 1981). The requirements for phosphate formation are only met in very specific depositional environment and during special ocean circulation patterns (Bentor, 1980), and a phosphate bed is therefore always of considerable significance as an environmental indicator. The Dogger Formation is about 10 m thick at Blea Wyke Point near Ravenscar but is much thinner at Hawsker and Saltwick Nab, which are located on the NW side of the Peak Fault (Hemingway, 1974).

Fig. 1. Key map showing the location of the study area.

The Blea Wyke Point section shows a coarsening up ward section with large-scale crossbedding and vertical distribution towards the top. Two distinct thin horizons of phosphate conglomerate occur in the lower parts of the Formation and phosphate pebbles are sometimes concentrated on foresets in the higher crossbedded part of the

sequence. It was noted by earlier workers that the phosphate nodules were not in situ but had been transported into their present position (Rastall, 1905). Hemingway (1974) interpreted the pebbles to be phosphatized fragments of Liassic carbonate concretions.

Petrography and Mineralogy

The nodules are 1–5 cm in diameter and subangular to subrounded; then occur in a matrix of feldspathic sandstone, cemented by microcrystalline siderite and minor pyrite. The nodules consist of dark coloured, fine grained, impure phosphatic mudstone, usually without structure. Subordinate clasts of phosphate which include coprolites, pellets, fish bones and fish scales are also recognized.

Petrographically, apatite occurs into two forms; (a) apparently amorphous "collophane" which composes most coprolites and pellets, and (b) a better crystalline variety, which composes most skeletal apatite. Both varieties produce identical XRD patterns, which indicates that "collophane" consists of submicroscopic crystallites. Partial diagenetic recrystallization of "collophane" into the better crystalline variety is widespread particularly around some pellets and along cracks.

The characteristic main reflections of apatite at 2.79–2.81 Å (121), 2.69–2.71 Å (112) and 2.62–2.63 Å (202) have been detected in all samples of phosphate nodules and phosphatic sediments analysed. The obtained XRD patterns (the main d-spacings are 2.79/100, 2.69/80, 2.62/30 3.05/30 and 1.93/30) correspond to the standard data for francolite (carbonate fluorapatite variety, Gruner and McConnell, 1937). The slow scanning diffractograms of several phosphate nodules show two reflections, at 2.787 Å

Fig. 2. Slow scanning diffractogram of a phosphate nodule from the Dogger Formation, Yorkshire Coast

and 2.805 Å (Fig. 2). The former reflection is believed not to be related to apatite but most probably due to contamination by the cementing siderite.

Geochemical analyses of whole rock were carried out by XRF, except for Na and K which were analysed by flame photometer, and H₂O and CO₂ by gravimetric methods. Samples of phosphate-bearing rocks from the Dogger Formation have a phosphate content from 1.3 to 28% (Table 1). High iron and CO₂ contents in some samples are due to siderite cement.

Analysis of individual well-crystallized bone fragments (Fig. 3) and nodules were carried out on scanning microprobe quantimeter (ARL) using 15 kV accelerating voltage and 5–10 mA (Table 2). A model containing 16 cation sites, except hydrogen, was followed for the calculations of the chemical formula. According to McConnell (1973), the theoretical requirements to

Table 1. Bulk chemical analysis data of phosphate-bearing sediments from the Dogger Formation of Yorkshire Coast

Oxides Wt %	S a m p l e s					N u m b e r						AVERAGE
	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	
SiO ₂	39.43	23.49	13.12	48.73	48.79	36.42	33.42	54.42	43.07	37.07	22.70	36.42
Al ₂ O ₃	8.87	5.10	3.38	5.44	7.64	6.37	5.44	9.75	7.05	4.03	5.56	6.24
TiO ₂	0.57	0.37	0.10	0.36	0.57	0.49	0.46	0.66	0.37	0.43	0.35	0.43
Fe ₂ O ₃	11.05	9.04	3.80	11.45	13.71	18.90	34.99	5.88	2.40	12.68	7.88	11.98
FeO	8.55	1.48	0.37	12.58	3.11	12.80	5.85	5.03	0.37	20.39	5.07	6.87
MgO	2.46	1.02	0.56	1.60	1.32	2.28	1.85	1.66	0.35	1.48	1.42	1.46
CaO	11.75	30.35	42.69	3.66	6.99	4.83	2.64	8.25	21.84	3.80	26.83	14.88
SrO	0.02	0.04	0.11	0.02	0.01	0.01	0.01	0.02	0.04	0.01	0.03	0.03
Na ₂ O	1.14	1.61	0.43	1.11	0.99	0.90	1.01	1.37	1.69	0.89	0.92	1.10
K ₂ O	0.49	0.58	0.65	0.30	0.51	0.37	0.43	0.61	0.51	0.26	0.48	0.47
MnO	0.42	0.40	0.42	0.44	0.32	0.48	0.53	0.35	0.33	0.41	0.40	0.41
P ₂ O ₅	7.58	21.16	28.23	1.82	4.25	2.44	1.30	5.43	16.24	2.26	20.97	10.15
H ₂ O total	6.99	5.39	5.56	4.47	7.37	7.55	8.35	3.78	2.78	3.69	4.77	5.52
CO ₂	0.90	0.24	N.D.*	9.71	4.82	7.90	4.68	4.04	1.82	12.61	0.85	4.86

* means not determined.

Fig. 3. A back scatter electron image of fractured bone fragment (left) mounted in siderite and coated by pyrite. Right is the distribution pattern of the K α -radiation of phosphorus.

complete the 10 sites of Ca are satisfied by adding H₃O⁺ group, which is represented by (OH) in the chemical formula where hydrogen is excluded.

Bones:

Nodules:

Both bones and nodules proved to have rather similar chemical formulae, which correspond to that of carbonate fluorapatite. Minor enrichment in the contents of F as well as the cations substituting for Ca is detected in the formula of nodules.

Some of the iron and silica calculated into the formula in the nodule analyses may, however, be due to fine grained contamination of quartz and iron minerals. The F/P₂O₅ ratio is 0.09 which is slightly lower than analyses from Blaks Plateau where

Table 2. SEMQ analysis of nodules and bones from the phosphate-bearing sediments of Dogger Formation, Yorkshire Coast

Ingredients	Analysis of Nodules (average of 12 analys.)					Analysis of Bones (average of 11 analyses)				
	Wt %	Cation Ratios	Anion Ratios	Cations= 16, except hydrogen	Cationic Charges	Wt %	Cation Ratios	Anion Ratios	Cations= 16, except hydrogen	Cationic Charges
CaO	53.510	0.9542	0.9542	9.503	19.006	53.274	0.9499	0.9499	9.316	18.632
Ce ₂ O ₃	0.118	0.0007	0.0011	0.007	0.021	0.159	0.0010	0.0015	0.010	0.030
MgO	0.242	0.0060	0.0060	0.060	0.120	0.175	0.0043	0.0043	0.042	0.084
MnO	0.098	0.0014	0.0014	0.014	0.028	0.187	0.0026	0.0026	0.026	0.052
Na ₂ O	0.283	0.0091	0.0046	0.091	0.091	0.470	0.0152	0.0076	0.149	0.149
Fe ₂ O ₃	1.541	0.0193	0.0290	0.192	0.576	0.423	0.0053	0.0080	0.052	0.156
SiO ₂	2.214	0.0369	0.0738	0.368	1.472	0.712	0.0119	0.0238	0.117	0.468
SO ₃	1.242	0.0155	0.0465	0.154	0.924	1.178	0.0147	0.0441	0.144	0.864
CO ₂	2.750	0.0625	0.1250	0.623	2.492	5.283	0.1200	0.2400	1.177	4.708
P ₂ O ₅	35.550	0.5009	1.2523	4.989	24.945	35.955	0.5066	1.2665	4.968	24.840
		1.6065	2.4939	16.000			1.6315	2.5483	16.000	
F	3.293	0.1733		1.807		3.048	0.1604		1.637	
H ₂ O	0.428	0.0475		0.495	0.495	0.420	0.0466		0.476	0.476
Total	101.387				50.170	101.284				50.459
Extra Oxygen	1.387					1.284				

this ratio is 0.11 (Manheim *et al.*, 1980).

Origin of the Phosphate Nodules

The present study has found no evidence to suggest that the phosphate pebbles and nodules have been phosphatized from carbonate clasts in place after deposition. The fine-grained composition of the phosphate pebbles, the absence of a concentric concretionary structures, and the presence of the admixed skeletal fragments of apatite suggest that the phosphate pebbles have been transported from an area where phosphate beds or possibly older phosphate concretions had formed. The fact that the phosphate clasts are subrounded to subangular and do not have a typical nodular appearance or coating from sediment matrix, suggest to us that they are broken clasts of a micritic phosphate bed. A similar model has been described by Riggs (1979) for Miocene phosphate deposits in Florida.

The original phosphate may have been deposited in relatively shallow water, possibly associated with turbid organic rich water. During periods of regression, the phosphate beds may have been eroded and broken up to form phosphate pebbles and also disintegrated into components of coprolites, bones, etc. The occurrence of the phosphate pebbles in the Dogger Formation is, therefore, evidence of a period of transgression associated with a reduced clastic supply and high biological productivity followed by a regression, during which the Dogger Formation was deposited. As this regression occurred during a period of slow sedimentation, it is clear that this was not a progradational regression and may have resulted from an eustatic lowering of sea-level. The Dogger Formation is Early Bajocian age (Hemingway, 1974) and its deposition seems to coincide with an eustatic drop in sea-level as deduced from seismic stratigraphy charts (Vail *et al.*, 1977). Also,

Kolodny (1980) has pointed out that phosphate formed in stagnant basinal mud may be concentrated in higher energy environments during low sea-level stands.

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北東イングランド, Yorkshire Coast の Dogger 層中の 燐酸塩ノジュールの組成と起源

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標記の Dogger 層 (中部ジュラ系) のクロスベットの発達した部分に、径 1~5cm の燐酸塩ノジュールが集積している。これらは細粒の不純燐酸塩質泥岩からなり、長石砂岩質マトリックス中の糞石、スケルタル燐灰石、および海緑石ペレットなどの混在物である。燐酸塩は炭酸塩-フッ素燐灰石で、ノジュールも骨片も同じ化学組成を示す。これらの燐酸塩物質は、海退期に破碎され分解したミクライト質燐酸塩層の破片と考えられる。