

Mineralogical alterations in a concretion from a fourteenth-century ship, caused by environmental changes

DURING excavation carried out by archaeologists from the Danish National Museum at St. Tornebakke, Vigsø, in Han Herved (UTM-grid 32VMJ880291) some apparently Fe-cemented concretions were found. The aim of this work was to establish the composition and structure of the cementing material in one of these concretions.

The formation of iron constituents in aqueous solution has been studied in laboratory experiments by Berner (1964). X-ray diffractometry and chemical methods identified iron sulphides as tetragonal FeS, pyrite, marcasite, a magnetic cubic iron sulphide, and pyrrhotine. Transformation models for the monosulphides in recent marine sediments resulting in pyrite have been described (Berner, 1967, 1970) whereas formation of siderite should not be possible under sea-water conditions, as it is not stable in marine sediments. To form siderite, reducing conditions are necessary, e.g. in connection with transformation of organic matter. Siderite is a common mineral, forming under reducing conditions in fresh-water sediments (Baas Becking, Kaplan, and Moore, 1960), though it is also found as a transformation product during corrosion of cast iron under sea-water conditions (North, 1976). Here skeletal CaCO_3 covering cast iron transforms to FeCO_3 as iron diffuses from the cast iron to the calcite zone. Krauskopf (1967) has pointed out that this transformation can take place when the $\text{Fe}^{2+}/\text{Ca}^{2+}$ ratio exceeds 1/150.

The coarser skeletal particles from the concretions are rounded with a major axis from about 40 mm to about 2 mm. Most of the particles constituting the coarser part of the skeletal material are quartz. From a particle size of 2 mm down to 0.5 mm the number of subangular particles increases, as do the number of non-quartz particles. In the fraction from a major axis of about 0.5 mm down to 0.25 mm the number of particles is considerably increased. These particles are arranged as a matrix between the coarser skeletal particles. The particles are rather closely packed while the space between them is more or less completely filled with material < 30 μm (plasma).

The salinity of the sea-water at the coast outside the excavation area is on an average 33 ‰. The mean sea-water temperature for the warmest and coldest months are 16.5 °C (July) and 3.0 °C

(February). The corresponding air temperatures are 14.9 °C (July) and 0.0 °C (February). The contents of Fe, Ca, and Na in the fresh water that filled the excavation area after pumping stopped are Fe 0.44, Ca 60.4, and Na 22.7 ppm. The pH in the same water sample was determined as 8.1.

A part of the concretion consisting of plasma material containing mineral particles up to a size of 4-5 mm was ground to < 500 μm in an agate mortar. From a part of this sample free iron oxides were determined by a sodium dithionite determination by AAS (after Olsen, R. V., in Black *et al.*, 1965). A corresponding sample was treated with 6N HCl for 8 hours at 100 °C to remove non-silicate bound materials. Total C and total S were determined by a Leco dry-combustion analyser on the ground sample. Loss on ignition was determined at 1000 °C. The mineral content in the matrix material was qualitatively determined in a powder sample by X-ray diffractometry. A part of the concretion was impregnated with polyester resin to make polished thin sections for optical microscopy and electron-microprobe analysis. Distribution patterns were made for Si, Al, Fe, and Ca by the electron microprobe.

The chemical analysis of the samples showed that only a very limited amount of iron was extractable by sodium dithionite, Table I, and thus

TABLE I

	1	2	3
Fe_2O_3	67.61	1.49	10.2
CaO	2.13		
Al_2O_3	2.07	—	
SiO_2	1.96		
MgO	1.34		
MnO	0.09	tr.	
Na_2O	0.30		
K_2O	0.39		
Loss on ign.	23.90		
Total	99.79		

1. Extraction with HCl 8 h % of loss.
2. Extraction with dithionite % of total sample.
3. Extraction with dithionite % of HCl loss.

could be considered as iron from free oxides. In the same extraction Al and Mn were determined but according to Table I there was no Al and only traces of Mn. The HCl extraction showed a total loss of 14.6% (110 °C basis). The distribution of this loss between the different elements is shown in Table I. The greater part of the HCl-extractable material, which can be considered as matrix material, consists of iron. Corresponding to the micromorphological investigation, there is some Ca present while the micromorphological analysis of the matrix material does not reveal Al, Si, and Mg. It is possible that some ions have been extracted from the skeleton material minerals. As can be seen from Table II, the results of the C- and S-analysis and the loss on ignition have been converted according to the HCl treatment loss. It is considered that the C- and S-contents as well as the loss on ignition are principally due to matrix material.

Assuming a very low content of organic matter and all the Ca to be present as CaCO₃, the average content of calcite in the matrix material is 3.8%. If the remaining carbonate is assumed to be present in FeCO₃, the siderite content will be 25%. As these amounts of siderite and calcite can be responsible for 9.4% loss on ignition and the sulphur responsible for only 2-3%, a major part of the loss on ignition must be due to loss of water from other iron compounds.

The sulphur content in the original, undisturbed environment presumably existed together with iron in pyrite, which, under the actual conditions, has been transformed into other sulphur compounds. During the dissolution of the iron from the ship, ferro compounds have been formed due to the presence of organic matter. The sand and gravel have been cemented by these iron compounds, and while the concretions have remained undisturbed under the sea-floor, not much has happened to them. As the character of the environment changed from salt to fresh water and the conditions probably became more oxidizing, pyrite for example was transformed. In the relatively sulphate-rich sea-water, it is not likely that siderite and calcite would be found. These compounds were probably formed under conditions like the present-day environment. X-ray diffractometry analysis of the

matrix material reveals quartz, siderite, calcite, and some feldspar, while there is no trace of pyrite. In similar concretions from a ship of the same age (from 1370) found in marine environment at Vejby on the north coast of Sjælland there is a much higher content of S and very strong pyrite lines in the diffractometer trace. The distribution patterns from the electron microprobe show quartz particles which has a thin coating of iron-bearing material. Upon this calcite crystals are growing out into the voids. Spot analysis on the calcite crystals showed a Ca content of 39.6%. With a theoretical value of 40.1% Ca in CaCO₃ there should be no doubt that the crystals are calcite.

The iron distribution indicates that the calcite must have been precipitated later than the iron compounds coating the quartz particles. The calcite crystals can only be recognized in that part of the concretion where there are rather large voids. Since Ca-rich water occurs in these old beach ridge materials which have a high content of chalk, precipitation of calcite may have taken place at a rather late stage and in the present environment. Siderite can be recognized in those parts of the concretion in which the voids are almost filled. Here the permeability was presumably so low that the iron concentration has become high enough for precipitation of siderite instead of calcite. According to the equation

$$\text{FeCO}_3 + \text{Ca}^{2+} \rightleftharpoons \text{CaCO}_3 + \text{Fe}^{2+}$$

$$K = \frac{[\text{Ca}^{2+}]}{[\text{Fe}^{2+}]} = \frac{[\text{Ca}^{2+}][\text{CO}_3^{2-}]}{[\text{Fe}^{2+}][\text{CO}_3^{2-}]} = \frac{4.7 \times 10^{-9}}{3.1 \times 10^{-11}} = 152$$

the concentration of Ca has to be about 150 × the Fe concentration before precipitation of calcite will take place in the presence of iron. The iron concentration in the low-permeable part of the concretion was probably high enough for siderite precipitation. In the high-permeable part the Ca-concentration was sufficient for calcite precipitation according to the Ca/Fe ratio measured in the fresh water. Siderite might have been precipitated first, to be later replaced by calcite, as possibly indicated by the distribution patterns.

TABLE II

C in % of total sample	C as % carbonate in matrix	S in % of total sample	S in % of matrix	Loss on ign. in % of total sample	Loss on ign. in % of matrix
0.44	15	0.65	4.5	3.48	23.9

Acknowledgements. The author wishes to thank Professor J. T. Møller and Museum Keeper O. Crumlin-Pedersen for their valuable discussions during preparation of the manuscript, and Lektor J. R. Wilson for his improvement of the English.

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[Manuscript received 7 May 1980;
 revised 9 June 1980]

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PER NØRNBERG

MINERALOGICAL MAGAZINE, DECEMBER 1980, VOL. 43, PP. 1050-2

Types of distribution of the minerals of the Meldon Aplite, Devonshire: Addenda

THE four figures in the above paper, published earlier in this volume (Chaudhry and Mahmood, 1979), were unfortunately omitted and are therefore reproduced here.

REFERENCE

- Chaudhry (M. N.) and Mahmood (A.), 1979. *Mineral. Mag.* **43**, 307-9.