

20. PYRITIZED DIATOMS IN THE SEDIMENTS AT THE DISTAL END OF THE BENGAL FAN¹

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ABSTRACT

Well-preserved fossil pyritized diatom valves were retrieved from the upper Pliocene (CN 12d) sediments of the distal end of the Bengal Fan. Energy-dispersive X-ray microanalysis of these valves and those subjected to pyrite extraction with concentrated HNO₃, documents the coexistence of original silica and pyrite within the fossil. Based on the preservation of untreated and treated valves, we postulate microcrystalline growth of pyrite within the matrix of the frustule.

INTRODUCTION

Pyrite is reported from many kinds of rocks from the Precambrian to Holocene and from numerous locations from all over the world (Love and Amstutz, 1966). Under favorable conditions it is formed in fresh, brackish, and marine sediments.

Biogeochemistry of sulfate reduction has advanced so that we can better understand the role of environmental parameters (deposition rate and the type of organic matter and inorganic iron, temperature, availability of alternative electron acceptors) in the rate of sulfate reduction and in the species of iron sulfides produced (Berner, 1969, 1985; Sweeney and Kaplan, 1973; Raiswell, 1982; Berner and Westrich, 1985; Morse and Cornwell, 1987). Less well understood are the processes that control the physico-chemical relationship between organic or other matter and precipitating pyrite (Vallentyne, 1963; Berner, 1970; Rickard, 1970; Raiswell 1982).

Reports on diatoms and other fossils such as foraminifers, radiolarians, and sponges filled with aggregations of framboidal pyrite are common. Our review of relevant literature indicates that "pyritized diatoms" reported are, in fact, pyrite in-fillings of the frustule casts with occasionally preserved minute fragments demonstrating original ornamentation (Kato, 1967; Georgi 1976; Geroch, 1978; Thomas and Gradstein, 1981, Bignot, 1983). Generally the surface of the cast consists of a layer of fram-boids. Other frequently reported diatom remnants associated with pyrite are unaltered siliceous frustules filled with framboidal pyrite (Vallentyne, 1963; Schallreuter, 1984). In both cases, pyritization takes place in small chambers (created within buried skeletons or resulting from dissolution of the frustule) acting as a favorable microenvironment for crystallization of the pyrite.

Other reports relate to the pyritized organic globules that retained some of the original organic matter either within or around fram-boids (Love and Amstutz, 1966; Rickard, 1970). These observations form a basis for biogenic models of the origin of framboidal pyrite (Rickard, 1970). Later experiments and elemental analyses of such pyritized globules failed to detect appreciable concentrations of organic carbon in the dissolved fram-boid residues, thus casting doubt on the model (Vallentyne, 1963; Elverhoi, 1977).

To the best of our knowledge, diatom remnants have never been reported in a pyritized state where FeS₂ and original diatomaceous silica co-occur. In this paper we report on the elemental composition and state of preservation of pyritized diatom valves and speculate on their possible origin.

MATERIALS AND METHODS

Pyritized diatom remains were fairly common in Pliocene sediments (Cores 116-117C-24 through -65). Only marine benthic and planktonic frustules were pyritized: e.g., *Thalassiosira oestrupii* (Ost.) Hasle var. *venrickae* Fryxell et Hasle, *Coscinodiscus marginatus* Ehr., *C. radiatus* Ehr., *Actinocyclus* spp., *Thalassionema nitzschioides* (Grun.) V.H., *Thalassiothrix* sp. cf. *Th. longissima* Cl. et Grun., *Biddulphia* sp., and *Triceratium favus* Ehr. For scanning electron microscopy (SEM) and elemental analyses, large valves were hand picked from the sieved fraction >64 μm. In all instances, the state of preservation was excellent. The frustules may have been fragmented, but the substructure of the valve revealed preservation of even the most minute details (Plate 1, Figs. 1-4; Plate 2, Figs. 2-3).

Under the dissecting microscope the frustules have a golden color. Under the light transmitting microscope all pyritized diatoms appeared black (Plate 2, Figs. 3-4).

Ten randomly selected specimens of various species were subjected to concentrated HNO₃ treatment to remove the pyrite. The dissolution process was observed and time recorded. Elemental composition of six intact and three HNO₃-treated diatom remnants was examined using an energy-dispersive X-ray system (EDS). Cleaned pyritized diatoms were transferred to carbon planchets. The samples were then sputter coated with approximately 20 nm of gold-palladium in a Hummer IV sputtering unit. SEM and energy-dispersive X-ray microanalyses were performed on a JEOL JSM-35C equipped with a Kevex Unispec System 7000 EDS. Vertical scales of the spectra are indicated on Plate 2, Figs. 1A-1C; Fig. 7.

The thinnest silicified portion of the diatom valve occurs in the region of the areola occlusions. These areas were sufficiently electron transparent to allow selected area diffraction (SAD) to be performed. The technique reveals information regarding the crystallinity (or lack of) in the sample within the region selected. SAD was performed on 10 such areas of 4 valves using a JEOL 100CX transmission electron microscope (TEM).

RESULTS AND DISCUSSION

Elemental analysis of the individual valves revealed that S and Fe are major constituents of the pyritized diatoms. The peak ratio of Fe to S is stable, approximately 1:2 (Plate 2, Figs. 1A-1C; Fig. 7). In addition to these two elements, all valves examined contained a variable amount of Si (Plate 2, Figs. 1A-

¹ Cochran, J. R., and Stow, D. A. V., 1990. *Proc. ODP, Sci. Results*, 116: College Station, TX (Ocean Drilling Program).

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1C; Fig. 7). Sporadic minute peaks of Ca, Al, and K were also detected. Their presence can be attributed to clay contamination. Sweeney and Kaplan (1973) report Ca and P in pyritic aggregates, some of which might represent pyrite infillings of the biotic casts (twigs, foraminifers). In pyrite grains from marine sediments Siesser (1978) found K, Si, Al, Ti, and Mg in quantities less than 0.05% by weight. Muza and Wise (1983) detected slightly higher quantities of these and Ca and Zr in sheet-like and framboidal pyrite.

Electron diffraction patterns of pyritized frustules show discrete spots and/or rings that indicate a microcrystalline organization of the matter. As diatom silica is consistently reported to be amorphous (Simpson and Volcani, 1981), we assume that this diffraction pattern represents a microcrystalline organization of the pyrite. Individual microcrystallites can be as small as 50 nm in diameter (Rickard, 1970) but are more commonly reported in the range of 200–300 nm (Criddle, 1974; Sweeney and Kaplan, 1973).

Individual microcrystallites were not resolvable in our SEM, on either the surface of the pyritized diatoms or on the broken edges. Lack of outgrowing crystals was observed earlier in framboidal pyrite, suggesting that it may be growing within an enclosure like an outer "skin" or within organic globules (Love and Amstutz 1966; Rickard, 1970; Sweeney and Kaplan, 1973).

Experimental removal of the pyrite from a clean, isolated pyritized diatom valve by dissolution in concentrated HNO₃ is a fast process lasting no more than 5 min. Upon drying, the residue becomes white and often collapses on itself. The residue retains its integrity nevertheless, conserving the size and shape of the diatom frustule after repeated rinsings in distilled water and embedding in a Hyrax resin. In all cases the structure of the original silica base layer and areolar ornamentation pattern were present (Plate 2, Fig. 8). The elemental spectra of the residue yielded counts for Si similar to those from pyritized valves. Minute quantities of Fe and some P were also detected (Plate 2, Fig. 7).

Love and Amstutz (1966) reported an organic, sponge-textured residue left after FeS₂ was dissolved from the framboids. Carbon constituted 35%–71% of the residual matter. The majority (75%) of organic matrix bodies from the framboids showed no distinct internal organization. Approximately 25% of the residues had puncture holes, presumably where pyrite crystals were. The organic matter, they concluded, did not control pyrite crystallization, but rather modified its own shape from within to that of crystals. Their evidence as to whether the organic matter was invested by pyrite and reformed or solidified around the pyrite was inconclusive.

Later efforts to investigate the residual organic matrix from dissolved framboids either failed or yielded such a minute amount of carbon that contamination could not be excluded (Vallentyne, 1963; Sweeney and Kaplan, 1973). Consequently, Sweeney and Kaplan (1973) and Elverhoi (1977) suggested that the matrix they detected must have been postcrystalline in origin. Therefore, the Love and Amstutz (1966) data are the only reports to date suggesting cohabitation of pyrite and biogenic matter.

In the case of pyritized diatoms from the Bengal Fan sediments, we speculate that the microenvironmental conditions are favorable for pyrite formation throughout the colloidal silica of the diatom frustule. At the same time, the fine structure of the silica matrix restricts the ultimate size of individual microcrystals. Pyrite microcrystallites must have invaded the frustules very gradually, permeating and/or replacing silica.

In contrast, conditions favorable for pyrite formation in fossil sponge spicules appear to exist only on their outer surfaces, and the fine structure of the spicule does not prevent free outgrowth of microcrystals (Plate 2, Figs. 5–6).

Evidence (see review in Simpson and Volcani, 1981) suggests that the silica in diatom valves is an aggregation of siliceous spheres. The primary building spherule diameter seems to be no smaller than 1–2 nm. The primary spherules aggregate into the secondary larger units, spheres commonly 30–50 nm in diameter but ranging between 10 and 200 nm in different species. These spheres seem to constitute building units of the tertiary, columnar aggregates. In *Ditylum brightwellii* (West) Grun., the width of columns (40–50 nm) corresponds to the diameter of the most common class of spheres. Such fine structure would provide suitable void spaces for pyrite microcrystalline growth.

We interpret the cryptocrystalline nature of the pyrite integrated into the diatom groundmass and lack of crystal outgrowth as an indicator of silica control of the space in which pyrite cryptocrystals were growing. Therefore, the diatomaceous silica demonstrates a different type of interaction between crystallizing pyrite and surrounding matter than that proposed for organic, sponge-textured matter by Love and Amstutz (1966).

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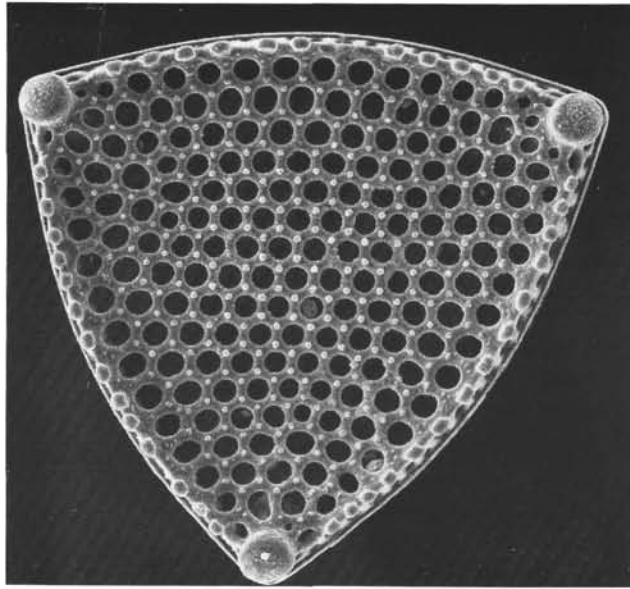
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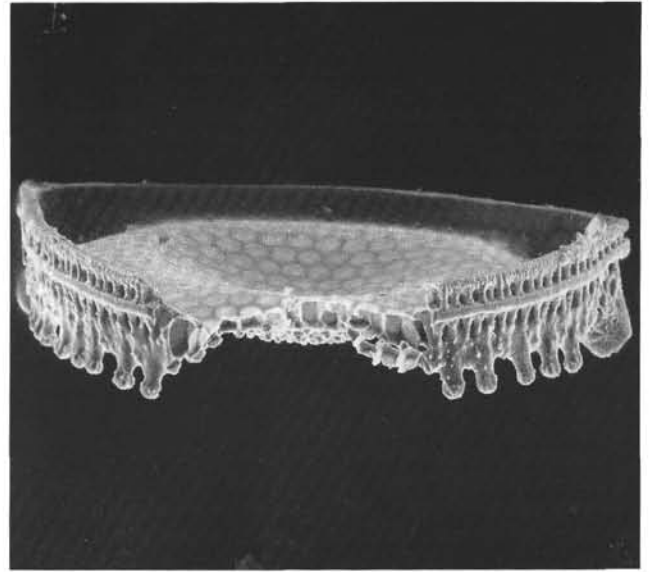
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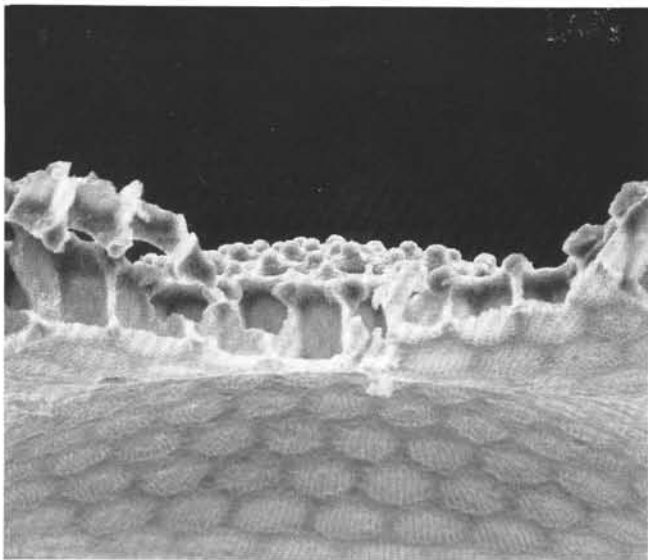
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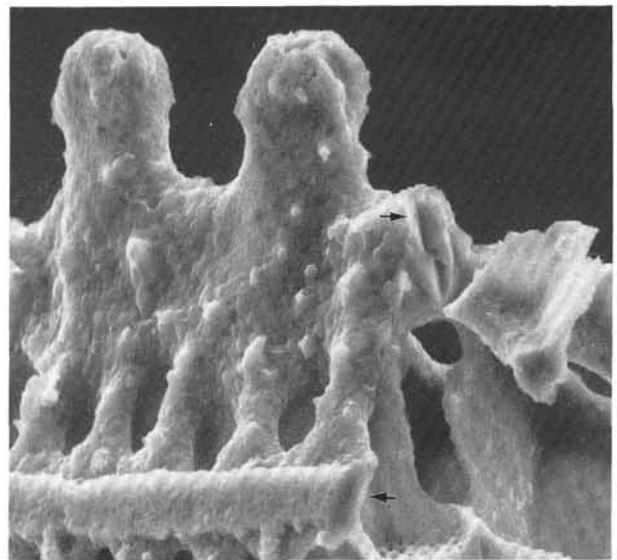
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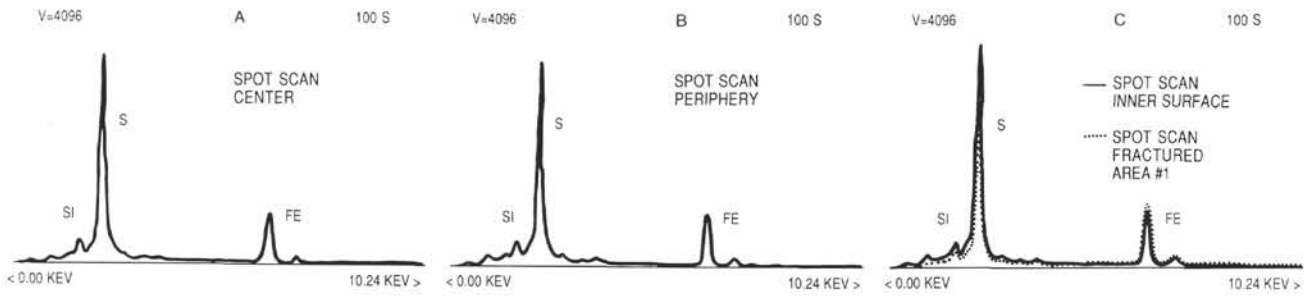


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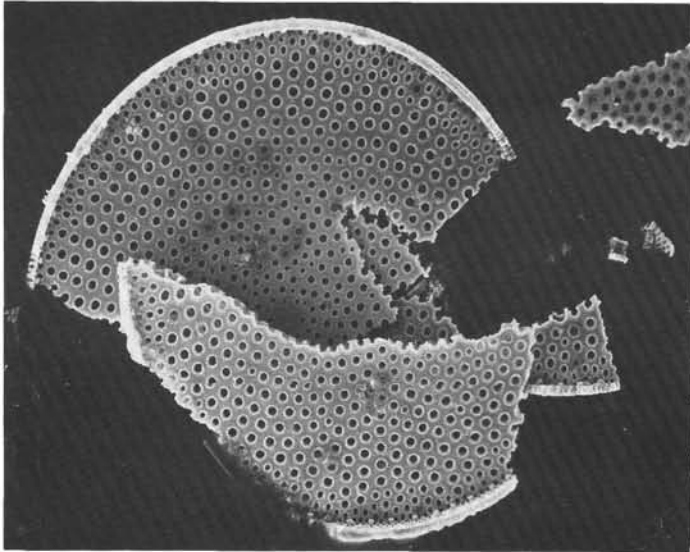


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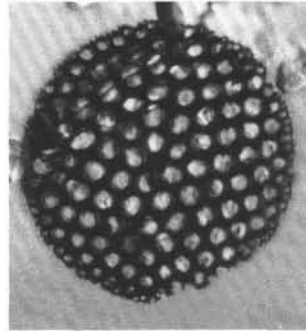
Plate 1. Pyritized specimens of *Triceratium favus* Ehr. Sample 116-717C-25X-5, 24–25 cm. On all SEM micrographs the bar represents 10 μm . 1. Details of the external surface of the valve face ornamentation. 2. Details of the valve mantle and internal valve face surface. 3. Cross-section of the areoles and the base layer of the valve. 4. Close-up of the mantle structure, even broken edges (arrows) of the valve do not resolve pyrite crystallites.



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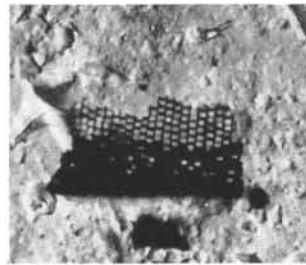
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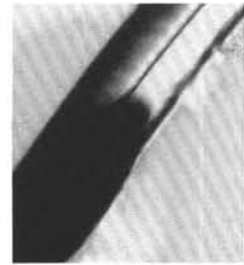
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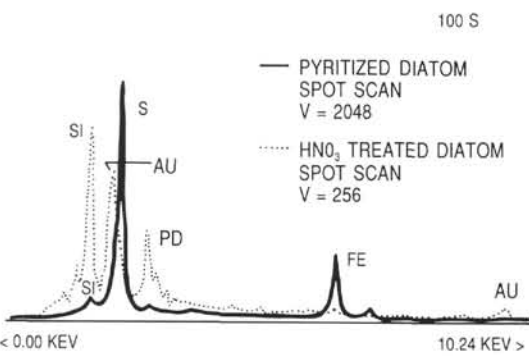
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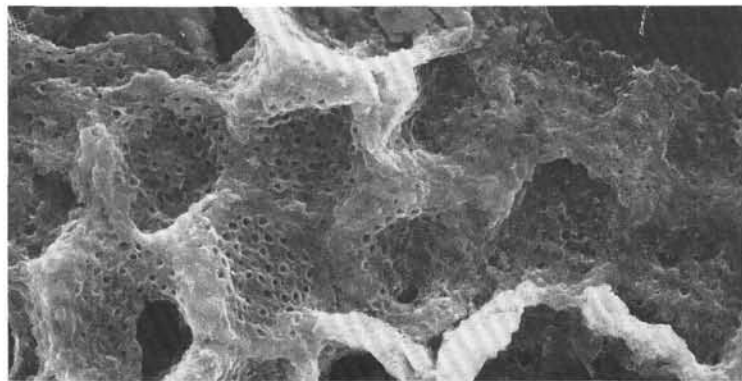
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Plate 2. Elemental spectra and photomicrographs of the pyritized diatoms and sponge spicules. Sample 116-717C-25X-5, 24-25 cm. 1. A-C. EDS elemental composition of three pyritized diatom valves; Figures 1A and 1B represent spectra of the same valve examined at different areas; Figure 1C demonstrates spectra of two different valves. The vertical scales of the spectra are indicated by V. 2. SEM micrograph of the internal surface of a pyritized *Coscinodiscus radiatus* Ehr. 3. Pyritized *Thalassiosira oestrupii* (Ost.) Hasle var. *venrickae* Fryxell et Hasle (LTM, 1900 \times). 4. Pyritized fragment of *Ethmodiscus* sp. (LTM, 700 \times). 5. SEM micrograph of partially pyritized sponge spicule. 6. Partially pyritized sponge spicule (LTM, 1900 \times). 7. Overlaid elemental spectra of a pyritized valve (solid line) and fragment of pyrite extracted valve (dashed line). Note two different vertical scales (V) for the spectra. 8. SEM micrograph of the pyrite extracted valve of *Triceratium favus* Ehr.; notice the base silica layer ornamentation and remnants of areoles.