Biogenic Pyrite from the Cretaceous Formations of Sakhalin and Hokkaido

Kato, George
Faculty of Science, Kyushu University

https://doi.org/10.5109/1543909

出版情報：九州大學理學部紀要 : Series D, Geology. 20 (1), pp.73-84, 1970-01-25. Faculty of Science, Kyushu University
バージョン：
権利関係：

Mem. Fac. Sci., Kyushu Univ., Ser. D, Geology, Vol. XX, No. 1,
pp. 73-84, text-fig. 1, pls. 10-17, Jan. 25, 1970

Biogenic Pyrite from the Cretaceous Formations of Sakhalin and Hokkaido

By

George KATO

Abstract

Innumerous tiny pyrite granules of various shape were found in the calcareous concretions of the Upper Cretaceous formations of Sakhalin and Hokkaido. The framboidal pyrite mostly replenishing in the tests of diatoms, foraminifers and radiolarians occurs in the majority of these granules. A reconsideration on the origin of the framboidal pyrite is given in the present paper, although it was discussed in some details in the previous paper (KATO, 1967).

Introduction

The present author described innumerous minute pyrite granules of various shape from a Miocene formation of Southwest Japan, discussed their origin, and pointed out that these pyrites were found also in the sediments of all the geologic age (KATO, 1967). In this paper, the author will give further detailed discussion on the origin of the biogenic pyrite and the mechanism of replacement of some micro-organisms on the basis of the observation of the abundant micro-pyrite granules which mostly consist of the framboidal pyrite in the calcareous concretions from the Upper Cretaceous formation of Sakhalin and Hokkaido.

Promising data to suppose the origin of sedimentary pyrite are got through the examination of the calcareous concretions in the Cretaceous sediments. Unfractured pyrites and the tests of micro-organisms are obtained from those concretions, because the concretions are soluble by HCl without extreme crushing. The author discriminated two types of pyrite granules. One shows the shape of diatom, but its surface ornamentation illustrates the aggregation of tiny pyrite crystals. The other also shows the same shape as the preceding one, but the surface ornamentation consists both of crystal and framboidal pyrites. These examples are considered to prove the same origin of both the crystal and framboidal pyrites, and the author will revise a part of idea about the genesis of sedimentary pyrite stated in the previous paper. Further he will introduce an idea about the mechanism of replenishment into some micro-organisms by pyrite, because he could detect the tests of micro-organisms which were replenished by framboidal pyrite.

This report, the author hopes, has some bearing as a basic data on the

---

Manuscript received July 24, 1969.

genesis of biogenic pyrite. The result owes much to many persons who kindly supported the author with suggestions, advice and criticism on the course of the study. The author wishes to express here his cordial thanks to these persons.

Professor Tatsuro MATSUMOTO and Dr. Hakuyu OKADA of Kyushu University gave him access to the necessary material and literature. Professor MATSUMOTO guided him also with useful suggestions and advice on the problems. Professor Ryuzo TORIYAMA and Dr. Tsugio SHUTO of the same university gave him attentive suggestions and advice especially on the biological side of the problems in the course of the study, and also gave careful criticism on the manuscript. Dr. Fumitoshi HIROWATARI and Mr. Nobutaka SHIMADA helped him on the observation and photographing under the ore-microscope, and gave necessary discussion on the mineralo-chemistry. Drs. Juichi YANAGIDA and Itaru HAYAMI made necessary criticism on the typescript.

Material

The samples examined in this study were offered by T. MATSUMOTO and H. OKADA of Kyushu University. MATSUMOTO provided with part of the calcareous concretion of the Cretaceous age from Sakhalin. The concretion (N401e)[*] consists of the matrix of clean micritic calcite and of the grains of quartz, feldspar and a small amount of heavy minerals in fine sand size, and contains a large ammonite, *Gaudryceras*. Most of the heavy mineral grains, of course, are pyrite granules. The locality: the third tributary of Naibuchi River, Sakhalin. The geologic horizon: Mh6β zone, the upper Yezo Group (Senonian), the Upper Cretaceous.

The material collected by OKADA from Hokkaido is quite similar to that from Sakhalin, though the former differs from the latter in containing the scattered chlorite and sericite in the matrix of the concretion. The concretion contains some ammonites, *Neophylloceras subramosum* (SPATH) and *Subptychoceras jimboi* MATSUMOTO (MS). The locality: Miginosawa, the upper stream of Haboro River, Hokkaido. According to MATSUMOTO (personal communication), its geologic horizon is almost the same as the preceding one.

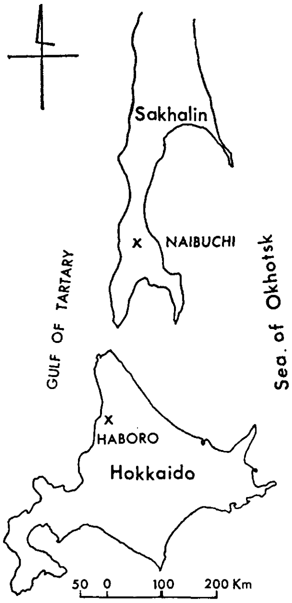


Fig. 1. Index map showing the localities of the Cretaceous concretions.

---

[*] See MATSUMOTO (1942).

Separation of pyrite granules

To separate pyrite granules, the author adopted the procedure as follows: the calcareous concretion is crushed by jaw-crusher until the grains pass through 16 mesh sieve; the grains are washed off the mud particles by water, and gently boiled in HCl (1:1) on sandbath for about half an hour; then the heavy minerals are concentrated by THOULET's solution, and the non-pyritized micro-fossils, diatoms and radiolarians, are found in the residues; the separated heavy fraction is cleaned by ultrasonic cleaner; a liquid of iodide methylene is used as medium of centrifuging in order to separate pyrite granules from other heavy minerals; the tests of micro-organisms, radiolarians, which are packed perfectly or imperfectly inside by some framboidal pyrites are found in the residues; further, for the X-ray and ore-microscopic examination, a part of the heavy minerals is attacked by hydrofluoric acid. After that procedure, pyrite granules clearly show the pattern of pyrite lattice in the diffraction of X-ray; these pyrite granules are enclosed in polyester resin (Rigorac 2004W) and polished for the ore-microscopic examination.

Shapes of the pyrite granules

The pyrite granules comprise the following three groups:

1. Framboidal pyrite
    a. single framboidal pyrite
    b. aggregated framboidal pyrite
    c. framboidal pyrite replenishing into the tests of some micro-organisms
2. Micro-crystal pyrite
    a. cubic crystal
    b. octahedral crystal
    c. pyritohedral crystal
3. Irregular shape pyrite.

Group 1 is the framboidal pyrite which is subdivided into three, a, b and c. As many workers have referred, the term, framboidal pyrite, is due to RUST (1935). Single framboidal pyrite (a) is rounded or ellipsoidal sphere of 2 to 100 μ in diameter, scattered in the matrix of concretion or inside of the tests of micro-organisms. Aggregated framboidal pyrite (b) is the aggregation of single framboidal pyrite and shows irregular form. Two varieties of aggregation are discriminated concerning the size of single framboidal pyrite, one is composed of single framboidal pyirte of similar size, and the other is of various size. They are also scattered in the matrix or inside of the tests of micro-organisms. Most of the framboidal pyrites (group 1) belong to c (framboidal pyrite replenishing into the tests of some micro-organisms). They replenish clearly in the whole inside of the tests of micro-organisms still showing the framboidal texture. This phenomenon seems to illustrate the process of formation of framboidal pyrite (1)*. The internal structure of framboidal pyrite, as described by LOVE and AMSTUTZ (1966), is represented by the assemblage of innumerous tiny pyrite crystals of regular or irregular arrangement. The difference in the crystal arrangement seems to reflect the divergence of the process of crystallization to pyrite from FeS_2-gel (2)*.

Group 2 is a single crystal or aggregation of crystals of $2\mu \sim 2$ mm in diameter. They illustrate three habits, cubic, octahedron and pyritohedron, but two kinds of habit are never co-existing in a single aggregation. A part of them replenishes into the tests of some micro-organisms. The problems of the difference in habits and the degree of aggregation are also discussed in the later article (3)*.

Group 3 comprises all the pyrite specimens which are excluded from the two groups mentioned above. Their form is irregular, and the size also spreads in wide range. However, there is another example which replenishes into the tests of some micro-organisms.

The pyrite bearing specimens examined contain not only a single group of pyrite, but also the mixture of two. For instance, Pl. 11, Figs. 12, 14, 15, 17 and 18 (framboidal and crystal pyrite), Pl. 12, Figs. 6 and 8 (framboidal and irregular pyrite) and Pl. 10, Figs. 5, 6 and 10 (crystal and irregular pyrite). The above mentioned facts suggest that all kinds of pyrite are the same in origin, and the morphological divergence is due to the difference of the micro-environments where FeS_2-gel is introduced (4)*. The example of mixture of three groups has not been found yet. The difference of the factors and the duration of the micro-environments where FeS_2-gel was originated should affect the formation of each form and the combination of the groups.

Further discussion on the genesis of pyrite

FeS_2-gel. LOVE and AMSTUTZ (1966) discriminated crystal form pyrite and framboidal one in a single specimen from the Devonian Chattanooga Shale and Rammelsberg Banderz. However, they didn't come to a solid conclusion on the origin of morphological difference between the two forms. The present author found the example, in which diatom was replaced by pyrite, and the surface ornamentation of the diatom reveals clearly the intermixture of crystal and framboidal pyrites. The fact suggests that the gel of pyrite of both forms was formed at the same time. The idea on the process of formation of FeS_2-gel was offered in the previous work, although it was a preliminary conclusion. It is summarized as follows: the sulfur bacteria and sulfate reducing bacteria symbiotic in sediment make up a colony; accordingly, the sulfur cycle is realized in the colony; ionized sulfur (S^{--}) appears in the cycle; S^{--} reacts with ionized iron (Fe^{++}); as a result of this reaction, FeS_2-gel is formed in the sediment. Fe^{+++} doesn't participate in the formation of pyrite, because it is inactive in

---

* (1), (2), (3) and (4) are discussed in details in the later article.

sediment. As pointed out in the previous paper, the reaction of Fe^{++} and H_2S is impossible under the normal marine condition. These problems shall be omitted from the present theme to keep off duplication. Concerning the co-operation of two kinds of bacteria, Butlin and Postgate (1954) concluded that the sulfur bacteria and sulfate reducing bacteria accumulated sulfur from H_2S through their co-operation in the lake sediment of Cyrenaica, North Africa. Rhodes W. Fairbride (Columbia University) succeeded in synthesizing jarosite from pyrite and illite with H_2SO_4 under the inorganic condition, and stated that "the yellow powder is always jarosite, not S" (personal communication). The present author thinks that it is rather difficult to break the S-O bond under the inorganic condition, but some microbes may have the ability of breaking the bond. Also, the S-H bond is not broken inorganically by the same reason as in case of the S-O bond. Azuma Iijima (the University of Tokyo) pointed out the possibility of following reaction in the sediment (personal communication):

$$FeS - \tfrac{1}{2}Fe^{++} \rightarrow Fe_{\frac{1}{2}}S = FeS_2$$

The present author thinks that, if the reaction mentioned above is realized in the sediment, the ionized iron which was free from mono-iron sulfide may react as oxidized iron, and such sedimentary environment should not allow the reaction of iron and sulfur and even the existence of iron sulfide, especially pyrite. The author still admits the conclusion mentioned in the previous paper about the genesis of FeS_2-gel. Molisch (1911) observed the diatom to concentrate iron in the internal part of the test through metabolism. That is to say, it is likely that a fair volume of ionized iron (Fe^{++}) is contained in the inside space of diatom. His observation supports the conclusion of the present author. It is, on one hand, improbable to supply sufficient Fe in such a way as quoted above to afford all the pyrite replenishing in the whole cell of diatom. It is, however, on the other hand, quite probable to supply the nucleus of crystal. In order that the crystal grows larger, the favorable condition for crystal growth must last longer and the gel must be sufficiently supplied. If FeS_2-gel in the sediment is supersaturated, the condition of the latter is out of question. When the term is unfilled, the cohesive strength between FeS_2-gel comes into question. The critical volume of the nucleus is a necessary condition for crystal growth, but is not sufficient. This time, the author will give some discussions about the problem of the origin of the different forms of pyrite within the micro-organisms such as diatoms, foraminifers and radiolarians, and about the problem why the FeS_2-gel is crystallized as crystal or framboidal form. The information about pyrite from the profile column of recent sediment should serve to solve this problem.

Sedimentary condition. The anaerobic zone in the bottom sediment of marine environment is rather thick in many cases. The distance of the horizon of *Eh* $-50\sim-150$ mV from the bottom surface is rather limited in a narrow zone, where is a favorable circumstance for the colony of sulfur bacteria and sulfate reducing bacteria. FeS_2-gel is formed there, and then infiltrates into the tests of micro-organisms such as diatoms, foraminifers and radiolarians. If the same anaerobic environment continues till the beginning of diagenetic hardening, FeS_2-gel is crystallized as a single form of the three groups. However, the anaerobic zone rises upward in keeping pace with the deposition of the overlying sediment, while FeS_2-gel stays where it is originally formed. Consequently *pH* and *Eh* conditions around FeS_2-gel at the original site are modified in correspondence with its relative position. That is to say, the difference of *pH* and *Eh* conditions at the time of crystallization of FeS_2-gel should be decided by the relative depth of the gel.

Sulfur isotopes. In the field of recent geochemistry, many excellent results of the study of the sulfur isotopes have been offered. Among them, it is worth noticing that pyrites of magmatic and biogenic origins are discriminated on the basis of the ratio of S^{32}/S^{34}. According to NAKAI and JENSEN (1960, 1964), the ratio of S^{32}/S^{34} of magmatic pyrite, on one hand, is in a narrow field and never scattered. On the other hand, biogenic pyrite shows rather dispersed distribution of the ratio and has much more S^{32} than magmatic one in many cases. They interpreted these phenomena as the bacteria prefer S^{32} which is lighter than S^{34} in the formation of FeS_2-gel. If their explanation proves true, it may throw light on the discrimination of biogenic pyrite. However, there are some different data from NAKAI and JENSEN's among the many publications of sulfur isotopes. For instance, RANKAMA (1963) concluded that the sulfides with S^{32}/S^{34} ratio higher than 22.3 were biogenic origin. That is to say, RANKAMA's biogenic field is wider than NAKAI and JENSEN's. Under such circumstance as mentioned above, it is difficult to discriminate the pyrites of magmatic and biogenic origins on the basis of the ratio of S^{32}/S^{34}. The problem of fractionation of sulfur isotopes in pyrite must be answered after the close examination of the occurrences of pyrite in sedimentary rocks, whether they are suffered by some hydrothermal igneous activities or not, and of the pyrite in recent sediment, which may be either reworked from ancient rocks or not.

NAKAI and JENSEN (1964) stated their success of pyrite formation by using the mixed culture of bacteria. Examining the isotope ratio of this pyrite, they proposed the idea of fractionation by bacteria. However, they didn't give any comments on the process of chemical reaction of FeS_2-gel. It seems that their "mixed culture of bacteria" corresponds to the author's "colony of bacteria". HALLBERG (1965) reported the success of formation of pyrite* in the bacterial colony. Unfortunately, there are few specified information of the chemical process concerning the formation of pyrite in sediment in which the bacteria act as a catalyzer during the diagenesis. It is difficult to explain the chemical process that the bacteria form pyrite directly, and that FeS_2-gel is formed by bacteria in the presence of H_2S. After all, as mentioned in the previous paper, it is the most reasonable supposition that ionized sulfur (S^{--}) is formed in the colony of bacteria and reacts with ionized iron (Fe^{++}) directly to form FeS_2-gel. If the fractionation of sulfur isotopes occurs actually in pyrite, it should originate at the stage of ionization of S^{--} in the colony of bacteria in sulfur cycle. However, as pointed out by NAKAI and JENSEN (1964), the ratio of biogenic pyrite

---

* He (HALLBERG) wrote in his personal communication that "It is found not to be pyrite".

doesn't always higher than the magmatic one. It is also examplified in VALLENTYNE's data (1963). If biogenic pyrite always shows the definite concentration of lighter isotope of sulfur, VALLENTYNE's framboidal pyrite must be of magmatic origin. In fact, however, the fields of S^{32}/S^{34} of magmatic and biogenic origins overlap partially. It is, in consequence, difficult to discriminate whether the framboidal pyrite is biogenic or magmatic origin only from the ratio of S^{32}/S^{34}. Therefore, the critical importance should be put on the detailed examination of the occurrence of framboidal pyrite.

Micro-environment. The present author pointed out in the previous work that the replenishment of the framboidal pyrite should begin from the inside of diatom, although this idea was not verified by the concrete evidence. In the present study it is proved by the material from Sakhalin and Hokkaido. The framboidal pyrite clearly replenishes into some micro-organism's tests in various degree. Some of the framboidal pyrites exist in the sedimentary matrix don't contact directly with the tests of micro-organisms. The author supposes that they were scattered in the sediment because of break-down of the tests by some reasons. And the break-down might be made before the complete replenishment of the framboidal pyrite into the tests, because the framboidal pyrite occur in a single or aggregated state, but never reveals the same particular forms as micro-organisms. If the tests might have been broken after the complete replenishment of the framboidal pyrite, the framboidal pyrite should reveal a special form such as diatoms, foraminifers or radiolarians. Therefore, the author further supposes that some space enclosed in any test should be required to form the framboidal pyrite. In the case of the "geopetal pyrite" of HONJO *et al.* (1965), it seems that some cavities in limestone play the role of space and screen. "Space enclosed with any screen" is considered to be the necessary condition for the formation of the framboidal pyrite. That is to say, a special micro-environment isolated and differentiated from the surroundings is needed for the formation of the framboidal pyrite. The tests of micro-organisms afford such micro-environment. FeS_2-gel is crystallized inside and outside the micro-environment mentioned above in respective shape because of the difference in the physico-chemical conditions during the diagenesis. Whether or not the tests of micro-organisms are preserved in sediment after the diagenesis depends well on the difference of the chemical and/or physical conditions and the original thickness of the test. The material from Sakhalin and Hokkaido illustrates the latter case. No foraminiferal tests are found in them, because the calcareous test might have been dissolved away during preparatory treatment. In fact, only the thick tests of foraminifers are rather well preserved in the thin section of concretion, but the thin test is never found. The interior part of the tests of micro-organisms is considered not only the ideal micro-environment for the formation of the framboidal pyrite as mentioned above, but also the favorable niche to the colony of sulfur bacteria and sulfate reducing bacteria. Furthermore, it may permit the infiltration of only Fe^{++} and keep off FeS, even if it existed in the surroundings, because the tests act the role of the screen.

Internal structure of framboidal pyrite. The observation of the polished section clarifies that most of the framboidal pyrites from Sakhalin and Hokkaido consist of the aggregation of innumerous tiny cubic pyrite crystals. However, a part of the framboidal pyrites are made of marcasite showing radiated structure. The marcasite must have been changed from pyrite, because the framboid includes a few minute cubic pyrites in the core. Many presumptions are instituted about the difference of the habit between the aggregated framboidal pyrites and the individual larger crystal. However, the environments, in which FeS_2-gel is formed and crystallized as pyrite don't always coincide with each other. The conditions of respective environment must be thought separately.

The interior structure of the framboidal pyrite is the aggregation of minute pyrite crystals. The crystal habit of those minute pyrites includes three forms same as magmatic pyrite, namely cubic, octahedron and pyritohedron. The mode of aggregation has correspondence to the crystal habit. For instance, the cubic one shows a scattered mode, Pl. 15, Figs. 2, 3. Although it is difficult to distinguish the three habits under ore-microscope, the crystals of respective habit seem to be arranged in different mode. LOVE and AMSTUTZ (1966, pl. 2, figs. 1, 2) reported that the pyritohedral crystals in the framboidal pyrite showed regular arrangement, but it is not denied that there are some space between crystals on the direction of c-axis. If FeS_2-gel is crystallized as the cubic form, the crystals attain larger size, take regular arrangement and don't become framboidal. It seems that undetermined matter other than pyrite molecule exists in the framboidal pyrite around the minute pyrite crystals. The difference of crystal habit of the framboidal pyrite is considered to be decided by the environmental factors where FeS_2-gel is formed and by the molecule of the undetermined matter in the gel.

Habit of micro-crystals in framboidal pyrite. At least, it is evident that two kinds of habit never co-exist in the framboidal pyrite. Two probable causes may be considered for this phenomenon. One is that the time needed for the transformation of FeS_2-gel to the framboidal pyrite may not be so long, because an environment of particular character in sediment may not last unchanged. Generally, the habit of crystal is decided by the character and the duration of the environment. The other is that the micro-environment such as in the tests of micro-organisms is able to maintain for long period a particular condition having the least connection with the surroundings. Judging from the mode of the framboidal pyrites in the sedimentary rocks, the latter case should be evaluated, because the time factor during crystallization in low temperature can not be ignored.

The environment at the time of crystallization of FeS_2-gel may be different from that at the time of formation of the gel. FeS_2-gel is formed only at a limited position in the profile of the sedimentary column. Generally, the sediment at sea bottom is composed of sand and mud particles transported altogether to form a single bed. The upper part of the bed is unable to become anaerobic because of continuous oxygen supply from the sea water. Accordingly, only the middle and lower parts may be anaerobic to stimulate the formation of FeS_2-gel. When the bed is attacked by the aerobic circulatory water, the whole bed should become aerobic with the exception of the closed micro-environment as in the tests of micro-organisms.

The crystallization of FeS_2-gel may proceed resulting a particular form in a particular environment. If the environmental condition changes even slightly, the crystallization of the particular form may stop and the gel may be transformed to another form. If the crystallization proceeds in such a way as mentioned above, it is not impossible that there are the mixture of three forms crystallized under the changing environmental condition, although such mixture have never been actually found yet.

Temperature. Generally speaking, temperature acts as the most important factor during the chemical reaction associated with some microbial action, and the most favorable range for most of the microbes is 20~40°C. While ZoBELL (1958) stated that the tolerance field of sulfate reducing bacteria is 0~100°C. There are two reasons why the thermophilic bacteria show the greatest activity at rather high temperature. One is that they get a large reaction speed to form their enzymes (ALLEN, 1950). The other is that they connote many stable enzymes at high temperature (MILITZER *et al.*, 1950; POSTGATE, 1950). However, the framboidal pyrite occurs not only in sediments or sedimentary rocks but also in sulfide ores formed at much higher temperature than the ordinary sedimentary environment. Whether the temperature is the most important factor or not for the formation of pyrite must be answered after the close examination of all factors other than temperature.

Pressure. ZoBELL and JOHNSON (1949) reported the results of the observation of some cultured microbes under various pressure (300~600 atm) and temperature (20~40°C). While ZoBELL and OPPENHEIMER (1950) reported that sulfate reducing bacteria were able to endure still higher pressure of about 1000 atm on the basis of the observation of their culture. Judging from the above mentioned facts, at least, it seems there is some combined effect of pressure and temperature to the formation of pyrite through the microbial action. For the solution of the problem about the habits of framboidal pyrite and individual crystal pyrite, accurate informations are needed about the depth and pressure at which the pyrites are originated in recent sediment.

Salinity. According to WERKMAN and WILSON (1951, *in* TSURU, 1962), microbes show much difference in the ability of permeation under the osmotic pressure and their opinion has been confirmed by many works about sulfate reducing bacteria (for example: ZoBELL, 1946a; ISACHENKO, 1929, etc.). However, the framboidal pyrites occur regardless the type of sedimentary environments, fresh, brackish or marine. It seems, therefore, the salinity doesn't contribute to the formation of FeS_2-gel. If the salinity effects the formation of the sedimentary pyrite, it should be reflected in the fractionation of the sulfur isotopes in pyrite, because NAKAI and JENSEN (1964) admitted that there were some difference in S^{34} between bottom water of the sea and of the lake. In future, the salinity problem must be examined in relation to the crystal habit of the framboidal pyrites, because the stenohaline bacteria may cause a special fractionation of S^{32}/S^{34} in pyrite corresponding to the salinity.

pH and Eh. It is said that most of the important physico-chemical functions of microbes such as the osmosis of cell-wall and the activation of enzymes are controlled and conditioned by *pH*. The function of free hydrogen ion is related not only to the dissociation of hydrogen carrier electrosis but also to the existence of salts, the oxidation-reduction potential and/or buffer action (RAVOTNOVA, 1957, *in* TSURU, 1962). STARKEY and WIGHT (1945), ZoBELL (1946b), and SHTURM (1951) offered many excellent data on the relation of *pH* with the culture of sulfate reducing bacteria under various condition. Their data give the conclusion that the greatest activity of sulfate reducing bacteria occurs at around *pH* 7. According to BAAS BECKING and KAPLAN (1956), the relation between the activity of sulfate reducing bacteria and *pH* is closely connected to *Eh* under the experimental and natural conditions. They reported that *Eh* −50∼−150 mV was the optimum for growth of microbes.

Synthesis. Yuji ENDO, Ichiro SUNAGAWA and Nobuyuki NAKAI* succeeded in the formation of framboidal pyrite through the following process: the starting materials are metallic iron (Fe) or oxidized iron (Fe_2O_3 or FeO), elemental sulfur (S) and distilled water, which are all inorganically refined; these materials are taken in the glass tube and heated in autoclave at 250∼350°C; after 5∼20 hours, pyrite is formed in the tube. The habit of the synthesized pyrite is cubic, but the habit transforms to octahedron in the course of the crystal growth. At crystallization of pyrite, *pH* is 0.18∼1.2. Pyrite changes to marcasite because of the ultra-acidic condition. After this procedure mentioned above, the experiment is further proceeded. The refined $CaCO_3$ is added to control *pH*. This results the rise of *pH* to 5∼6 and the formation of framboidal pyrite in the tube. SUNAGAWA** stated that the addition of $CaCO_3$ was not the necessary condition for the synthesis of pyrite, but for the formation of framboidal pyrite, because pyrite was always formed regardless of the change of *pH*. In the system added with $CaCO_3$, pyrite crystallized from the nucleus stops its growth to a limited size and, in consequence, the size of the pyrites is even. Then the aggregate of minute crystals forms framboidal pyrites. SUNAGAWA** explained that the growth of pyrite might stop due to the coating of the crystal-surface by $CaCO_3$ and that the appearance of the framboidal pyrites closely resembles those in the sedimentary rocks. He concluded that all the mechanism of formation of framboidal pyrites is clarified in the experiments just mentioned. However, the present author thinks that the process of chemical reaction of S and Fe (what kind of sulfur ion reacts with Fe to form FeS_2) is not yet solved, because the temperature is higher and *pH* is also lower than that of the ordinary sedimentary condition. The problem of ionization of sulfur, the time factor and the catalyzer must be pursued sufficiently. Further, it is highly probable that the difference of the molecule of the gel and/or the volume and character of the crystal nucleus in FeS_2-gel control the form and habit. The question remains to be solved in future.

---

* Preprint of the annual meeting for 1969, the Mineralogical Society of Japan.

** Personal communication.

Concluding remarks

It is said that some biogenic sulfur has some isotopic ratio different from that of magmatic origin. If the fractionation is aroused by some microbes, a particular value of the ratio should correspond with each microbe. In other words, the ratio may point to the kind of microbes. Accordingly, if the kind of microbes is made clear on the basis of the ratio of the sulfur isotopes, the conditions of the sedimentary environment may be concluded.

Microcrystals constituting the framboidal pyrite illustrate three crystal habits. The three habits must be reflected the difference and/or the duration of the physico-chemical conditions where FeS_2-gel was introduced. Therefore, the freqeuncy of habits in every framboidal pyrite may indicate the sedimentary condition at the time of precipitation of the gel.

Marcasite which shows the framboidal texture in appearance is found intermixing with the framboidal pyrite. It is clearly a pseudomorph of the framboidal pyrite. If the transitional point is examined experimentally, it may verify the change of diagenetic condition after crystallization of pyrite.

Pyrite is valuable to presume the paleo-sedimentary environment, because it has a high stability as compared with other syngenetic minerals.

References

ALLEN, M. B. (1950): The dynamic nature of thermophily. *Jour. Gen. Physiol.*, **33**, 205–214.

BAAS BECKING, L. G. M. and KAPLAN, I. R. (1956): The microbiological origin of the sulfur nodules of Lake Eyre. *Trans. Roy. Soc. S. Aust.*, 79, 52–65.

BUTLIN, K. R. and POSTGATE, J. R. (1954): The microbiological formation of sulfur in Cyrenaica lakes. *In* Biology of Deserts. Inst. Biol. London, 112–122.

HALLBERG, R. (1965): Notes on biosynthesis of pyrite. *Acta Univ. Stockholm Contri. Geol.*, **13**, (4), 35–37.

HONJO, S., FISHER, A. G. and GARRISON, R. (1965): Geopetal pyrite in fine-grained limestones. *Jour. Sedi. Petr.*, **35**, (2), 480–488.

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

KATO, G. (1967): Biogenic pyrite from a Miocene formation of Shimane Peninsula, Southwest Japan. *Mem. Fac. Sci., Kyushu Univ., Ser. D*, 18, (2), 313–330.

LOVE, L. G. and AMSTUTZ, G. C. (1966): Review of microscopic pyrite from the Devonian Chattanooga Shale and Rammelsberg Banderz. *Fortschr. Miner.*, 42, (2), 273–309.

MATSUMOTO, T. (1942): Fundamentals in the Cretaceous stratigraphy of Japan. Pt. I. *Mem. Fac. Sci., Kyushu Univ., Ser. D*, 1, (3), 129–280.

MILITZER, W. E., SONDERREGGER, T. B., TUTTLE, L. C. and GEORGI, C. E. (1950): Thermal enzymes. II. Cytochromes. *Arch. Biochem.*, **26** ,299–306.

MOLISCH, H. (1911): Die Eisenbakterien. *Zentr. Bakteriol. Parasitenk.*, **11**, (29), 241–243.

NAKAI, N. and JENSEN, M. L. (1960): Biogeochemistry of sulfur isotopes. *Jour. Earth Sci., Nagoya Univ.*, 8, 181–196.

——— and ——— (1964): The kinetic isotope effect in the bacterial reduction and oxidation of sulfur. *Geochim. et Cosmochim. Acta*, 28, 1893–1912.

POSTGATE, J. R. (1959): Sulfate reduction by bacteria. *Ann. Rev. Microbiol.*, **13**, 505–520.

RANKAMA, K. (1963): *Progress in isotope geology.* Interscience Publishers, John Wiley & Sons. New York, London, 1–705.

RAVOTNOCA, I. L. (1957): Roles of physiochemical conditions in the life activity of micro-organisms. (*in* TSURU, 1962).

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

SHTURM, L. D. (1951): Roles of the sulfate reducing bacteria in the life and history of petroleum deposits. Pamyati: I. M. *Gubkina Akad., Nauk SSSR,* 275–286.

STARKEY, R. L. and WIGHT, K. M. (1945): Anaerobic corrosion of iron in soil. Am. Gas. Assoc., New York, N.Y., 1–108.

TSURU, S. (1962): Geomicrobiology. *Jour. Jap. Chem.,* **17**, 35–50.

VALLENTYNE, J. R. (1963): Isolation of pyrite spherules from recent sediments. *Limnol. Oceanog.,* 8, 16–30.

WERMAN, C. H. and WILSON, E. B. (1951): The cell in Development and Heredity. (*in* TSURU, 1962).

ZOBELL, C. E. (1946a): Function of bacteria in the formation and accumulation of petroleum. *Oil Weekly,* **120**, 30–36.

——— (1946b): Bacteriological process for treatment of fluid-bearing earth formations. U. S. Patent No. 2413278, Assigned to the American Petroleum Institute.

——— (1958): The ecology of sulfate-reducing bacteria. *In* Sulfate reducing bacteria, their relation to the secondary recovery of oil. New York: St. Bonaventure Univ., 1–24.

——— and JOHNSON, F. H. (1949): The influence of hydrostatic pressure on the growth and viability of terrestrial and marine bacteria. *Jour. Bacteriol.,* **57**, (2), 179–189.

——— and OPPENHEIMER, C. H. (1950): Some effects of hydrostatic pressure on the multiplication and morphology of marine bacteria. *Jour. Bacteriol.,* **40**, 771–781.

George KATO

Biogenic Pyrite from the Cretaceous Formations of Sakhalin and Hokkaido

Plates 10～17

Plate 10

Explanation of Plate 10

Figs. 1–4, 7–9, 11–16, 18 and 20. Diatoms replaced by pyrite perfectly...Page 76
Figs. 5, 6 and 10. Diatoms replaced by pyrite imperfectly ....Page 76
Figs. 17, 19 and 21–24. Framboidal pyrite replenished in diatom ....Page 76

All figures are in the same magnification (×400), and all the specimens came from one and the same locality (the third tributary of Naibuchi River, Sakhalin).

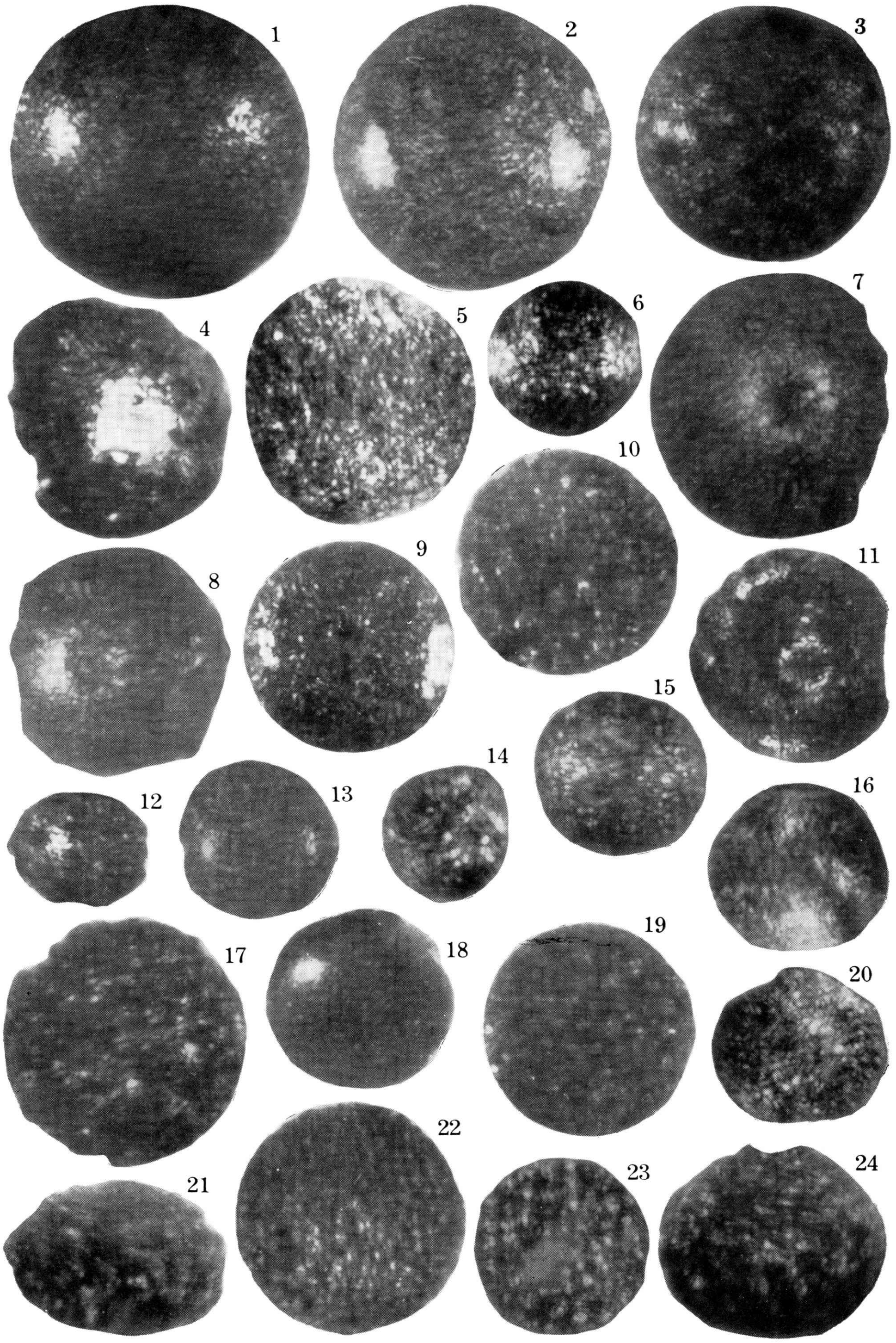
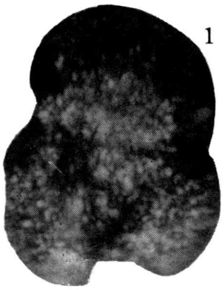

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24

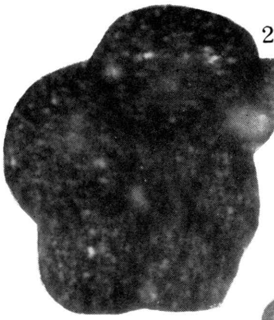
Plate 11

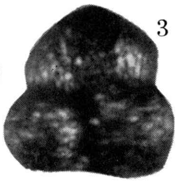
Explanation of Plate 11

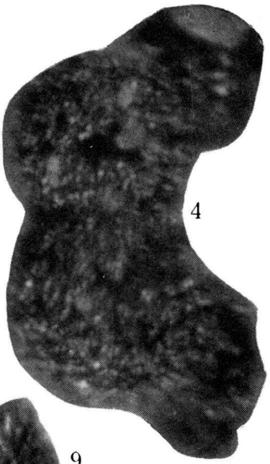
Figs. 1–10. Foraminifers replaced by pyrite ....Page 76
Figs. 11 and 13. Break-down specimens of diatom replaced by pyrite...Page 76
Figs. 12, 14, 15, 17 and 18. Diatoms replaced by framboidal and crystal pyrites ....Page 76
Figs. 16. Side view of radiolaria replaced by framboidal pyrite.........Page 76
Figs. 19–22. Side view of diatoms replaced by framboidal pyrite ....Page 76
Figs. 23. Octahedral pyrite ....Page 76

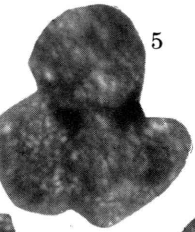
The magnification of figures and the locality of the specimens are all the same as that of Plate 10.

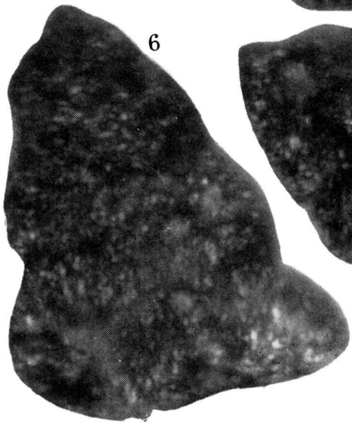

1


2


3


4


5

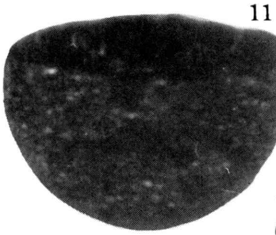

6

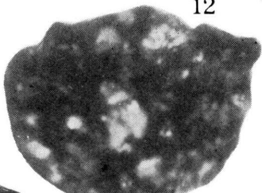

7


8

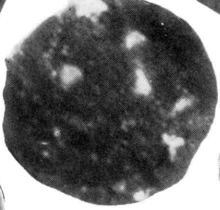

9

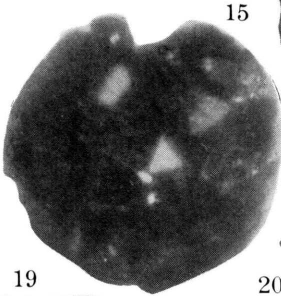

10


11

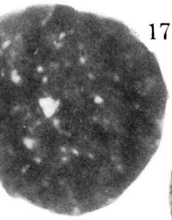

12

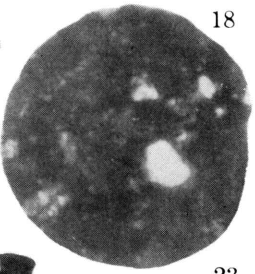

13

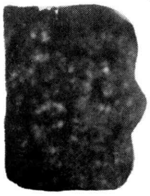

14

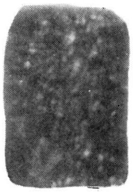

15


16

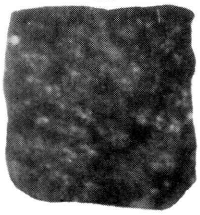

17

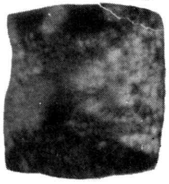

18


19


20


21


22


23

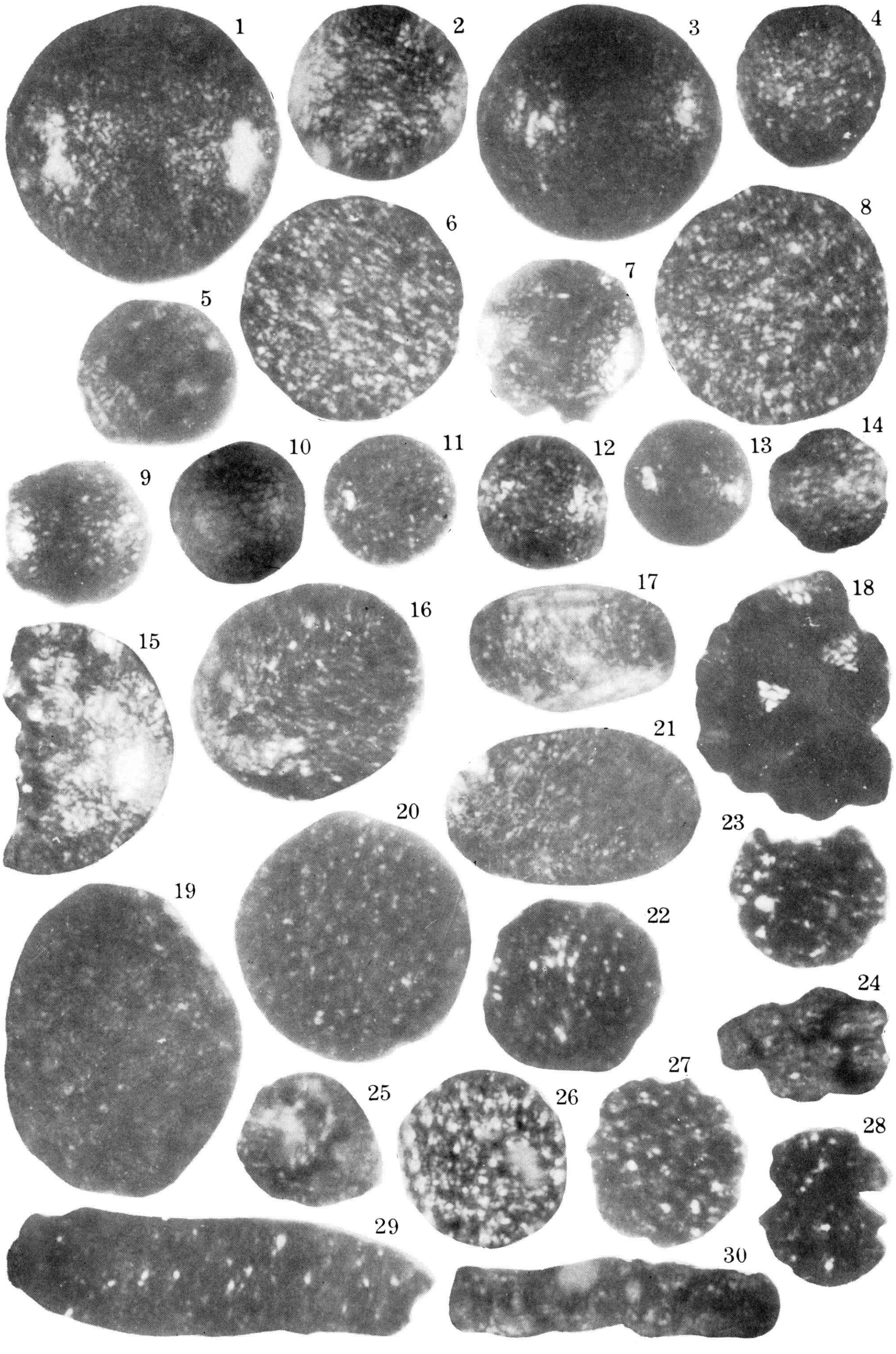
G. KATO: Biogenic Pyrite

Plate 12

Explanation of Plate 12

Figs. 1–5, 7, 9–14, 16 and 21. Diatoms replaced by pyrite perfectly .....Page 76
Figs. 6 and 8. Diatoms replaced by pyrite imperfectly ....Page 76
Figs. 15. Break-down specimen of diatom replaced by pyrite ....Page 76
Figs. 18. Diatom replaced by framboidal and crystal pyrites ....Page 76
Figs. 19, 20, 22, 23 and 26–28. Framboidal pyrite replenished in diatoms. Page 76
Figs. 24. Aggregated framboidal pyrite, irregular form ....Page 76
Figs. 25. Radiolaria replaced by pyrite ....Page 76
Figs. 29 and 30. Probably some micro-organisms replaced by framboidal pyrite ....Page 76

All figures are in the same magnification (×400), and all the specimens came from one and the same locality (Miginosawa, the upper stream of Haboro River, Hokkaido).



G. KATO: Biogenic Pyrite

Plate 13

Explanation of Plate 13

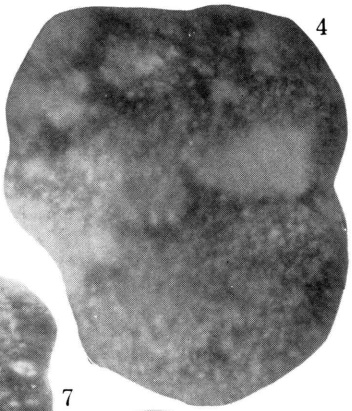
Figs. 1–11. Foraminifers replaced by pyrite	Page 76
Figs. 12, 16 and 17. Irregular pyrite	Page 76
Figs. 13. Aggregated framboidal pyrite	Page 76
Figs. 14 and 15. Probably some micro-organisms replaced by pyrite	Page 76

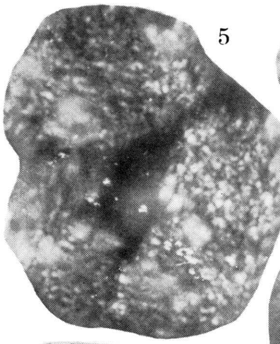
The magnification of figures and the locality of the specimens are the same as that of Plate 12.

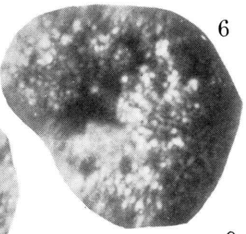

1

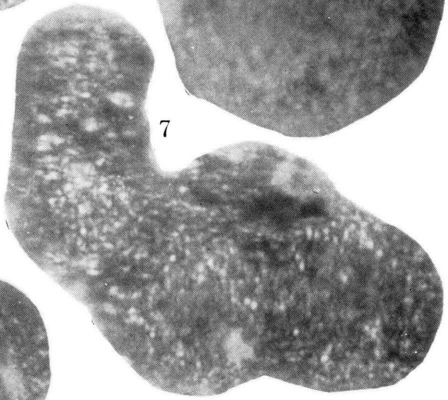

2

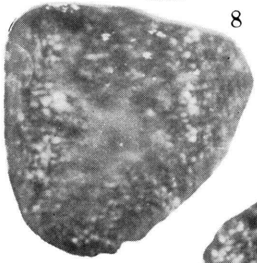

3

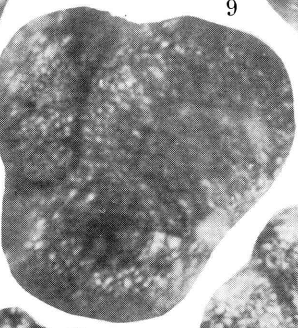

4

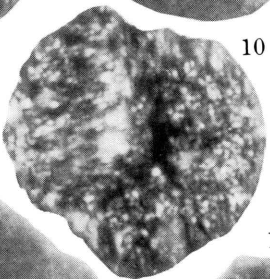

5

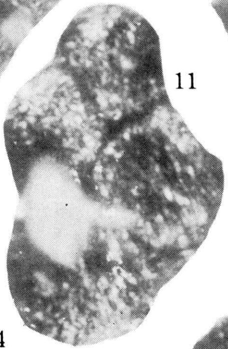

6

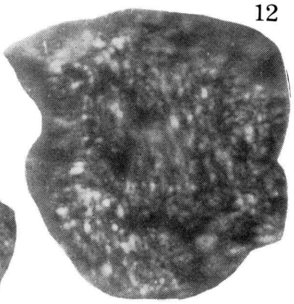

7

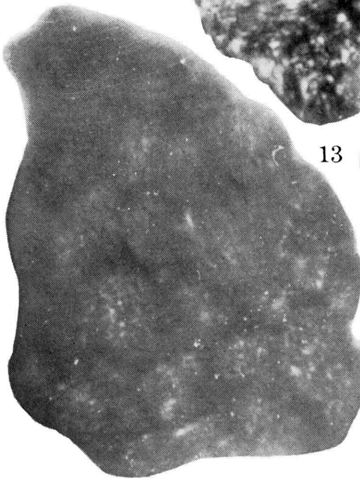

8


9

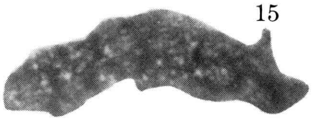

10

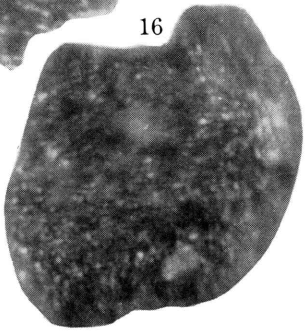

11


12


13


14


15


16

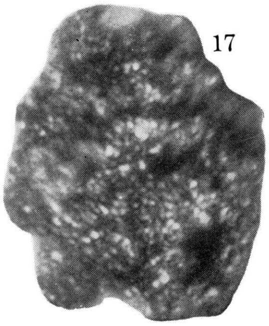
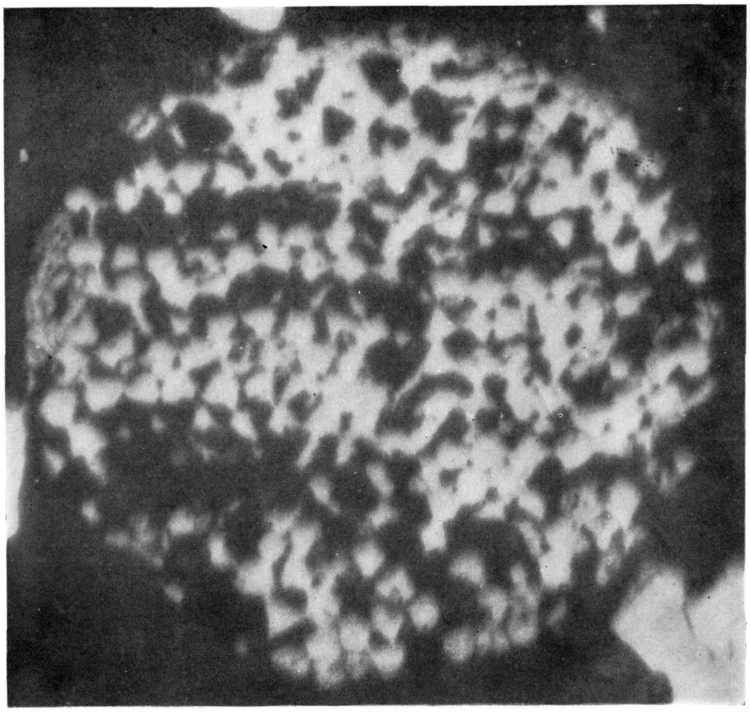

17

Plate 14

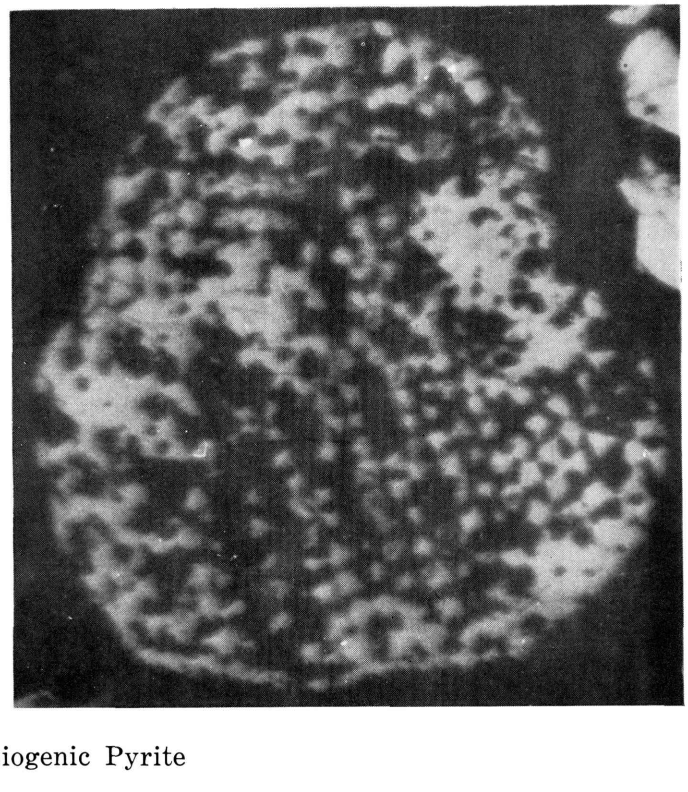
Explanation of Plate 14

Figs. 1 and 2. Polished section of framboidal pyrite ....Page 76
Both framboidal pyrites are probably the aggregation of octahedral crystals and show something ordered arrangement (×1200).

The locality of the specimens is all the same as that of Plate 12.



1



2

G. Kato: Biogenic Pyrite

Plate 15

Explanation of Plate 15

Figs. 1–4 and 6. Polished framboidal pyrites.

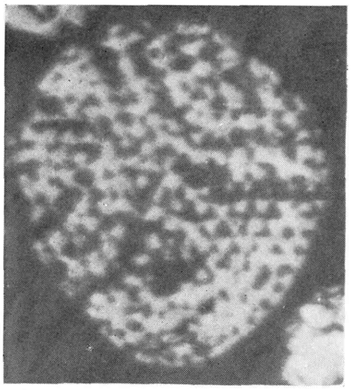
Fig. 1. Octahedral micro-crystals showing something ordered arrangement .... Page 76

Figs. 2–4. Cubic octahedral micro-crystals of irregular arrangement.. Page 76

Fig. 6. Cubic micro-crystals of concentric arrangement .... Page 76

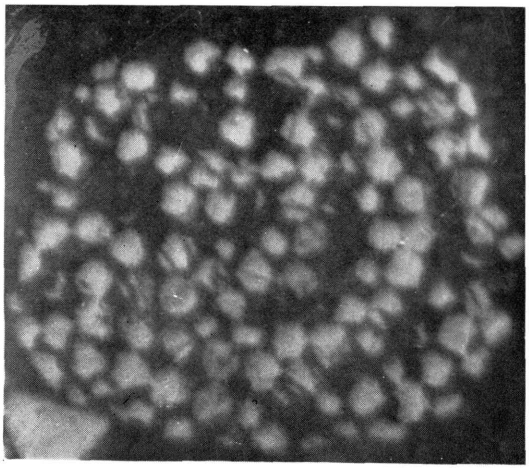
Fig. 5. Aggregation of cubic octahedral pyrite crystals, not framboidal (polished section) .... Page 76

The magnification of figures and the locality of the specimens are all the same as that of Plate 12.

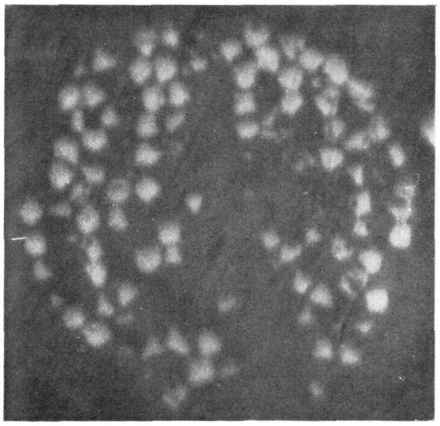


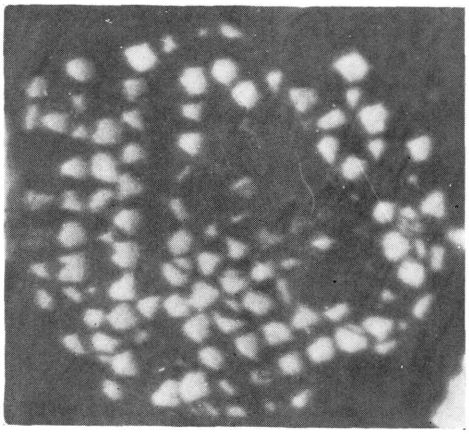
1

2



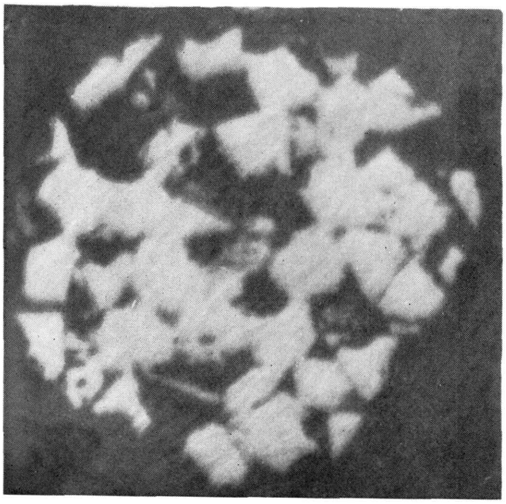
3



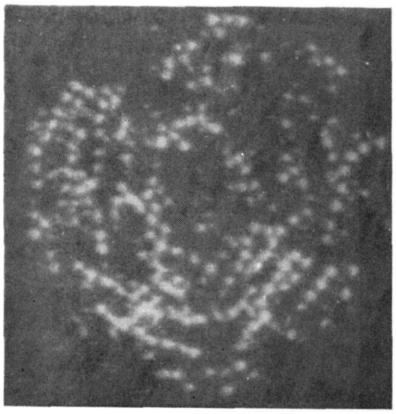


4

5



6



G. Kato: Biogenic Pyrite

Plate 16

Explanation of Plate 16

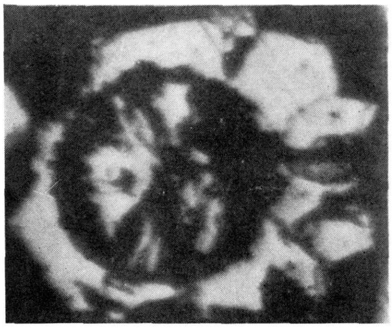
Figs. 1–3. Pyrite presenting two stages of crystallization .... Page 76
Fig. 1 and 2 is in same material, but showed by different magnification (×1200, ×400).
Fig. 3. ×400.
Figs. 4–6. Framboids presenting radiated structure.
They may be marcasite (×400) .... Page 76

All the specimens are in the polished section. The locality of them is all the same as that of Plate 12.

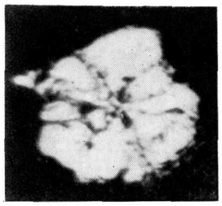

1


2


3


4


5


6

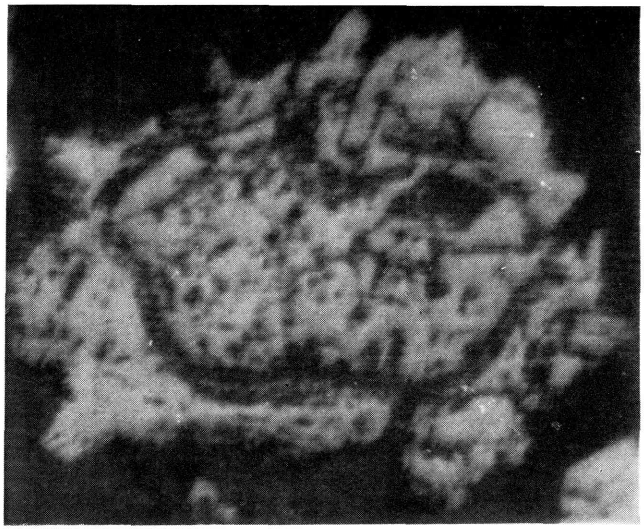
G. KATO: Biogenic Pyrite

Plate 17

Explanation of Plate 17

Figs. 1 and 3–7. Pyrites showing two stages of crystallization ....Page 76
    Figs. 1 and 4–7. ×1200.
    Fig. 3. ×400.
Fig. 2. Foraminifer replaced by pyrite (×400) ....Page 76

All the specimens are in the polished section. The locality of them is all the same as that of Plate 12.



1

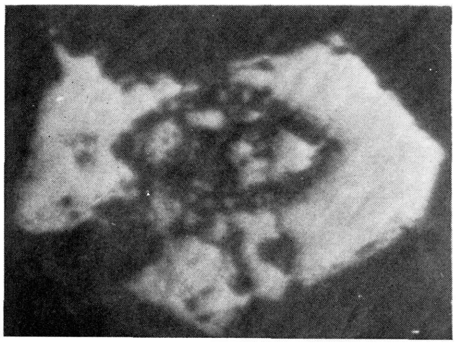
2

3

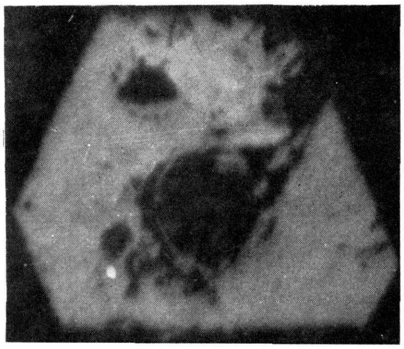
4

5

6



7



G. KATO: Biogenic Pyrite