24. FRAMBOIDAL PYRITE IN DEEP-SEA SEDIMENTS[1]

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ABSTRACT

The framboidal form of pyrite from two different types of sediments at DSDP Site 530 (Angola Basin) was examined by scanning electron microscopy (SEM). In foraminifer-nannofossil-diatom oozes, pyrite framboids occur only as assemblages in microfossils forming a separate microenvironment, whereas in black shales they occur throughout the sediment. The formation mechanism of the framboids is reviewed, but many questions still exist.

INTRODUCTION

As Regnéll has observed (1960, p. 305), "formation of iron sulphide in deep-sea sediments seems not to be an ordinary process," noting that "abundant pyrite has rarely been found in deep-sea sediments" (p. 313). Qualitatively, however, pyrite is one of the most common minerals in deep-sea sediments. It appears in different forms and sizes, from cryptocrystalline pyrite to macroscopic nodules or irregular concretions. In certain sediments (e.g., black shales) it is one of the dominant constituents and "may be more responsible for the characteristic colouration than the organic matter" (Hallam, 1980, p. 123).

The most common form of the mineral in the sediments investigated on Deep Sea Drilling Project (DSDP) Leg 75 was framboidal pyrite. It is probable that in sediments from other legs this will be the most common form of pyrite. Nonetheless, few contributions to the *Initial Reports* discuss the framboidal form of pyrite. Some papers present good SEM micrographs of framboids, but only one paper is dedicated exclusively to framboidal pyrite (Criddle, 1974).

This contribution is only a preliminary report. During its preparation, many new questions arose, which will necessitate investigations of many more samples.

OCCURRENCE

According to the (incomplete) list of occurrences of framboidal pyrite made by Love and Amstutz (1966), this form of pyrite occurs in Precambrian, Phanerozoic, and Recent sediments. Framboids are reported from very different rocks, but they are especially common in sapropels (Love and Amstutz, 1966). Framboidal pyrite is also reported from deposits of possibly hydrothermal origin (Love and Amstutz, 1966).

Framboidal pyrite has been reported from deep-sea sediments by several authors. The first recognition of pyrite framboids in deep-sea sediments is not certain, but among the oldest publications concerned with this form of pyrite is—according to Vallentyne (1963a)—an 1897 paper by Androussow. In DSDP's *Initial Reports,* pyrite framboids have been reported since the first leg (Beall and Fischer, 1969).

TERMINOLOGY

"Framboids" are more-or-less spheroidal aggregates (from <1 μm to >100 μm) of randomly or nonrandomly distributed, entirely discrete pyrite microcrystallites (from $<1/5$ μm to >5 μm across).

The term was introduced by Rust (1935) for clusters of tiny pyrite cubes and grains after *framboise* (French for "raspberry"), because of the external similarity. It was later used for similar aggregates of other minerals (magnetite—Jedwab, 1965; greigite—Bobrovnik, 1967; limonite—Love, 1967); but according to Rickard (1970) these cases may be related to the processes of formation of pyrite framboids: "the framboid texture is virtually exclusive to pyrite" (p. 279). Farrand (1970), however, described framboidal sulfides not only of iron but also of copper, lead, zinc, nickel, and arsenic. Lougheed and Mancuso (1973) described hematite and limonite framboids from the middle Precambrian Negaunee iron formation (Michigan); they considered these to be pseudomorphic after pyrite framboids.

Most framboids fall into the size range given above, but Farrand (1970), described framboids >0.2 μm whereas Sweeney and Kaplan (1973) found framboids about 250 μm in diameter. Most framboids are smaller than 20 μm (Love and Amstutz, 1966, text-figs. 1, 2; Lougheed and Mancuso, 1973, figs. 2–6; Sweeney and Kaplan, 1973, p. 628). In describing framboids, the following size classes are used in this chapter: <1 μm: very small; 1–3 μm: small; 3–10 μm: medium-sized; 10–100 μm: large; >100 μm: very large.

"Framboid aggregates" (*Rogenpyrit*) are masses of framboids, of irregular or regular shape. The regular-shaped spheric aggregates are called "polyframboids." Framboid aggregates are presumably formed by different pathways. One group is represented by steinkerns of fossils.

The term "polyframboids" was introduced by Love in 1971 for textures in which "the framboidal texture itself is compounded, so that the body is of a higher

[1] Hay, W. W., Sibuet, J.-C., et al., *Init. Repts. DSDP*, 75: Washington (U.S. Govt. Printing Office).

order of complexity and correspondingly greater size. It is, however, still a spheroid when not deformed" (p. 1038). Fabricius (1962) had already observed such polyframboids and called them *Kugeln II. Ordnung* ("spheres of the second order"). Love (1971) wrote that the *Rogenpyrit* of Fabricius are polyframboids, but Fabricius himself included also single framboids (*Kugeln I. Ordnung*) (Love 1971, fig. 4).

Polyframboids had been observed during earlier micropaleontological work. Wicher (1938, p. 12, plate 1), for example, called them *Pyrithäufchen—Zusammenballungen feinster Pyritkugelchen,* for which later the descriptive name *Rogenpyrit* came into use (Fabricius, 1962). Here the name *Rogenpyrit* is used for all framboid aggregates.

FRAMBOID FORMATION

Inorganic Formation

Laboratory Synthesis

Several investigators have been successful in synthesizing framboids. Berner (1969) first described the synthesis of framboidal pyrite at low temperature (65°C) and neutral pH by the reaction of FeS with elemental sulfur in saturated H_2S solution. Farrand (1970) obtained framboidal sulfides of iron, copper, lead, zinc, nickel, and arsenic from aqueous solution of hydrogen sulfide in the absence of any bacterial agent. Farrand considered the formation of framboids to be a normal result of the precipitation of discrete sulfide particles in suspension from reactants in true solution at a concentration between two and ten times the solubility of the sulfides; but the preservation of framboids demands, according to Farrand, protection from additional solvent within a few days of precipitation. "Although it has proved possible to synthesize framboids as a somewhat transient phenomenon in a purely aqueous laboratory system," he wrote, "organic compounds may play a key role in the formation and, particularly, in the preservation of framboids in a natural sedimentary environment" (p. 245).

Sweeney and Kaplan (1973) tried "to reproduce the formation of pyrite in the laboratory by simulating processes which are believed to occur in marine sediments" (p. 618). They produced framboids by reactions between iron sulfide and elemental sulfur (1) in aqueous solutions and (2) separated from solution (but wet) at atmospheric pressure (which does not occur in marine sediments) within 4 to 6 days at 60° to 85°C. Sweeney and Kaplan (1973) published the first good SEM micrographs of synthetic framboids (figs. 4.4–6, 6.1–2) and polyframboids (fig. 6.4).

Natural Inorganic Origin

Framboidal pyrite was reported originally by Rust (1935) in copper ores at Cornwell Mines in SE Missouri. Rust cited evidence which indicates a hydrothermal ancestry for the mineralizing solutions and very moderate temperatures. To him, the framboidal texture indicated a colloidal condition of the ore material at the time of deposition.

Schouten (1946) discovered pyrite spheres in a pyrite-marcasite mass from the tin veins of Cornwall and emphasized that the ores of Rio Tinto in Spain, considered to be of hydrothermal origin, are rich in analogous spheres.

Ramdohr (1975) also suggested a hydrothermal genesis for pyrite spheres.

Steinike (1963) described an occurrence of inorganic pyrite spheres from Permian andesites near Halle (Germany). Love and Amstutz (1969) reported framboidal pyrite from the same andesite and from a Tertiary andesite-porphyry from Peru, but they recognized that only "a very small proportion of the pyrite clusters in the Plötz and Antachajra deposits, being at the extreme end of the whole textural range, could be indistinguishable from less well organized framboidal pyrite spherules" (p. 106).

Kanehira and Bachinski (1967) described framboidal pyrite from Newfoundland ores without hypothesizing about its genesis.

Kalliokoski and Cathles (1969) suggested that the occurrence of framboids from hydrothermal environments might indicate that thermal waters contain organo-colloidal substances. Raybould (1973) described framboidal pyrite associated with lead-zinc mineralization and concluded that organo-colloidal substances were not involved and that the framboidal pyrite is a primary product of epigenetic mineralization.

Organic Formation

Vallentyne (1963b) emphasized the important distinction between two different usages of the term "biogenic": "direct biogenesis" and "indirect or secondary biogenesis." In the first sense, the word is used "to refer to materials that have originated as a direct result of the metabolic activities of one or more living organisms, i.e., to diffusible metabolic products or to solids deposited in or around living cells." The second usage refers to "materials that have been formed nonbiologically, or more often in an unknown manner, from reactants that are themselves directly biogenic."

Indirect Biogenic Formation

Vallentyne's (1963b) contention was that pyrite spherules are secondarily biogenic; many other authors are of the same opinion.

Kalliokoski and Cathles (1969), for one example, assumed that framboids form "by a process of coacervation and particulation due to the reaction of ferruginous humic acid with biogenic H_2S." "As further evidence of the control by organic debris on framboids, the senior author has noted elsewhere that the pyrite of pyritized fossil matter in the Wabana pyrite bed is abundantly framboidal, whereas the pyrite of adjoining hematite-chamosite oolites is structureless, granular, or fibrous (Kalliokoski, 1966, p. 880). The correlation is too perfect to be fortuitous" (p. 128).

Lougheed and Mancuso (1973) suggested that "framboidal pyrite in Phanerozoic sediments is invariably as-

sociated with fossils or material or features of biogenic origin," but "it should be emphasized that framboidal pyrite never replaces biogenic material as such... but develops in bacterially decaying protoplasm...."

Framboids as Fossil Microorganisms

Some authors have thought that framboids are the remains of microfossils (or nannofossils). Schneiderhöhn (1923) considered chalcopyrite framboids from the Kupferschiefer of Mansfeld (Germany) to be mineralized microorganisms and mineralized sulfur bacteria (*vererzte Bakterien*). Bergh (1928) recorded fossil sulfur bacteria from the alum shale (Cambrian) of the Kinnekulle (Sweden). Schouten (1937, 1946) regarded the notion of the existence of fossil sulfur bacteria, as proposed by Schneiderhöhn, to be highly questionable—morphologically, physiologically, chemically, and from the standpoint of ore genesis. Fabricius (1962) also interpreted the so-called *Rogenpyrit* as sulfur bacteria or colonies thereof. Skripchenko (1970) investigated framboids from pelagic ooze from the Pacific Ocean and found additional confirmation of the theory that "pyrite crystals are metabolic products of globular bacteria" (p. 133). He considered "mineralized bacteria" to be a special group of sulfate-reducing microorganisms which "secrete the main reduction product (pyrite) in their bodies and isolate it from the external medium." Recently, Locquin and Weber (1978) described framboids as *bacteries coccoides exosymbiotes.* In another paper Locquin described (1981, plate 7, figs. 4–5) two chitinozoans "avec les spores apparaissant en relief a travers le corps." Presumably the spores represent framboids, as in many other cases (Wrona, 1980, plate 32, figs. 8–9; Schallreuter, 1981).

Love (1958) demonstrated that pyrite framboids leave HNO_3-insoluble residues. He considered them to be microfossils and established the two monotypic genera *Pyritosphaera* and *Pyritella.* Vallentyne (1963b) could not support the idea that the microfossils of Love (microforms) are composed of organic matter and concluded that they are predominantly if not exclusively inorganic. By 1963 Love himself no longer considered the framboids to be microfossils (Love, 1964, p. 14).

Rickard (1970) concluded that framboid formation may proceed through several pathways, including the pseudomorphism of single-celled microorganisms. The absence of organic matter from a large percentage of framboids may, according to him, be partly explained by evaporation, dissolution, or dispersion after pyritization and is therefore no argument against the organic nature of those framboids.

MORPHOLOGY OF FRAMBOIDS, LEG 75

The morphology of framboids observed in deep-sea sediments obtained during Leg 75 is shown in the plates which accompany this chapter. Many of the plate figures are presented as stereo pairs. In order to obtain maximum information from these, it is essential to view the micrographs stereoscopically by means of a stereoviewer[2]; with some experience, however, it is possible to view the stereomicrographs with the naked eye (which is preferable because the printing screen is not visible, contrary to the magnifying stereo-viewer.).

All micrographs were taken by the author with the STEREOSCAN 180 of the Geologisch-Paläontologisches Institut und Museum (GPIMH), University of Hamburg, Germany (F.R.). Magnifications are those indicated by the instrument and may be 10% too high. The GPIMH numbers are those of the originals which are deposited in the museum.

Framboids from Nannofossil Oozes

METHODS

Framboids in oozes occur as assemblages in microfossils forming a separate microenvironment—for example, foraminifers, diatoms, radiolarians, sponge spicules, and plant cysts. For the present investigations, diatoms were preferred—first, because it is relatively easy to open them, and second, because, given the composition of silica, it is possible to enrich the sample in diatoms and to disperse the sample at the same time by treatment with hydrochloric acid. The following method was used: A few cubic millimeters of sample were treated with HCl and washed with distilled water; the black diatoms (e.g., those with framboids) were picked out by a pipette under the binocular microscope and fixed on SEM stubs by means of double-face sticky tape. The stubs with the diatoms were then brought wet into a vacuum in order to allow the escaping, vaporizing water to open the diatoms. In other cases the diatoms were opened mechanically by a one-hair brush. The stubs were then coated with gold by sputtering.

Size

The smallest framboids in the oozes investigated are < 1 μm in diameter (Plate 5, Fig. 5), the largest are > 20 μm in length (Plate 5, Fig. 2).

Shape

The ideal shape, formed presumably only in the case of free growth, is spheroidal. If space is limited, all forms which could be produced by deformation of a growing spheroid are possible. In Sample 530B-2-3, 13 cm, for example, many elongated framboids occur (Plates 4 and 5). In other assemblages the framboids look as if they had grown until the free space was exhausted (Plate 1). This had already been observed by Skripchenko and Lytkin (1969, p. 1139, resp. 166) who wrote, "Colonies of 'bacteria' are generally recognizable through the fact that their individuals display signs of competitive growth, because of which the shape of 'bacteria' within colonies deviates from spherical." Most framboids in an assemblage seem to start growth simultaneously, but there are also examples of assemblages with framboids at all "ontogenetic" stages (Plate 3). The framboids of an assemblage grew until the free space was filled; there are no signs of overgrowth and disruption of the shell structures.

Surface

Some of the framboids show more or less rough surfaces, but most exhibit "smooth" surfaces, as if they "fit against an unseen outer wall" (Love and Amstutz, 1966) (Plate 5). Sweeney and Kaplan (1973) gave exam-

[2] Three suppliers of small pocket-sized stereoviewers are: Air Photo Supply Corpn., 158 South Station, Yonkers, NY 10705; C. F. Casella & Co. Ltd., Regent House, Britannia Walk, London N1 7ND, England; Dr. Walter Hert Mikrotechnik GmbH, Kunigundenstraße 66, 8000 München 40, Federal Republic of Germany.

ples of the "presence of membrane during growth indicated by impeded growth of surficial octahedral crystals" and a "pyrite framboid with surface membrane intact." A similar example from the samples investigated seems to be the framboids shown in Plate 6, Figures 1-3.

Crystallites

The Crystallites are normally octahedral, but there are also examples of cubic crystallites (Plate 2, Fig. 6). Within a framboid the crystallites seem to be regular, but at the outer side of smooth framboids they exhibit a triangular, square, or polygonal outline (Plate 5 and Plate 6, Fig. 5) or even an irregular outline (Plate 6, Fig. 3). Irregular crystallites have previously been observed by Nöel and Melguen (1978, p. 506, plate 7, fig. 6) in Sample 361-23-2, 140–143 cm (Cretaceous dark-gray very fine shale). The crystallites of a framboid are normally approximately equidimensional. Small framboids have small crystallites (Plate 3, Fig. 4: the diameter of the framboid shown is about 1.2 μm, the diameter of the crystallites about 0.12 μm), and large framboids have large crystallites (Plate 5, Fig. 3: the diameter of the framboid is about 10 μm, the diameter of the crystallite is about 0.9 μm; Plate 5, Fig. 4: the diameter of the framboid is about 12 μm, the length is about 17 μm, the diameter of the crystallite is about 0.7 μm; Plate 3, Figs. 2, 5: the diameter of the framboid is about 24 μm, the diameter of the crystallite is about 2 μm). There generally exists a direct proportionality between framboid diameter and crystallite size, but the ratio of the crystallite-to-framboid diameter varies within certain limits (Plate 6, Fig. 3, 1:10, Plate 7, Fig. 3, 1:20). As in Criddle's (1974) sample (p. 605), there are no signs of geometric regularity in the ordering of the crystallites in any of the framboids. In only a few cases are the crystallites roughly ordered in rows (Plate 7, Fig. 2). Normally the crystallites are loosely packed and could be disintegrated very easily into single crystallites. The so-called nebuloids of Criddle seem to be disintegrated framboids. Some crystallites exhibit signs of disturbed growth (Plate 3, Fig. 5), but many crystallites are corroded, especially those of framboids near the border of the diatom (Plate 2, Figs. 5–6). Corroded crystallites often exhibit a discontinuous crystal structure. It seems that the inner parts of the crystallites are less stable than the outer parts (Plate 2, Fig. 3). In Sample 530B-2-2, 32 cm, a framboid was observed with some hollow crystallites. These structures may be identical with the "unexplained minute depressions...on the faces of individual crystals" observed by Kalliokoski (in Love and Amstutz, 1966).

Framboids from Black Shales

METHODS

Smear slides of the black shales from Hole 530A normally exhibit much pyrite (1–25%), but no or few (often pyritized) microfossils. Therefore, the black shale samples were brought under the SEM untreated. The high content of pyrite and carbon made coating unnecessary.

Size and Shape

The diameter of the generally spheroidal framboids observed in black shale samples varies between 3 and >30 μm (Plate 9, Fig. 3: left framboid about 4 μm in diameter; Plate 10, Fig. 1: framboid diameter about 31 μm).

Surface

The surface of the observed framboids is more or less smooth (cf. Plate 8, Figs. 3, 5; Plate 9, Fig. 3, and Plate 10, Figs. 1, 2, 3). Some framboids look as if they are coated by a membrane (Plate 9, Fig. 3).

Crystallites

The crystallites—normally octahedra—are approximately equidimensional in a framboid. Crystallite size and framboid diameter are related, the ratio varying within certain limits (Plate 8, Fig. 3: framboid diameter about 3.4 μm, crystallite size about 0.5 μm; ratio 1:7; Plate 10, Fig. 2: framboid diameter about 31 μm, crystallite size about 1.4 μm, ratio 1:22).

In addition to framboids the black shale samples contain many nonframboidal assemblages of pyrite microcrystallites in the form of continuous layers of unordered octahedra (Plate 8, Fig. 1; Plate 10, Fig. 1). It seems that all or at least parts of these layers were formed by framboids that had been destroyed, because the crystallites of the framboids are all loosely packed and disintegrate readily.

DISCUSSION

The formation of pyrite framboids in sediments or during sedimentation requires an anaerobic environment. This environment could be formed within the sediment (or the water column above) as a whole, or it might exist as a microenvironment inside microfossils.

According to Love (1964, p. 13) and other authors, "it is safe to say that the sulphide radical is essentially the resultant of micro-biological processes in an anaerobic environment," the result of the breakdown of organic matter by decaying and sulfate-reducing bacteria. The iron is usually brought in as detritus, according to Rolfe and Brett (1969, p. 229). Criddle (1974, p. 603) concluded that the major source of iron for pyrite formation in a calcareous nannoplankton ooze is unlikely to be clastic iron minerals and clay fraction iron, but suggested that nannoplanktons were the source.

According to Berner (1970), the essential requirements for the production of microcrystalline pyrite in normal marine waters are not only organic matter for the metabolism of sulfate-reducing bacteria, but also diffusion of sulfate into the sediment (Criddle 1974) or to the place of formation of the framboids. The framboid aggregates in microfossils also show that diffusion of iron is necessary. Many diatoms are completely filled with framboids. Their organic matter would not provide sufficient sulfur and iron for all the framboids; these elements must, therefore, diffuse into the diatom from outside.

Framboids could form where and when the necessary conditions are fullfilled. In the experiments of Farrand (1970), the first framboids appeared half an hour after the conditions for their precipitation had been established. Framboids are formed in the laboratory within hours or a few days. This implies that framboids found in deep-sea sediments could form or at least begin to form in the water column. In this respect the discovery of framboids as suspended material within the H_2S zone of Lake Kivu by Degens et al. (1972) is very important. It proves that framboids can form syngenetically as postulated by Schneiderhöhn (1923) for the framboids of the Kupferschiefer.

Most authors believe that framboids are formed in the sediment during early diagenesis (e.g., Love and Amstutz, 1966; Lougheed and Mancuso, 1973; Rolfe and Brett, 1969; Wiedmann and Neugebauer, 1979), whereas Wiedmann and Neugebauer (1979) "proved" a relatively late formation of the framboidal pyrite.

Wiedmann and Neugebauer (1979) investigated pyritized ammonites from Sites 363 (Walvis Ridge) and 364 (Angola Basin) of Leg 40 and found that most or perhaps all ammonites are fractured and collapsed. According to these authors, the mass of framboidal pyrite was formed only after the overburden produced shell fracture.

The framboids investigated here are all loosely packed as are those described by Wiedmann and Neugebauer (plate 4, figs. 4-7). It is hard to imagine how such loosely packed framboids, showing no sign of depression, are formed under "certain stress" (p. 718). Rather, stress destroyed many of the framboids and formed continuous layers of unordered octahedra, forming a soft bed for the surviving framboids as in the black shale samples investigated (see above and Wiedmann and Neugebauer, 1979: plate 4, figs. 1–3). Therefore, the late formation of framboidal pyrite is questioned.

The precise mechanism of framboid formation is still unknown (Lougheed and Mancuso, 1973, p. 206). The first question is whether framboids grow up from scratch (that is, from small framboids with small crystallites to larger framboids with larger crystallites, thus forming a continuous "ontogenetic" series) or whether the crystallites of a framboid fill out a preformed spheroid (for example, inorganic or organic globules or microorganisms)? Kalliokoski and Cathles (1969, p. 132), for example, advocated a "diagenetic growth of individual pyrite granules.... As the granules grow, the framboids increase in size." Papunen (1966) on the other hand, suggested that the "framboidal pyrite spherules, with their varying sizes resemble small emulsion drops."

As mentioned, the framboids of the assemblages that we investigated show no signs of overgrowth; on the contrary, the diatom wall left impressions (Plate 1, Fig. 2). Together with the smooth surface of many framboids, this could be interpreted as an argument that the framboids formed by filling out of some soft sac. Such sacs have been observed frequently (e.g., Love and Amstutz, 1966, Wiedmann and Neugebauer, 1979, pl. 5, fig. 1).

Crystals can grow explosively—like ice—and it can be seen (Plate 11) that the crystallites of the framboids have the capability of overgrowth (the sample also shows that in this case the crystallites can be different sizes). However, framboids in diatoms ceased formation once the available space was completely filled.

Many of the framboids of an assemblage show signs of secondary solution, especially framboids at the wall. In this respect the experiments of Farrand (1970) are important. He found that the "preservation of framboids demands protection from further access to a solvent within a few days of precipitation."

The west coast of Africa is an area of regional upwelling. The water at depth may have been reducing at the time the sediments were deposited, but as with the present situation off India or Peru, the deeper water is oxidizing as a result of the supply of water from the Antarctic. If such a situation existed from time to time in the Angola basin, the dissolution features on the surface of crystallite faces observed in certain horizons may be explained. We could further suggest that some of the microfossils lost all their framboids as a result of oxidation at depth.

CONCLUSIONS

On the basis of the studies presented here it is tempting to speculate on the origin of framboids. In my opinion, however, no conclusive statement can yet be made. We are, however, studying 300 samples from the Angola Basin, and attention will be given to the organic and inorganic content of the sediments. Once these data are in, additional light will perhaps be thrown on framboid formation.

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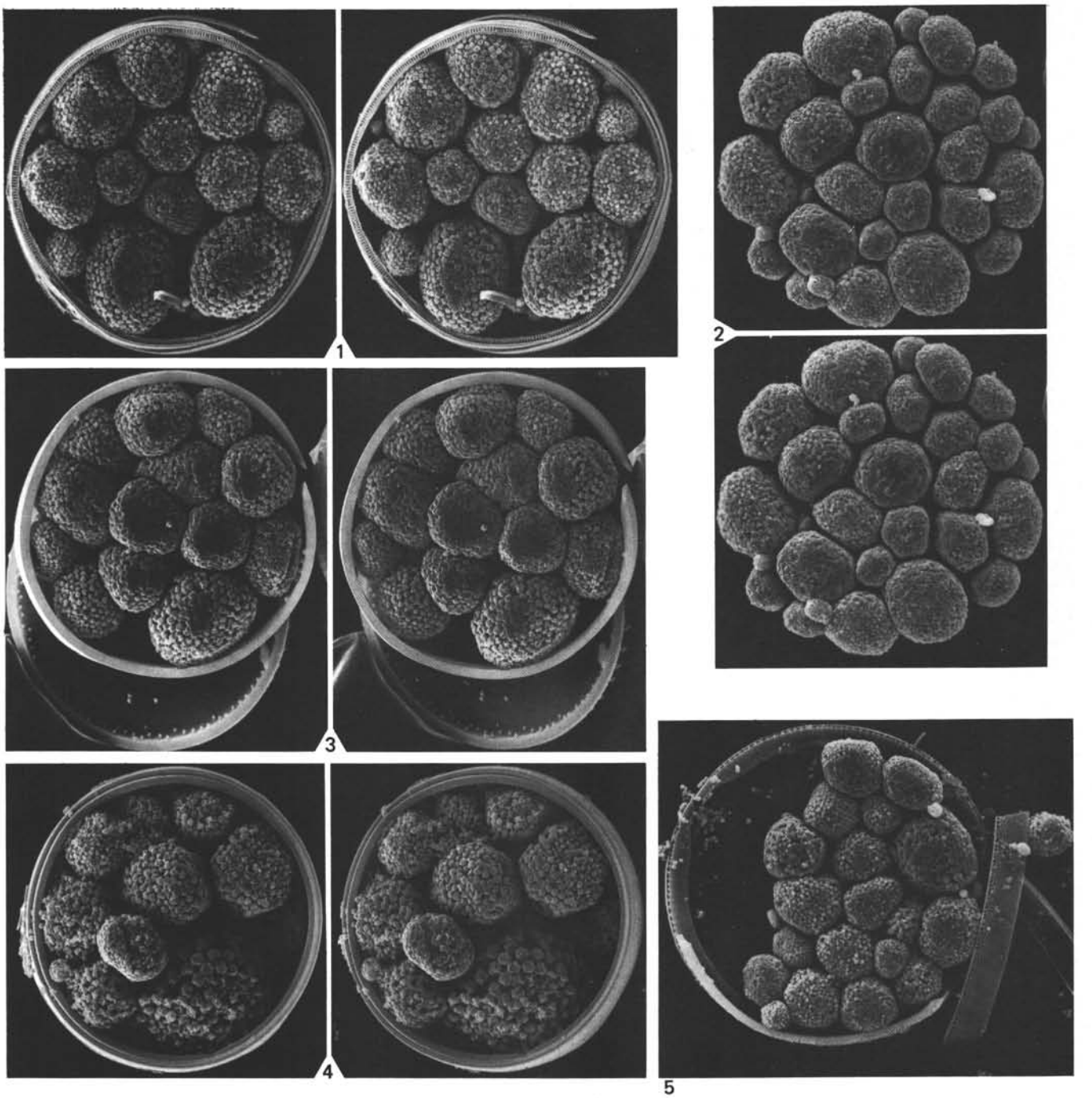

Plate 1. Five framboid assemblages in or from diatoms, Sample 530B-2-2, 32 cm, foraminifer-nannofossil-diatom ooze, HCl residue, Au coated. **1, 2.** Stub GPIMH no. 2575 (Fig. 1, ×1275; Fig. 2, ×950). **3, 4.** Stub GPIMH no. 2576, (Fig. 3, ×930; Fig. 4, ×1275). **5.** Stub GPIMH no. 2577, ×950. (Stereopairs, except Fig. 5.) Note the different sizes of the framboids and the adaptations of their shapes to each other and to available space. Note especially deformation of the central framboids in Figures 1–3 and 5, the marked border of the diatom in the marginal framboids in Figure 2, the plane surface of the central framboids caused by the plane diatom valve in Figure 2, and the deformation of the diatom girdle in Figure 1.

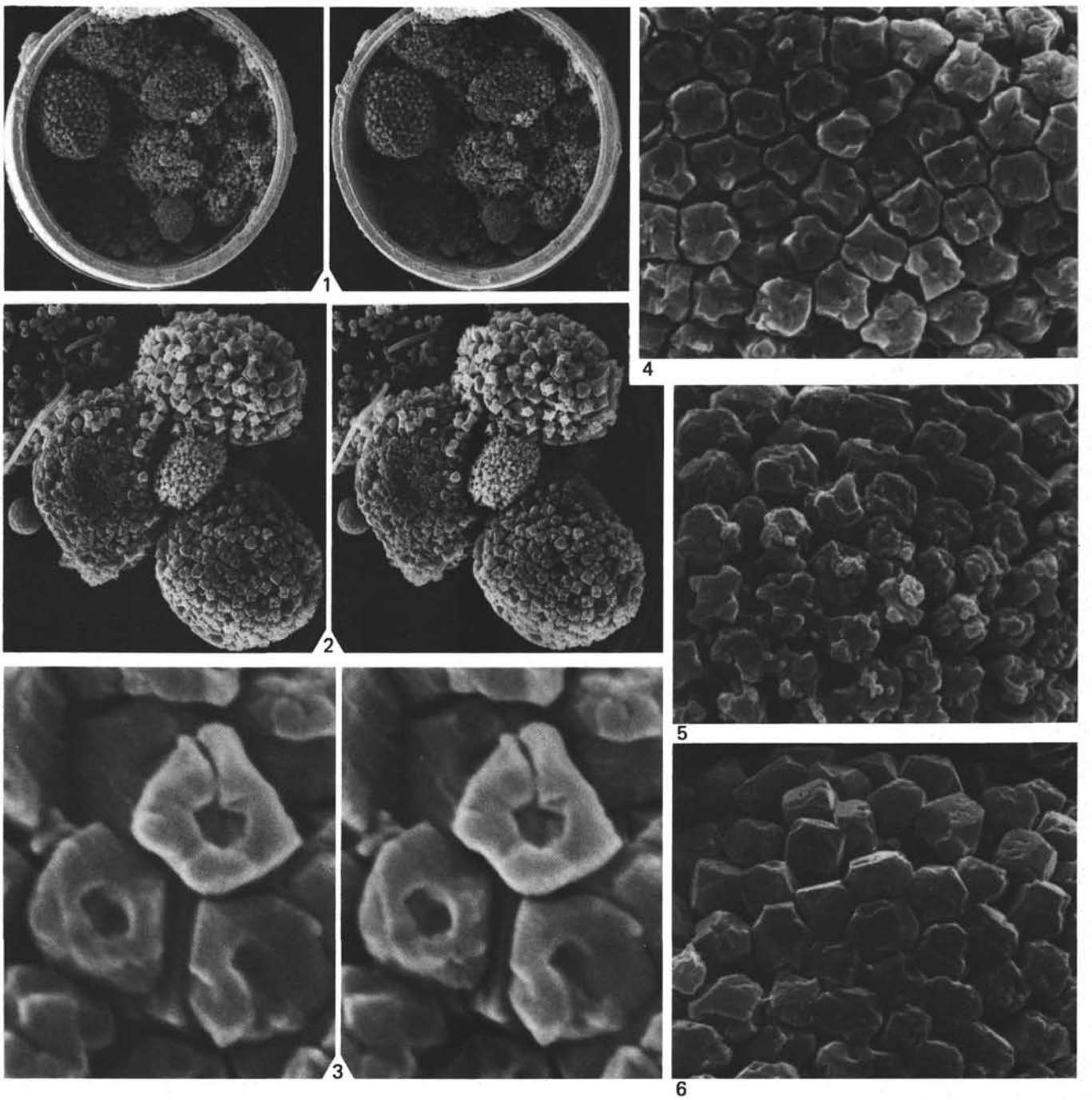

Plate 2. Sample 530B-2-2, 32 cm, foraminifer–nannofossil–diatom ooze, HCl residue, Au coated. **1.** A framboid assemblage in a diatom valve (stub GPIMH no. 2576), ×1200 (stereo pair). **2.** Part of a framboid assemblage in a diatom valve (stub GPIMH no. 2575), ×2200 (stereo pair). **3.** Crystallites of the uppermost large framboid near midline of the assemblage shown in Plate 1, Figure 1, ×27,000 (stereo pair). **4.** Crystallites of the lower-left large framboid of the assemblage illustrated in Plate 1, Figure 1, ×9100. **5–6.** Detail of the surface crystallites of the lower-right large framboid of the assemblage shown in Plate 1, Figure 2, ×7000; (5) crystallites at the outer side (near the border of the diatom girdle); (6) crystallites at the inner side (nearer to the center of the diatom).

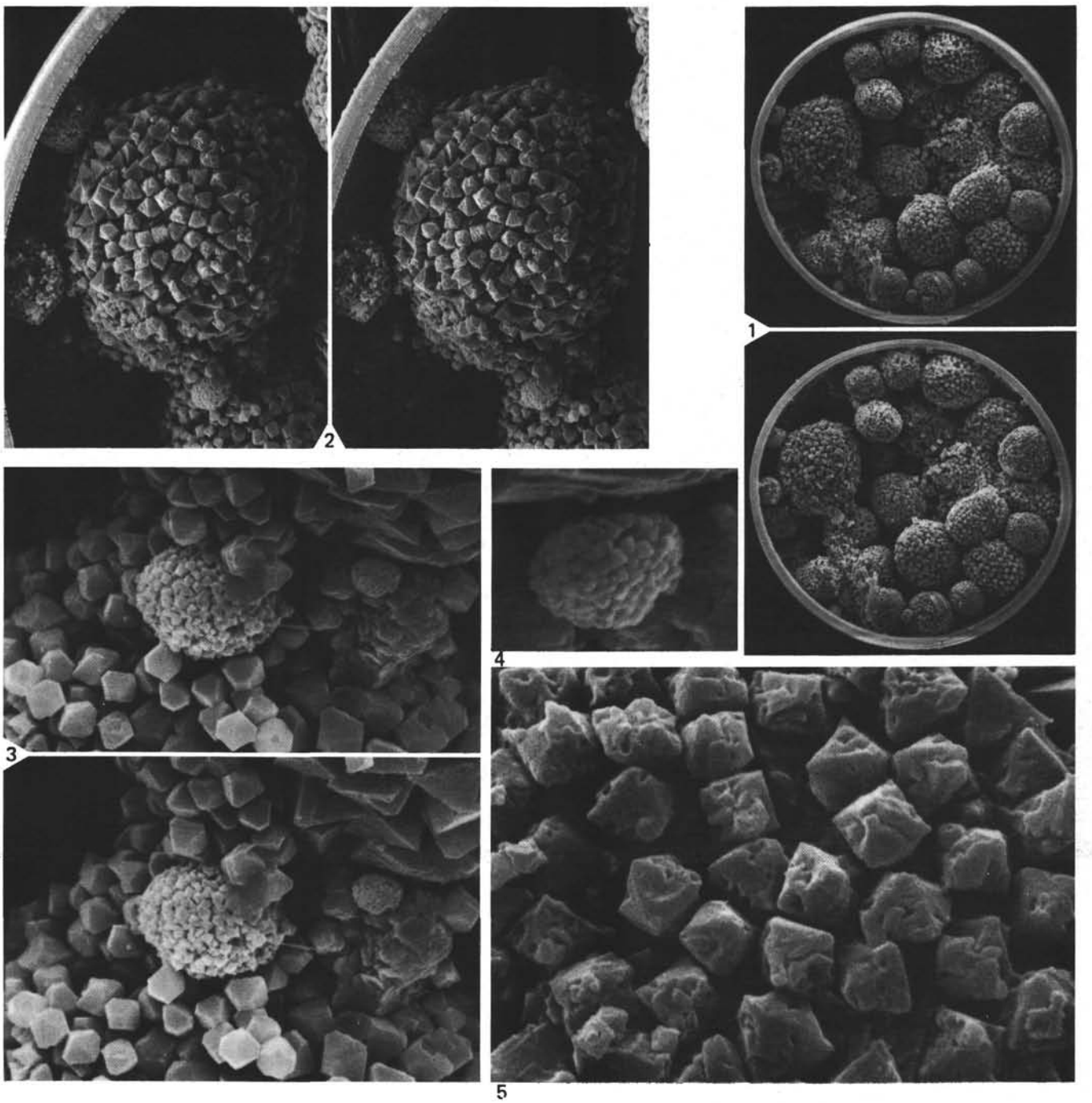

Plate 3. Sample 530B-2-3, 32 cm, foraminifer-nannofossil-diatom ooze, HCl residue, Au coated. **1.** A diatom with an assemblage of framboids of different sizes (stub GPIMH no. 2578), ×680. **2.** Detail of Figure 1, ×2100. **3–5.** Details of Figure 2; respectively, ×6800, ×22,500, ×8500. (Stereo pairs except Figs. 4, 5.)

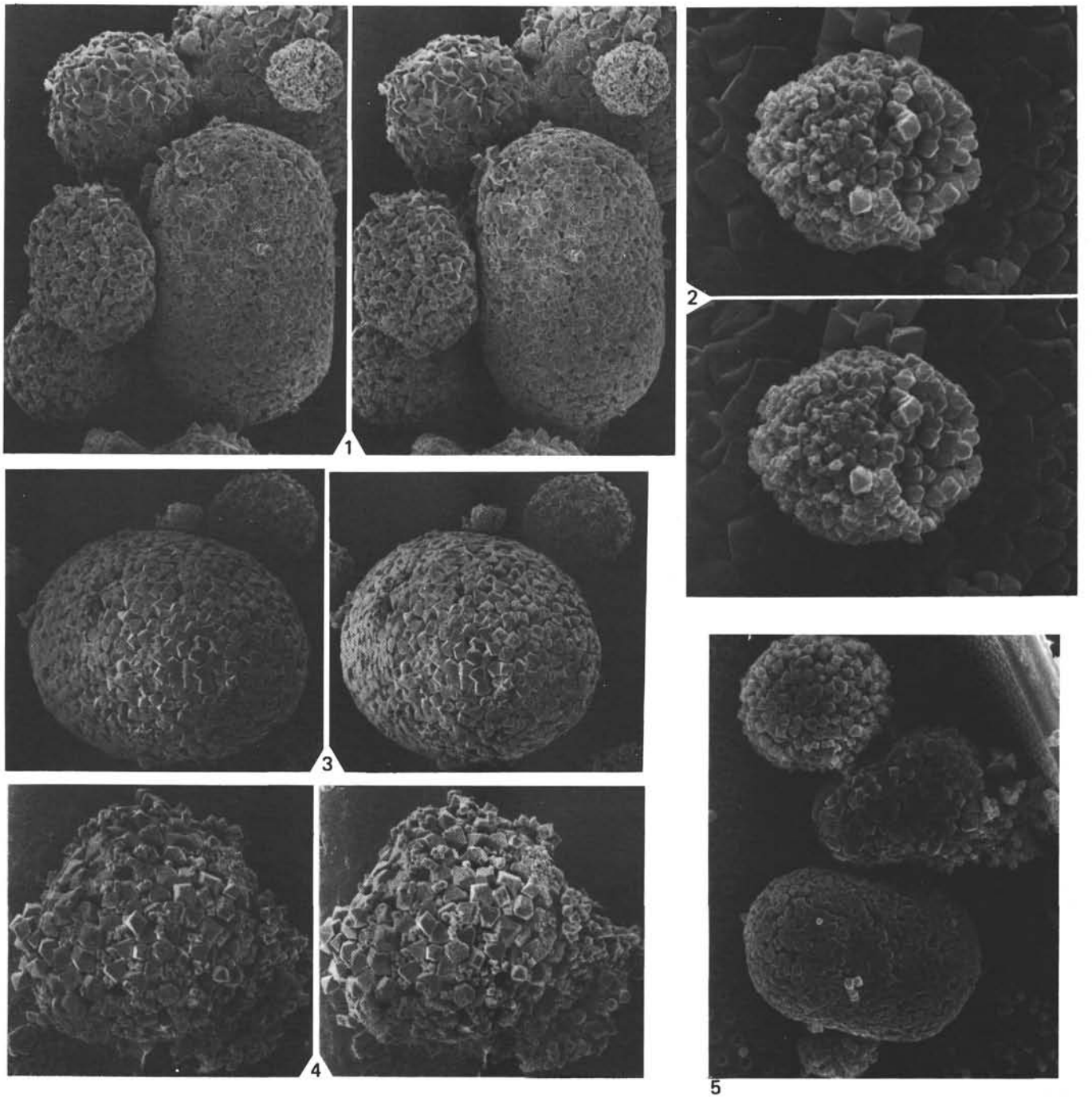

Plate 4. Sample 530B-2-3, 13 cm, foraminifer-nannofossil-diatom ooze, HCl residue, Au coated. Several framboids of different sizes presumably from one diatom (stub GPIMH no. 2579). **1.** ×2200. **2.** Detail of Fig. 1., ×6200. **3.** ×2100. **4.** ×3150. **5.** ×3400. (Stereopairs, except Fig. 5.)

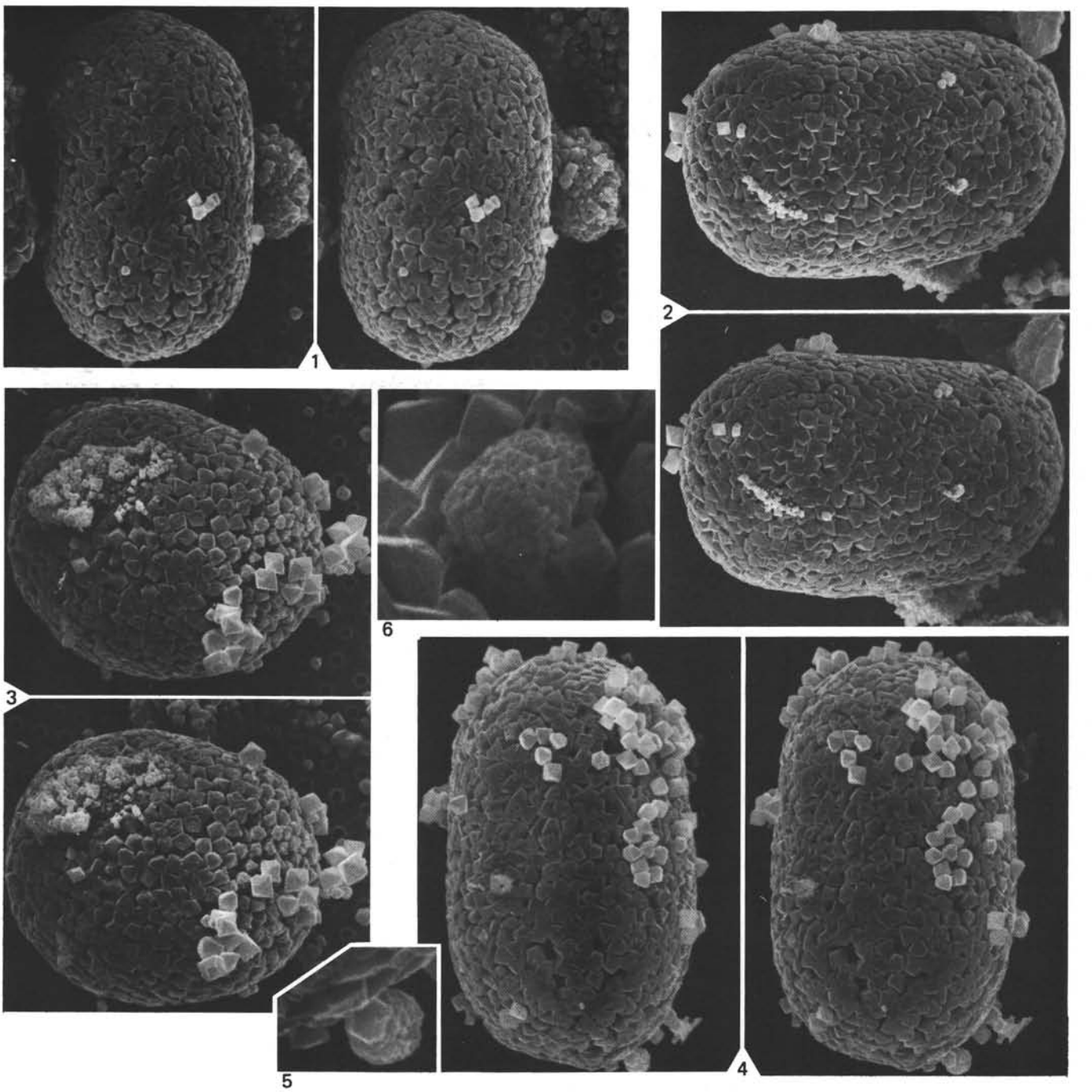

Plate 5. Sample 530B-2-3, 13 cm, foraminifer–nannofossil–diatom ooze, HCl residue, Au coated. **1.** The elongated framboid from the assemblage shown on Plate 4, Figure 5, ×4600 (stereo pair). **2.** An elongated framboid presumably from the same assemblage as the framboids of Figure 1, ×2900 (stereo pair). **3.** An elongated framboid presumably from the same assemblage as the framboids of Figure 1, ×4150 (stereo pair). **4.** An elongated framboid presumably from the same assemblage as the framboids of Figure 1, ×4100 (stereo pair). **5.** The very small framboid from the lower-left side of the framboid of Figure 4, ×13,500. **6.** The small framboid on the left side of the uppermost framboid (in the middle of the figure) of the assemblage illustrated in Plate 4, Figure 1, ×15,000.

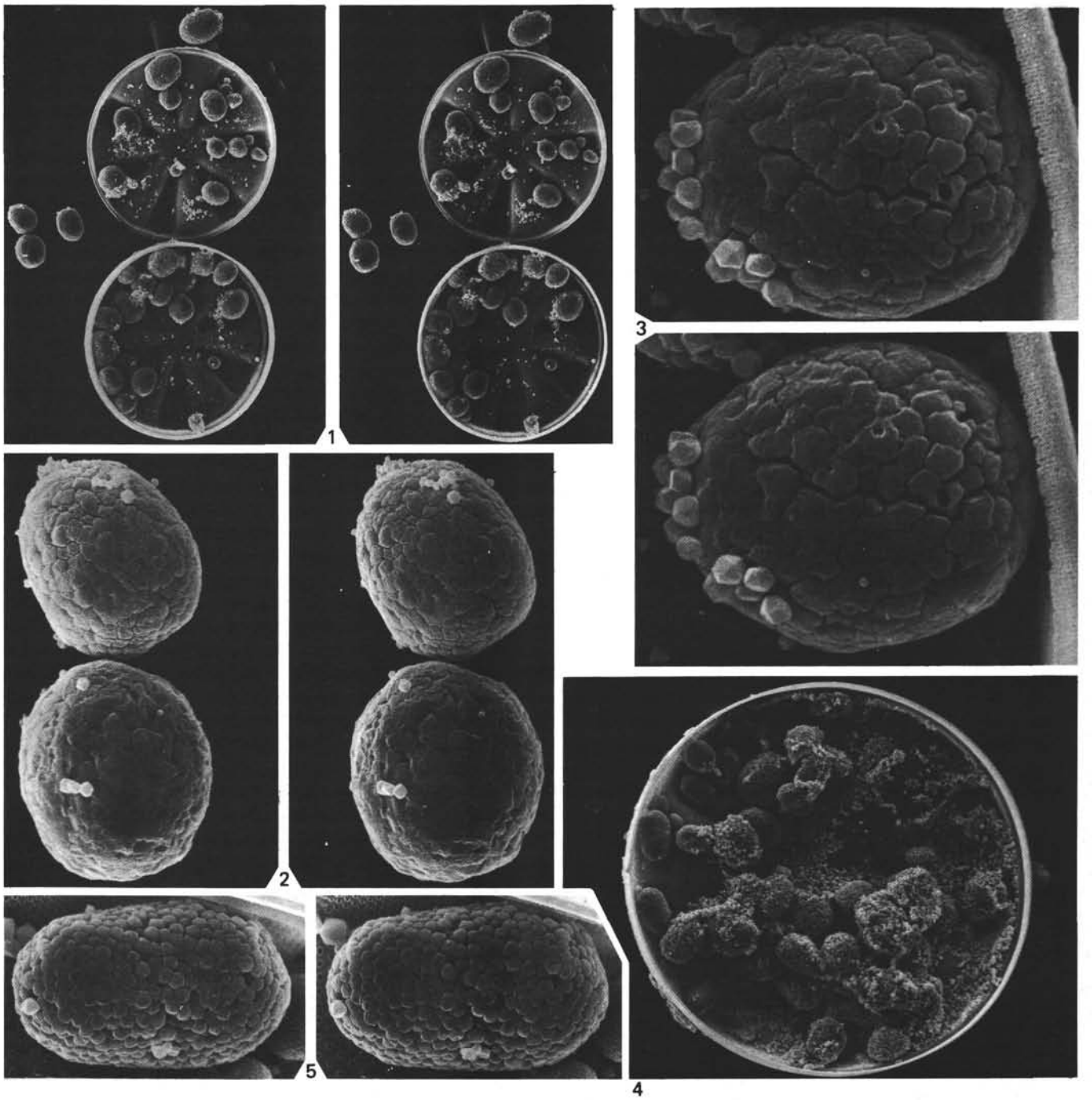

Plate 6. Sample 530B-2-3, 13 cm, foraminifer-nannofossil-diatom ooze, HCl residue, Au coated. **1.** A diatom with a framboid assemblage (stub GPIMH no. 2580), ×520 (stereo pair). **2.** The two framboids on the left side of Figure 1, ×3300 (stereopair). **3.** A framboid of the diatom shown in Figure 1, ×7000 (stereopair). **4.** A diatom with a framboid assemblage (stub GPIMH no. 2580), ×650. **5.** A framboid of the diatom illustrated in Figure 4, ×3600 (stereopair). Note the elongated shape of the framboid.

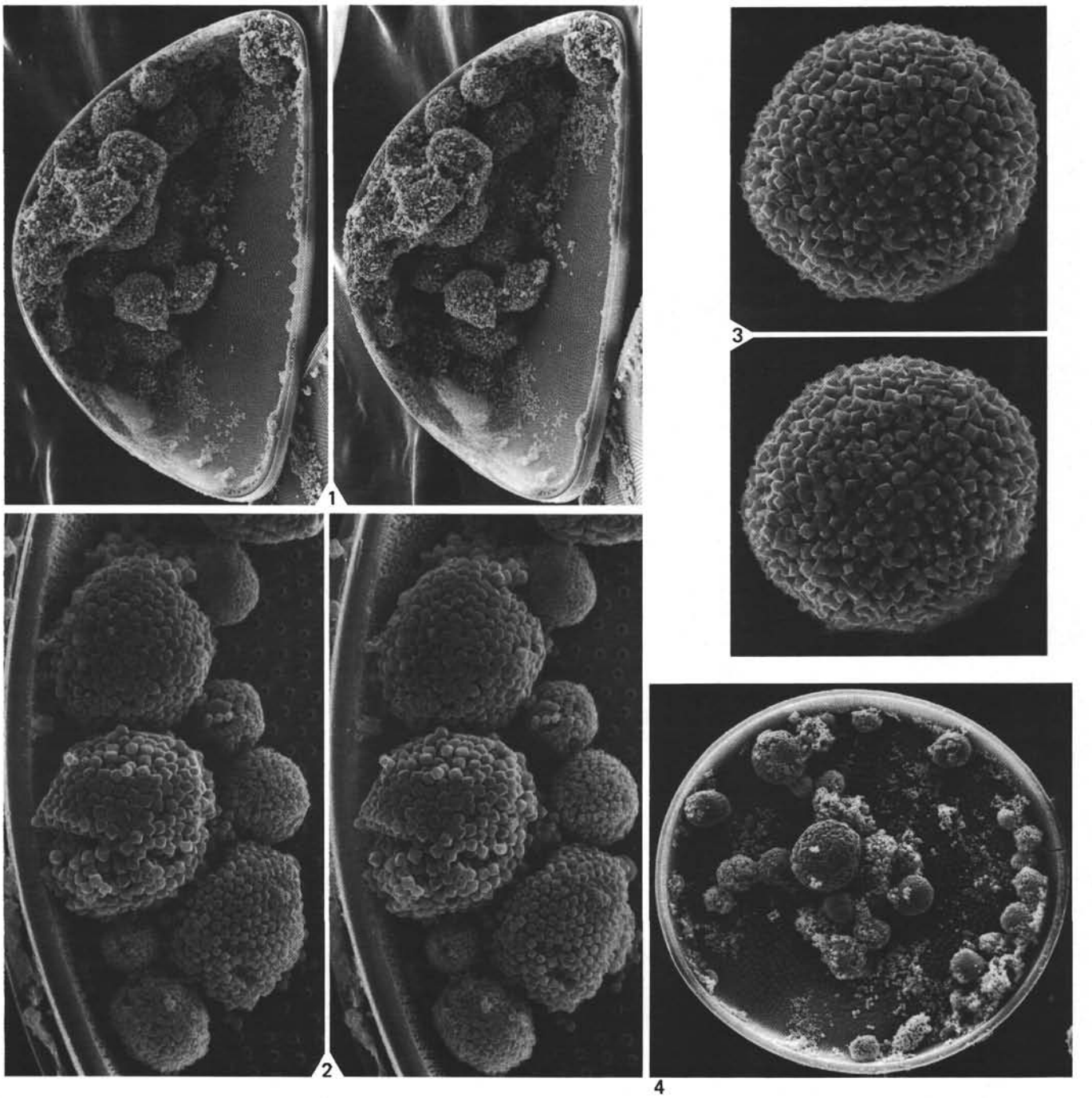

Plate 7. Sample 530B-2-3, 13 cm, foraminifer–nannofossil–diatom ooze, HCl residue, Au coated. **1.** A diatom with a framboid assemblage (stub GPIMH no. 2582), ×620 (stereopair). **2.** Part of a framboid assemblage of a diatom (stub GPIMH no. 2581), ×2800 (stereopair). Largest framboid about 15 μm in diameter. **3.** A large framboid (diameter about 20 μm) (stub GPIMH no. 2579), ×2500 (stereopair). **4.** A diatom with a framboid assemblage of medium-size to large framboids (4–12 μm) (stub GPIMH no. 2582, ×840.

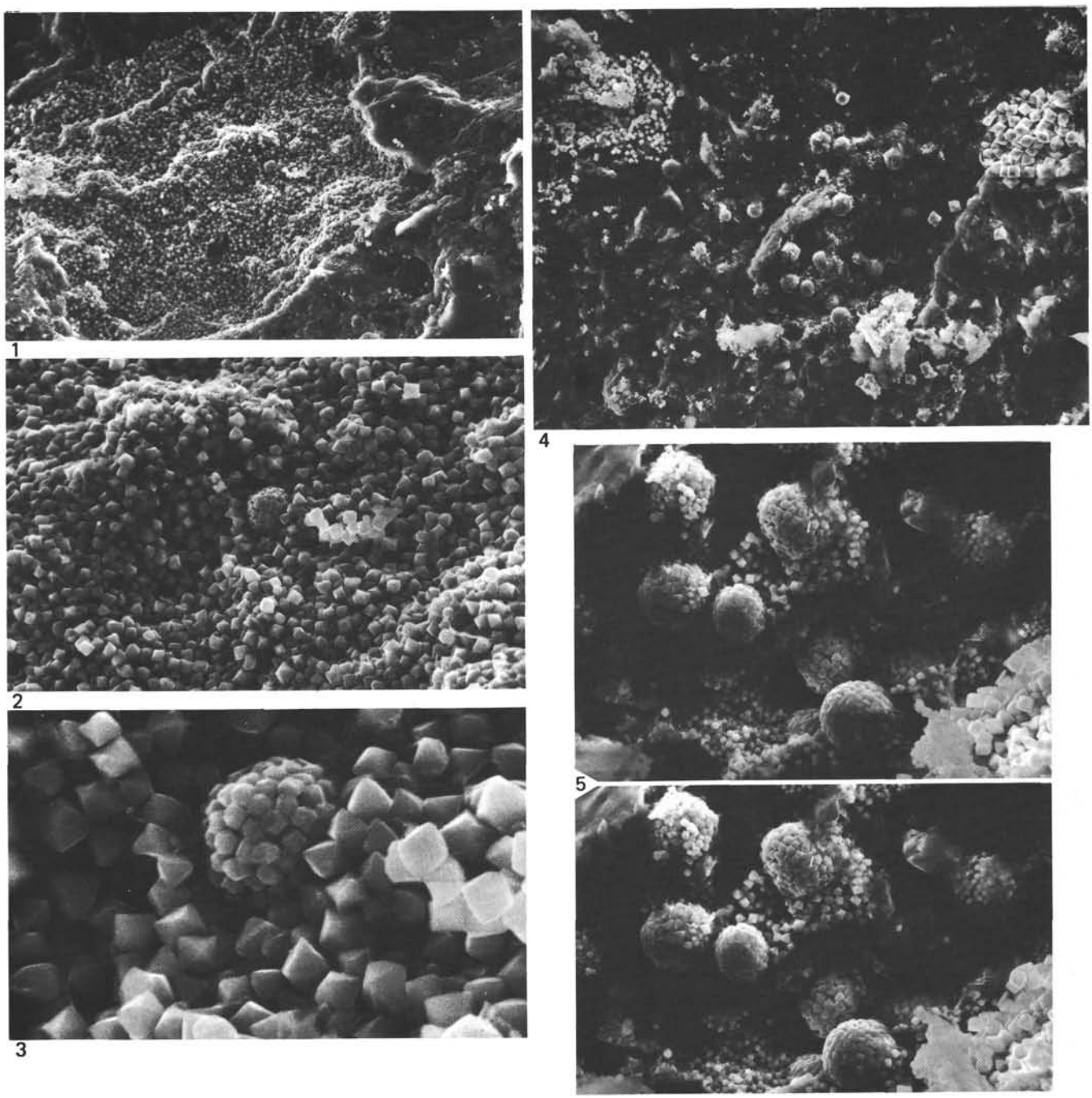

Plate 8. Sample 530A-101-7, 7 cm, black shale, uncoated (stub GPIMH no. 2583). **1–3.** A medium-size framboid (diameter about 3 μm) within a mass of pyrite crystallites (1) ×740, (2) ×2300, and (3) ×7400. **4, 5.** Surface of a cleavage plane with several medium-size framboids (diameter 4—6 μm), (4) ×600, and (5) ×2100 (stereopair).

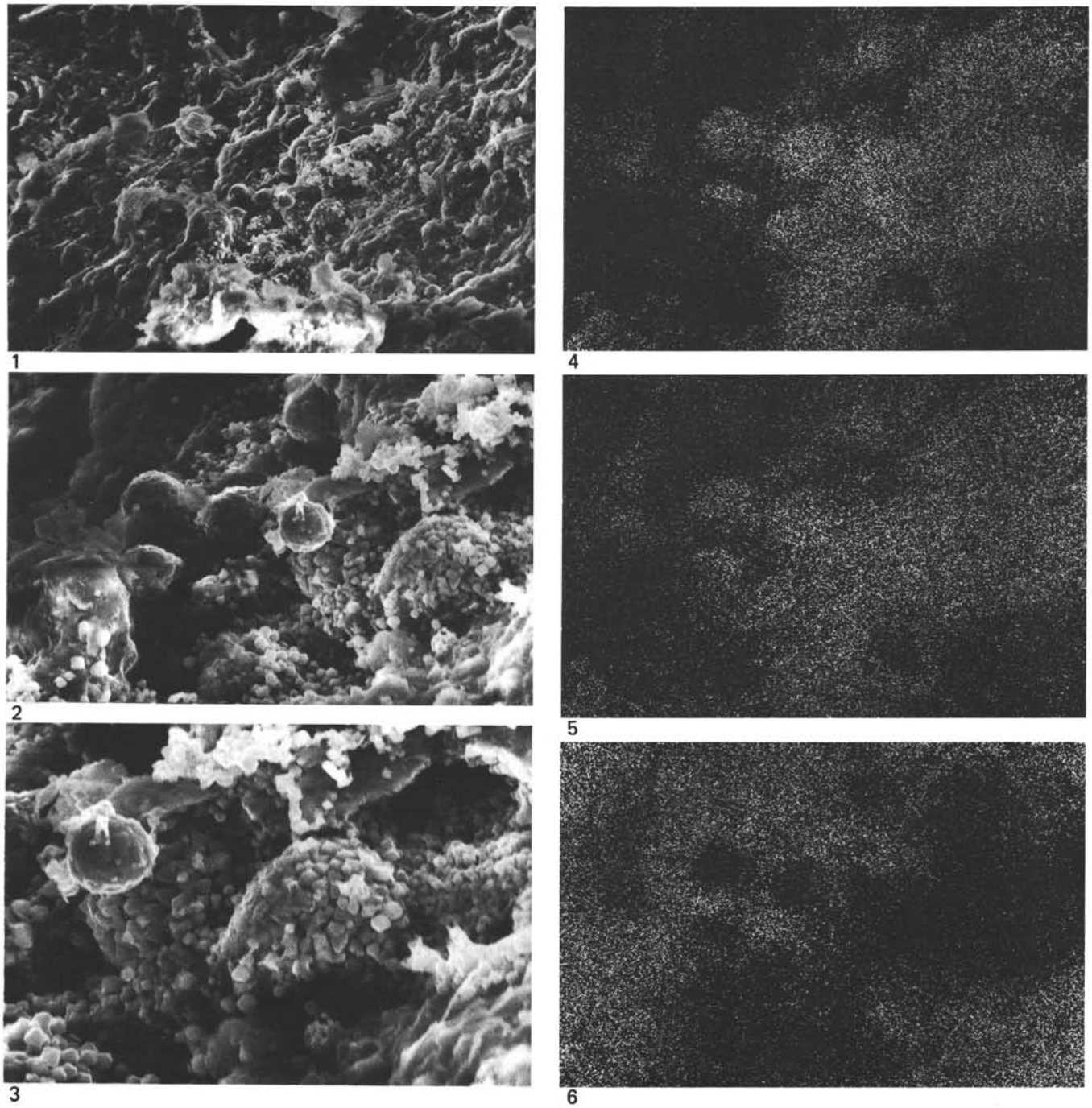

Plate 9. Sample 530A-101-7, 7 cm, black shale, uncoated, (stub GPIMH no. 2583). **1.** Surface of a cleavage plane with several medium-sized framboids (diameter 4–8 μm), ×750. **2.** Detail of Figure 1, ×2300. **3.** Detail of Figure 2, ×3700. **4.** Sulfur X-ray map of Figure 2, 20 kV, ×2300. **5.** Iron X-ray map of Figure 2, 20 kV, ×2300. **6.** Silicon X-ray map of Figure 2, 20 kV, ×2300.

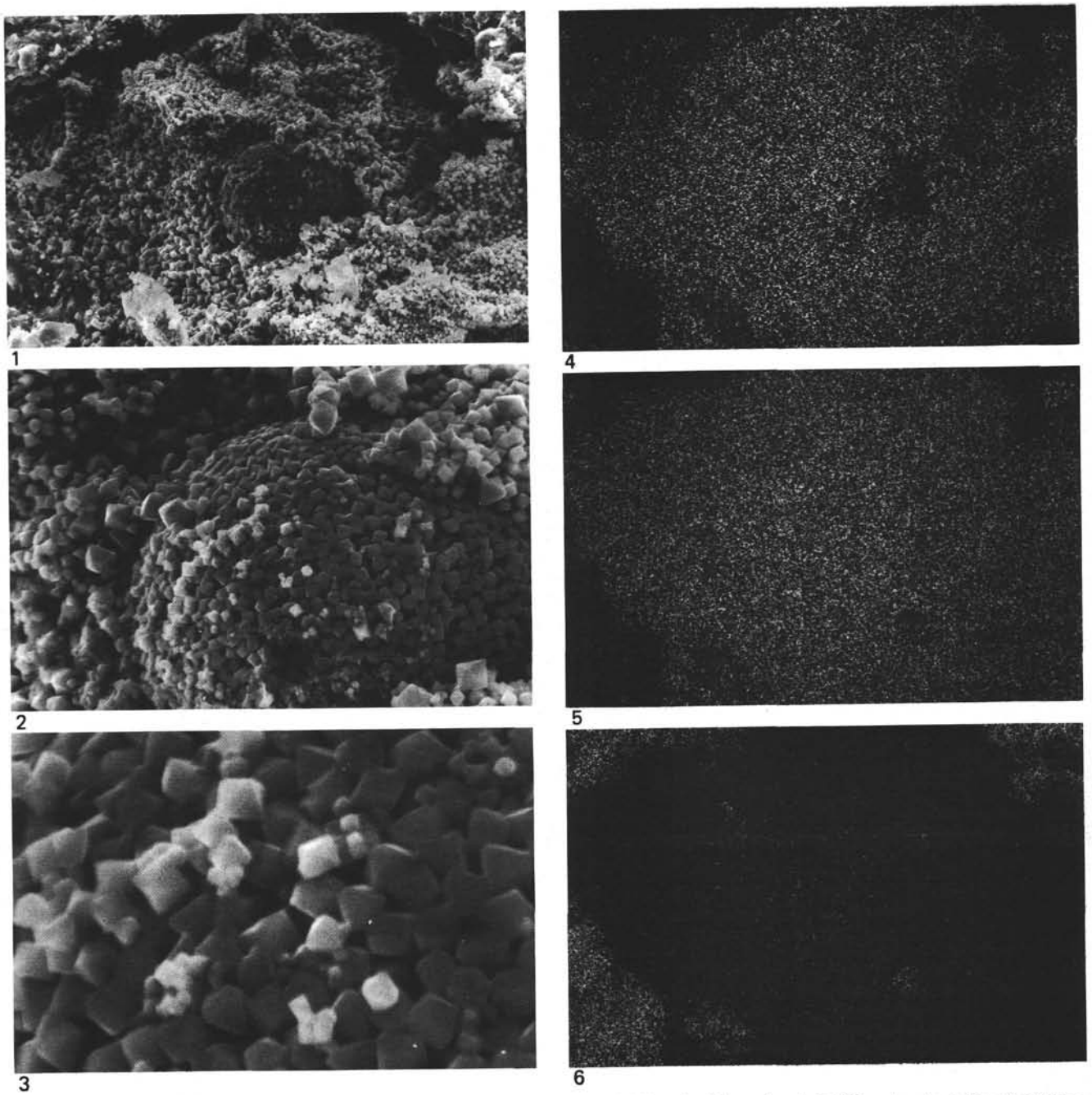

Plate 10. Sample 530A-101-7. 7 cm, black shale, uncoated (stub GPIMH no. 2583). **1.** A large framboid (diameter about 30 μm) within a mass of pyrite crystallites, ×730. **2.** The framboid in Figure 1, ×2300. **3.** Detail of the framboid in Figure 1, ×7300. **4.** Sulfur X-ray map of Figure 1, 20 kV, ×730. **5.** Iron X-ray map of Figure 1, 20 kV, ×730. **6.** Silicon X-ray map of Figure 1, 20 kV, ×730.

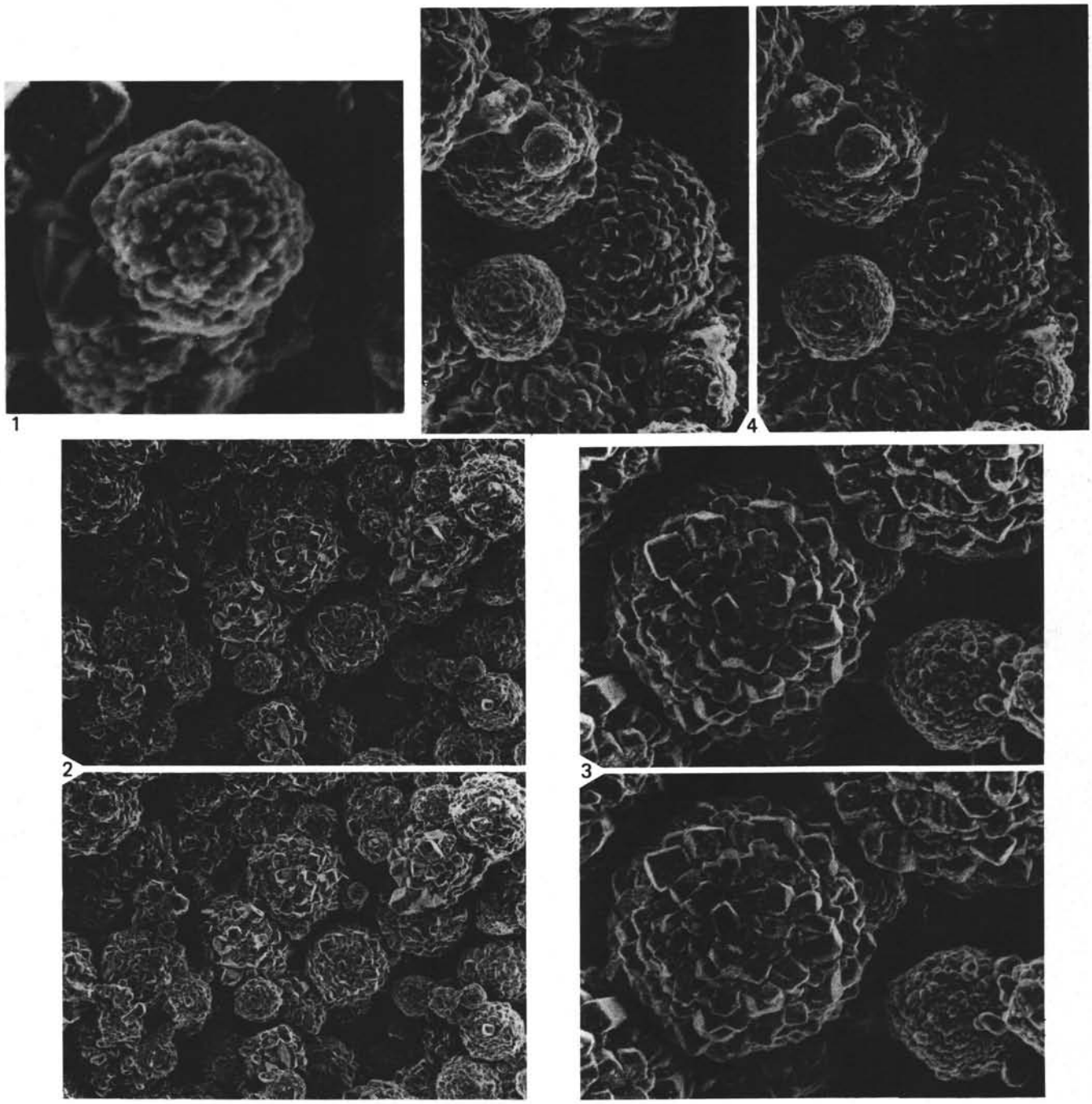

Plate 11. Pyrite framboids from an Ordovician black shale (middle Ordovician) Sularp shale of Scania, southern Sweden; boulder from the beach at Gislovshammar (no. Gis29). **1–3.** Framboids from a small mat-like assemblage (later destroyed). Figures 1 (×6700) and 3 (×2100) (both stereopairs) are details of Figure 2 (×670). Note the recrystallization of the crystallites in many framboids and the different sizes of the crystallites as a result. **4.** Framboids from a pyrite steinkern of the fossil problematicum *Labyrinthotuba* (stub GPIMH no. 2584), ×2400. Note the different sizes of the framboids (stereopair).