Biogenic Pyrite from a Miocene Formation of Shimane Peninsula, Southwest Japan

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Biogenic Pyrite from a Miocene Formation of Shimane Peninsula, Southwest Japan

By

George KATO

Abstract

Abundant micro-pyrite granules of various shapes occur in the hard black shales of the Aishiro alternation member of the Miocene Furue Formation in Shimane Peninsula, Southwest Japan. These granules are composed of micro-pyrite crystals, micro-pyrite spherules, and diatoms replaced with pyrite.

The mechanism of replacement and the origin of pyrite are discussed in relation to the micro-pyrite spherules and diatoms. The results of these studies seem to support the interpretation that sulfur bacteria and sulfate reducing bacteria work as a catalizer during the precipitation of sedimentary pyrites. A general description of the geology and paleontology of the area is also given.

Introduction

Throughout the last ten years or so there has been a great deal of informations published concerning the origins of sedimentary pyrites. Unfortunately not a single report on this subject can be found in the numerous volumes of Japanese geology although pyrite spherules with framboidal texture have been reported from several localities of various formations in Japan.

Recent contributions on sedimentary pyrites and their origins by L. G. LOVE (1957), J. R. VALLENTYNE (1963) and so on show wide differences of opinions. LOVE made an excellent contribution with the descriptions and genetical notes to the study of the sedimentary pyrites. He pointed out the existence of the pyrite spherules with framboidal texture and concluded that they were some organisms replaced by pyrite. VALLENTYNE was especially conspicuous, supporting BAAS BECKING's (1956) and BERNER's (1962) interpretations that some of the framboidal pyrite was inorganic products.

Field and laboratory studies were started in the summer on 1964 to see if pyrites from the Aishiro alternation member could possibly illuminate or confirm one of the already proposed theories.

The result supports the interpretation that sulfur bacteria and sulfate reducing bacteria work as a catalizer during the precipitation of sedimentary pyrite.

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Geologic Note of Shimane Peninsula

Shimane Peninsula is situated with an E-W direction in the central part of Southwest Japan facing the Sea of Japan. Although the Neogene formations are somewhat limited in distribution in Southwest Japan, they are extensively developed in Shimane Peninsula with a thickness of more than 2,000 m. The basement rock, although unexposed in Shimane Peninsula, is presumed to be the Cretaceous granitic rocks which are widely distributed in Chugoku province of Southwest Japan around the Neogene basin.

The geologic sequence in Shimane Peninsula is as follows in ascending order:

Koura Formation	Chigo tuff member
	Koura shale member
Ushigiri Formation	Josoji sandstone member
	Ushigiri alternation member
Furue Formation	Aishiro alternation member
	Furue mudstone member
Matsue Formation	

Koura Formation: The Koura Formation consists of two members: the lower, the Chigo tuff member; and the upper, the Koura shale member. The Chigo tuff member, about 100 m thick, is composed of stratified coarse black tuffs with the intercalation of several thin basaltic lavas. Its lower limit is not exposed. No fossils are known to be in this member. The Koura shale member is in contact with the Chigo tuff member by faults and is composed of alternation of siliceous fine greenish sandstones and shales at the lower part and hard black shales at the upper. The thickness is 100 m. The following fossils have been found in this formation: *Cinnamomum schuchzeri* HEER, *Comptonia naumanni* (NATHORST), *Glyptostrobus europaeus* (BRONGNIART), *Laurus promigenius* UNGER, *Metasequoir japonica* (ENDO), *Planera ungeri* ETTINGSHAUSEN, *Quercus glauca* THUNBERG, *Salix* sp., *Ulmus* sp. (plants); *Corbicula* sp., *Cristaria muroii etomoensis* SUZUKI, *Cuneopsis* sp., *Hyriopsis* sp., *Lamprotula sakaii* SUZUKI, *L. shimanensis* SUZUKI, *Parreysia nipponensis* SUZUKI, *Semisulcospira* sp., *Viviparus* sp. (molluscs). The fossil assemblage clearly indicates that the Koura Formation was deposited in a fresh water.

Ushigiri Formation: The Ushigiri Formation overlies the Koura Formation conformably, and is composed of two members: the lower, the Josoji sandstone member; and the upper, the Ushigiri alternation member. The lower part of the

Josoji sandstone member consists of loose conglomerate cemented by coarse tuffaceous sand. The pebbles of conglomerate range in size from pebbles to cobbles. The middle part consists of greenish coarse sandstones, and the upper part comprises hard black shales and massive thick green tuffs. The thickness of this member is 500 m. Although some fossils have been reported from the Josoji sandstone member by the previous workers, the author doubts whether the horizon from which the fossils came actually belongs to the Josoji sandstone member or not. The Ushigiri alternation member attaining a thickness of 1,500 m is composed of hard black shales and green tuffs. Known fossils are as follows: *Bathyamussium* sp., *Delectopecten peckhami* GABB, *Megayoldia* sp., *Nuculana* sp., *Propeamussium tateiwai* (MAKIYAMA), *Solemya* sp., *Yoldia* sp. (molluscs); *Brissopsis* sp. (echinoid). The nature of the environment of the Josoji sandstone member at the time of the deposition is not clear because of lack of necessary data. The Ushigiri alternation member is clearly marine sediments.

Furue Formation: The Furue Formation overlies the Ushigiri Formation conformably, and is composed of two members: the lower, the Aishiro alternation member; and the upper, the Furue mudstone member. The Aishiro alternation member is composed of boulder conglomerate cemented by tuffaceous material at the lower part, and alternation of fine to medium compact sandstones and hard black shales at the upper. The thickness is 600 m. The following fossils came from this member: *Cardita shiobarensis* YOKOYAMA, *Cardium* sp., *Delectopecten peckhami* GABB, *Dentalium* sp., *Dosinia* sp., *Fulgoraria* sp., *Glyptoamussium* sp., *Acesta goliath* (SOWERBY), *Nautilus izumoensis* YOKOYAMA, *Neptunea koromogawana* NOMURA, *Ostrea* sp., *Patinopecten kimurai ugoensis* HATAI & NISIYAMA, *Phos* sp., *Shichiheia yokoyamai* (NOMURA & HATAI), *Thyasira* (*Conchocele*) *nipponica* YABE & NOMURA, *T.* sp., *Yoldia* (*Yoldia*) *laudabilis* YOKOYAMA (molluscs); *Coptothyris* sp. (brachiopod); *Globorotalia fohsi fohsi* CUSHMAN & ELLISOR, *G. tumida* (BRADY), *Orbulina universa* D'ORBIGNY, *O. suturalis* BRONNIMANN (planktonic foraminifers). The samples of pyrite treated in the present paper were found in this member.

The Furue mudstone member is composed of massive grey mudstone. The thickness is 600 m. The fossils occurring in this member are as follows: *Acila* sp., *Delectopecten peckhami* GABB, *Lucina* sp., *Lucinoma acutilineatum* CONRAD, *Nuculana* sp., *Ostrea* sp., *Solemya tokunagai* YOKOYAMA, *Thyasira* (*Conchocele*) *bisecta* (CONRAD) (molluscs); *Globorotalia bykovae* (AISENSTAT), *Globigerina pachyderma* (EHRENBERG) (planktonic foraminifers). The fossil assemblage and sedimentary feature of the Furue Formation show that the Aishiro alternation member was deposited in a shallow brackish environment and the Furue mudstone member under a pure marine condition, although the depth was not too great.

Matsue Formation: The Furue Formation grades up into the Matsue Formation conformably. The latter in turn is covered with the Pleistocene lacustrine sediments unconformably and composed of loose yellowish fine to medium sandstones with an intercalation of shales and lignites at some horizons at the upper part. The thickness is 300 m. Known fossils are as follows: *Anadara ogawai* (MAKIYAMA), *Cardium nuttari* CONRAD, *Cerithium* sp., *Chlamys cosibensis* (YOKO-

YAMA), *C. swifti etchegoini* (ANDERSON), *C.* sp., *Cultellus izumoensis* YOKOYAMA, *Dosinia* (*Phacosoma*) *japonica nomurai* OTUKA, *Glycymeris cisshuensis* MAKIYAMA, *G.* sp., *Lucinoma acutilineatum* CONRAD, *Ostrea* sp., *Pitar itoi* (MAKIYAMA), *Procopecten akihoensis* MATSUMOTO, *Prototheca tateiwai* (MAKIYAMA), *Solemya tokunagai* YOKOYAMA, *Tectonatica janthostoma* (DESHAYES), *Thyasira* (*Conchocele*) *bisecta* (CONRAD) (molluscs). These fossils indicate that the Matsue Formation was deposited in a shallow sea.

The Koura shale member is correlated with the Daijima Formation in Oga Peninsula which is the type-locality of the lower Miocene in Japan, because *Metasequoia japonica* (ENDO), *Comptonia naumanni* (NATHORST) and others in the Koura shale member comprise the *Comptonia-Liquidambar* association, the so-called "Daijima-flora". *Globorotalia fohsi fohsi* CUSHMAN & ELLISOR occurs in the upper part of the Ushigiri Formation together with *G. tumida* (BRADY). The known range of the combination of *G. fohsi fohsi* and *G. tumida* is only very short, being restricted to the uppermost part of *G. fohsi fohsi* zone. Accordingly there is no doubt that the upper part of the Ushigiri Formation is included in the uppermost of *G. fohsi fohsi* zone. *G. bykovae* (AISENSTAT), the index species of the next higher zone in Japan, occur in the lower part of the Aishiro alternation member.

Above mentioned facts lead to the conclusion that the Koura, the Ushigiri, the Furue, and the Matsue Formation are correlated respectively to the Aquitanian, the lower Burdigarian, the upper Burdigarian to the Helvetian, and the Sarmatian.

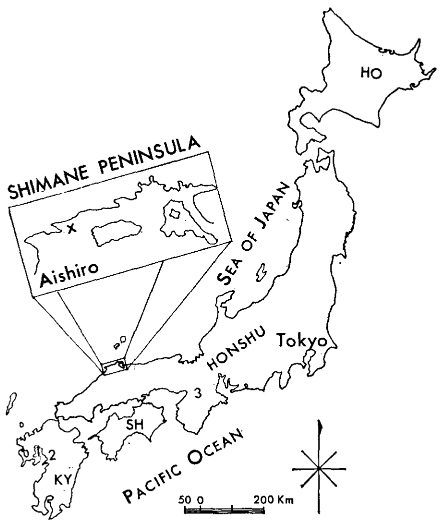


Fig. 1. Index map showing the locality of framboidal pyrite in Japan.
KY. Kyushu island, SH. Shikoku island, HO. Hokkaido island.
1. Ariake bay, 2. Miike coal field, 3. Gojo mine.

Occurrence of Pyrite in the Aishiro Alternation Member

The pyrite granules dealt with in the present paper were obtained from the shales in the upper part of the Aishiro alternation member. The lower part of the Aishiro alternation member is composed of boulder conglomerate consisting of granitic rocks and andesites. The upper part is composed of fine to medium compact sandstones and hard black shales, the former of which consists of clean and well sorted sand while the latter is remarkably rich in the organic matter such as a high percentage of wood fragments. Some fossils deposited in a shallow brackish water occur in the Aishiro alternation member. Besides, the overlying Furue mudstone member and the underlying Ushigiri alternation member, both of which are in contact with the Aishiro conformably, are pure marine sediments although their facies are not so deep. It is presumed that the Aishiro alternation member which was once deposited in a shallow brackish environment might have been redeposited on the Ushigiri alternation member by turbidity currents. Considering the distribution of the Aishro alternation member, it is probable that they originally had a lenticular form as a whole thinning out towards the eastern part of Shimane Peninsula, where the Furue mudstone member overlies directly on the Ushigiri alternation member without any stratigraphical gap. However, the original stratigraphical relation is not clear in the western part because of the intense intrusion of igneous rocks. Although it is very difficult to presume a sedimentary environment for the Aishiro alternation member in details, it is, at least, reasonable to suppose that the shales were deposited in an anaerobic environment with a high content of organic matter.

Two kinds of pyrite occur in side by side. The pyrite granules, on one hand, occur in the shales in the form of laminar bands without any sign of scattered distribution. On the other hand, there is another form of pyrite, impregnated veinlets. Various shapes of pyrite granules are readily distinguished among the pyrites in the laminar bands. The pyrite granules were carefully treated to avoid the mixing of materials from the bands and veinlets. Groups 1 and 2 of the four groups discussed later are considered to be especially important in the regard of their origin, and a discussion on the origin of sedimentary pyrite is given here in some detail. Group 1 (Pl. 15, Figs. 1–18) is diatoms replaced by pyrite. Pl.16, Figs. 17 and 28–38 show diatoms imperfectly replaced by pyrite also belonging to group 1. Group 2 is framboidal pyrites. They show the different stages of aggregation. The specimens, illustrated in Pl. 16, Figs. 1–16, are single framboidal pyrites, and those shown in Figs. 18–27 are aggregated framboidal pyrites. Very interesting is the inner casts of diatoms showing neither the framboidal aggregation nor the ornamental feature of the outer surface of diatom tests. They clearly indicate the last stages of replenishment by framboidal pyrite in the bivalves of the diatoms. The above mentioned facts indicate that the pyrite under consideration must originate in the framboidal pyrite.

Isolation of Pyrite

A large number of pyrite granules with various shapes were found unexpectedly by the author during the preliminary heavy mineral analysis of the shales from the Aishiro alternation member. Then the author systematically sampled the shales from the same locality for collecting more pyrites. There are two kinds of pyrite, each showing a different occurrence. One occurs as laminar bands in strata, while the other occurs as veinlets which cut across the strata as mentioned in the preceding article. On sampling, the author took care to avoid the mixing of both, and collected only the shales having the banded parts.

The shale samples were treated by the following procedure: The shale was crushed by jaw-crusher until the grains would pass through the 80-mesh sieve; the grains were washed off the mud particles by water in a glass beaker, and gently boiled in 50% HCl to extract $CaCO_3$ on a waterbath for about 15 minutes; then heavy minerals were concentrated by THOULET's solution, and cleaned by the ultrasonic generator (Son Blastor) to take away the surface pigments of grains; in order to separate pyrite granules from them, a liquid of iodide methylene was further used by means of centrifuging; the residues were mounted in slide-glasses with geratine. Observation was made under the microscope under a high magnification.

Description of Pyrite

The pyrite granules comprise the following four groups of various form:

1. Micro-organisms replaced by pyrite
2. Microspheres
3. Microcrystals
4. Irregular shapes.

Almost all the micro-organisms of group 1 belong to diatoms comprising 4 species of 2 genera, *Coscinodiscus* sp. cf. *C. argus* EHRENBERG, *C. lineatus* EHRENBERG, *C. stellaris* ROPER, and *Actinocyclus* sp. aff. *A. ingens* RATTRAY, replaced by pyrite. They are showed in Pl. 15. The specimens shown in Pl. 16, Figs. 17 and 28–38 are also diatoms, which are imperfectly replenished by many microspheres of pyrite. The other members of group 1 are micro-organisms other than diatoms ranging in size from 2 to 200 μ, although they can not be classified taxonomically because of imperfect replenishment. Group 2 is the microspheres which RUST (1935) named "Framboidal pyrite". They occur as single framboidal pyrites ranging from 2 to 50 μ or as aggregated forms including different stages of aggregation. All the single framboidal pyrites show practically spherical form with uneven surface. Examination under the microscope under a high magnification with oil immersion reveals that the surface ornamentation consists of innumerous minute pyrite crystals. LOVE (1962) divided the pyrite spherules into a few groups based on their form and size. However, his division seems to be unreasonable, for it considers all of these pyrite spherules to be of the same origin, the difference lying only in form and size.

Group 3 is single or aggregated minute crystals like group 2. Their size ranges from 5 to 50 μ. The crystal habits include cubic, pyritohedron and octahedron. Group 4 is comprised of all the specimens which are excluded from the three groups mentioned above. Nearly all of them do not show regular shapes, especially of framboidal texture, nor regular size. It is not clear whether they were originally the framboidal pyrite and melted later or they are quite different from the framboidal pyrite in origin. The group 3 and 4 are omitted from the subject of the present paper, because the scope of this paper is to examine the framboidal pyrite.

Historical Review

NAUMANN (1919) studied the pyrite spherules in the fresh water deposits and reported wide-spread distribution of the pyrite spherules in the deposits. He also reported their occurrence within microfossils. THIESSEN (1920) observed pyrite spherules with diameters of 30 to 40 μ associated with the wood fragments in peat. They were powdery spherules which appeared pyritous, varied from light yellow the black opaque in color, were easily stained and gave the appearance of micro-organisms. In a single preparation all the intermediate stages were seen and the spherules were regarded as bacteria replaced by pyrite. SAWJALOW (1922) described the *Actinomyces*-bearing grains of black sulfide within the radiating mycerial filaments. SCHNEIDERHÖHN (1923) reported spherical pyrite bodies of diameter 5 to 20 μ from the Mansfeld Kupferschiefer in Germany. He classified the spherules into four different types on the basis of size, surface feature and mineralogical character. He considered the spherules to be fossilized bacteria, each spherule corresponding to a single large bacterium, and concluded that the spherules were formed synchronously to the deposition as a result of bacterial action. BERGH (1928) reached a similar conclusion concerning the origin of the pyrite spherules in the Swedish alumina shale. ISSACHENKO (1929) described the formation of pyrite within the individual cells of bacteria. He assumed that the pyrite was produced as a result of biological activity. RUST (1935) regarded the formation of pyrite spherules as a non-biological process, that is, it resulted from metacolloidal crystallization of globules of FeS_2-gel. He introduced a term, framboidal texture, for the texture of the surface of the smaller spherules, and concluded that the framboidal texture was due to simultaneous crystallization in a gel-structure. SCHOUTEN (1937; 1946a, b, c) was also strongly opposed to the sulfur bacteria theory in relation to the formation of pyrite spherules in the Kupferschiefer, and concluded that the framboidal spherules were attributable to the recrystallization of iron-sulfide gel, but admitted the activity of the sulfur bacteria for the origin of the gels. NEUHAUS (1940) classified the spherules in two types, which are modifications of SCHNEIDERHÖHN's four-folded classification. They are *Kieskügelchen* and *Kiesklümpchen*, the former of which is 5 to 20 μ in diameter with the typical framboidal texture, while the latter is larger in size with coarser crystals on the surface. He concluded that the pyrite spherules were produced through the action of metal-bearing water and sulfur grains originated from the sulfur bacteria. BASTIN (1950) reached a similar conclusion to that of RUST. RAMDOHL (1950, 1953) considered framboidal pyrite as mineralized bacteria. DEANS and EAGER (in EAGER, 1952) noted the occurrence of framboidal pyrite spherules in the various kind of rocks, and suggested that they were formed under marine conditions, although he did not imply any particular mode of origin. HIGASHIMOTO (1956) reported sulfide minerals having colloidal textures from the Gojo mine in Nara Prefecture, Japan. FABRICIUS (1961) concluded that the framboidal pyrite represented individual bacteria. KANNO (1962) found diatoms which were replenished by black FeS mineral in recent sediments from the Ariake Bay in North Kyushu. NAKAYANAGI (1964) also found pyrite spherules of framboidal texture from the Miike coal field.

Genesis of Pyrite

The origin of framboidal pyrite has been discussed by many investigators as mentioned above. These discussions can be classified in three groups: a) Framboidal pyrites are replaced fossil organisms (ex. SAWJALOW, 1922 and LOVE, 1957); b) framboidal pyrite is formed of inorganic gel (ex. RUST, 1935 and VALLENTYNE, 1963); and c) the so-called "bacteria theory", that is to say, bacteria work as a catalizer during the process in which the framboidal pyrite is formed (ex. THIESSEN, 1920 and NEUHAUS, 1940). Each of the hypotheses has merit but no one is conclusive.

Discussion: a) In his hypothesis LOVE (1957) stressed the fact that the framboidal pyrite left some organic residues after being treated with nitric acid. It may appear reasonable that the organic material exists in some of the framboidal pyrites because NAKAYANAGI (1964) also reported similar result as LOVE's. However, it does not mean that all of the framboidal pyrites always contain the organic material in them, as VALLENTYNE (1963) mentioned. It seems to be a more reasonable conclusion that only part of the framboidal pyrites contains the organic material. Furthermore the framboidal pyrite with organic material does not necessarily lead to a single conclusion as to its origin. This has led, NAKAYANAGI and the present author, who found the organic residue in the framboidal pyrite, to disagreement with LOVE's interpretation.

LOVE proposed generic and specific names for some of the framboidal pyrites, *Pyritosphaera barbaria* and *Pyritella polygonalis*. The former is smaller and the latter is larger. It is premature to give the generic and specific names to the framboidal pyrite for the sole reason that the organic material was retained in them because the organic material is not necessarily the organism itself. Moreover, the organisms which correspond to the framboidal pyrites have not been found anywhere in spite of common occurrence of the framboidal pyrite in recent sediments. If the organisms which LOVE described were to be found

in recent sediments, his conclusion would have a concrete basis.
b) VALLENTYNE mentioned that the framboidal pyrite was formed of inorganic gel, referring to BAAS BECKING'S and BERNER'S opinions. He concluded that the organic material which LOVE described should be the result of contamination during the processes of the chemical treating of the pyrite sample, yet NAKAYANAGI extracted the organic material from the framboidal pyrite. The author also reached substantially the same result as they, after carefully avoiding contamination during all the processes for detecting the organic material from the framboidal pyrite. From the evidences above mentioned, no one will deny that the organic material exists in a part of the framboidal pyrite.

The "inorganic theory" may be apparently the most reasonable interpretation about the origin of framboidal pyrite without organic material. However, it can not interpret the origin of the framboidal pyrite with organic material. That is to say, it can not give a satisfactory interpretation concerning how the organic material is taken in inorganic gel and, moreover, why the framboidal pyrite was replenished in the cells of the organisms selectively.
c) Although some revision must be given to the formation of the framboidal pyrite, the author supports the third interpretation in the sense that (i) the organic material exists, at least, in a part of the framboidal pyrites, (ii) the environment of recent sediments and sedimentary rocks with the framboidal pyrite is restricted in foul condition and (iii) the framboidal pyrite replenishes the cell of certain kind of organisms selectively.

Further, LOVE mentioned that the framboidal pyrite was produced under an anaerobic condition. Certainly all of the sediments and sedimentary rocks with framboidal pyrite have a more or less intimate relation to a foul environment during the deposition and the diagenesis. For the iron-sulfide gel the supply of H_2S is indispensable even when sulfur bacteria and sulfate reducing bacteria work as a catalizer. If H_2S is supplied freely, an anaerobic condition is not necessarily needed for the formation of the iron-sulfide gel because the bacteria do not need the foul environment but H_2S for the vigorous breeding. Long lasting foul environment, of course, has some importance to the generation of H_2S and is not necessitated the supply of inorganic H_2S. In Japan almost all of beds with framboidal pyrite are associated with the mines of sufide minerals. For example the Aishiro alternation member seems to have been influenced rather by the sulfuric spring or sulfide gas by volcanic activity than by the foul environment in its dense concentration of framboidal pyrite. It seems to be impossible to form the abundant framboidal pyrite from H_2S which is generated only in the foul environment. Furthermore, in the Aishiro alternation member in which the dense concentration of the framboidal pyrites are found, the rapid reaction of Fe and S should be required. H_2S supplied from the anaerobic environment seems to be insufficient to form necessary amount of FeS_2-gel. Because the maximum volume of dissolved H_2S and Fe^{++} in water is constant, something must work as a catalizer to utilize H_2S as much as possible.

Selective replenishing of framboidal pyrite in diatom tests should not be inevitable, if the framboidal pyrite was formed by inorganic gel. As shown in Pl. 2, Figs. 17 and 28–38, however, it is clear that the replenishment of the framboidal pyrite starts inside the bivalves of the diatoms. If the framboidal pyrite was formed of inorganic gel, it should be precipitated on the outer surface of the valves. Many examples of pyrite which fill up the inside of organisms have been reported by various investigators. The question of why FeS_2-gel is replenished within the cell of organisms is a critical problem. It may be solved by supposition that sulfur bacteria and sulfate reducing bacteria worked as a catalizer.

Even supposing that sulfur bacteria and sulfate reducing bacteria work as a catalizer, the chemical process of the formation of FeS_2-gel should be clarified. To date, the previous investigators who treated the framboidal pyrite seems to have been misled by idea that mere co-existence of Fe^{++} and H_2S resulted in the formation of FeS_2. After the experiment on the reaction of Fe^{++} and H_2S under the same condition of sea water, BAAS BECKING (1961) recognized that the precipitation from that solution was not FeS_2 but FeS. While he (1956) supposed that the hypothetical material with the molecular formula of $Fe(SH)_2$ is formed as the transitional substance before FeS_2 is ultimately formed during the reaction of Fe^{++} and H_2S, this is very doubtful. Even if $Fe(SH)_2$ is formed, it should be resolved immediately following the equation given below:

$$Fe(SH)_2 \rightarrow FeS + H_2S$$

Accordingly there is no chance to obtain FeS_2 as purely a chemical precipitate. BERNER (1962) proposed the following formula as a normal reaction:

$$FeS + S^0 \rightarrow FeS_2$$

The reaction of the solid S with any other element, however, is impossible at room temperature with low pressure. These facts lead to the hypothesis that Fe^{++} and S^{--} react directly to form FeS_2 under the above mentioned condition.

GARRELS (1956) stated that S could not be ionized through any inorganic process under the condition mentioned above, no matter what kind of material S originated from. The following fact, however, throws light on the formation of S^{--}; he found also a minute quantity of S^{--} in recent sediments, and supposed that S^{--} might have been ionized by the activity of the organism. FeS_2 has never been synthesized from Fe^{++} and H_2S. S^{--} also has never ionized from S through any inorganic process at room temperature with low pressure. However, both FeS_2 and S^{--} actually exist in recent sediments. These facts seems to contradict each other. The problem, however, may be solved through the introduction of the recent knowledge on the action of sulfur bacteria and sulfate reducing bacteria.

As pointed out by BAAS BECKING, he could not succeed to synthesize FeS_2 from Fe^{++} and H_2S in his experiment even under the influence of sulfur bacteria. It seems that the reaction of Fe^{++} and H_2S proceeded before S^{--} was formed by the bacteria in BAAS BECKING's experiment. Moreover the observation concerning the activity of sulfur bacteria which ionized S to S^{--} has never been reported. Although this data seems to be disadvantageous for the bacteria theory, this is not conclusive. He might have avoided his failure, if he had used the colony of both sulfur bacteria and sulfate reducing bacteria. It is actually observed that both sulfur bacteria and sulfate reducing bacteria are symbiotic and make up a colony.

GALLIHER (1933) pointed out that a sulfur cycle may be realized through the serial activities of the colony. The author supports this interpretation that there is a possibility of ionizing S to S^{--} in the organic sulfur cycle, even if S is supplied as H_2S or H_2SO_4, irrespective of their organic or inorganic origin. If the condition is such that H_2SO_4 is supplied continually, the formation of pyrite is obstructed because Fe^{++} reacts much more readily to SO_4^{--} than to S^{--}. $FeSO_4$ is hardly preserved in sedimentary rocks because of its low stability at room temperature with low pressure. If S^{--} is formed in the colony of the bacteria, it may react with Fe^{++} directly to form the gel of FeS_2 which is more stable than FeS at room temperature with low pressure. The process in which the FeS_2-gel transforms to the framboidal form can be explained through application of colloidal chemistry.

In the process of crystallization of the FeS_2-gel, whether it becomes pyrite or marcasite depends on the physico-chemical condition through the diagenesis. Under an acidic condition FeS_2-gel is crystallized as marcasite which has low stability compared with pyrite at room temperature with low pressure, and is scarcely preserved in sedimentary rocks which are in many cases neutral or weak alkaline. This is the reason why pyrite is much more than marcasite in sedimentary rocks.

Summary

1. A large number of framboidal pyrites which replenish the cells of diatoms were found from the Aishiro alternation member of the Miocene Furue Formation in Shimane Peninsula, Southwest Japan.

These diatoms, *Coscinodiscus* sp. cf. *C. argus* EHRENBERG, *C. lineatus* EHRENBERG, *C. stellaris* ROPER, and *Actinocyclus* sp. aff. *A. ingens* RATTRAY are described systematically in the present paper.

2. To date, several interpretations concerning the origin of the sedimentary pyrite have been given by many investigators.

3. However, all of these interpretations seem to have been based on the misunderstanding that pyrite is formed in normal sedimentary condition merely by the co-existence of Fe^{++} and H_2S.

The precipitation by the purely chemical reaction of Fe^{++} and H_2S at room temperature with low pressure is not FeS_2 but FeS.

4. Ionized sulfur (S^{--}) and iron (Fe^{++}) may react directly with each other to form FeS_2-gel.

5. Although the latest knowledge of chemistry teaches that sulfur is never ionized to S^{--} through any inorganic process at room temperature with low pressure, S^{--} is actually found in recent organic sediments.

6. It is generally believed that sulfur bacteria and sulfate reducing bacteria are symbiotic and build up a colony, and that a sulfur cycle is realized in the colony.

7. The sulfur bacteria and sulfate reducing bacteria seem to work as a catalizer for the formation of FeS_2.

Systematic Description of Diatom

Class Bacillariophyta
Order Centrales SCHÜTT, 1896
Family Discaceae SCHÜTT, 1896
Subfamily Conscinodiscoideae SCHÜTT, 1896
Tribe Coscinodisceae SCHÜTT, 1896
Genus *Coscinodiscus* EHRENBERG, 1838

Coscinodiscus sp. cf. *C. argus* EHRENBERG
Pl. 15, Figs. 1, 2, 3, 4.

1840. *Coscinodiscus argus* EHRENBERG, *K. Akad. Wiss. Berlin, Phys. Abh.*, 1938, p. 129 (inaccessible).
1929. *Coscinodiscus argus*, HUSTEDT, *Kieselalgen*, Teil 1, p. 422, fig. 226.
1941. *Coscinodiscus argus*, LOHMAN, *U.S. Geol. Surv. Prof. Papers* 196-B, p. 70, pl. 13, figs. 1, 3.
1957. *Coscinodiscus argus*, KANAYA, *Sci. Rep. Tohoku Univ. 2d ser. (Geology)*, vol. 28, p. 84, pl. 4, figs. 1a, 1b, 2a, 2b, 3.
1959. *Coscinodiscus argus*, KANAYA, *ibid.*, vol. 30, p. 73, pl. 3, fig. 4.

Specimen no.—GK-W 4001-a, b, c, d (Slide).

Horizon and locality.—Middle Miocene, the Aishiro alternation member; a quarry about 100 m north of Aishiro-iriguchi, Hirata City, Shimane Peninsula.

Description.—The valve is almost flat or slightly concave without the rosette. The areolation is complete; each areole is hexagonal and enlarges the size from center (3–4 in 10 μ) toward margin (5–6 in 10 μ). The radial and secondary spiral rows of areoles are clear.

Distribution.—LOHMAN (1941) mentioned that this species had its heyday in the geologic past, but it is still living in the neritic environment as a "distinct warm water marine species". This species has been found from the following localities: The upper Eocene-lower Oligocene formation of Barbados Island [DE TONI, 1894 and SCHMIDT, 1878 (cited from KANAYA, 1957)], the upper Eocene Oamaru deposit of New Zealand [DE TONI, 1894 (cited from KANAYA, 1957)], Monterey shale of California (HANNA, 1928), the upper Miocene Megeri Formation (REINHOLD, 1937), the middle Calvert Formation ? of Maryland [DE TONI, 1894 (cited from KANAYA, 1957)], North Atlantic deep-sea cores, Pleistocene (LOHMAN, 1941), the Pacific, Atlantic and Indian Oceans equatorial deep-sea cores (KOLBE, 1957), the Miocene formation of Oga Peninsula, Japan (KANAYA, 1959).

Remarks.—All of the specimens are replaced by pyrite. The sculpture on the valve is well preserved, but it can not be observed whether the hyaline area is present or not. Neither marginal processes nor apiculi is present.

Size range of measured specimens.—60–150 μ in diameter.

Coscinodiscus lineatus EHRENBERG

Pl. 15, Figs. 5, 6, 7.

1840. *Coscinodiscus lineatus* EHRENBERG, *K. Akad. Wiss. Berlin, Phys. Abh.*, 1838, p. 129 (inaccessible).
1928. *Coscinodiscus lineatus*, HUSTEDT, *Kieselalgen*, Teil 1, p. 392, fig. 204.
1941. *Coscinodiscus lineatus*, LOHMAN, *U. S. Geol. Surv. Prof. Papers* 196-B, p. 68, pl. 12, fig. 10.
1955. *Coscinodiscus lineatus*, KOKUBO, *Plankton diatoms*, p. 77, fig. 58.
1959. *Coscinodiscus lineatus*, KANAYA, *Sci. Rep. Tohoku Univ., 2nd ser. (Geology)*, vol. 30, pl. 4, fig. 3.
1960. *Coscinodiscus lineatus*, ICHIKAWA, *Sci. Rep. Kanazawa Univ.*, vol. 5, no. 1, pl. 2, figs. 17, 18.

Specimen no.—GK-W 4002-a, b, c (Slide).

Horizon and locality.—Same as GK-W 4001.

Description.—The valve is disc-shaped with almost flat surface. Its margin is slightly thin with radial striae and marginal spinules are present there. The areolation is perfect. The areoles are hexagonal and arranged on the straight lines while those of the many genera are arranged on the curved line, similar in size (6 in 10 μ) over the surface of valves.

Distribution.—According to LOHMAN (1941), this cosmopolitan species has a world-wide distribution as the oceanic and neritic plankton of temperate and subtropical seas, and occurs from the Late Cretaceous to Recent. This species has been known from the following localities: The upper Cretaceous Moreno shale (HANNA, 1934), the middle Miocene Sharktooth Hill deposits (HANNA, 1932 and KANAYA, 1957), the Miocene of the Maria Madre Island, the West Coast of Mexico (HANNA and GRANT, 1926), the Pliocene San Joaquin and Etchegoin Formations at Kettleman Hills, California (LOHMAN, 1938), the upper Miocene and the Pliocene strata in eastern Java (REINHOLD, 1937), the Miocene formation of Japan (OKUNO, 1952), the Miocene formation of Oga Peninsula (KANAYA, 1959), and Noto Peninsula (ICHIKAWA, 1960), the North Atlantic deep-sea cores, Pleistocene and Recent (LOHMAN, 1941), the equatorial cores of the Pacific, Atlantic and Indian Oceans (KOLBE, 1957).

Remarks.—All the specimens at hand are replaced by pyrite and not perfect in preservation, and the detailed observation can not be carried out. The girdle part, however, is generally preserved very well and enables the concrete comparison with other genera and species.

Size range of measured specimens.—50–90 μ in diameter.

Coscinodiscus stellaris ROPER

Pl. 15, Figs. 8, 9, 10, 11, 12.

1858. *Coscinodiscus stellaris* ROPER, *Quart. Jour. Micr. Sci.*, vol. 6, p. 21, pl. 3, fig. 3 (inaccessible).
1905. *Coscinodiscus stellaris*, JÖRGENSEN, *Bergens Mus. Skrifter*, ,vol. 7, p. 196.
1928. *Coscinodiscus stellaris*, HUSTEDT, *Kieselalgen*, Teil 1, p. 396.
1941. *Coscinodiscus stellaris*, LOHMAN, *U. S. Geol. Surv. Prof. Papers* 196-B, pp. 68–69, pl. 13, fig. 2.

Specimen no.—GK-W 4003-a, b, c, d, e (Slide).

Horizon and locality.—Same as GK-W 4001.

Description.—The valve is convex. The sculpture on valves is delicate. The areolation is perfect and the radial and secondary rows appear sharply. Each areole is small and hexagonal. The 6–8 large dots scatter in the central part. The areoles arrange on 10–12 in 10 μ.

Distribution.—This species is said to range from Tertiary to Recent. There is some doubt concerning its specific identification in the previous works. The detailed description regarding localities can not be given.

Remarks.—Although the specimens are replaced by pyrite, the sculpture is well preserved. *Coscinodiscus stellaris* ROPER and *C. stellaris* var. *symbolophora* (GRUN.) JÖRG. closely resemble each other in the general features. The former, however, can be distinguished from the latter by having much finer sculpture. Many specimens have been reported as *Coscinodiscus stellaris* ROPER from the various localities of the world. A considerable number of the mentioned species, however, should be referred to *C. stellaris* var. *symbolophora* (GRUN.) JÖRG. While MANN (1907) stated that there were so many intermediate forms between *Coscinodiscus stellaris* ROPER and *C. stellaris* var. *symbolophora* (GRUN.) JÖRG., therefore the distinction between the two is not practical. So far as the specimens treated in the present paper are concerned, the former and the latter, however, can be distinguished clearly. This fact suggests a strong possibility that *Coscinodiscus stellaris* var. *symbolophora* is revised to *C. stellaris* subsp. *symbolophora*, but the conclusion should be suspended until enough specimens shall be examined. In Japan, ICHIKAWA (1960, p. 186–187, pl. 1, fig. 12a, pl. 2, fig. 12b) reported *Coscinodiscus stellaris* ROPER from the Miocene formation of Noto Peninsula and his identification has been accepted by some Japanese authors. However, the author considers that ICHIKAWA's specimens really belong to *C. stellaris* var. *symbolophora* (GRUN.) JÖRG. This discrepancy must be answered by a close examination of two forms.

Size range of measured specimens.—80–120 μ in diameter.

Subfamily Eupodiscoideae SCHÜTT, 1896
Tribe Eupodisceae SCHÜTT, 1896
Genus *Actinocyclus* EHRENBERG, 1838

Actinocyclus sp. aff. *A. ingens* RATTRAY
Pl. 15, Figs. 13, 14, 15, 16, 17, 18.

1890. *Actinocyclus ingens* RATTRAY, *Quekett Micr. Club. Jour., 2nd ser.* vol. 4, p. 149, pl. 11, fig. 7 (inaccessible).
1959. *Actinocyclus ingens*, KANAYA, *Sci. Rep. Tohoku Univ., 2nd ser. (Geology)*, vol. 30, p. 97, pl. 7, figs. 6–9, pl. 8, figs. 1–4.
1960. *Actinocyclus ingens*, ICHIKAWA, *Sci. Rep. Kanazawa Univ.*, vol. 7, no. 1, p. 185, pl. 1, figs. 11a–d.

Specimen no.—GK-W 4004-a, b, c, d, e, f.

Horizon and locality.—Same as GK-W 4001.

Description.—The valve is disc-shaped, and the surface undulates concentrically and rises gradually from center to about 2/3 of radius and slopes down outwardly. The sculpture is coarse. The areoles are round to subangular and arranged in radial rows. Their size changes from center to the submarginal zone (6 in 10 μ) through the highest zone (4 in 10 μ), where the areoles are largest.

Distribution.—KANAYA (1959) stated that the geologic age was unknown, though most of the localities were probably of the Miocene. This species has been reported from the following localities: Brunn Tegel, Moravia, Santa Monica, Los Angeles, Monterey [RATTRAY, 1890 (cited from KANAYA, 1959)], the Miocene formation of Oga Peninsula, Japan (KANAYA, 1959), and Noto Peninsula (ICHIKAWA, 1960).

Remarks.—All of the specimens are replaced by pyrite. The hyaline area can not be discriminated, therefore, it can not be concluded whether the dots are originally present in it or not.

Size range of measured specimens.—40–75 μ in diameter.

References

BAAS BECKING, L. G. M. (1956): Biological processes in the estuarine environment. VI. The state of the iron in the estuarine mud iron sulfides. *Koninkl. Nederl. Akad. Wetensch. Amsterdam*, **59**, 181–189.

———, KAPLAN, I. R. and MOORE, D. (1960): Limits of the natural environment in terms of *pH* and oxidation-reduction potentials. *Jour. Geol.*, **68**, 243–284.

——— and MOORE, D. (1959): The relation between iron and organic matter in sediments. *Jour. Sedi. Petr.*, **29**, 454–458.

——— and ——— (1961): Biogenic sulfides. *Econ. Geol.*, **56**, 259–272.

BASTIN, E. S. (1926): A hypothesis of bacterial influence in the genesis of certain sulfide ores. *Jour. Geol.*, **34**, 773–792.

——— (1950): Interpretation of ore textures. *Mem. Geol. Soc. Amer.*, **45**, 1–101.

BERGH, S. V. (1928): Fossilifierade svavelbacterier uti alunskiffern på Kinnekelle. *Geol. Fören. Förhandl.*, **50**, 413–418.

BERNER, R. A. (1962): Experimental studies of iron sulfide formation. Paper presented at a symposium on "Biogeochemical Cycle of Sulfur Isotopes", Yale University.

DEANS, T. (1948): The Kupferschiefer and the associated lead—zinc minerallization in the Permian of Silesia, Germany and England. *Rep. Int. Geol. Congr. 18th sess. Gt. Britain*, Pt. 7, 340–352.

DE TONI, G. B. (1891–1894): Sylloge algalum omnium hucusque cognitarum. *Padova*, 2, Bacillatieae, 3 pls., 1556 pp. (inaccessible).

EAGER, R. M. C. (1952): The succession above the soft bed and Bassy mine in the Pennine region. *Liverpool & Manchester Geol. Jour.*, **1**, 23–56.

——— (1952): Growth and variation in the non-marine lamellibranch fauna above the Sand Rock mine of the Lancashire Millstone grit. *Quart. Jour. Geol. Soc. London*, **107**, 339–379.

——— (1953): Additions to the non-marine fauna of the Lower Coal Measure of the North-Midlands Coalfields. *Liverpool & Manchester Geol. Jour.*, **1**, 328–369.

——— and RAYNER, D. (1952): A non-marine shelly limestone and other faunal horizons from the Coal Measure near Wakefield. *Leeds Geol. Assoc. Trans.*, **6**, 188–209.

EHRENBERG, C. G. (1838 (1840)): Über die Bildung der Kreidefelsen und des Kreidemergels durch unsichtbare Organismen. *K. Akad. Wiss. Berlin, Phys. Abh.*, 59–147, pls. 1–4 (inaccessible).

FABRICIUS, F. (1961): Die Strukturen des "Rogenpyrits" (Kössener Schichten, Rät) als Beitrag zum Problem der "Vererzten Bakterien". *Geol. Rundschau*, **51**, 647–657.

GALLIHER, E. W. (1933): The sulfur cycle in sediments. *Jour. Sedi. Petr.*, **3**, 51–63.

GARRELS, R. M. and CHRIST, C. L. (1965): *Solutions, minerals, and equilibria.* Harper & Row, and John Weatherhill, Inc. Tokyo.

GRUNOV, A. (1884): Die Diatomeen von Franz Josepfs-Land. *K. Akad. Wien, Denkschr.*, 48, 53–112, pls. 1–5.

HANNA, G. D. (1928): The Monterey shale of California at its locality with a summary of its fauna and flora. *Amer. Assoc. Petr. Geol. Bull.*, **12**, (10), 969–983, pls. 7–10.

——— (1932): The diatoms of Sharktooth Hill, Kern Country, California. *California Acad. Sci. Proc. 4th ser.*, **20**, (6), 161–263, pls. 2–18.

——— (1934): Additional notes on diatoms from the Cretaceous of California. *Jour. Paleont.*, 8, (3), 352–355, 1 pl.

——— and GRANT, W. H. (1926): Miocene marine diatoms from Maria Madre Island, Mexico (Expedition to the Revellagigedo Islands, Mexico in 1925 II). *California Acad. Sci. Proc. 4th ser.*, 15, (2), 115–193, pls. 11–21, 1 text-fig.

HIGASHIMOTO, S. (1958): Colloidal texture of the ore minerals of the Gojo mine, Nara Pref. *Jour. Geol. Japan. Assoc. Min. Petr. Econ. Geol.*, 42, (3), 136–144.

HUSTEDT, F. (1927–1937): Die Kieselalgen Deutschland, Oesterreichs und der Schweiz mit Berücksichtgung der übrigen Länder Europas sowie der angrenzenden Meeresgebiete. *in* Dr. RABENHORST's Kryptogamen-Flora von Deutschland, Oesterreichs und der Schweiz, 7, Leipzig: Pt. 1, Secs. 1–5, 920 pp., 542 figs., 1927–1930; Pt. 2, Secs. 1–5, 736 pp., 1105 figs., 1931–1937.

ICHIKAWA, W. (1960): On the fossil marine diatoms in the Wakura beds, Noto peninsula, Japan. *Sci. Rep. Kanazawa Univ.*, 5, (1), 175–214, pls. 1–9.

ISSACHENKO, B. L. (1929): Zur Frage der biogenischen Bildung des Pyrits. *Internat. Rev. Hydrobiol. Hydrogr.*, 22, 99–101.

JÖRGENSEN, E. (1905): The protist plankton and the diatoms in bottom samples, hydrographical and biological investigations in Norwegian fjords. *Bergens Mus. Skrifter*, 7.

KANAYA, T. (1957): Eocene diatom assemblages from the Kellog and "Sidney" shales, Mt. Diablo area, California. *Sci. Rep. Tohoku Univ. Sendai, Japan, 2d ser. (Geology)*, 28, 27–124, pls. 3–8.

——— (1959): Miocene diatom assemblage from the Onnagawa Formation and their distribution in the correlative formation in Northeast Japan. *ibid.*, **30**, 1–130, pls. 1–11.

KANNO, I. and others (1960): Clay minerals of recent shallow sea (near-shore) sediments from Ariake bay in Kyushu. *in* Proceedings of the Fourth Annual Meeting on Clays and Clay minerals. Clay Research Group of Japan. Nagoya Inst. Technol. 4, 227–238.

KOKUBO, S. (1955): *Plankton diatoms.* Nippon Gakujutsu Shinkokai, Tokyo.

KOLBE, R. W. (1954): Diatoms from equatorial Pacific cores. *Rep. Swedish Deep-Sea Exped.*, **6**, (1), 48 pp., 4 pls.

——— (1956): Diatoms from equatorial Atlantic cores. *ibid.*, 7, (3), 151–184, 6 text-figs,. 2 tables, 2 pls.

——— (1957): Diatoms from equatorial Indian ocean cores. *ibid.*, **9**, (1), 50 pp., 6 text-figs., 5 tables.

LOHMAN, K. E. (1938): Pliocene diatoms from the Kettleman Hills, California. *U. S. Geol. Surv. Prof. Papers* 189-C, 81–94, pls. 20–23.

——— (1941): Pt. 3 Diatomaceae *in* Geology and biology of North Atlantic deep-sea cores, between Newfoundland and Ireland. *ibid.*, 196-B, V-XIV-55–86, pls. 1–2 and 11–17.

LOVE, L. G. (1957): Micro-organism and the presence of syngenetic pyrite. *Quart. Jour. Geol. Soc. London*, **113**, 429–440.

——— (1962): Further studies on micro-organisms and the presence of syngenetic pyrite. *Paleontology*, **5**, 444–459.

——— (1962): Biogenic primary sulphide of the Permian Kupferschiefer and Marl slate. *Econ. Geol.*, **57**, 350–366.

——— and ZIMMERMAN, D. O. (1961): Bedded pyrite and micro-organisms from the Mount Isa shale. *ibid.*, **56**, 873–896.

——— and MURREY, J. W. (1962): Biogenic pyrite in recent sediments of Christchurch Harbour, England. *Amer. Jour. Sci.*, **261**, (5), 433–448.

MANN, A. (1907): Diatoms of the *Albatross* voyages. *Contr. U. S. Nat. Herbarium*, **10**, pt. 5, 220–419, pls. 44–54.

NAKAYANAGI, Y. (1964): Iron sulphide mineral of Miike coal field. *Jour. Fuel Soc. Japan*, **43**, (45), 808–819.

NAUMANN, E. (1919): Om Jarnets Forekomstatt I Limniska Avlagringer. *Sver. Geol. Undersökn.* C, **289**, 1–47.

NEUHAUS, A. (1940): Über die Erzführung des Kupfermergels der Haaseler und der Gröditzer Mulde in Schlesien. *Z. Angew. Mineral.*, **2**, 304–343.

OKUNO, H. (1952): Atlas of fossil diatoms from Japanese diatomite deposits. *Botanical Inst. Fac. Textile, Kyoto Univ. Indust. Arts, Textile Fibers*, 49 pp., 29 pls.

RAMDOHL, P. (1950): *Die Erzmineralien ihre Verwachsungen.* Akad. Verlag, Berlin.

——— (1953): Mineralbestand, Strukturen und Genesis der Rammersberg-Lagerstatte. *Geol. Jahrb.*, **67**, 367–495.

RATTRAY, J. (1890): A revision of the Genus *Actinocyclus* Ehr. *Quekett Micr. Club, Jour. 2d ser.*, **4**, 137–212 (inaccessible).

REINHOLD, T. (1937): Fossil diatoms of the Neogene of Java and their zonal distribution. *Nederl. Koloniën Geol. Mijn. Gen. Verh. Geol. ser.*, **12**, 43–132, 21 pls.

ROPER, F. C. (1858): Notes on some new species and varieties of British marine Diatomaceae. *Quart. Jour. Micr. Sci.*, **6**, 17–25, 3 pls. (inaccessible).

RUST, G. W. (1935): Colloidal primary copper ores at Cornwall mines, southeastern Missouri. *Jour. Geol.*, **43**, 398–426.

SAWJALOW, W. (1922): Über die Schwefelwasserstoffgärung im Schwarzen Heilschlamme. *Centralbl. Z. Bakt. Parasitenkunde* (for 1913–1914), **39**, (2), 440–447.

SCHMIDT, A. (1885–1937): *Atlas der Diatomaceenkunde, Zweite revidirte Auflage.* Leipzig. Last plate issued to date, pl. 416, *in* August, 1937, *by* F. HUSTEDT. (inaccessible).

SCHNEIDERHÖHN, H. (1923): Chalkographische Untersuchung des Mansfelder Kupferschiefers. *N. Jahrb. Z. Min.*, **47**, 1–38.

——— (1926): Erzführung und Fefüge des Mansfelder Kupferschiefers. *Metall und Erz*, **23**, 143–146.

SCHOUTEN, C. (1937): *Metasomatische Probleme.* Amsterdam.

——— (1946a): Some notes on micropseudomorphism. *Econ. Geol.* **41**, 348–382.

——— (1946b): The role of sulfur bacteria in the formation of the so-called sedimentary copper ores and pyrite ore bodies. *ibid.*, **41**, 517–538.

——— (1946c): Synthetic replacements as an aid to ore-genetic studies. *ibid.*, **41**, 659–667.

SCHÜTT, F. (1896): Bacillariales (Diatomeae) *in* Engler und Prantl. Die Naturlichen Pflanzen familien. Ist ed. I Teil, 1 abt. b, Bacillariales, 31–150 (inaccessible).

THIESSEN, R. (1920): Occurrence and origin of finely dissemunate sulfur compounds in coal. *Trans. Amer. Inst. Min. Eng.*, **63**, 913–931.

VALLENTYNE, J. R. (1960): On fish remains in lake sediments. *Amer. Jour. Sci.*, 258-A, 344–349.

——— (1961): On the rate of formation of black spheres in recent sediments. *Verhandl. Internat. Verein. Limnol.*, **14**, 291–295.

——— (1962): Concerning LOVE, microfossills, and pyrite spherules. *New York Acad. Sci. Trans. ser. 2*, **25**, 177–189.
——— (1963): Isolation of pyrite spherules from recent sediments. *Limnol. Oceanog.*, 8, 16–30.
——— and SWABEY, Y. S. (1955): A reinvestigation of the history of Lower Linsley Pond, Conneticut. *Amer. Jour. Sci.*, **253**, 313–340.

George KATO

Biogenic Pyrite from a Miocene Formation of
Shimane Peninsula, Southwest Japan

Plates 15 ～ 17

Plate 15

Explanation of Plate 15

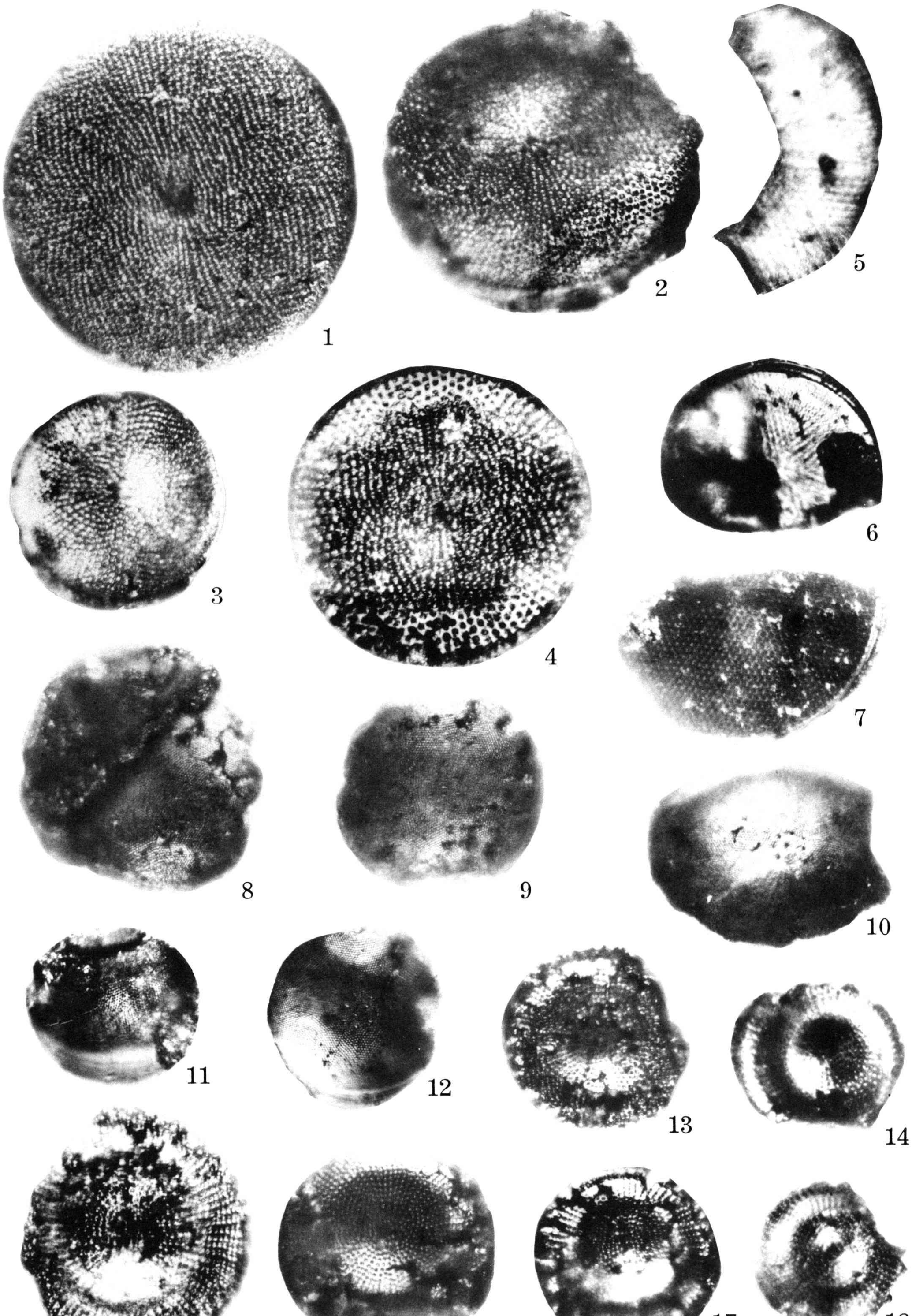
Figs. 1–4. *Coscinodiscus* sp. cf. *C. argus* EHRENBERG ....Page 324
1, GK-W 4001-a (Slide); 2, GK-W 4001-b (Slide); 3, GK-W 4001-c (Slide); 4, GK-W 4001-d (Slide).

Figs. 5–7. *Conscinodiscus lineatus* EHRENBERG ....Page 325
5, GK-W 4002-a (Slide); 6, GK-W 4002-b (Slide); 7, GK-W 4002-c (Slide).

Figs. 8–12. *Coscinodiscus stellaris* ROPER ....Page 325
8, GK-W 4003-a (Slide); 9, GK-W 4003-b (Slide); 10, GK-W 4003-c (Slide); 11, GK-W 4003-d (Slide); 12, GK-W 4003-e (Slide).

Figs. 13–18. *Actinocyclus* sp. aff. *A. ingens* (GRUN.) JÖRG. ....Page 326
13, GK-W 4004-a (Slide); 14, GK-W 4004-b (Slide); 15, GK-W 4004-c (Slide); 16, GK-W 4004-d (Slide); 17, GK-W 4004-e (Slide); 18, GK-W 4004-f (Slide).

All figures are in the same magnification ($\times 400$), and all the specimens came from one and the same locality (a quarry at Aishiro-machi, Hirata-city).



G. KATO: Biogenic Pyrite

Plate 16

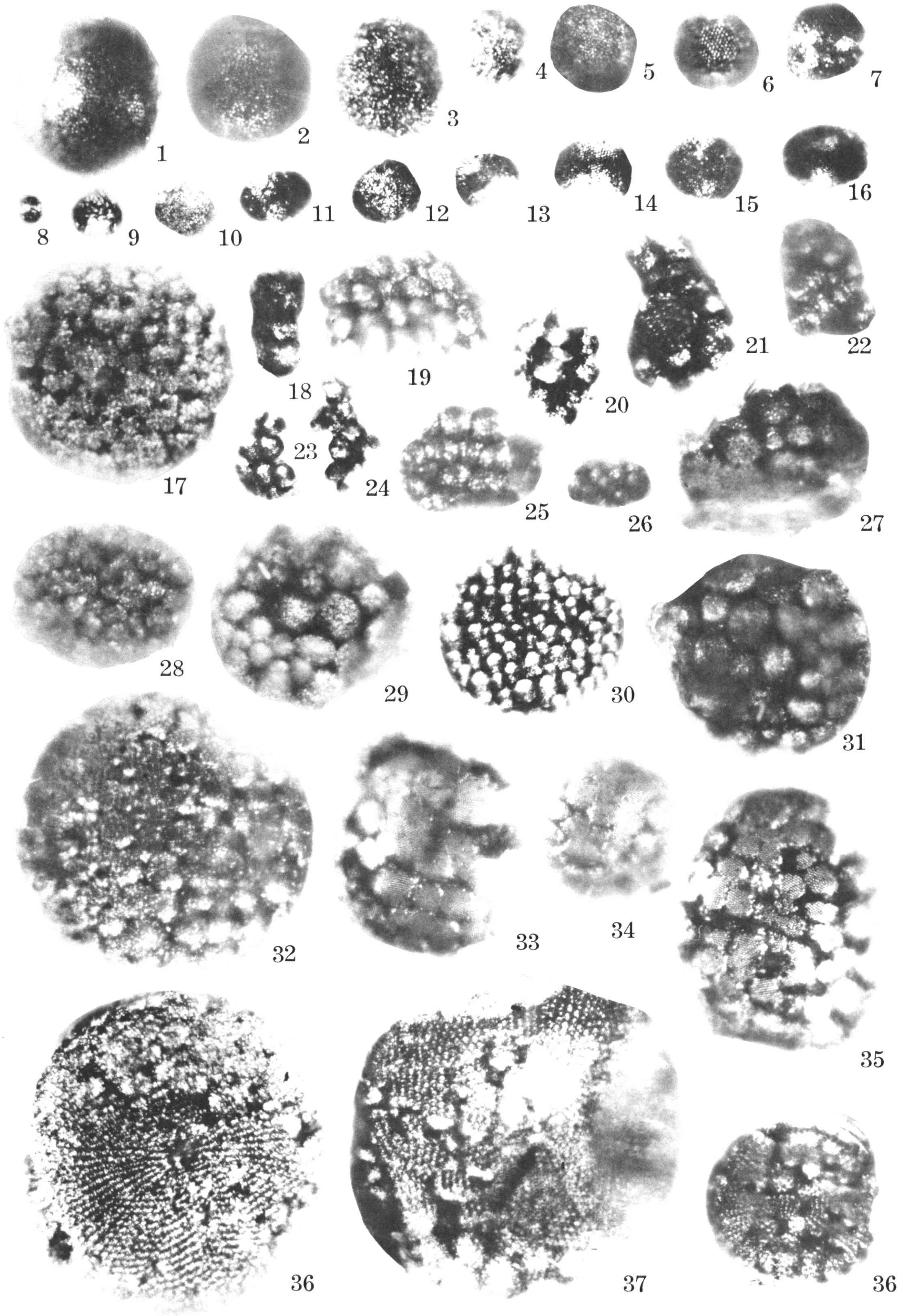
Explanation of Plate 16

Figs. 1–16. Single framboidal pyrite .... Page 318
1–7 and 9–16, ×1000; 8, ×400.

Figs. 18–27. Aggregated framboidal pyrite .... Page 318
21, ×1000; 18–20, 22, 25 and 27, ×400; 23, 24 and 26, ×250.

Figs. 17, 28–38. Framboidal pyrite replenished in diatom .... Page 318
17, 28, 29 and 31–38, ×400; 30, ×250.

All the specimens came from one and the same locality, a quarry at Aishiro-machi, Hirata-city.



G. KATO: Biogenic Pyrite

Plate 17

Explanation of Plate 17

Figss. 1–9, 16 and 17. Microcrystal ....Page 319
1 and 7–9, ×400, Single crystal: 2–6, ×400; 16 and 17, ×250, Aggregated crystal.

Figs. 10–15. Framboidal pyrite replenished in micro-organism ....Page 318
10–15, ×400.

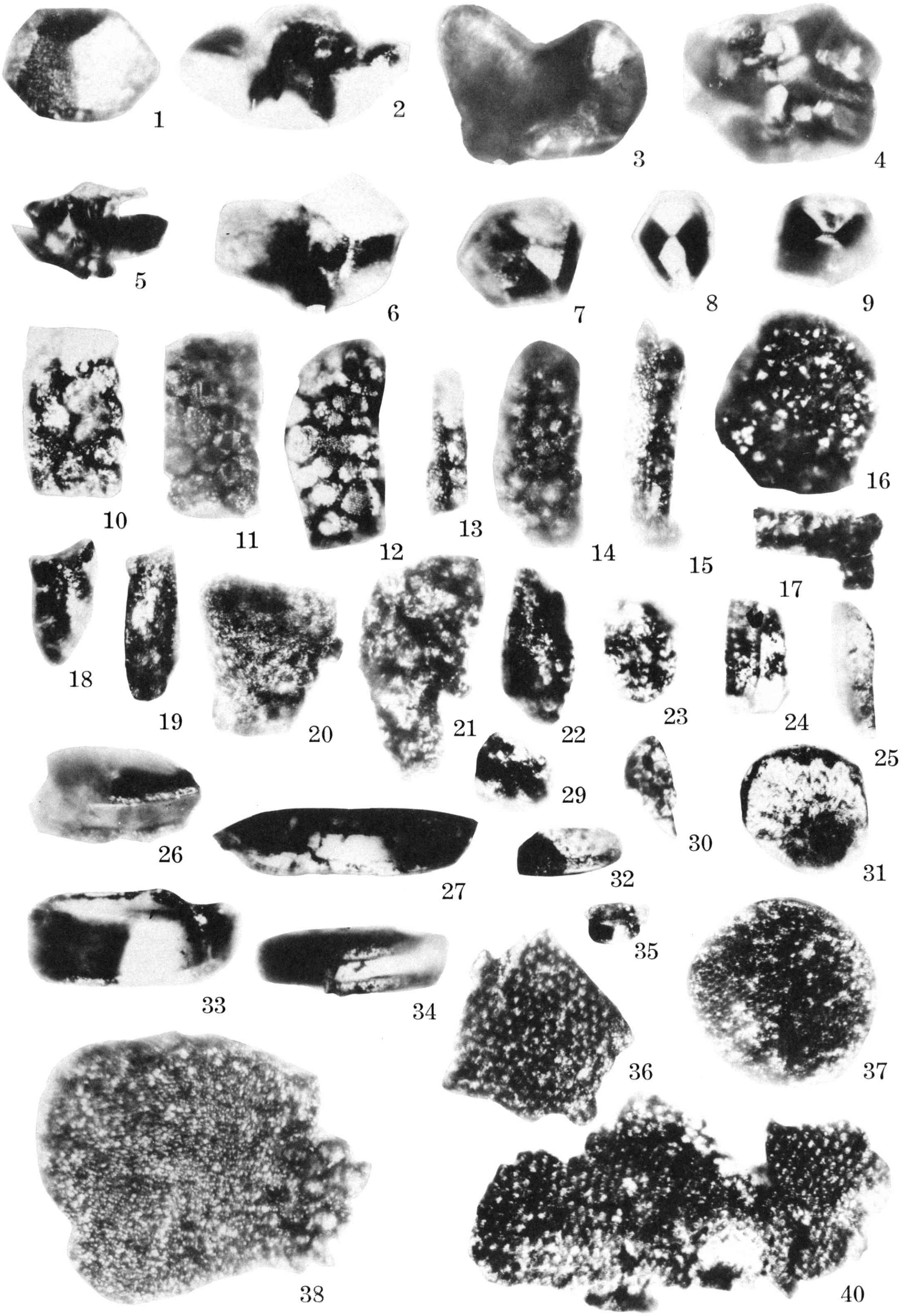
Figs. 18–25, 29 and 30. Irregular type pyrite ....Page 319
18–25, 29 and 30, ×400.

Figs. 26, 27, 32–35. Side view of diatom replaced by pyrite ....Page 318
26, 27, 33 and 34, ×400; 32 and 35, ×250.

Figs. 36, 37 and 40. Smaller framboidal pyrite replenished in daitom. Page 318
36 and 40, ×400; 37, ×250.

Fig. 38. Framboidal pyrite and irregular pyrite replenished in diatom. Page 318
38, ×400.

All the specimens came from one and the same locality, a quarry at Aishiro-machi, Hirata-city.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