

On Pyrite in Deep-Sea Sediments

By

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On a detour from its fixed course the vessel "Albatross" of the Swedish Deep-Sea Expedition 1947-1948 secured two cores from stations off the west coast of North Africa. This was done at request of Professor A. HADDING, Lund. From data obtained, *inter alia*, by the "Meteor" Expedition it was evident that recent glauconite is formed in quantities in this area. The purpose was to collect material for further investigation of glauconite. However, the cores (Albatross 224 and 225) were sampled too far off-shore (approx. 215-240 km) and at a greater depth than calculated and accordingly beyond the very area of formation of glauconite. Core 224, which measured 890 cm in length, was taken at lat. N 18°50', long. W 18°24' at a depth of 2810 m. Core 225 had a length of 970 cm; it was taken from a depth of 2978 m, at lat. N 18°44', long. W 18°44'. Glauconite or aggregates of a mineral similar to glauconite were extremely sparse in the sediment. Instead, another authigenic iron-mineral was present, namely pyrite.

The sediment in the cores is mainly of the type detrital Globigerina ooze, according to the classification of REVELLE (1944). Certain parts in the lower portion of core 225 contain more than 50% CaCO₃, while in other horizons the sediment would be characterized adequately as clayey or silty mud. In addition, there are seams of almost pure fine-sand. The colour of the sediments as observed on fresh-cut surfaces varied principally between light olive grey, dusky yellow green, and dark greyish green (Rock-color chart, U.S. Nat. Research Council, 1948).

Below a level of about 150 cm below the surface more or less abundant thin black streaks in the moist sediment were visible to the naked eye. These streaks were caused by small soft sticky aggregates which had been dragged along the blade on lengthwise splitting of the core sections. Chemical analysis and X-ray diffraction showed that the aggregates consist of pyrite. They are not confined to the distinctly green portions of the sediment.

Formation of iron sulphide in deep-sea sediments seems not to be an ordinary process. ARRHENIUS (1952), in his extensive material from the Pacific, mentions one instance only in which precipitation of sulphide may have occurred. Relating to sediments from the Atlantic, CORRENS (1936, p. 295) remarked that "Sulfid konnte weder mikroskopisch, noch röntgenographisch, wohl aber ... chemisch nachgewiesen werden". The content of FeS₂ in "Blauschlick" ranged between

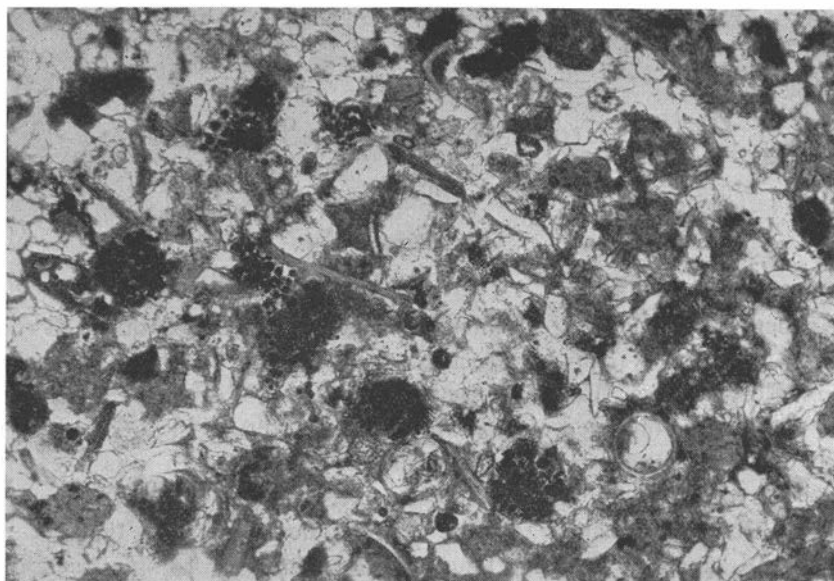


Fig. 1. Solution of calcite in connexion with formation of pyrite. The foraminiferal shells have disappeared almost completely, but their external shape can still be traced. Core 224. 593 cm level. $\times 100$.

0.04 and 0.47%. BRAMLETTE *et al.* (1940) recorded insignificant quantities of iron sulphide in two deep-sea cores from approx. 50° N in the Atlantic. A limited formation of pyrite in marine sediments has been established in cores from basins of varying depth and at varying distance from the coast off South California (EMERY and RITTENBERG 1952). There are no continuous records of echo-sounding in the area from where our cores were sampled, nor were any investigations of the bottom water made. But data available on the bottom topography from this area¹ do not indicate any restriction of the circulation of water due to basin formation. Recent sediments at least have been deposited in an open-sea environment.

The kind of sulphide precipitation on the sediment surface that is a normal phenomenon in near-shore areas with stagnant bottom water (euxinic environments) will not be considered in this connexion.

Chemical analyses of samples from different horizons in the material at my disposal revealed a minimum content of 0.26% FeS_2 (core 224, 28 cm), and a maximum content of 1.8% FeS_2 (core 224, 873 cm) calculated on a dry matter basis. In spite of the fact that pyrite is more abundant below the 3 m level (particularly so in core 224), the increase is not continuous. Some horizons in the lower portion of core 225 are very poor in pyrite.

The pyrite is clearly a subsurface formation. It appears mostly as aggregates

¹ Echo-soundings of the "Meteor" Expedition (1933); HEEZEN's topographic map of the N. Atlantic (1957).

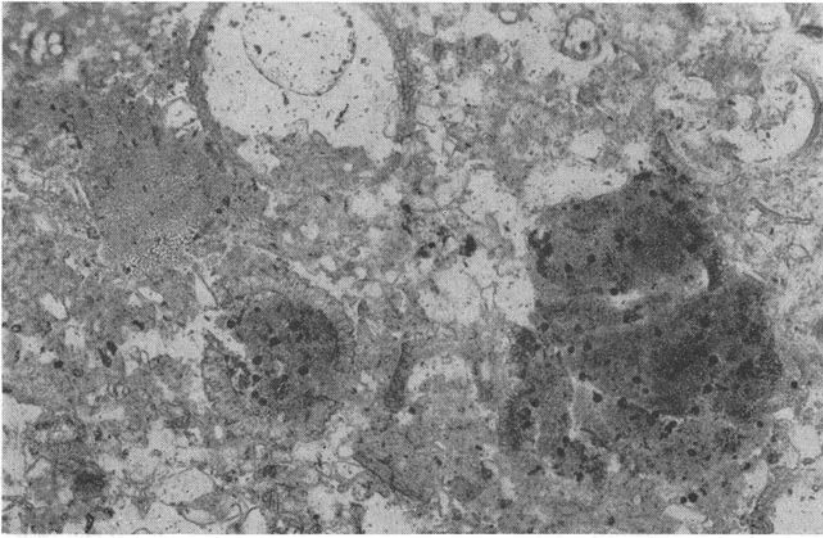


Fig. 2. Common form of pyrite showing rounded grains (appearing dark in the photograph) in a ground-mass of extremely fine-grained pyrite. There are only insignificant remains of the test of the foraminifer to the right. Core 224, 715 cm level. $\times 100$.

of tiny spherical bodies that fill the chambers of foraminiferal shells. In thin sections a slight remainder of the shell is frequently visible around the pyrite or the shell has been dissolved completely, yet the soft smeary sulphide aggregate has retained its shape (see text-figs. 1 and 2). This will be possible under the condition only that the formation of pyrite has taken place *below* the sedimentary layer exposed to the action of mud-eaters.

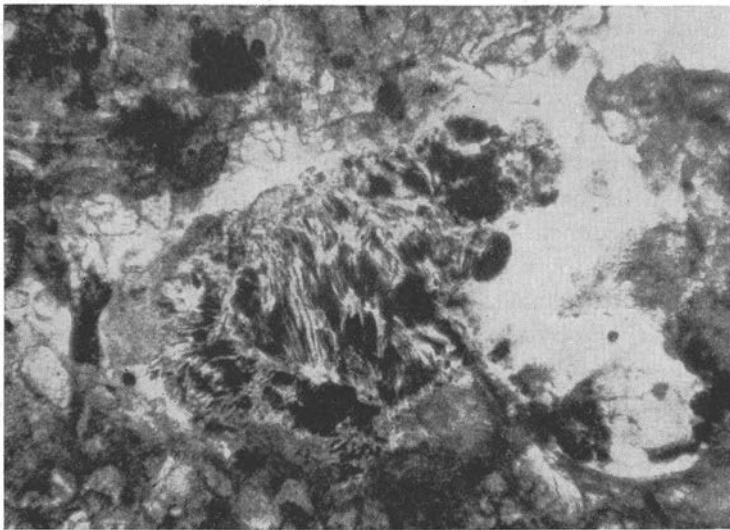


Fig. 3. Authigenic clay mineral partially replaced by pyrite. Same thin section as that pictured in Fig. 1. $\times 100$.

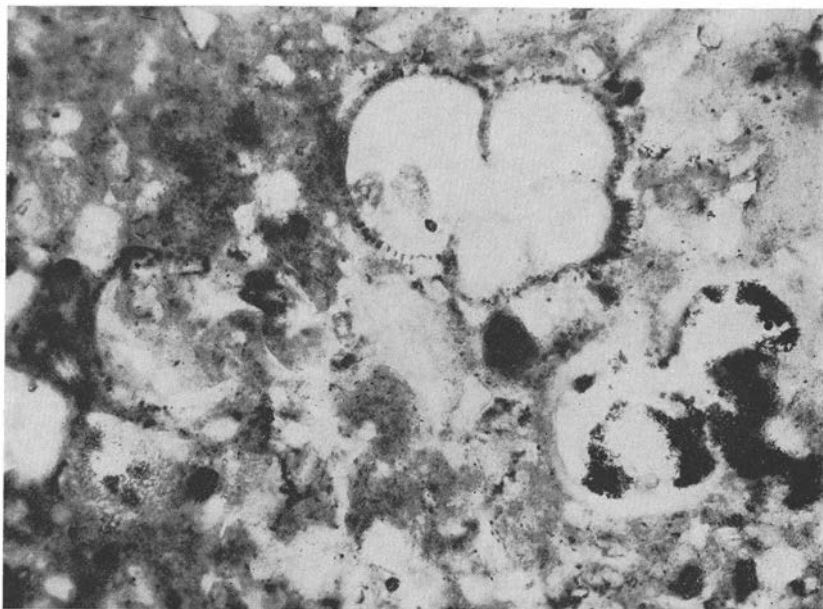


Fig. 4. Sediment rich in pyrite, showing disintegration (in the lower right) and recrystallization of foraminiferal shells; opaque inclusions in each individual calcite crystal. Core 225. 383 cm level. $\times 150$.

In some instances, the pyrite forms irregular lumps and sometimes it appears as threads, about 1 cm long, occasionally branching, which replace organic matter entirely or partially. In some few horizons with abundant pyrite I have noticed partial replacement of a clay mineral which is probably authigenic itself, considering its size in relation to surrounding mineral grains (text-fig. 3) (cf. NORIN 1953).

After-burial or diagenetic dissolution of calcium carbonate in recently formed marine sediments has received little attention in the literature. The general opinion seems to be that the varying and in many cases quite considerable dissolution of shells that has been stated in cores from all oceans has occurred essentially at the sediment-water interface. This may well be the case. But in the present material there is a close connexion between formation of pyrite and dissolution of carbonate. This is clearly seen in thin sections and is demonstrated, *inter alia* by the above-mentioned shells destroyed entirely or in part that enclose the pyrite concretions. In beds rich in pyrite there are also examples of disintegration (according to REVELLE and FAIRBRIDGE 1957, p. 275 = transformation into a micro-granular or amorph-looking structure) and recrystallization of the shelly material (text-fig. 4). The formation of pyrite has taken place without affecting the calcium carbonate in those cases where the pyrite content is sparse, filling scattered shells only.

There is also an obvious parallelism between the percentage of sulphide

and "the grade of crushing" measured at different levels (the grade of crushing means here the number of fragments per 100 complete shells in the fraction $> 150 \mu$). The connexion between pyrite and grade of crushing is often more evident than the connexion between grade of crushing and the percentage of organic matter. The metabolism of living organisms and the decomposition of organic substance produce the carbon dioxide which may be the main cause of dissolution of carbonate at the sediment surface (cf. KOCZY 1953).

The parametres that may control the formation of pyrite are pH, Eh, certain mechanical processes, and, of course, the supply of sulphur and iron.

pH. Almost all reliable measurements of pH in open-sea sediments vary between 7 and 8.5 (BAAS BECKING *et al.* 1960). Accordingly, pH does not restrict the formation of pyrite, because pyrite is stable at least between pH 6 and 9 (GARRELS 1960). Yet the pH of the sediment is of interest, because the "limestone fence" is at about pH = 7.8 (KRUMBEIN and GARRELS 1952). If formation of pyrite has occurred below pH 7.8, simultaneous dissolution of carbonate is likely. No measurements of pH or Eh of the sediments were made on board the ship. This means that the values calculated long afterwards in this laboratory may differ considerably from those prevailing in the sediment *in situ*. OPPENHEIMER (1960) has pointed out that a low pH in an anaërobic sediment will rise very rapidly after removing the sample from its natural environment. Irrespective of this and other sources of error, if any (for example, diluting the sample with water), there is a clear tendency of lower pH-values in beds rich in pyrite as compared with the mean value of the cores (which is 8.17). In a few horizons, however, I have observed abundant pyrite along with higher than normal pH.

From a theoretical point of view, both decreasing and increasing pH is conceivable in connexion with formation of pyrite. In case hydrogen sulphide¹ and carbon dioxide have been formed by decomposition of organic matter, pH must be expected to decrease. On the other hand, if sulphate-reducing bacteria transfer the strongly acid sulphate radical into sulphide, a weak Brönsted base, the pH of the interstitial water may be raised and dissolution of CaCO₃ will not occur (REVELLE and FAIRBRIDGE 1957). Both processes can be considered to occur simultaneously in the sediment. The net result may depend on the kind of organic matter available and the types of bacteria thriving on it.

Deposition of marine plankton should be abundant in the actual area with upwelling waters rich in foodstuff. The great frequency of silt and fine-sand in the sediment makes it probable that even remains of terrigenous or near-shore organisms have been carried out and embedded in the sediment. Mean values of carbon and nitrogen are 0.97% and 0.094%, respectively, in core 224,

¹ MOSEBACH (1952) found by laboratory experiments that H₂S dissolves calcium carbonate as vigorously as does CO₂.

and 0.66% and 0.063%, respectively, in core 225. Also core 224 has more pyrite and higher percentage of detritus than core 225. This would indicate that the organic matter washed out from comparatively shallow sea-areas plays a decisive rôle in the formation of pyrite.

Eh. The oxidation-reduction potentials of the sediments depend, too, on the microbial activity and the kind of organic matter available. According to the pH-Eh diagram of GARRELS (1960), which was calculated on theoretical grounds, the stability range of the pyrite is below -200 mV in the relevant pH range. It must be assumed that Eh is an important controlling factor of the formation of pyrite. Normally, the redox potential of sea water is positive, average surface sea water having $Eh = +400$ mV. Even the Eh of bottom water is believed to be weakly positive. The only measurements of abyssal sediments published so far (BAAS BECKING *et al.* 1960) originate from a couple of mid-Pacific cores which have throughout positive Eh. The South California coastal sediments referred to above show as a rule negative Eh below 0.5-1 m under the surface, but one single core only showed potentials lower than -200 mV. In spite of a high percentage of carbon in these sediments (mean value 3.5% C) and an amount of hydrogen sulphide big enough to give strong odour occasionally, the percentage of FeS_2 in the horizons richest in pyrite is only of the order of 0.01% of the whole dried sample. In the material under discussion, Eh must have been lowered locally to such a point that a steady growing of pyrite was permitted.

Mechanical factors. The particle size and interstitial space of the sediments may influence the formation of pyrite (as well as other diagenetic processes) in various ways. Smaller particles with larger surface area adsorb more organic materials and bacteria than coarser. On the other hand, arenaceous and shelly sediments have larger interstitial spaces and allow the development of a more varied and vividly migrating bacterial life and more effective diffusion of food and metabolic wastes (OPPENHEIMER 1960). A certain mobility is also required for fresh supply of sulphur and iron to the spot where formation of pyrite occurs. Stagnation of the interstitial water must lead to all chemical reactions soon coming to a standstill, and no diagenesis will occur even though the environment be favourable in other respects. This may be the case in the California basin sediments mentioned above. These are characterized by emitting hydrogen sulphide and by pH being frequently as low as 7.5. In spite of this, the formation of pyrite is insignificant, and the foraminiferal shells are said to show no signs of dissolution. These cores consist chiefly of clay (median diametres finer than 4μ).

The grain-size varies a good deal in my cores. Lumps or beds of fine-sand alternate with denser portions. The foraminiferal shells, too, are often irregularly distributed in the sediment. Microscopic examination shows that there is a

tendency towards vigorous formation of pyrite at the very interface between two types of facies. Optimal conditions should exist at an interface where one type of facies (mud with a high percentage of organic matter) offers the requisite for the proper physical and bacterial environment, while the other (silt facies) by its mobile interstitial water is favourable for fresh supply of the chemical elements involved.

In two ways, the rate of sedimentation may influence the formation of pyrite. By incomplete space packing of the grains rapid accumulation will give the sediment a higher permeability (GRIM and BRADLEY 1955). In addition, on rapid accumulation complete oxidation of the readily disintegrating organic compounds does not occur at the sediment surface. Instantaneous covering up of the sediment surface by dust fall or by deposition from turbidity currents may be particularly efficient in this respect. Both phenomena can be assumed for the sediments under discussion here. The average rate of deposition in core 224 has been calculated at 15–20 cm/1000 years which is considerably above the mean of deep-sea sediments.

Sulphur. The hydrogen sulphide, or, in solution, rather (HS)⁻ ions, that is required for the formation of pyrite may be derived either from sulphur compounds in organic matter, or, by action of sulphate-reducing bacteria, from (SO₄)⁻ in the interstitial water. The latter is probably the main source. In this case, the factor of enrichment is as low as 3, (provided the pore-water has the same composition as the sea-water, the water contained in the sediment be 50%, and 0.5% pyrite has been formed). Taking solely the protein in organic substance as source-material will make the enrichment factor unreasonably high. The supply of sulphur must be considered a limiting factor in the formation of pyrite only in case the mobility of the interstitial water is restricted.

Iron. Iron in solution occurs in sea-water in very low concentrations. The total amount of iron, most of which is present as colloids or combined with organic compounds, is only 2–50 mg Fe/m³ (DIETRICH and KALLE 1957). In deep-sea sediments iron is deposited mainly as colloidal iron oxide aquate (GOLDBERG and ARRHENIUS 1958; CORRENS 1942), flocculent and/or adsorbed to organic substance. The hydrous iron oxide is unstable with respect to both hematite and goethite (GARRELS 1960). But prior to this aging, iron oxide is supposedly highly disposed to reactions and is easily reduced. The organic matter here serves the double purpose of concentrating iron and giving it the reduced state wanted.

In certain portions of cores 224 and 225 the sediment contains some ferrous compound which is extremely unstable. Of every freshly cut core section two or more analyses of Fe⁺⁺ were made. The samples were extracted, on the one hand, from the least green portions, on the other, from portions having the most vivid green colour. The values obtained by the analytical method used do not account

for the iron of the pyrite. After air-drying, new analyses of Fe^{++} were made of samples from the same horizons. The values then obtained gave smoother curves (0.4–0.7% FeO), while values relating to moist samples (re-calculated on a dry matter basis) demonstrated much greater variation, particularly in core 224. A definite connexion between the percentage of Fe^{++} in a moist sample and green colour (but not blackness) of the sediment could be established: the deeper the green hue of the sediment, the higher the Fe^{++} values, rising to twice the value of that of corresponding dry sample. In all instances, equal values of the percentage Fe^{++} were obtained of fresh and dried samples from horizons that on ocular inspection of the cores had been recorded as non-green.

Fe^{++} maxima do not as a rule coincide with pyrite maxima, even though pyrite may often abound in, or in the neighbourhood of, the greenest parts of the sediment.

In describing basin sediments from off South California EMERY (1960) has given colour symbols which are similar to those that apply to the green portions of the cores dealt with by me. EMERY suggests that the illite and montmorillonite which make up the bulk of the sediment are responsible for the green colour. He also states that the colour returns approximately to the original when the dried muds are wetted again. The clay fraction in my material is also made up largely of montmorillonite and illite (approx. 10% of the whole dry sample), but X-ray and DTA give much the same picture regardless of whether the sediment was originally green-coloured or not. Nor does the original green colour return on wetting the sample. It is evident that the colour is dependent on iron in a reduced state, but Eh has not been low enough to permit but a partial formation of pyrite. If, on the other hand, formation of glauconite was initiated in the green portions, the process could not develop into the stable mineral because interaction between reducing and oxidizing environments, which seems to be essential to the formation of this mineral, did not occur. In my opinion, the formation of glauconite, for instance from defective three layer clay lattices (BURST 1958), has to be initiated when iron is in the ferrous, reactive, state. The glauconite becomes stable only in the case of the greatest part of the iron becoming oxidized. This may be due to differences in the ionic radii, Fe^{+++} having the more suitable size (Fe^{+++} 0.74 Å; Fe^{++} 0.64 Å; Al 0.51 Å).

Iron originating from minerals in the terrigenous fine-sand has probably not contributed to the formation of pyrite. A characteristic element of the sand are "limonite"-looking grains of about the same size as the quartz grains that make up the bulk of the detritus. Quartz may occasionally form a nucleus in the red grains (cf. "Wüstenquartz", RADZIEWSKI 1938, and "Crôutes ferrugineuses", DUPLAIX and CAILLEUX 1952). X-ray analysis showed that the red grains are aggregates of quartz, clay minerals, and hematite (maybe goethite as well). In thin sections these grains may be seen to lie occasionally close to pyrite concretions, entirely unaffected, as it seems, by the strongly reducing

environment in which they had been resting. In other connexions, too, it has been previously observed that hematite is very resistant (cf. e.g. GRIM 1951). Also in GARRELS' stability-relation diagram, referred to above, a point can be found (pH approx. 7.5, $E = -200$ mV) in which pyrite and hematite are in equilibrium.

The amount of iron in marine sediments does not control the formation of pyrite. High percentages of pyrite in cores 224 and 225 do not coincide with horizons characterized by iron percentages above the average. It is essential, however, that the iron is in, or can be transformed into, a state ready to react.

Summary. In two cores from off the west coast of North Africa diagenetic pyrite has been stated to occur in various horizons and in varying concentrations, the maximum amount of FeS_2 being 1.8%. The sediment may be characterized as Globigerina ooze with silty sand as an important component. Abundant formation of pyrite is invariably accompanied by transformation or solution of the calcium carbonate shells. There is probably a relation between the pyrite and the formation of glauconite nearer to the shore. Both are authigenic iron minerals and require the presence of some organic matter for being formed. But pyrite is a subsurface form which is stable at a very low Eh, the formation of which is favoured by a rapid rate of deposition, while glauconite is formed on the sedimentary surface in a semi-reducing environment with agile water and very slow rate of deposition.

Abundant pyrite has rarely been found in deep-sea sediments. pH and the supply of sulphur and iron are no limiting factors. Controlling factors in the formation of pyrite are the permeability and redox potential of the sediment. The redox potential is in its turn dependent on the microbial activity. The material now dealt with should be classed as deep-sea and open-sea sediments (depth of water approx. 3000 m, no basin formation). Nevertheless it would seem that nearness to the shore is vital in the formation of pyrite. This view is based on the following facts:

(1) Comparatively high concentration in the sediment of organic matter derived in part from near-shore waters or a terrigenous source which may support a bacterial flora favourable to the formation of pyrite.

(2) High rate of accumulation, allowing part of the readily disintegrating organic matter to get buried in the sediment without having been oxidized. This will give the prerequisites for low Eh-values within the sediment.

(3) Sufficient mobility, at least partially, of the interstitial water due to high rate of sedimentation and to deposition of a fair quantity of silt or fine-sand.

(4) In places very inhomogeneous sediments with frequent change of micro-facies. This renders the system "non-balanced", which should improve the prerequisites for diagenesis. The most abundant formation of pyrite seems to occur at interfaces between oozes or muds containing organic matter and sand facies.

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