

33. MARCASITE IN MIOCENE CALCAREOUS SEDIMENTS FROM HOLE 315A.

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ABSTRACT

This chapter notes the occurrence of the pyrite dimorph, marcasite, as a minor diagenetic cement in light purple to bluish-white Miocene calcareous oozes. It occurs as the only mineral phase cementing small, elongate, gray aggregates with the morphology of worm burrows and may represent a worm's last stand. Scanning electron micrographs reveal clumps of typically fluted or curved orthorhombic dipyrramids of marcasite supporting a framework of broken and corroded siliceous fossil fragments. Pyrite co-occurs in the same stratigraphic horizons. Marcasite has apparently formed in association with animal decay that creates a microenvironment where pH is near or below 6.0. It may later invert to pyrite, possibly in association with the initial cementation and compaction processes leading to a chalk marked by pyritic liesegang rings. Iron sulfide occurrences in Hole 315 are consistent with the very high sedimentation rates reported in the variegated Miocene oozes and chalks.

INTRODUCTION

Marcasite is a common iron sulfide mineral in peat or coal areas (e.g., Edwards and Baker, 1951), but has not commonly been reported from the open marine environment. Accepted theories postulate that it is formed under more acid conditions whereas pyrite is favored at neutral or slightly alkaline pH values (Fairbridge, 1967; Blatt et al., 1972; Love, 1967; Edwards and Baker, 1951).

Pyrite has been noted in deep-sea sediments from almost every DSDP cruise, while marcasite has rarely been reported. In one instance, Donnelly and Nalli (1973) described rectangular iron sulfide crystals of possible marcasite which, however, were identified as pyrite. They speculated that these might originally have been marcasite crystals which have inverted to pyrite as the sediment matured. Berger and Von Rad (1972) in a careful study of DSDP Leg 14 calcareous sediments noted only the presence of pyrite. Pyrite and marcasite have generally not been differentiated. The lack of occurrences reported in DSDP volumes may be the result of several factors: (1) it is a very minor constituent and commonly co-occurs with, but is dominated by pyrite, (2) the routine X-ray analysis is not programmed to recognize this mineral in the search mode, or (3) most iron sulfide identifications are made by optical methods. The confusion is understandable. Marcasite (FeS_2) is the metallic-yellow orthorhombic dimorph of pyrite and can best be differentiated by its characteristic X-ray diffraction d -spacings (and intensity): 2.71(100), 1.76(63), 3.44(40), 1.19(30), 2.41(25), 2.32(25) in Angströms. Possibly marcasite is more common than hitherto reported.

GEOLOGY

Hole 315A penetrated approximately 400 meters of Miocene foram and rad-nannofossil ooze to chalk (Cores 3A to 5A, 85-465 m). Within this highly calcare-

ous sequence, X-ray analysis showed that pyrite is a significant diagenetic mineral in the decalcified fraction (Cook and Zemmels, this volume). The purplish and bluish patina of the oozes and chalks is apparently imparted by variations in the content of disseminated sulfide. Ultrathin iron sulfide coatings, some identified as pyrite, are common on scattered radiolarian and sponge fragments (see Figure 1). A few rare black laminae were encountered which were found to be rad-spicular oozes with pervasive iron sulfide coatings (e.g., 315A-5-2, 125 cm, 343 m). Mottling, as evidence of burrowing activity,

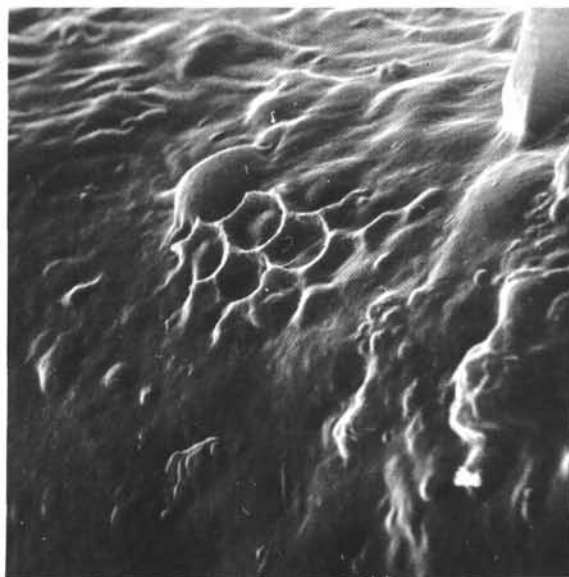


Figure 1. High magnification SEM micrograph of an ultra-thin, yellowish-gray iron sulfide coating on a triaxon sponge spicule. Sample 315A-1, CC (85 m), Miocene (HCl treated). Scale bar = 2 μm .

is common throughout the sediments. Maximum pyrite concentrations (43% of the decalcified fraction) occur as clumps in a redeposited foram-grainstone containing palagonite and plagioclase. This implies that redeposited sediments are an important source of sulfate minerals (315A-4-3, 103 cm, 260 m). Within the calcareous sediments, pyrite commonly ranges from 4% to 15% of the decalcified fraction and is accompanied by barite (50%-70%) and minor terrigenous components (Cook and Zemmels, this volume).

The ooze to chalk transition occurs at a depth of roughly 300 meters. Pyrite also occurs within the chalk section, outlining or filling burrow traces surrounded by typical liesegang rings (see Figure 2). These rings document a diffusion phenomenon of periodic alterations between solution mobility (diffusion) and supersaturation (nucleation and precipitation) (Fairbridge, 1967). Because this process is dependent primarily on a diffusion gradient away from a burrow locus, it might be expected to form concentric circles in a homogeneous medium such as the chalks. In Figure 2 note that the ellipsoid rings show a flattening of about 3:5. If this is a result of compaction, about 30% has taken place in the time between the beginning of ring formation and the conversion from ooze to chalk.

MARCASITE

Within the Miocene pyrite-bearing, calcareous sediments marcasite was only identified from Samples 315A-1, CC (85 m) and 315A-3-3, 54 cm (145 m). The fragments were isolated by sieving, washing, and hand picking from a light purple splotch in the nannofossil oozes. In these samples marcasite was also the only sulfide phase. It occurs as hard, elongate, irregular gray clumps up to 1 cm long and 2 mm in diameter which apparently represent the internal molds of burrow tubes.

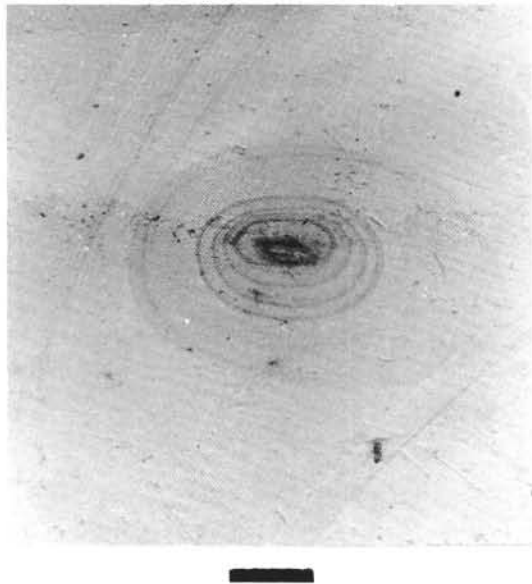


Figure 2. Lower Miocene nannofossil chalk with pyrite concretions in a burrow surrounded by liesegang rings. Sample 315A-8-2, 120 cm (592 m). Scale bar = 1 cm.

Scanning electron micrographs (Figure 3) illustrate such an aggregate. Note that marcasite is a binding cement for corroded and broken diatoms, radiolarians, and spicules. They have probably passed through the digestive tract of a worm. Note the criss-crossed, fluted, spindle-like irregular orthorhombic dipyramids which contrast sharply with typical pyrite framboids.

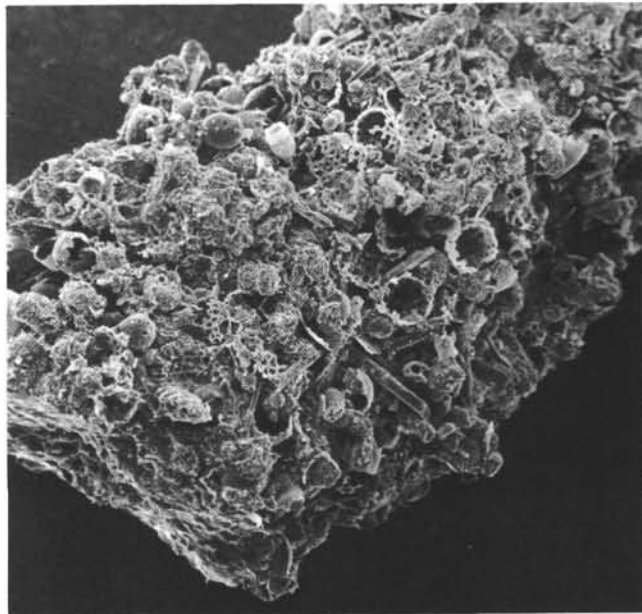
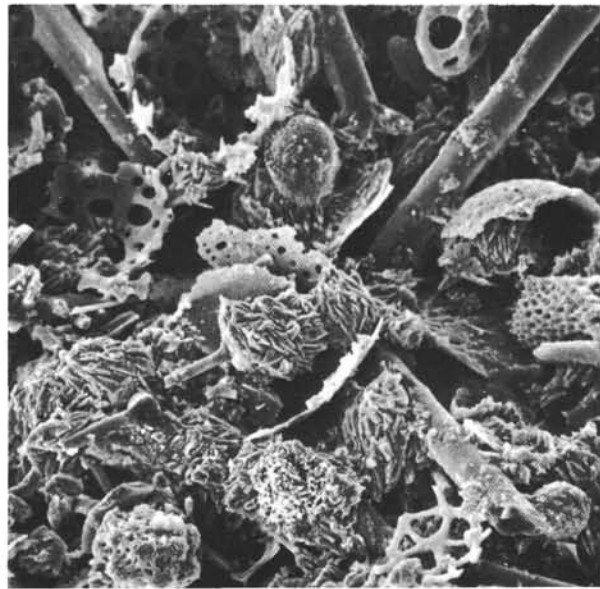


Figure 3a. Scanning electron micrograph of a light gray, elongate, irregular rod-shaped aggregate of siliceous fossils held together by a marcasite cement. Sample 315A-3-3, 54 cm (146 m), middle Miocene) Scale bar = 0.2mm.



(b) Detail of aggregate showing the broken or corroded condition of siliceous fossils. Criss-crossed pattern of marcasite clumps visible. Scale bar = 70 μ m.

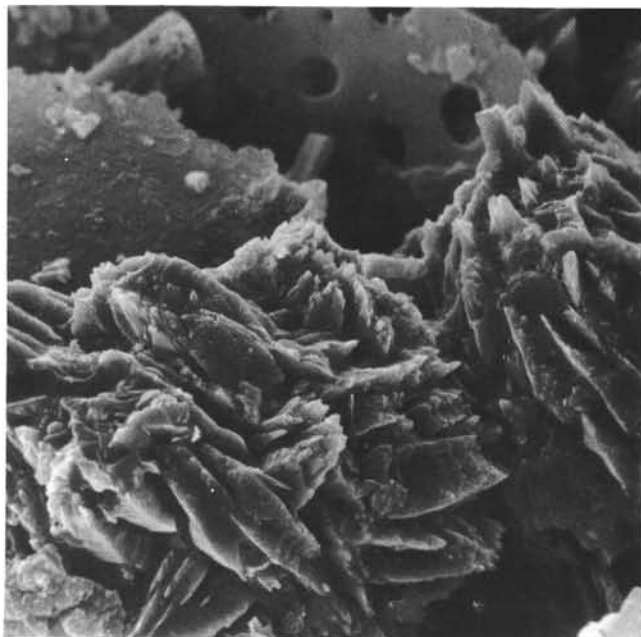


Figure 3c. Close-up of marcasite cement. Cris-crossed, irregular, and curved crystal aggregate. Note the spongy texture on some crystal surfaces. Scale bar = 10 μm .

Why is marcasite favored at these local sites? Berner (1971) has discussed the processes involved in pyrite formation from primary iron mono-sulfides. Special local conditions are necessary. Undoubtedly, the formation is related to the relative alkalinity of the microenvironment around a decaying worm. Sulfate reducing bacterial activity produces CO_2 and H_2S and initiates a drop in pH from the pH values above 7.0 common in a calcite-buffered ooze. The physicochemical conditions in the microenvironment of many organic processes remains largely unknown. But, if pH is lowered and held to about 6.0 some calcite may dissolve and, in addition, conditions favor the direct formation of marcasite rather than pyrite (Fairbridge, 1967; Tröger, 1967; Rickard, 1969). Once initiated, marcasite proceeds to precipitate as the stable form. pH measurements of interstitial waters in Hole 315A indicated that pH is lowest in the Miocene sediments. It drops to 7.0 near 85 meters and increases linearly to 7.4 near 500 meters. As diffusion normalizes the microenvironment to that of the surrounding calcareous oozes, a conversion of marcasite to pyrite may take place. The Miocene age of the sediments containing both marcasite and pyrite suggests that any inversion is more complex than a maturation model. Marcasite has not been identified in any samples from the chalk zones. Possibly compaction and cementation of the oozes to chinks is an initiating factor for an inversion.

Pyrite formation in deep-sea nannofossil sediments has been interpreted to indicate rapid accumulation rates (Berger and Von Rad, 1972). The very rapid sedimentation rates of 10 to 20 m/m.y. from Miocene oozes in Hole 315A are in agreement with this observation (Schlanger, Jackson, et al., this volume). Organic compounds are removed from the seawater-sediment in-

terface before they are completely oxidized. Further destruction by aerobic bacteria removes the last vestiges of O_2 from the pore waters. *Desulforibrio desulfuricans* activity releases H_2S which mobilizes iron sulfate compounds leading to the conversion of iron sulfide to pyrite. Rapid nucleation favors a very small crystallite size disseminated in the oozes, (Berner, 1970, 1971). For some reason of organic surface chemistry, the sulfides are commonly present as an ultrafine, meshwork coating on radiolarians (see Figure 4a, b). The purple and blue hues

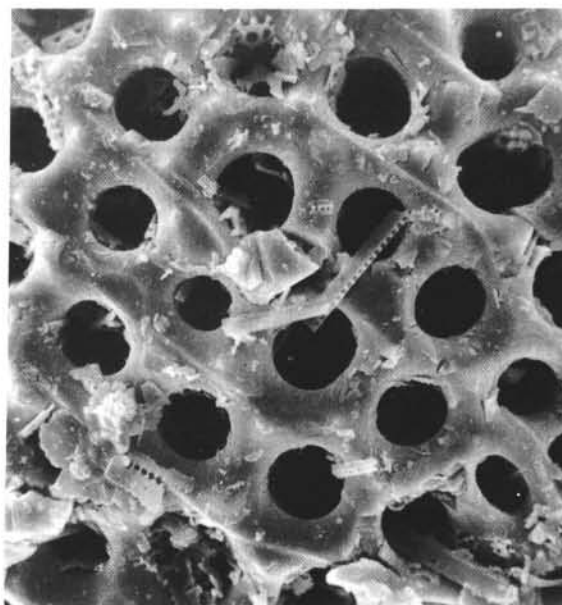


Figure 4a. Pyrite-coated radiolarian lattice from the acid residue of a black, pyritic rad-spicular ooze, Sample 315A-5-2, 125 cm (373 m), lower Miocene. Scale bar = 6 μm .

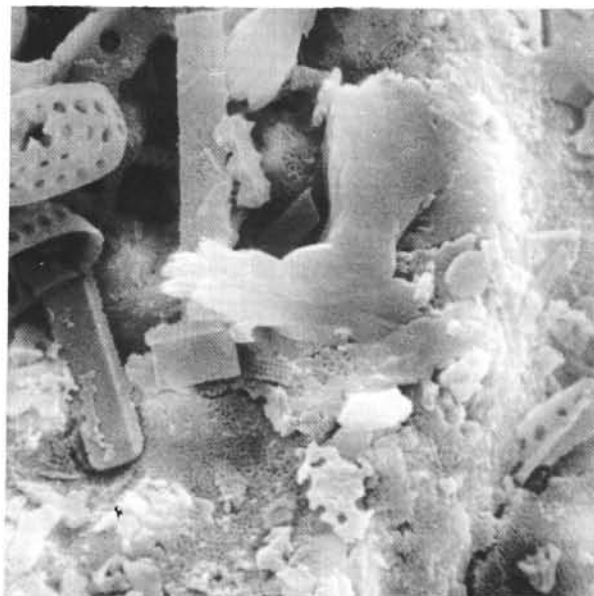


Figure 4b. Close-up shows a mass of various siliceous fragments imbedded in a fine meshwork of pyrite which coats the whole test. Scale bar = 2 μm .

from Miocene variegated oozes in Hole 315A may therefore represent variations both in radiolarian content and in accumulation rate (slower in bluish-white horizons).

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