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Katsu KANEKO, Director

Variation in Crystal Habit of Pyrite

By

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Abstract

Pyrite is one of the most popular and persistent minerals, and it shows various kinds of crystal habits.

To clarify the origin of habit variation of this mineral and the relation between each habit and crystallization condition, the present writer has made systematic observations and statistics on the habit variation of pyrites from various occurrences and localities, in close connection with their crystallization environment. Consequently, he could clarify some unexplored facts concerning the origin of the habit variation, and obtained a systematic figure of the habit variations of pyrite.

These facts are difficult to be explained by the interpretation method which was proposed by crystal chemists and now is a popular view.

From his observations and considerations, it is considered that the fundamental cause of the habit variations of pyrites is the differences of the conditions of crystallization environments. Crystal habit is controlled by whether pyrites grow under suitable conditions and sufficient supply of solution or not. Under suitable conditions, pyrites appear in pentagonal or octahedral habit; and they take cubic habit when they grow under unsuitable conditions. Influence of impurities upon habit change is recognized only under some limited condition. Thus, this is considered as a minor factor than the factors above.

The facts observed and the above relations are satisfactorily interpreted from the standpoint of a new idea of crystal growth.

Acknowledgement

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Introduction

The phenomenon that one species of crystals shows various external forms, despite the same crystal structure, chemical composition, etc., resulting from different assortments of crystal faces, is one of the problems being observed with deep interest by many crystallographers, mineralogists, crystal chemists, etc. Anyone, who is interested in crystals, will feel doubtful on why this variation of crystal habits appears. Many workers have endeavored to solve this problem from the mineralogical, crystal-chemical, and crystal-physical standpoints. Consequently, many results have been achieved specially in the field of crystal chemistry.

However, since these are the results obtained in the case of the artificial crystals grown under laboratorial circumstances, they can not be applied carelessly to the case of the crystals which are grown in nature under very different circumstances. Many of the observations of minerals are only the descriptions of individual minerals, and no unified interpretation as obtained in the case of artificial crystals has yet been succeeded to the present time.

The author has been interested in this problem since ten years ago, and has studied the problem of persistent minerals in nature, such as pyrite, calcite, and chalcopyrite. From the standpoint of study that we must not deal with minerals as an individual specimen, but must consider them in connection with their crystallization environment, the author's research is mainly on the relation between the habit and the differences of the mode of occurrences. Therefore, the results obtained are inductive; however, the author discovered some unexplored relations between the habit variation and the crystallization environment.

These relations can not be explained by the interpretation method which has been proposed by crystal chemists and now is a popular view on the origin of habit variations. Thus it is believed that the author's results will add some new information to this question.

In this paper, the writer intends to describe systematically about his observations concerning the origin of habit variation of pyrite, and attempt some interpretations from the standpoint of crystal growth.

On the same problem about calcite$^{42)}$ and chalcopyrite$^{39)}$ as well as the detailed description of pyrite, the reader may refer to the author's individual papers.

I. Historical Review of the Habit Problem

Former researches on crystal habits can be classified roughly into two lines. One is experimental studies by crystal chemists and the other is observations on natural minerals by mineralogists.

Studies by crystal chemists mainly concern the influence of the impurities in solution upon crystal habit. The oldest discovery of this phenomenon is the experiment by de l'Isle$^{27)}$ who succeeded in the formation of octahedral habit of common salt from brims containing urea, and the experiment by Leblanc$^{23)}$ who succeeded in the crystallization of cubic habit of alum by means of alkali. After these discoveries, many researchers have been interested in the phenomenon that crystals from solution containing foreign materials differ in habit from the crystals obtained in a pure one, and many experimental results have been reported by Beudant, Von Hauer, Von Foullon, Retgars, Gaubert, Wenk, Bunn, Buckley, and Frondel, etc. At first, the inorganic ions were used as the impurities. However, after the first discovery, by Retgars[28)], of strong influence of the dye impurities, Buckley[7)], Frondel[11)], etc. have studied mainly on the influence of the dye ions. Especially, the results obtained by Buckley reach to a vast number, and consist of the main core of the crystal chemical studies.

Gaubert[12)] first analyzed the phenomenon scientifically. His idea is the so-called syncrystallization theory. Namely, because the microscopical fine crystals of impurity adsorb only on the specific face of the substratum crystal, the deposition of the molecules of the substratum crystal on that face are disturbed, and cause the variation in habit. The interpretations proposed afterwards by Bunn, Frondel, and Buckley, etc. are similar to this theory in the fundamental meanings. Meanwhile, somewhat different interpretations were proposed by Walcott[47)] and Saylor[33)], though they could only succeed in the interpretation of the local facts.

Starting from the syncrystallization theory, Bunn and Royer developed the theory more strictly. According to Bunn, mixed crystal, oriented overgrowth and habit variation caused by impurities are all related phenomena. He considered that these phenomena all occur as the result of surface adhesion of fine crystals of the impurities on the specific face of substratum crystal in the parallel position. In order to cause this adhesion, the next factors are necessary to be satisfied between the impurity molecules and the substratum crystal; i.e., the resemblance of crystal structure and the approximate similarity of distance between the atoms of the same type as well as the sufficient amount of the impurities for being adsorbed in parallel position. An idea similar to this was proposed by Royer and Frondel[10)]. Certainly, in many cases of the inorganic impurities, the factors above are satisfied. However, it is known from the experiments of the dye impurities that there are many dye impurities which affect strong influence upon habit, although the impurities not satisfy the above factors. The following are the arranged and quoted results from the experiments by Buckley.

1. Average concentration of the inorganic impurities is the order equal to the crystallizing substance where an effect is observed and maximum is about 1 out of 1,000 portions, while that of the dye impurities is the order of one out of few ten thousand portions, molecularly calculated, and maximum is more than one out of 330,000 portions.

2. The inorganic impurities which show some effect on habit have structural similarity with crystal, but the structure of the dye impurities is very complicated and not so similar to that of crystal.

3. Even a very powerful modifier may not affect some special salts.

4. There are a number of impurities which are either poor or ineffective on almost all substances but one single substance which have a strong effect.

5. Almost all impurities modify the same type of face only differing from each other in their effectiveness.

6. A dye impurity which has powerful influence on one member of isomorphous crystals often does not effect the other member.

7. When changing the crystal habit by dies, some will be scarcely tinted at all, whereas the others are so deeply tinted that they remove almost all the color from the solution.

From the aspects mentioned above, Buckley pointed out the serious difficulty in the way of interpreting habit change in the terms of surface adhesion, but he did not propose a new idea in return. He considered that there is one sequence of events taking place between the crystal-solution interface which results in habit modification, another one which causes selective deposition with zoned structures, and a third, the choice whether parallel growth or mixed crystals are formed—and no necessary connection between these processes is evident. He also noted that they go on simultaneously quite often, but they can be proceeded independently in the same crystal at the same time.

Subsequently, Bunn3) explained these difficulties from the results of his experimental studies on crystal growth. Namely, he proposed the next two different processes in which the impurity has influence on habit; i.e., (1) Fine crystals of the impurity precipitate on a specific face of crystal in parallel position, and results to modify the development of this face. 2) The surface of the growing crystal forms a fairly stable two-dimensional complex with the impurity ions, and no new molecules or ions can attach themselves there, then the growth of the layer ceases, and crystal habit changes. According to Buckley, although such an explanation may have some objections, it seems that his supposition is probably closer to the truth than any of the views offered up to this point, and is the most satisfactory explanation at the present time.

Besides his explanation, Buckley5) discovered the fact that the effectiveness of the impurity usually changes according to the different conditions of crystallization, such as temperature, speed of crystallization and grade of cooling. He took the fact seriously, but did not explain it systematically.

Crystal chemists explain the fundamental cause of habit change by the terms of surface adhesion of the impurity, and do not consider the other factors. This explanation is generally accepted and has been the main current interpretation of habit change resulting from its glorious appearance.

Against this, some mineralogists made many observations on mineral specimen in museums and found some relations between habit and crystallization stage and the mode of occurrences as well as crystallization temperature on individual minerals. Nevertheless, no unified interpretations about such relations has appeared to the present time.

Typical mineralogical studies are found in the literatures of G. Kalb and his scholars. The following relations are cleared by them.

Calcite...Crystal habit of calcite varies as the temperature of crystallization decreases17).

High Quartz...Crystal habit differs between crystals in basic rocks and acidic rocks18).

Olivine, Rutil...Magmatic crystals, contact crystals, and druse crystals of these minerals show each characteristic habit17).

Zincblende...Crystals of the earlier stage differs in color, luster, and habit from that of the later stage16).

After these studies appeared, no valuable reports were seen for a while. However, since 1940 many studies have been reported, such as the work of L. Maklári, A. F. Seager, G. P. L. Walker, A. Pabst, I. Kostov, M. O. Kliya, S. Watanabe, P. Ramdohr, K. Muta and the present writer. Main part of them are quoted here in a short word.

Barite. . .By Maklári25) and Seager31), it is observed that the habit of this mineral varies according to the different stage of crystallization.

Calcite. . .It is explored by Kliya22) and Sunagawa28) that successive variation of habit can be observed according to crystallization stage and temperature.

Garnet. . .Pabst26) found the fact that habit changes successively from small grain to large grain in garnet crystallized in schist at Fort Wrangel, Alaska. Against this conclusion, I. Kostov19) proposed the next as the main controlling factors from his observation on many specimen from Bulgaria; chemical composition, ratio of ionic radius between R^{+} and R^{3+}, and crystallization environment.

Chabazite. . .Walker48) drew a distribution map of different habit of chabazite in basaltic plateau in Ireland, and concluded that the habit of chabazite is mainly controlled by the temperature of crystallization.

Arsenopyrite. . .Watanabe49) explored that the habit of this mineral from the Ashio mine in Japan differs according to the temperature of growth.

Magnetite. . .Macroscopic crystal of magnetite always shows octahedral habit and a poor development of *a(100)* face. Ramdohr30) found that very fine crystals of magnetite of 4μ or under show cubic habit, and interpreted this phenomenon as a function of the growth rate of the different faces and the grade of supersaturation

Pyrite. . .Kinoshita and Muta21) reported the variation according to different depth of deposits, and Hayashida and Muta13) described the relation between *o(111)* face and minor contents of As.

Chalcopyrite. . .Genesis of the triangular chalcopyrite, a peculiar habit of the mineral from Japan, was clarified by Sunagawa39).

It is evident, as described above, that the cause of habit variation of natural crystals is somewhat different from that of artificial crystals. Habit variation in natural crystals seems mainly resulting from the difference in temperature of crystallization. Furthermore, we cannot neglect the relationship between habit and grain size which was explored by Pabst, Ramdohr and the author. In the case of solid solution, differences in chemical composition seem to play a great role on the habit change.

However, even in the case of natural minerals, there are some instances which will be explained by the terms of surface adhesion.

Fluorite. . .Iwase14) explained the difference of octahedral and cubic habits of fluorite by the presence of the impurity ions such as rare earth.

Galena. . .Development of octahedral face of galena is interpreted by the selective adsorption of Ag.

Zincblende. . .According to Becke4), crystals associated with galena and carbonate minerals show octahedral habit; they crystallize in tetrahedral habit when they are associated with pyrite.

Calcite. . .The relationship between soluble silicate and special habit of calcite from Andreasberg was created artificially.

In the present time, the so-called adsorption theory is most generally accepted, and able to explain many phenomena from the structural standpoint or the view point of crystal growth.

On the other hand, results of minerals are only the description that there will be some relationship between habit and crystallization conditions, and no satisfactorily explanation from the structural or crystal growth standpoint, has appeared.

II. Morphology of Pyrite

Pyrite belongs to the cubic system, Diploidal 2/m3. $a_0 = 5.40$A. It shows the best crystalline state among natural minerals, and is rich in sorts of faces as well as in crystal habit. The number of crystal faces reported in Japan amounts to twenty-seven. As the result of two-circle goniometry of 25 specimens from the Hanaoka mine, the author decided sixty-six faces which show good reflection. In the Dana's 6th edition, eighty-five faces are reported; and the 7th edition

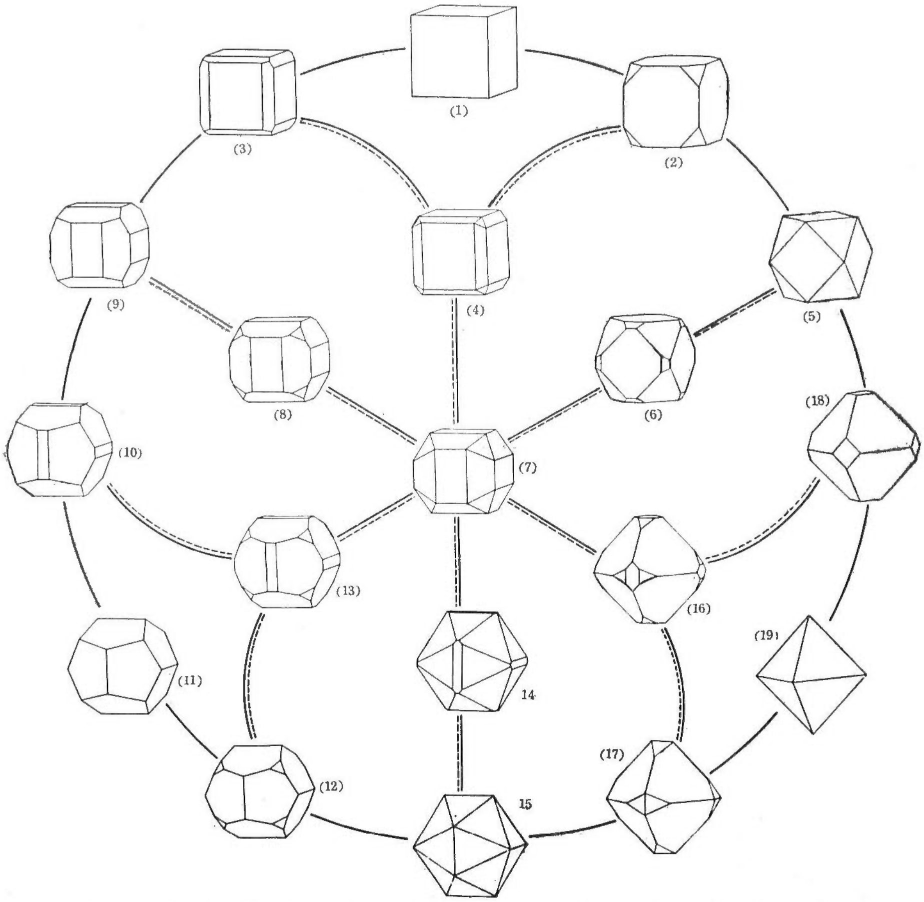

Fig. 1 Typical combinations of three dominant faces *a*(*100*), *o*(*111*) and *e*(*210*) of pyrite

describes seventeen faces as dominent and 222 faces as uncertain. The greater part of this large number of faces is low in frequency of appearance as well as in the grade of development. Three faces of $a(100)$, $o(111)$ and $e(210)$ are most frequent in appearing as dominant face, and $d(110)$, $D(540)$, $\vartheta(430)$, $h(410)$, $p(221)$, $n(211)$, $s(321)$, $t(421)$, etc. also often appear. However, the frequency of appearance of faces under $d(110)$ is much lower compared to the frequency of the first three faces. Therefore, it is convenient to set the subject of observations within the assortment of three dominant faces when we treat the problem of crystal habit of pyrite. The main assortment of them is shown in Fig. 1. The majority of pyrites show these habits; however, pyrites often have faces, such as $p(221)$, $n(211)$, etc. as accessory faces, and sometimes they become the first predominant faces.

The surface structures of crystal faces such as vicinal face, striation, lineage structure and growth layer is important, as such structures show the process of crystal growth indirectly. Microphotographs of the surface structures of dominant faces are shown from plates one to ten, and the characteristic features of each face are schematically drawn in Fig. 2, and described in the following.

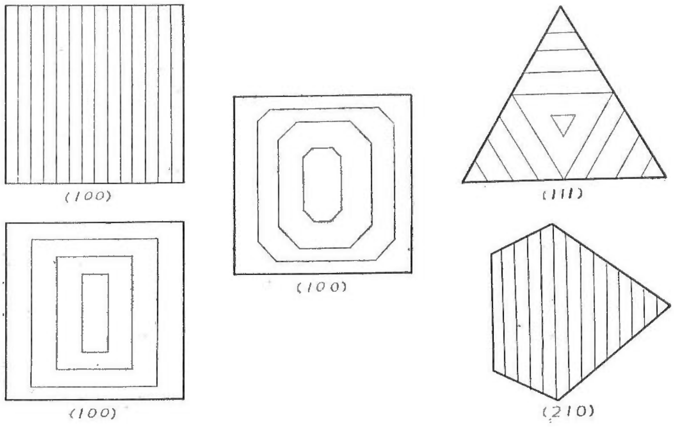

Fig. 2 Idealized figures showing the characteristics of the surface structures on three faces $a(100)$, $o(111)$ and $e(210)$. Only positive crystals are drawn.

1. $a(100)$ face
   Striations parallel to the edge $a\wedge e$; cubic form consisting of $[010]$ and $[001]$ directions; octagonal form which consists of two directions parallel to the edge $a\wedge e$ and $a\wedge o$; sometimes cubic form consisting of $[011]$ and $[0\bar{1}1]$ directions.
2. $o(111)$ face
   Triangular form parallel to the edge $o\wedge a$.
3. $e(210)$ face
   Striation parallel to the edge $e\wedge a$. It does not show the closed form. Vicinal faces are mostly developed in the zone $[001]$.

Furthermore, the rate of development of the vicinal faces and type of construction of the pyritehedral face $\{hk0\}$ characteristically differ according to the mode of occurrences as described below (Fig. 3).

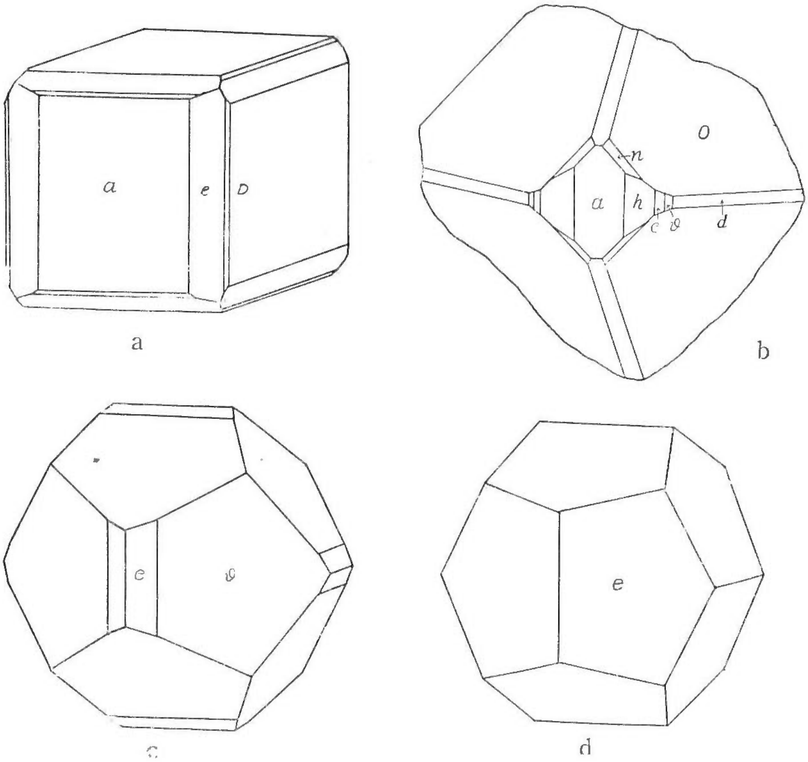

Fig. 3 Several constitution types of pyritehedral faces $\{hk0\}$
a. b. c. ....characteristics of pyrite of the replacement type
d. ....characteristics of pyrite of the vein type
a(100), *o*(111), *e*(210), *h*(410), ϑ(430), *D*(540), *d*(110), *n*(211)

1. Vicinal faces are developed more on crystals of the replacement type than crystals of the vein type.
2. The pyritehedral face $\{hk0\}$ generally consists of *e*(210) alone, in the case of the vein pyrite.
3. While it is common that the $\{hk0\}$ face consists of two or more faces, including *e*(210), in the case of the replacement pyrite.
4. In the case of the replacement pyrite, judging from observations in the case of the Hanaoka mine, sorts of predominant developed $\{hk0\}$ faces differ according to the differences of habit; i.e., in pentagonal habit, ϑ (430) predominates, *D*(540) predominates in cubic habit, and h(410) predominates in octahedral habit.

III. Crystallization Circumstances of Pyrite

Pyrite is one of the so-called persistent minerals. It grows under a wide range of temperature and acidity; however, it crystallizes only under reductional condition; it is known from synthetic experiments that under strong acidity and low temperature marcasite crystallizes out instead of pyrite. The mode of occurrences of pyrite is as follows:

1. magmatic segregation
2. in pegmatite
3. in contact replacement deposits
4. in hypothermal, mesothermal, epithermal veins
5. in hydrothermal replacement deposits (for instance, Kuroko deposit, clayey deposit, etc.)
6. impregnation in country rocks near ore body
7. impregnation in altered rock by hot spring action
8. in bottom clay of volcano lake
9. in non-mineralized sedimentary rock (for instance, impregnation in black shale, coal or replacement of fossils)
10. in metamorphosed rocks
11. in amygdaloidal druse of basaltic lava

The above mode of occurrences can be roughly classified as follows from the standpoint of growth mechanism.

a. Direct precipitation from hydrothermal solution
b. Crystallization as a result of reaction of sulphur in mineralizer and iron mainly in mother rocks which takes place simultaneously with metasomatism of country rocks
c. Crystallization by the action of sulphur bacteria, etc. under strong reductional circumstance without the help of igneous action
d. Sublimation at the latest stage of solidification of lava
e. Magmatic segregation

As the properties of mineral vary sensitively according to the differences of crystallization conditions, we can never neglect this difference and treat crystals of different occurrence indiscriminately.

Therefore, the author has made his observation after drawing a clear line between different occurrences.

The author's observations were mainly made on pyrite from epithermal veins, hydrothermal replacement deposits, such as Kuroko, clayey deposits of the Tertiary age, and impregnated pyrite in altered rock by hot spring action. He has observed only a few instances about pyrite from contact deposits, kieslager deposits, pegmatite, and sedimentary origin. Thus, the descriptions in this paper are mainly on the former pyrite, and in reference to the latter, it will be confined to information.

For the sake of convenience in description, pyrite which is directly formed from ore solution is named the vein type, and pyrite grown by the reaction between sulphur in mineralizer and iron in mother rocks is named the replacement type.

IV. Pyrite of the Replacement Type

Pyrite of the following occurrences is treated as this type.

1. Impregnated pyrite in country rocks near ore body
2. Impregnated pyrite in clay deposits, such as sericite, kaoline, pyrophyllite, diaspore deposits
3. The so-called powder pyritic ore in Kuroko deposit and impregnated pyrite in altered clay zone surrounding ore body

4. Impregnated pyrite in clay altered by hot spring action, as well as in clay near the volcanic fumaroles

These pyrites are not considered as being directly crystallized from ore solution, but they will be thought as crystallization by the reaction between mineralizer and rock simultaneously with hydrothermal alteration of mother rocks.

Usually, a lot of crystals are crystallized within a narrow scope, and they are smaller than 8 mesh. Grain size of crystals is very widely distributed in one specimen, and crystals commonly show good crystalline state, even the crystals which are smaller than 200 mesh.

These crystals are characterized by the remarkable development of vicinal faces and the construction type of the pyritehedral form $\{hk0\}$ as already described.

IV. 1 Habit Variation According to Grain Size

Now, an elutriation of a specimen collected together with mother material to select out pyrite will be made, and crystals will be classified into some classes of mesh, and statistics of the frequency of appearance of each habit in each mesh under binocular microscope will be made.

Figures 4, 5, and 6 show the results of statistics of one specimen from the Hanaoka, Wanibuchi and Kambe mines, respectively. In the figures of Hanaoka and Wanibuchi, the results of statistics are directly plotted on a graph, in the case of the Kambe mine, the result is plotted on a triangular graph after converting

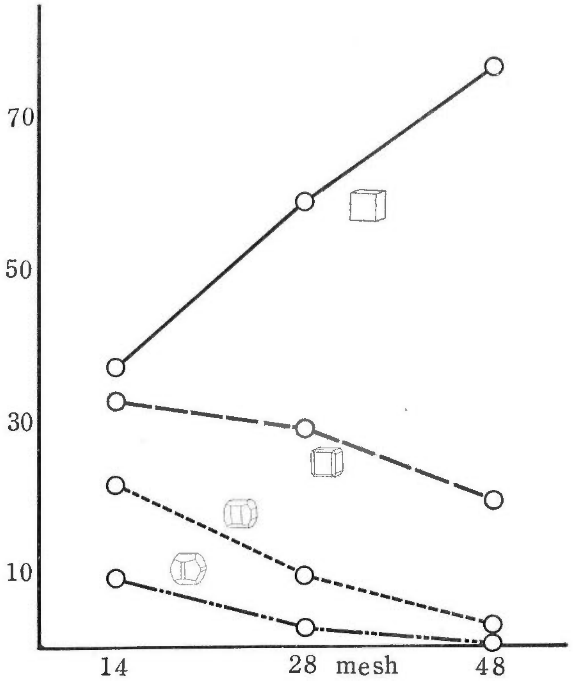

Fig. 4 Variation in frequency of appearance of different habits of pyrite according to grain size (Hanaoka mine)

the result of statistics into the percentage of surface area of the three dominant faces *a, e,* and *o.*

These figures show that the frequency of appearance of each habit or each dominant face is varying successively from small crystal to large one. Furthermore, the frequency of each habit seems to vary in the definite tendency as crystals become larger.

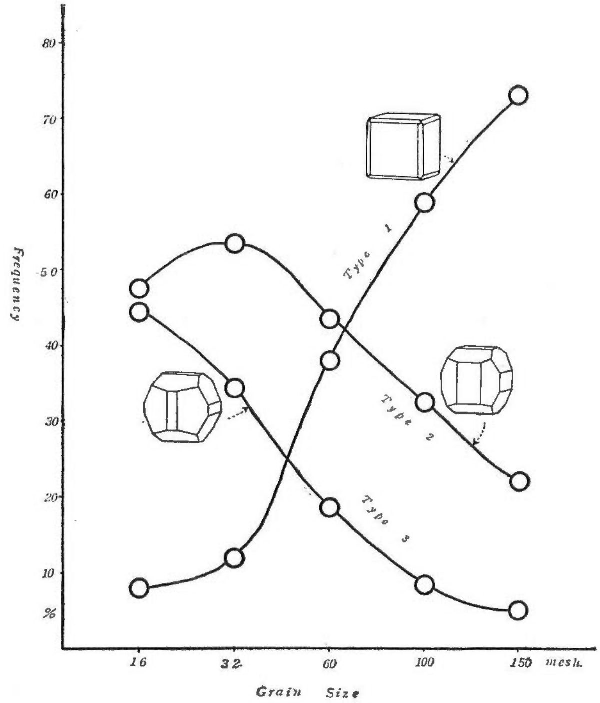

Fig. 5 Variation in frequency of appearance of different habits of pyrite according to grain size (Wanibuchi mine)

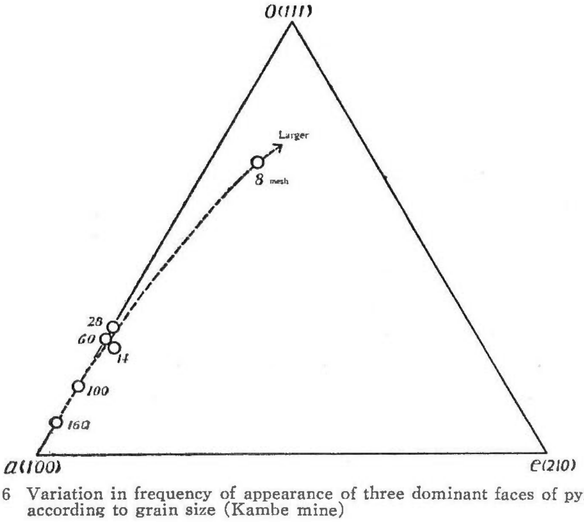

Fig. 6 Variation in frequency of appearance of three dominant faces of pyrite according to grain size (Kambe mine)

This kind of variation is observed not only in the above three instances, but also in almost all instances in which the author has made statistics, even though the rate of variation differs in each of the cases. In almost all cases, the variation has a definite tendency in general. That is, frequency of appearance of pentagonal habit increases as the grain size becomes larger, and of cubic habit shows the opposite tendency. Octahedral habit has an intermediate tendency between these two. As the grain size becomes larger, octahedral habit has an increasing tendency against cubic habit and a decreasing tendency against pentagonal habit. Similarly, this tendency is observed in the case of the change in development of the three dominant *a*, *o*, and *e* faces.

The writer has made similar statistics on many specimen of different occurrences in the Hanaoka mine and obtained the results as shown in Table 1. There are some exceptions in this case, perhaps this is so since this observation was made confined from only eight to forty-eight mesh and not under forty-eight mesh. But, the general tendency of habit variation as crystals become larger is similar to the case described above. Therefore, the general tendency of habit variation as grain size becomes larger can be represented in the diagrams below.

Table 1 Statistic on Crystal Habit of Pyrite in the Hanaoka Mine

R Habit (L) Habit (H)	Pentagonal	Cubic	Octahedral	Total number
Pentagonal	0.125	9	5	14
Cubic	60	0.74	25	85
Octahedral	38	21	0.66	59
Total number	98	30	30	158

Number in each column shows frequency of cases. For instance, 60 in column of cubic of habit (H) and pentagonal of habit (L) shows that frequency of cases in which pentagonal habit increases and cubic habit decreases as grain size grow larger is 60.

R is the ratio of win, and shows the grade of increase of appearance with decrease of grain size. R=Total (L)/Total (L)+Total (H)

cubic habit→octahedral habit→pentagonal habit

$a(100) \rightarrow o(111) \rightarrow e(210)$ or $\{hk0\}$

This phenomenon involves an important meaning and makes the premise of furthergoing studies.

Detailed genetical consideration about this phenomenon will be described later, nevertheless, it is clear that there is a close connection between this phenomenon and the growth of crystal. If we do not consider this as the variation which varies according to the growth of crystal, but as variation resulting from the coexistence of crystals which have grown in different stages, then we will be unable to interpret the definite tendency of the variation which is observed in almost every different occurrences of the replacement type.

Crystals drawn in Fig. 7 show this relation directly. These crystals are impregnated in weak altered tuff near an ore body of the Hanaoka mine. As shown in the figure, no striations on small crystals are observed on *(100)* face, yet, the striations soon make themselves visible as the crystals grow larger, and *e(210)* face appears in the next stage and finally crystals become pentagonal habit. Here,

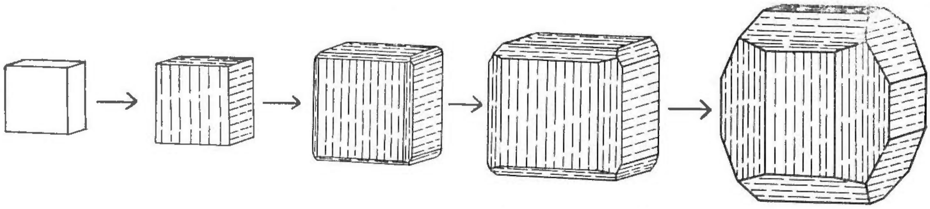

Fig. 7 Variation in crystal habit and property of crystal faces of pyrite (Crystals impregnated in weak altered tuff near onp body in the Hanaoka mine)

the *e*(*210*) face consists of striations or small steps of *a*(*100*) face. Therefore, this phenomenon is considered to show, directly and successively, the process of habit change as crystals grow larger.

By the way, this phenomenon of variation is considered as involving two meanings. They are the rate and the series of variation. The former is a problem of whether even dominant faces vary, within the definite range of grain size, or the accessory faces alone; the latter is a problem of difference of the assortment of faces: For instance, in some cases crystal habit varies from cubic to octahedral without *e*(*210*) face, in other cases it varies from cubic to pentagonal and *o*(*111*) face does not appear, and in another case, it varies in the assortment of the three faces. The origin of habit variation will not be explored, unless the origin of the grade and series of variation is discovered. Next, the writer will describe these separately.

IV. 2 Grade of Variation

Several instances showing the cause of the differences of the grade of variation will be described below. For detailed descriptions, the reader may refer to the author's individual reports.

Wanibuchi mine[38)]

The Wanibuchi mine is made up of gypsum deposits which are hydrothermally replaced from black shale and green tuff of Tertiary age. In the deposit, gypsum crystallizes as an ore ball, and also impregnates in green, brown, and yellowish white clay. Pyrites also impregnate mainly in these clays and sometimes in gypsum. From various observations, the differences of clay are considered as resulting from the differences of the original rocks. In Table 2, the distribution of each habit of pyrites in different mesh is shown. From this result, it can be said that the grade of variation is not the same in different clays; that is, it is very high in green clay and yellowish-white clay and is very low in brown clay. Furthermore, it is observed that the amounts of impregnated pyrite and gypsum differ in different clays. From this, it is considered that as tuff and shale receive equal mineralization, the grade of alteration differs according to the difference of their properties, and a different clay will be produced; i.e., green clay and yellowish-white clay, of which the original is green tuff and calcarious patch, is the strongest altered product; and brown clay, of which the original is black shale, is a production of low grade alteration. Therefore, the grade of habit variation is high in the case of strong mineralization and vice versa. That is, the grade of variation is controlled by the grade of mineralization.

Table 2 Difference in the Grade of Habit Variation in Different Clays (Wanibuchi Mine)

Mesh / Sample No.	14	28	60	100	150	Clay
24071606	—	—	C	C	C	brown clay
504	C	C	C	C	C	
604	—	Cpo	Cpo	Cpo	Co	
505	C	C	C	C	C	
605	C	C	C	C	C	
506	C	C	C	C	C	
501	Pc	PC	Cp	Cp	C	green clay
701	—	P	P	P	Cp	
609	P	P	Pc	Pc	PC	
608	—	P	P	P	Cp	
704	PC	PC	PC	Cp	C	
502	—	P	Pc	Pc	PC	
610	Pc	CP	Cp	C	C	
702	P	Pc	C	C	C	
503	P	P	P	Pc	PC	
612	P	Pc	Pc	Co	Co	yellow clay
613	PC	PC	Cpo	Cpo	Cp	
508	Oc	Oc	Oc	Oc	Co	
703	CP	Cp	Cp	Cp	C	
507	Oc	Oc	CO	C	C	

C, P, O show the cases in which cubic, pentagonal and octahedral habit is predominant, respectively. Small letters show that each habit appears in small proportion, and enumerated capital letters show that two habits appear about equally.

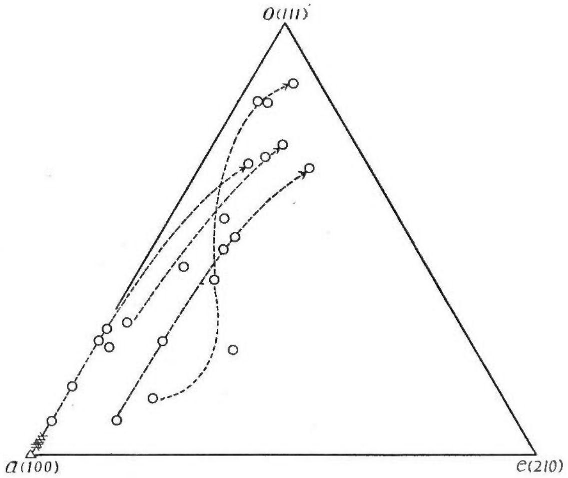

Fig. 8 Difference in the grade of habit variation according to grain size in different altered zones in the Kambe sericite deposit
○....ore deposit (sericite) ×....weak altered zone △....outermost zone

Kambe mine41)

The Kambe mine is composed of sericite-stibnite deposits seated in diorite. There, three zones of mineralization are observed from the inner to outer part of the deposit. Fig. 8, the triangular diagram of the three dominant faces, shows the mode of habit variations according to grain size in each zone. Here, it will be also understood that the grade of variation is high in strong mineralized zone of inner part, and is low in outer weak altered zone.

Hanaoka mine

If we classify the frequency of dominant habits observed on 158 specimens from the Hanaoka mine according to the different mode of occurrences, Fig. 9 can be obtained. As it is clearly visible from this figure, crystals in yellow ore which received the strongest mineralization are much more abundant in pentagonal habit than in cubic ones, and in weak altered tuff cubic habit is much abundant than pentagonal ones. This comparison is made on crystals of the same grain size. As already described, crystal habit in this mine varies according to grain size, and pentagonal habit increases as crystals become larger. Therefore, the grade of variation corresponds to the grade of mineralization in this case also.

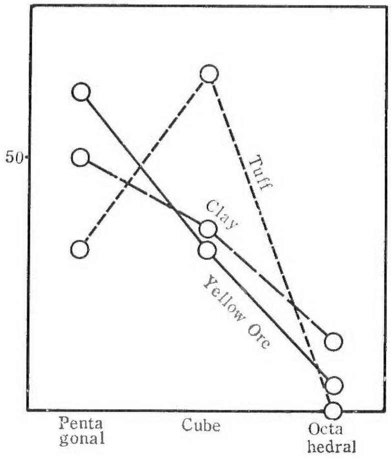

Fig. 9 Difference in frequency of appearance of three habits in the different modes of occurrences (Hanaoka mine) Vertical axis shows frequency of cases.

Goto mine43)

The Goto mine consists of many diaspore-pyrophyllite deposits embeded in sedimentary rocks of Tertiary age and granite porphyry which intrudes the former. The results of statistics, which were made on the ratio of surface area of *a*, *e*, and *o* faces according to the different grade of mineralization, are shown in Fig. 10. From this figure, it is clear that as the grade of mineralization becomes higher, the rate of frequency and development of *o*(*111*) increases, and that the crystals impregnated in mother rocks show cubic habit. On the other hand, cubic habit generally becomes predominant as crystals become smaller in this case also. Therefore, we can also consider that the grade of variation appears according to the grade of mineralization.

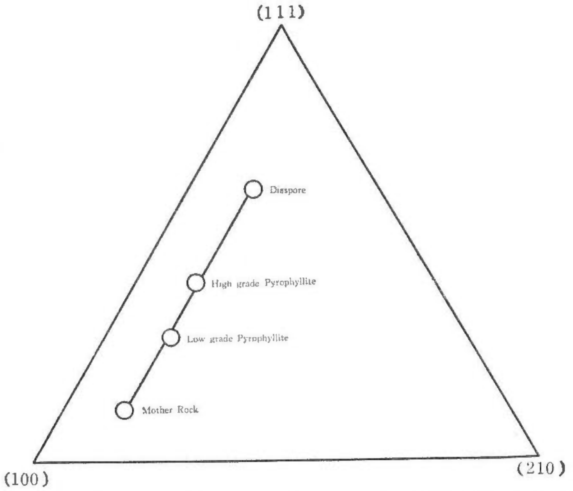

Fig. 10 Variation in average frequency of appearance of three faces with progress of mineralization (Goto mine)

Yonago mine[45]

The Yonago mine is composed of diaspore-pyrophyllite deposits embedded in diorite. Table 3 shows the result of observation concerning the differences of crystal habits between strong and weak mineralized parts within one specimen. Prescribing the same principle as above, it can be concluded that the difference in the grade of variation corresponds to the difference of the mineralization grade.

Table 3 Difference of Crystal Habits Between High and Low Parts of Mineralization Grade (Yonago Mine)

Sp. No.	Occurrence	Habit (No.) Mineralization grade high....low	Face Mineralization high....low
14	weak altd. green pyrophyllite	11, 10......10, 9, 3	*e*(*210*)......*a*(*100*)
15	〃	11, 10......3–9 rich, sometimes 9, 10	*e*......*a*
39	green pyrophyllite	19......11, 12	*o*(*111*)......*e*
45	country rock	3, 1......1	*o*......*a*
51	green-pyrophyllite	15, 18......11	*o*......*e*
53	clayey pyrophyllite	10......3 rich sometimes 9	*e*......*a*
73	low grade pyrophyllite	9 rich with 10, 3......1, 3	*e*......*a*

Number in the column of habit is habit number of the author. (Ref. to Fig. 1)

Although the results above show a different style of appearance respectively, the results that the grade of variation in crystal habit corresponds to the difference in the grade of mineralization have been obtained. Thus, crystals which are grown under a sufficient supply of ore solution, will show a wide change in habit within definite range of grain size, while, crystals which are grown slowly under a poor supply of solution, will show smaller change.

IV. 3 Series of Habit Variation

There are four series of variation. They are shown in Fig. 11 and are described below.

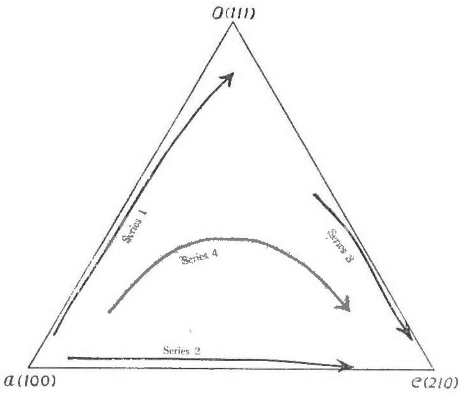

Fig. 11 Triangular diagram showing the sequence of habit variation

Table 4 Variation in Crystal Habit of Pyrite in Different Zones of the Yonago Mine

	Zone	Mode of occurrences		Amount and grain size of pyrite	Crystal habit of pyrite
Inner part of deposit ↑	Diaspore	upper	enclosed only in the red-pyrophyllite zone as small pockets or lenses	rare	octahedral +*e*
		lower	vein mainly embedded in red-pyrophyllite zone, but often impreg. in green-pyrophyllite zone as lenses	increase in amount and grain size	mainly octahedral
	Red-pyrophyllite	upper	surrounded by green-pyrophyllite zone	no	octahedral +*a*
		lower	sometimes silicified	rarely appears	
	Green-pyrophyllite	upper	surrounding red-pyrophyllite,	much, small size	pentagonal
		lower	diaspore impregnated in lower part	much, medium size	pentagonal +*o*, *a*
	Silicified zone	upper	silicified product of red- and green-pyrophyllite	no	cubic∼cubo-pentagonal and sometimes octahedral
		lower	common silicification which surrounds the green-pyrophyllite zone	rarely appears	
Outer part ↓	Country rock	upper	with sharp boundary between green-pyrophyllite zone	rarely appears	mainly cubic
		lower	gradually change to silicification zone	slightly increase in amount	cubic, rarely cubic +*o*, *e*

Series 1 The variation mainly from cubic to octahedral, including the case with small *e(210)* face.
Series 2 The variation mainly from cubic to pentagonal, including the case with small *o(111)*.
Series 3 The variation mainly from octahedral to pantagonal, including the case with small a*(100)*. This series appears very seldom.
Series 4 The variation from cubic to pentagonal through octahedral.

The causes of this difference is not so completely cleared.

Here the author intends to describe only his former observations and his present guesses.

Yonago mine[45)]

The following zonal distribution is observed from inside to outside of the deposit.

diaspore zone → red-pyrophyllite zone → green-pyrophyllite zone → silicified zone → mother rock.

Mineralogical characteristics and dominant habit of pyrite of each zone are tabulated in Table 4. From this table, the following relations are detected.

1. Pyrites show characteristic habit and series of variation in each zone. Namely, pyrite in mother rock is mainly cubic and shows series 2, and in the green pyrophyllite zone crystal habit is pentagonal and shows series 2; and octahedral and series 1 is particular to the diaspore and the red-pyrophyllite zone.
2. Octahedral face predominates in the depth where diaspore enriches.

Therefore, series of variations in mother rocks and the green pyrophyllite zones clearly differ from the series of variations in the red-pyrophyllite and the diaspore zones.

Goto mine[43)]

In the above case, the difference of series is observed in different zones within one ore deposit, while in this case, the difference is observed in zonal arrangement of many ore deposits within one province.

Within this province, many small diaspore-pyrophyllite deposits are distributed as illustrated in Fig. 12. From the mineral assemblages in each deposit, these deposits are classified into three zones, i.e., the corundum zone, the diaspore zone, and the pyrophyllite zone. These are zonally arranged from the higher temperature (deeper) to the lower temperature (shallower). The characteristics of deposits and predominant habit of pyrite in each zone are shown in Table 5 from which the following will be concluded.

1. Pyrite in the corundum and the diaspore zone shows series 1, while in the pyrophyllite zone pyrite shows series 2.
2. Predominant habit is cubic in the corundum zone, octahedral in the diaspore zone, and pentagonal or cubic in the pyrophyllite zone.

Therefore, the series of variation differs between deep and shallow zones, namely, series of *a→e* is characteristic of a shallow zone, and series of *a→o* is characteristic in a deep zone.

Thus, it can be said, in spite of many differences between the two, that the mode of differences of series is almost similar in two diaspore-pyrophyllite deposits

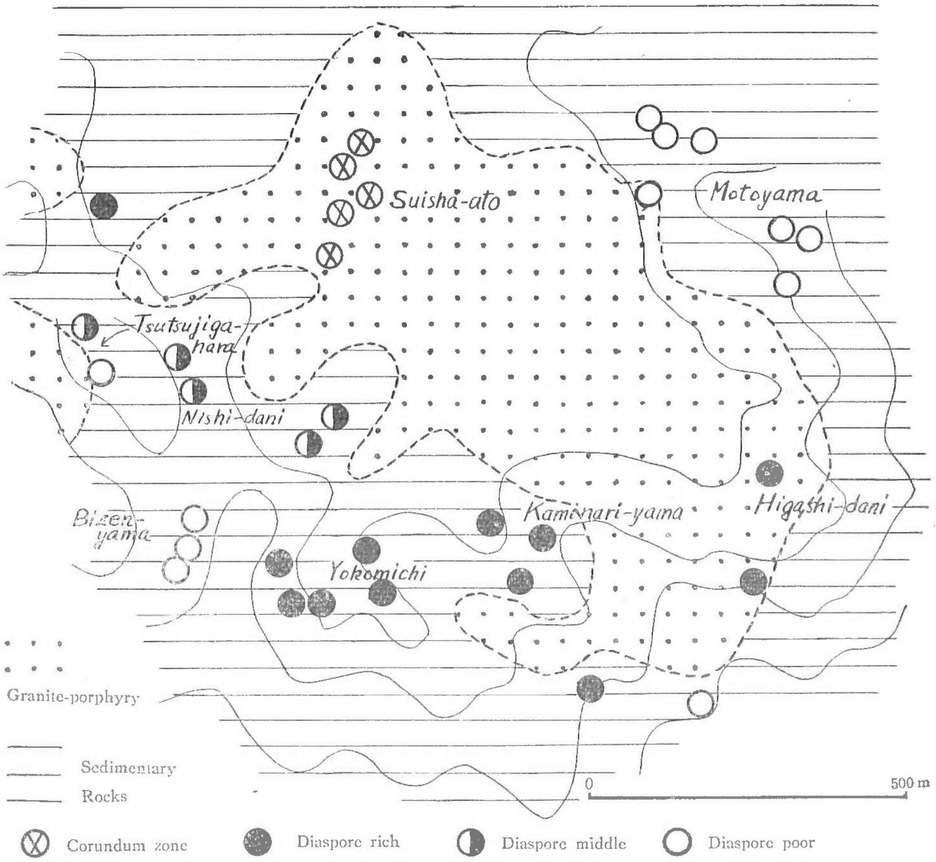

Fig. 12 Distribution and geological sketch map of ore deposits in the Goto mine

Table 5 Mineral Assemblage and Crystal Habits of Pyrite in Each Ore Deposit of the Goto Mine

Ore deposits	Zone		Mineral Assemblage			Pyrite		
			Corundum Andalusite Dumortierite	Dia-spore	Pyro-phyllite	Amount	Dominant habit	Series of habit variation
Suisha-ato	↑ inner or deeper facies	Co-rundum	○	◎	◎	○	Cubic	$a \to o$
Higashi-dani		diaspore zone	×	○	○	◎	octahedral+o	$a \to o$
Nishi-dani			×	◎	○	○	cubo-octahedral	$a \to o$
Yokomichi			×	◎	○	◎	octahedral+a	$a \to o$
Kaminari-yama			×	○	○	○	cubic+o, e	$a \to o \to e$
Obori	↓ outer or shallower facies		×	○	◎	○	octahedral+e	$o \to e$
Tsutsuji-ga-oka		pyro-phyllite zone	×	×	◎	○	cubic+e	$a \to e$
Bizen-yama			×	×	◎	○	cubic+e	$a \to e$
Moto-yama			×	×	◎	○	pentagonal+a	$a \to e$

× no or very rare ○ common ◎ abundant

which are different in the age of deposition, mother rocks, etc. That is, in both cases, series 1 is characteristic of the central part (higher temperature and lower pH) of the deposit, while series 2 is characteristic of the outer part (lower temperature and higher pH).

On the other hand, the author has observed some interesting phenomena and they will be described below:

Wanibuchi mine[38)]

In this case, as shown in Table 2, pyrite in brown and green clay almost shows series 2, pyrite in yellowish white clay, which occurs only in the central part of the deposit as a pocket, shows series 4. The yellowish white clay is a product of the strongest mineralization and its original rock is considered as a calcarious patch.

Hanaoka mine[36)]

From the result of statistics on many specimens from this mine, it is found that the differences of series in the different mode of occurrences can not be recognized; while the differences of series in the different ore bodies are detected as shown in Table 6.

Table 6 Difference in the Series of Habit Variation in Different Ore Deposits of the Hanaoka Mine
(Number shows frequency of cases)

Type or series / Ore deposit	1 $a \to o$	2 $a \to e$	3 $o \to e$	4 $a \to o \to e$	No. Total
Doyashiki	8	8	0	2	18
Ochiai-zawa	0	5	1	1	7
Kami-yama	0	7	0	0	7
Kan'nondo	0	5	0	0	5
Moto-yama	0	7	5	0	12
Tsutsumizawa	1	3	0	1	5
Oyama	1	2	2	7	12
Total	10	37	8	11	66

Furthermore, the following tendency is generally observed.

1. Pyrite crystals impregnated in weak altered mother rocks almost show series 2.
2. Pyrite, which are crystallized near the earth's surface, such as impregnation in clay altered by hot spring action, generally shows series 1.
3. Pyrite in the Kuroko deposits shows all of the series, yet it is comparatively more abundant in series 4.

Complete generalization may not be obtained yet from the above observation alone. However, while the difference of the grade is considered mainly controlled by the difference of the mineralization grade, this difference will be looked upon as being controlled by change in the physical chemical conditions, such as temperature, acidity or minor elements in ore solution. For instance, observations on the diaspore-pyrophyllite deposits show that the series change from 1 to 2* as temperature decreases or as the acidity becomes weak alkalic. The fact that pyrite impregnated in mother rocks are generally series 1 is also one proof for this consideration. The fact that pyrite in Kuroko deposits includes various series, is considered to be caused by the telescoping characteristics of the deposits.

Furthermore, the fact that the series differ in the different ore bodies in the Hanaoka mine is also considered as another proof for the above consideration.

Considering the cause of the difference of the series only from the above observations, it seems that pyrite formed under lower temperature shows series 2 and under a comparatively higher temperature shows series 1; however, it would be too far to conclude that the difference of series is controlled only by temperature condition.

Therefore, further studies are required, since which series will appear under certain conditions is the direct result of integrating the complicated factors.

IV. 4 Summary of the Replacement Type Pyrite

From the above results, observations on habit variations in the replacement pyrite are summarized below.

1. This sort of pyrite has the following morphological characteristics when it is compared to the vein pyrite.
    a. Pyritehedral face $\{hk0\}$ almost consists of two or three faces.
    b. Kinds of pyritehedral faces which predominate, vary according to habits.
    c. Vicinal faces develop remarkably.
2. The replacement pyrites show a wide range of grain size within one specimen, and even very fine crystals under the 200 mesh usually show good crystalline state.
3. The statistical observations on many crystals within a narrow range of environment, which is considered the crystallization under same conditions of growth, show that the frequency of appearance of habits or dominant faces varies according to the grain size.
4. The variation of habit from small to large grain has this general definite tendency.

    Cubic habit→octahedral habit→pentagonal habit
    $a(100) \rightarrow o(111) \rightarrow e(210)$ or $\{hk0\}$
5. The grade of variation differs in different specimen, and this difference appears according to the difference of the mineralization grade.
6. The series of variations is classified into four types. The reason for the appearance of the difference of series has not yet been clarified; however, it is presumed that the difference will mainly be related to the physical and chemical conditions of environment, such as temperature or acidity.
7. Generally speaking, each habit has the following tendency of occurrence.

    Cubic habit...in the weak altered mother rocks; in the weak mineralized

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* See p. 18

zone; in the highest and the lowest temperature zone of pyrophyllite-diaspore deposits; and in range of small grain.

Octahedral habit...in moderate temperature zone of pyrophyllite-diaspore deposits and in strong mineralized zone. Generally, this habit predominates in sericite deposits, alunite deposits, pyrophyllite-diaspore deposits and in altered clay by hot spring action. It shows intermediate position of variation between cubic and pentagonal habit according to grain size.

Pentagonal habit...in comparatively lower temperature zone in pyrophyllite-diaspore deposits and in strong mineralized zone in general. Generally, it predominates in Kuroko deposits more than in other clay deposits. Looking from the standpoint of variation according to grain size, this habit's frequency increases as crystals become larger.

Among the above results, the most important new discovery is the phenomenon of variation according to grain size. This phenomenon, as previously described, is interpreted as the variation which occurs with crystal growth. The variation according to grain size was discovered on other minerals simultaneously by other researchers. A. Pabst found this on garnet in 1943, and P. Ramdohr reported the similar phenomenon of magnetite in 1955. Pabst did not interpret its genesis, while Ramdohr considered this as function between growth rate of the face and the grade of supersaturation of the mother solution.

However, the author would like to seek its brief origin into the structural point, and to interpret as the successive variation according to crystal growth from the next facts; i.e., 1) The fact that the tendency of variation is nearly regular in almost every specimen from different occurrences, 2) the morphological characteristics, such as remarkable development of vicinal faces, style of construction of pyritehedral faces, and the surface structure of faces.

The fundamental idea of this consideration consists in the layer growth theory, which was proposed theoretically by Kossel[39] and Stranski[34], and was confirmed experimentally by Bunn and others[41].

It is considered that crystals do not grow by three dimensional precipitation around the nucleus but grow by piling up the layers, which spread two-dimensionally by adsorption and adhesion of the crystal molecules at the kinks of layer edges.

Now, if we consider the variation in habit according to grain size from this viewpoint, it will be thusly interpreted. In the case of pyrite, it is considered that the two-dimensional layers spread mainly on *(100)* plane, and not on *{hk0}*, *(111)*, and other faces. This consideration can be detected from the surface structure of each face, such as the growth layers, striations, etc. For instance, surface structure observed on *(100)* and *(111)* faces show the closed form, while that on *{hk0}* and *(210)* faces show only the straight line parallel to the edge with *(100)* face. This shows that *{hk0}* and *(210)* faces consist of the edge of the layers which spread on *(100)*. Most of the triangular forms on *(111)* face are considered to consisting the layer edges on *(100)*, but the question whether the layers do or do not spread on *(111)* in some cases, still remains unsolved, because the surface structure of *o(111)* face shows the closed form, and because there is a series of *o→e*, though this series frequently does not appear. However, if this series is observed to smaller crystals, there are some possibilities that this series be corrected to the series of $a \rightarrow o \rightarrow e$. Therefore, the writer would like to leave this question as a future problem.

Now, the mode of spreading and piling of the layers on *(100)* will be traced. According to observations by Bunn[2)], and by A. F. Seager[32)], a growth layer which starts from the center spreads outwardly and laterally. The rate of spreading becomes slow as the layer is going outwards, and the lateral spreading ceases when it reaches the edge of the prespread layer. Before this layer ceases its spreading, a new layer begins to form and continues its two-dimensional spreading. Thus, crystal grows by spreading of the two-dimensional layers and the piling of these layers.

On the other hand, it is theoretically explained that the probability of accretion of the molecules on the kinks of the steps or the edges is much higher than that on the surface of the layers when the molecules are transported from solution to the surface of growing crystals. From this point, the layer growth theory has started.

From this consideration, it is supposed that when the molecules are insufficiently transported from solution, the molecules will be mainly adsorbed at the kinks and not adhere on the surface, and two-dimensional layers will mainly spread. Therefore, the layers always reach the edges of the former spreaded layers, and the resulting crystal will not change its external form throughout the course of growth; i.e., pyrite crystal will show cubic habit. Contrary to this process, if the molecules are sufficiently supplied, the better part of the molecules will be adsorbed at the kinks of the edges, but simultaneously the spare molecules will adhere on the surface of the layer and make a new aggregation of the molecules. This aggregation becomes the nucleus of the new layer. Therefore, the frequency of the beginning of the new layers, i.e., the rate of piling of the layers, will increase more than the former case. Consequently, the layers which start later will successively stop their spreading before they reach the edges of the former layers; thus, the external form of the growing crystal will change to a polygonal form having more faces than the cube. The external shape will appear related to the contour of the layers. If the shape of the layer is a cube, the surface which consists of the edges of the layers will become a $\{hk0\}$ face, and pentagonal habit will appear. If the shape is cube parallel to the edge $o \wedge a$, an octahedral habit will appear. If the shape is octagonal, crystal will show a habit consisting of three faces *a*, *o*, and *e*.

Furthermore, if the impurity molecules such as arsenic are eventually adsorbed at the definite directions of the layers and make up a stable two-dimensional complex together with the structure of the layers, the spreadings in this direction will be interrupted and cause to form an octahedral habit.

With this consideration several facts which have been observed on crystal habit of the replacement pyrite will be satisfactorily explained. That is, the facts, such as the characteristics of pyritehedral faces, the remarkable development of vicinal faces, and striations on *[001]* zone, are considered as resulting from the piling of the edges. That the vicinal faces consisted of the edges of the layers was experimentally ascertained by Bunn[2)] and Mier[32)]. The facts that vicinal faces develop mostly on *[001]* zone and that the pyritehedral face usually consists of two or three faces are considered as the result that the surface which is composed of the edges of the layers can not form a simple *e*(*210*) face resulting from the rapid piling of the layers. The phenomenon of habit variation according to grain size can also be interpreted satisfactorily as the result of the above process. Furthermore, the fact that the grade of habit variation is strong under forceful mineralization, and weak under strengthless mineralization, is accounted for the change in the ratio of the rate of two-dimensional spreading to the rate of three-dimensional piling. One of the arguments which support the explanation above is that the grade of variation is mainly controlled by the grade of mineralization, while the differences in the series of variation is presumed to be related to the change in physical or chemical conditions of the environment.

Furthermore, viewing the mode of occurrences in which each habit predominates, cubic habit occurs in an environment unsuitable for crystallization, whereas octahedral and pentagonal habit predominates in a suitable environment. This tendency is considered as supporting the above explanation.

However, (1) why the layers spread mainly on the (*100*) face, and (2) why the surface, which is composed of the edges of the layers, forms a rational and simple index face are two questions that arise from the above explanation.

The solution to the first of the two questions should be seeked for in the sense of structural characteristics of the face. If the mesh area of the dominant faces are calculated according to the Donnay-Harker's Law[9)], the sequence of theoretical predominancy of faces is as follows;

(*111*), (*100*), (*210*), (*211*), (*110*)....

It is clear that three faces *a*, *o*, and *e* show particularly high predominancy, yet *a*(*100*) face does not predominate more than the other two, and the above sequence is not perfectly similar to that in nature. Therefore, this question will be unable to explain only by the geometrical characteristics of the structure. It will be necessary, perhaps, to consider the difference in the binding forces of the different faces at the surface, such as van der Walls force. Calculation of this force on pyrite is very difficult at the present time. However, we will here recall the idea of incomplete and complete plane of Stranski[35)], which leads the way of layer growth theory. As the result of his calculation on the binding energy on different faces of NaCl, Stranski concluded that {*001*} face is the only one physically possible plane to appear; he named this the complete plane. The other {*110*}, {*111*}, etc. are composed of regular stepwise pile of (*001*) and (*100*), and they are named incomplete plane. Although the binding energies cannot be calculated on real pyrite, it is considered that the case of pyrite will be similarly explained by the above idea.

Why the surface of the piling of the edges forms a low index face will now be explained. According to the experiment by Bunn, etc.,[2)] crystal growth is promoted just by the existence of high index surface at the edges of the layers. That is, most of the molecules do not precipitate or are not adsorbed on the perfect part of the edges, but on the imperfect part, such as the kinks. Therefore, as long as the imperfect part is still alive, crystal growth will be maintained. Conversely, when the edges of the layers or the surface of pile of the edges become perfect low index faces, only then will crystal growth be stopped. Therefore, it is the natural result of crystal growth that the pile of the layer edges forms the faces which conform to the law of simple index face.

V. Pyrite of the Vein Type

Pyrite from the following occurrences was classified to the group of vein type.

1. Pyrite crystallized in druse of vein type deposits.
2. Pyrite crystallized in vein together with the other ore minerals or pyrite enclosed in gangue minerals.
3. Pyrite crystallized as euhedral crystals in chalcopyrite having slight space between the both minerals.
4. Pyrite in veins of the network deposits or pipelike deposits.

These pyrites, which differ from the case of the replacement type, are considered as the direct precipitation from ore solution. They show different state in the mode of crystallization or state of crystallinity from the replacement pyrite. For instance, if it is compared with the replacement pyrite, it is generally larger in size, and uniform in distribution of grain size and is poor in variety of habit within a small scope of environment. Therefore, treatment of this type of pyrite differs considerably from that of the replacement type. It is convenient in this case to observe variation in habit according to the differences of coexisting minerals, to the different depth of vein and to the different position of vein, etc.

Pyrite crystals of this type have some morphological characteristics as it is illustrated below.

1. Vicinal faces are not so remarkably developed as that of the replacement type.
2. Pyritehedral face is composed of *e(210)* face alone.

V. 1 Variation According to the Differences of Coexisting Minerals

Some examples in which habit varies according to the differences of coexisting minerals are described below.

Coexisting with enargite

Pyrite coexisting with enargite always shows simple octahedral habit. However, octahedral habit appears only at the vicinity of enargite crystals, and the pyrite crystallized at some distant part from enargite crystals shows cubic habit. Specimen from Aiki village, Nagano pref., from the Hokuetsu mine, Niigata pref., from the Oage mine, Aomori pref., etc. are excellent examples. It is considered that this phenomena is caused by the selective adsorption of As on *o(111)* face. About this, detailed consideration will be described later. But, there are many reverse cases; e.g., some pyrites coexisting with other minerals or pyrites containing no As often show octahedral habit, and at the same time, some pyrites do not show octahedral habit even when they contain a high amount of As.

Hanaoka mine

Pyrites, which are crystallized in a druse of massive yellow ore at the third level of Doyashiki ore body, are associated with barite alone on one side of the specimen and quartz alone on the other side. The distance between their outer surfaces is within a few centimeters. The result of statistics of frequency of different habits on both sides is shown in Table 7. It is clear that pyrites coexisting with quartz show only octahedral habit, yet the other side is mainly cubic habit.

Table 7 Difference of Crystal Habit of Pyrite According to Different Coexisting Minerals (Hanaoka Mine)

Habit / Coexisting minerals	Cubic (%)	Cube+$o(111)$ (%)	Cubo-octahedral (%)	Octahedral +$a(100)$ (%)	No. counted
Barite	17.3	80.0	0.9	1.8	112
Quartz	0	0	1.0	99.0	133

Ogoya mine

In the case of pyrite from the Ogoya mine, as general, pyrites coexisting with chalcopyrite or enclosed in chlorite show octahedral habit and pyrites crystallized in quartz vein are cubic or cubo-octahedral crystals, while pyrites coexisting with barite always show cubic habit.

The above described are all instances which the writer has observed previously, and it is rare in general that crystal habit clearly changes according to the different coexisting minerals, except in the case of enargite. It seems that there will be some relations between barite and cubic habit, but they are not so distinct as in the case of enargite.

The habit variation by the coexisting minerals seems to show that the selective adsorption of foreign molecules, or special condition of growth which is shown by coexisting minerals, or the both together have influence on changes in crystal habit of pyrite. However, such phenomena are not generally observed, and this fact is considered as a negative proof for the explanation that the impurity particles have a strong influence on habit. In the case of enargite, selective adsorption of As is considered to change habit to octahedral, but influence of As on habit is limited within a narrow scope of growth conditions. The writer will describe this later.

V. 2 Implanted Crystal and Enclosed Crystal

In some cases, crystal habit of pyrite in druse (implanted crystal) differs from that of euhedral crystals enclosed in the other minerals. In the case of the Ashio mine, pyrites in druse are generally cubic habit with curved faces and rarely show small cubic crystals having largely developed $s(321)$37). Contrary to this, pyrites enclosed in massive chalcopyrite having narrow space between both minerals show various kinds of habit such as cubic, octahedral, pentagonal, peculiar habit which has developed $t(421)$, and sometimes deformed habit. Crystalline state of the latter is much better than the former40). Pyrites in the Ogoya mine generally show octahedral habit, but crystals enclosed in chalcopyrite in the similar mode of occurrences as the case above mainly show pentagonal habit. In the "Minerals of Japan", it is described that pyrites of the same occurrence from the Washiaimori mine show various kinds of habit, whereas pyrites in druse are cubic habit only.

Although pyrites of the above occurrence rarely appear, their habit differs greatly from crystals in druse, and generally show various kinds of habits within a narrow scope. The cause why this difference appears has not been clarified yet, but the mechanism of crystallization is certainly different between the both. That is, the pyrites in druse are considered as direct precipitation from ore solution, while the pyrites enclosed in chalcopyrite are considered as differential crystallization from mixed ore solution or liquid melt of chalcopyrite and pyrite on the way of its solidification.

V.3 Differences of Crystal Habits Between the Inner and Outer Parts of Vein, and Between Veins and Mother Rocks

These differences are considered as terminating from the differences in the cooling rate of the solution. Several observations are described below.

Ogoya mine

As shown in Fig. 13, pyrites in the inner part or druse of a pyrite-quartz vein are large and show simple octahedral habit, pyrites in the outer part are small

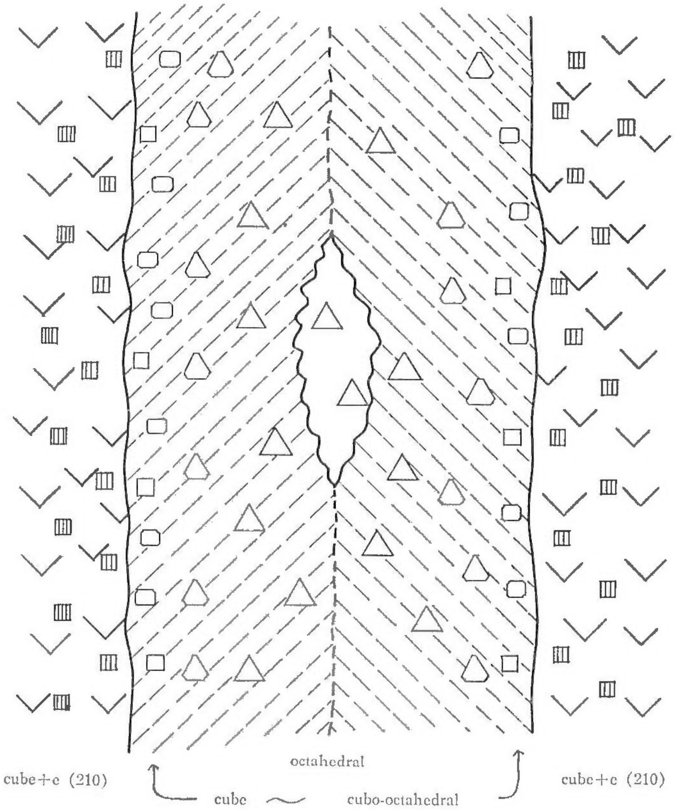

Fig. 13 Differences of crystal habits of pyrite between the inner and outer parts of a vein, and between vein and mother rock (Idealized figure) (Ogoya mine)

and mainly cubic habit or cube+small *o*. Similar relation is also observed in the other chalcopyrite-chlorite veins.

Kishu mine

Pyrites in the inner part of chalcopyrite-chlorite veins show pentagonal habit, while cubic face develops, and frequently cubic habit occurs near the wall of the veins.

Osarizawa mine

In the Murasaki vein, pyrites which crystallized toward the inner part of druse have octahedral habit, and pyrites in the wall side of the vein are mainly minute cubic crystals.

Similar relations are often observed in many cases. Cubic face generally develops more in the wall side than in the central position. The reverse relations have been unobserved. When pyrites in the central part of a vein are cubic, pyrites in the wall part are also cubic and do not show any other habits. As it is seen in the case of the Ogoya and Osarizawa mines, grain size of pyrites in the wall part is generally smaller than the grain size in the inner portion. Considering this tendency, it may be concluded that cubic face will develop under the condition of rapid cooling.

Similar relation is observed on the differences of habits between the vein and country rocks. Generally speaking, pyrites in country rocks are simple cubic or cubic with a small *e* face, and an octahedral face rarely appears. Octahedral and pentagonal habits do not appear in country rocks, except in a few cases, such as the Ani mine. In the Ani mine, pyrites in the country rocks show pentagonal

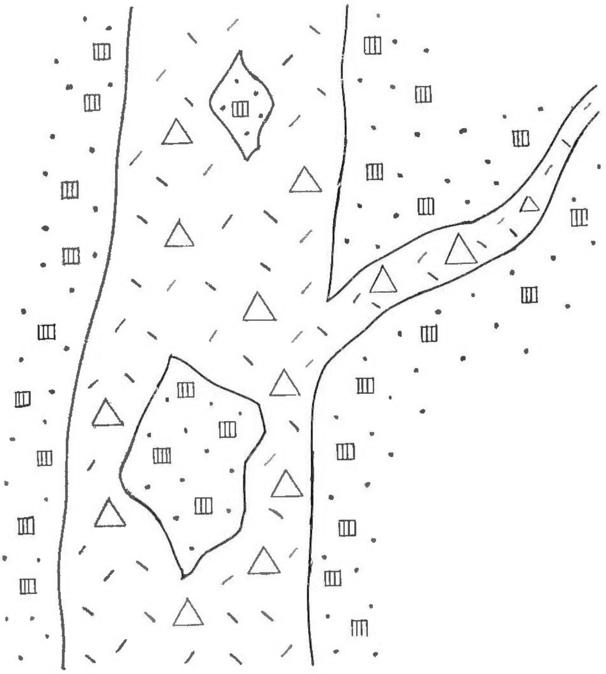

Fig. 14 Differences of crystal habits of pyrite between in vein and in mother rock (Udo mine)

habit, but all pyrites are negative crystals.

The pyrites in the country rocks usually show cubic habit, but on the contrary, pyrites in the veins show different habits according to the differences of the veins. Fig. 14 schematically shows this relation which is observed in the Udo mine. Crystals in this vein always show octahedral habit, even they crystallize in small veinlets or branches, while crystals impregnated in country rocks have cubic habit, even when they crystallize in the horse stones in the vein. It is considered that this difference of habit is caused by difference in the cooling rate and crystallization temperature.

Similar facts are the difference of habit between the inner and outer parts of vein. Thus, it is considered that in pyrites crystallized under rapid cooling condition or low temperature, or under unsuitable condition for crystallization, cubic face will develop more than other faces.

V. 4 Difference According to the Depth of Vein

It seems rather rare that different habits occur according to the depth of a vein.

According to the report on the Yoshino mine by K. Kinoshita and K. Muta, they ascertained that the cubic habit predominates in the upper and lower parts of the ore body, while pentagonal habit predominates in the middle portion.

As shown in Table 8, the writer observed the main No. 1 vein in the Ogoya mine that pyrites in this vein mainly show octahedral habit, but accessory *a*(*100*) face predominates in lower, accessory *e*(*210*) face predominates in the upper part of the vein, and in the middle part of the vein *o*(*111*) face develops. Furthermore, after inspecting the difference of habit in a metallogenic province of the Ogoya district, including the Kanehira and Iwabuchi mines, it was found that pentagonal habit predominates in the shallower part of the zonal arrangement, and octahedral habit predominates in the deeper part. Namely, crystal habits differ in different depth in a vein or, in this case, in a zonal arrangement. However, this kind of difference is not usually observed in other cases.

Table 8 Variation in Crystal Habit of Pyrite According to the Depth of Vein (Ogoya Mine)

Mines		Dominant metals	Dominant habit	Development of faces				
				e	*o*	*a*		
Iwabuchi		Pb, Zn	pentagonal +*o*	L	S	—	↑ shallow	*e* (*210*)
Kanehira		Cu, Pb, Zn	penta-octahedral	M	M	—		
Ogoya	upper	Cu	octahedral +*e*	S	L	—		*o* (*111*)
			octahedral	—	L	—		
	lower		octahedral +*a*	—	S	S		*a* (*100*)
			cubo-octahedral	—	M	M	deep ↓	

L....Large M....Middle S....Small — No

For instance, almost all pyrites show pentagonal habit in different depths of the veins in the Kishu mine. In the Ikuno mine, pyrites are only the habit of cube with a small *o* face in almost every depth of the veins. As the result of observations on pyrites from various veins of Au, Ag, Pb, Zn, Cu, etc. of more than twenty mines which are distributed in the vicinity of the Nikko and Kidogasawa mines, which belong to the same metallogenic province, the author found that pyrites from an assortment of veins showed only cubic habit, and did not vary according either to the depth of a vein or to the different mines which were situated in different depths of zonal arrangement.

The author observed pyrites from more than ten mines which were vein deposits of different ores belonging to a metallogenic province of the Nishimurayama district, Yamagata pref., and he found that every pyrite in different parts of this district showed cubic habit, even though the zonal arrangement was observed in a vein as well as in the whole district.

The above fact makes a remarkable contrast to the pyrites of the replacement type, which show a notable variety of habit within a narrow scope. This contrast is considered to be caused by the difference of crystallization process between the two types. Namely, the origin of this contrast is imagined that the replacement type is in telescoping condition, and the crystallization environment of the vein type is not telescoping but it is the condition of a comparatively slow gradient in temperature, pressure and acidity.

The genetical differences between the deposits, such as the Ogoya and Osarizawa mines in which pyrites are rich in variety of habit, and the deposits, such as the Kishu mine in which habit is very simple, it is considered to be searched out at this point.

Observing the fact that crystal habits do not vary so remarkably in different parts of zonal arrangement, it can be said that habits are controlled more greatly by the change in physical conditions, such as temperature gradient or cooling rate rather than the change in chemical conditions of ore solution.

V. 5 Habit Change According to Crystallization Stage

In some cases, crystal habits vary according to the different stages of crystallization. For instance, although it is not a quantitative observation, the writer observed that in the Osarizawa mine, cubic habit mainly occured in the earlier vein, and pentagonal, sometimes octahedral habit, predominates in the later vein. Of course, there are some cases in which crystal habits are same in different stages. For an example, in the case of the Nishimurayama district, pyrites show cubic habit in both the earlier Pb-Zn-Cu veins and the later Cu-quartz veins, which cuts the former vein. In the Funauchi mine, pyrites in the main Cu-Pb-Zn veins and pyrites coexisting with triangular chalcopyrites, which are considered as the later crystallization than the main veins, show cubic habit, and no differences are observed between them.

Pyrites crystallized in a druse sometimes show different habits according to the different crystallization stages. From the specimen out of the Arakawa mine, it is sometimes observed that small crystals grow on and cover the large crystals, and each shows a different habit. The writer observed the following three examples in the collections of Geological Survey of Japan.

1. Small pentagonal or cubo-pentagonal crystals grow on large cubic crystals.
2. Fine cubic crystals grow on large cubic ones.
3. Small cubic or cubo-octahedral crystals grow on large cubic ones.

That is, occasionally habit varies according to the different stages and sometimes it does not. When habit varies, it seems that the earlier one shows cubic habit, and in later stage *o*(*111*) or *e*(*210*) faces appear or predominate. Of course, this relation is not so strictly ascertained. There will be the reverse relation in some cases, especially in the latest generation of whole crystallization stage.

Although there are very few examples, it seems that generally a(*100*) face may predominate in the earlier stage, and *o*(*111*) or *e*(*210*) faces will develop in the later stage. It is also assumed from the former observations that *a*(*100*) face will begin to develop once more in the latest stage of crystallization.

V. 6 Summary of the Vein Type Pyrite

The observations of the vein pyrites are summarized below.

1. The vein pyrites have the following morphological characteristics, when these pyrites are compared with the replacement pyrites.
    a. Pyritehedral face usually consists of only *e*(*210*) face.
    b. Vicinal faces do not develop so remarkably like that of the replacement pyrites.
2. Generally, the range of grain size within a specimen is very narrow. Pyrites within a small scope of occurrence are not so rich in variety of habit as that of the replacement pyrites.
3. In some cases, habit variation appears as resulting from coexisting special minerals; however, this is not general phenomena.
4. Crystal habit of enclosed pyrites differs from that of implanted pyrites in some cases. For instance, pyrites enclosed in chalcopyrite with a narrow space between both minerals generally show different habits from that of druse in the same vicinity. The former is rich in variety of habit.
5. In many cases, the rate of development of the faces changes from the inner to the outer part of the vein. In general tendency *a*(*100*) face develops more in the outer part than in the inner. This change is considered due to the difference of cooling rate.
6. Generally, crystal habit of pyrite in vein differs from that in country rocks. Pyrites in country rocks have cubic habit and show the series of *a*→*e*, but *o*(*111*) face appears very rarely. Pyrites in vein show various habits and habits are peculiar to each vein.
7. Except for a few special cases, habit variation according to the depth of a vein is not very remarkable. This tendency is also observed in many ore deposits which are situated at different positions of zonal distribution within a metallogenic province. If the variation is observed according to the depth, it seems that the variation is in sequence of *a*→*o*→*e* from the lower to the upper, and in the still upper part *a*(*100*) face develops again.
8. Within a mine or a metallogenic province, pyrites are rich in variety of habit in few cases, and show almost a definite habit in the most cases.

This difference is considered due to the difference of the temperature gradient.

9. In some cases, pyrites vary in habit according to the different stages of crystallization.

The most striking phenomenon among the above observations is the contrasting relation that crystals of the vein pyrites are not rich in variety of habit within a fairly wide range of circumstances except for a few special cases, while habits of the replacement pyrites are very rich in variety within a narrow scope of occurrence. As one of the causes of this dissimilarity, the writer should like to point out the difference of temperature gradient between them. Namely, the replacement pyrites are considered as a telescoping crystallization product*; most of the vein pyrites are considered as precipitated from environment of which temperature condition does not fluctuate so strongly. Therefore, this difference shows that temperature condition is one of the controlling factors upon habit variation.

The next noteworthy fact is that pyrites do not show much variation of habit according to different depths of a vein or of a metallogenic province, while these pyrites show much variation according to the horizontal position across a vein, e.g., there are considerable differences in the inner and outer parts of a vein and between vein and country rocks, and also cubic face is predominant more in the wall side of vein and in country rocks than the vein itself. This fact shows that the crystallization temperature and the cooling rate are one of the controlling factors of habit variation, and the condition of either rapid cooling or low temperature will cause a cubic face to develop. Furthermore, the fact that the vein pyrites show almost a definite habit in different positions, in zonal distribution, and in many veins which belong to a metallogenic province, is considered to show crystal habits of pyrites are more sensibly effected by the physical conditions such as temperature or cooling rate than by the chemical conditions.

The third important point is that cubic habit mainly appears in the environment which is unsuitable for crystallization; e.g., cubic habit appears in the country rocks, or in the outer part of the vein or in the early or the latest stage of crystallization. Namely, cubic habit has the general tendency to appear in both the extreme parts of higher and lower temperatures, and under rapid cooling conditions as well as under the condition in which there are many disturbances for crystal growth. Conversely, pentagonal and octahedral habits are comparatively predominant in the environments of which conditions are suitable for crystallization; i.e., these habits occur in the inner part of the vein, under slow cooling condition, and under slow crystallization at the moderate temperature. This tendency is very similar to that of the replacement pyrites.

Finally, the point that is worthy of some recognition is that variation resulting from the difference of coexisting mineral is not generally observed but observed only in special cases. This fact proves to support the idea that the habit variation caused by selective adsorption of the impurities will not be the general case as the crystal chemists presume. The detailed discussion of this problem will be described later.

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* Here, the word " telescoping " means the environment of ore precipitation of which temperature and pressure gradient is narrow, and does not mean the rapid cooling condition of individual crystals.

VI. Pyrites of Other Occurrences

The pyrites from the following occurrences are mainly described above;

1. pyrites in the epithermal replacement deposits
2. pyrites in the country rocks and altered clay near ore body as well as in altered clay by the hot spring action
3. pyrites in the epithermal vein deposits
4. pyrites in the pyrophyllite-diaspore deposits as well as other kinds of clay deposits of hydrothermal origin

and pyrites are not described from or of

1. the kieslager deposits
2. the contact replacement deposits
3. the mesothermal and the hypothermal and the pneumatolytic vein deposits
4. sedimentary origin
5. magmatic segregation origin
6. pegmatites
7. sublimation in druse of lava

About these pyrites, the writer has not yet made systematic observations. Therefore, he will attempt to discover some general tendencies from his former observations and data described in literatures.

First, if crystal habits described in the "Minerals of Japan" are classified by the different modes of occurrence, Table 9 is obtained. In this table, "variable" represents the cases in which crystals are rich in variety of habit, "uncommon" represents the special habits of which the first predominant face is uncommon face, "rock" represents both the sedimentary origin and the sublimation pyrites in lava, and the number is frequency of appearance which is counted one for one locality. Since the data collected in the "Minerals of Japan" do not represent general appearance in a locality but mainly describe characteristic habit, it is dangerous to draw a general conclusion from this table only. Yet, the following tendencies are recognized as preliminary.

Table 9 Frequency of Appearance of Different Habits in the Different Modes of Occurrences. (Statistic Made on Data Described in the "Minerals of Japan 3rd. Ed.")

Occurrence	Crystal habit					Total
	Cubic	Pentagonal	Octahedral	Variable	Uncommon	
Vein	6	10	3	4	0	23
Contact	3	2	0	2	0	7
Rock	5	1	1	1	1	9
Replacement	1	0	1	3	1	6
Clay deposits	0	1	0	3	1	5
Kieslager	2	0	0	0	0	2
Total	17	14	5	13	3	52

1. Pyrites in vein deposits are rich in "single" and poor in "variable". Pentagonal occurs at the highest frequency and cubic as the next, while octahedral habit is rare. One among the numbers of octahedral is the case of coexisting with enargite.
2. Pyrites in the contact deposits do not show characteristic feature except that the cubic habit shows rather higher appearance than that of the vein pyrites.
3. In the case of "rock", cubic habit predominates by an overwhelming majority. In this case "*o*", "uncommon", and "variable" are of the exceptional occurrences; i.e., "*o*" is pyrite from druse of basaltic lava in Oogago, "variable" is pyrite from Subara of which the mode of occurrences is not clear but is supposed as impregnation in clay, and "uncommon" is a peculiar habit which mainly consists of β and this peculiar habit is the only one species observed in specimens from Mobara of which the normal habit is cubic one. Therefore, the last two cases can be excluded from consideration.
4. Frequency of "variable" is higher in the replacement and clay deposits than in the other cases.
5. Pyrites from the kieslager deposits show only cubic habit.
6. Viewing the frequency of each habit, cubic habit shows the highest frequency and the next are pentagonal and "variable". Octahedral and "uncommon" are very rare. Three instances out of the five of octahedral are from special occurrences such as druse of lava and coexisting with enargite.

From the above tendencies, it will be considered as follows.

1. Tendencies of the vein, the replacement, the clay deposits, and rocks almost completely agree with the writer's observations described in the previous two chapters.
2. Pyrites from the contact deposits show intermediate tendency between the replacement and vein types, and are higher in frequency of cubic habit than that of the vein type.
3. Cubic habit seems to predominate under high or low temperature and under an environment of which the condition is considered to be unsuitable for crystallization of pyrites.
4. Octahedral habit shows less frequency than the other habits and appears in the exceptional occurrences.

VII. Relation Between As and *o*(*111*)[44]

In trying to ascertain how extensively the presence of impurity molecules have an influence on crystal habit, the author made a spectrochemical study of the minor elements in pyrites with his co-worker, K. Takahashi. Analogized from the relation between enargite and octahedral habit, he took the relation between As and *o*(*111*) face seriously and examined the minor elements in pyrites from 6 mines; Kambe, Wanibuchi, Udo, Ogoya, Kishu, and Hanaoka. Consequently, the following facts became clear.

1. No definite relations are observed between As % and the rate of develop-

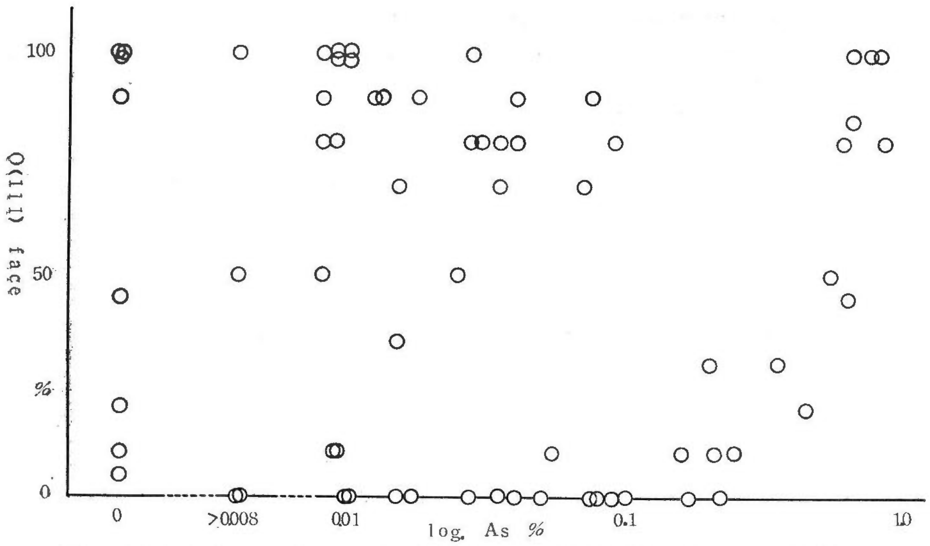

Fig. 15 Relation between As contents and development of *o(111)* face. Percentage of *o(111)* face shows percentage of the surface area of the face.

ment of *o(111)*, when the relation without any considerations of the localities or occurrences are examined (Fig. 15). Therefore, it can be said that adsorption of As is not the strongest factor superior to all the other factors which have influence on the development of *o(111)* face.

2. In the case of the Kambe mine, it becomes clear that the selective adsorption of As on *o(111)* face is promoting the development of the face (Fig. 16). This adsorption carries out not in the form of the enargite particles, but perhaps, in the form of As elements.

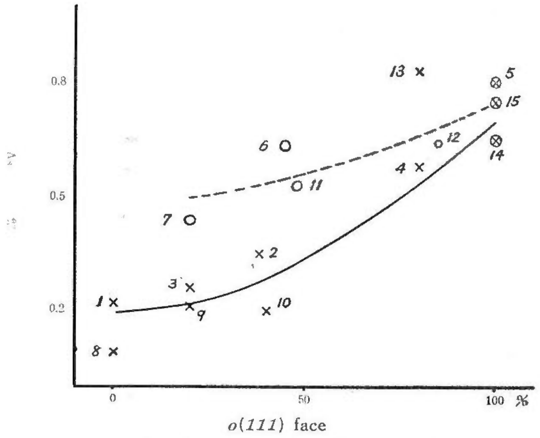

Fig. 16 As contents and surface area of *o(111)* of pyrite from the Kambe mine
×....shows crystals consisting of *a(100)* and *o(111)* faces
○....shows crystals consisting of *e(210)* and *o(111)* faces

3. However, clear relation between As % and development of *o(111)* is observed only in the above case and not in the other five mines.

4. The grade of As content is considered as one cause of this difference, yet many instances were observed in which pyrites containing large amounts of As did not show octahedral habit, and on the contrary, pyrites containing no As showed octahedral habit (Table 10).

Table 10 Average As % and Dominant Habit of Pyrite in Each Mine

Name of mine	Type of ore deposit	No. of analysis	Average As (%)	Dominant habit
Kambe	stibnite-sericite hydrothermal dep.	15	0.480	octahedral
Hanaoka	Cu-Pb-Zn epithermal replacement dep.	12	0.053	pentagonal and cubic
Wanibuchi	epithermal replacement gypsum dep.	8	0.033	cubic and pentagonal
Udo	epithermal Cu-pyrite-chlorite vein	28	0.026	octahedral
Ogoya	epithermal Cu-pyrite vein	8	0.008	octahedral
Kishu	epithermal Cu-pyrite vein	40	0.450	pentagonal

5. Therefore, other causes for this difference, in addition to the amount of As, must be sought.

From the results above, it is concluded that As may have an influence on the development of the octahedral face under only some limited conditions of growth, and may not have an influence when pyrites grow under other conditions even the pyrites contain a large amount of As.

The following facts are considered as the phenomena which show these limited conditions.

1. Pyrites coexisting with enargite always show simple octahedral habit.
2. Among the six mines examined, the Kambe mine alone is shallow-seated stibnite-sericite deposit.
3. The writer's observation on pyrites from the Saimoku mine shows that pyrites coexisting with realgar always show simple octahedral habit.

From these facts, it is supposed that the limited condition, As has an influence on the octahedral face, is the condition of low temperature, weak alkaline and containing high amount of As in solution in which enargite, stibnite, realgar, etc. precipitate.

On the other minor elements, the author examined qualitatively, but could not find any definite relationship between the minor elements and the habit variations.

VIII. Summary and Discussion

Here, summaries from the above described will be attempted by the writer. They are as follows:

1. The vein pyrites differ from the replacement pyrites in the morphological characteristics.
2. The replacement pyrites have a wide range of grain size and are rich in variety of habit within a narrow scope. The frequency of appearance of each habit varies with a nearly definite tendency according to grain size.

3. The rate of habit variation, according to grain size, is controlled by the grade of mineralization. The rate is great under the condition of strong mineralization, and vice versa. The difference of the series of habit variation is assumed that this difference is controlled by temperature and acidity of solution, though it has not yet been completely clarified.
4. The phenomena of habit variation according to grain size as well as the morphological characteristics of the replacement pyrites can be explained by the idea of layer growth.
5. The vein pyrites have a small range of grain size and are poor in variety of habit within a narrow scope and often within a wide scope.
6. Generally speaking, the vein pyrites do not show a remarkable variation of habit according to the depth of a vein and the different zones in zonal arrangement. However, they show variation according to the horizontal position across a vein, such as, in the inner and outer parts of a vein, in a vein and in country rocks, or in accordance with the difference of crystallization stage. This seems to show that the cooling rate or crystallization temperature is one of the controlling factors of habits, and also physical condition has a greater influence on habit than chemical conditions.
7. Except in the special cases, habit does not change by the difference of the coexisting minerals. This shows that the habit variation by means of adsorption of the impurity particles is not a general case. Crystal habit of the implanted pyrite differs from that of the enclosed pyrite in some cases. This difference seems to be caused by the difference of crystallization mechanism.
8. As the result of the spectrochemical studies on the relation between $o(111)$ face and minor content of arsenic, it is clear that the habit variation by means of selective adsorption of As can appear only under the limited physical-chemical condition, and arsenic has no influence on habit under other conditions.

Considering the main cause of habit variation of pyrite from the results above, it gives a conclusion which is considerably different from the idea of surface adhesion which was proposed by crystal chemists. Namely, it is clear that habit variation, caused by the presence of the impurities, is not a common phenomenon, but a special one which occurs under the limited physical-chemical condition. Therefore, it can be said that the idea of surface adhesion cannot explain the whole cause but only a part of habit variation.

Consequently, the causes for more general conditions other than the accidental conditions such as the presence of impurities must be sought. If the above results are taken into consideration, these more general conditions would be temperature, cooling rate, mineralization grade, grade of supply of solution (concentration), and acidity of solution. More correctly speaking, we may reach to the conclusion that crystal habit of pyrite is controlled by whether pyrites grow under suitable environments for crystallization or not. Then what habit appears under what conditions? To answer this question, the following are the summaries according to the author's observations.

1. Cubic habit

   a. In the case of the replacement pyrites, cubic habit predominates in the weak altered country rocks, in the weak mineralized parts, in high temperature part of the pyrophyllite-diaspore deposits, and in part of small grain.
   b. In the vein pyrites, cubic habit predominates in the country rocks, and in the outer part of a vein or in the early stage of crystallization.
   c. In the kieslager deposits and pyrites of sedimentary origin (in sedimentary rocks of non-igneous action), most of the crystals show cubic habit. Crystals of the contact deposits show a higher appearance of cubic habit than the crystals of the vein deposits.
2. Pentagonal habit
   a. In the replacement deposits, pentagonal habit predominates in part of large grain, in strong mineralized part, and in comparatively low temperature but strong altered zone of the pyrophyllite-diaspore deposits.
   b. In the vein deposits, pentagonal habit predominates in the inner part of a vein, in a comparatively shallow but not the shallowest depth of zonal arrangement, and in the later but not the latest stage of crystallization.
   c. Pentagonal habit appears more frequently in the vein deposits than in the contact deposits. If the pentagonal habit's frequency is compared with the Kuroko deposits to other clay deposits such as sericite, alunite, pyrophyllite-diaspore deposits, it is found that pentagonal habit occurs more frequently in the former of the two.
3. Octahedral habit
   a. In the replacement deposits, octahedral habit predominates in part of medium or large grain size, in strong mineralized zone, and in medium temperature zone of the pyrophyllite-diaspore deposits. Octahedral habit shows a higher frequency in sericite, alunite, and pyrophyllite-diaspore deposits than the Kuroko deposits.
   b. In the vein deposits, octahedral habit shows nearly a similar appearance as pentagonal habit, however, the difference of these two habits according to the characteristics of the veins has not yet been clarified systematically. If pyrites crystallize in shallow depth from a low temperature and weak alkaline solution containing a comparatively large amount of As, the pyrites show octahedral habit.
   c. Frequency of the octahedral habit is much lower than the frequency of the other two habits.
4. In the case of pyrite from vein, kieslager, and sedimentary origin, crystal habit is usually very simple; in the case of the replacement deposits, clay deposits, contact deposits, as well as the pyrite enclosed in chalcopyrite, pyrites are very rich in varieties of habits.

From these observations, the following are supposed to show the conditions under which each habit will predominate.

   1. Cubic habit predominates under the condition which is unsuitable for crystallization of pyrite. For instance, it predominates in pyrites crystallized by rapid cooling, under very high or very low temperatures, at weak mineralization, and under the condition of unsufficient supply of ore solution.
   2. Generally, pentagonal and octahedral habits appear if pyrites grow under

suitable environments for crystallization. For instance, these habits predominate in pyrites crystallized by slow cooling, at moderate temperature, under strong mineralization, and under sufficient supply of ore solution.

3. Difference of conditions between pentagonal and octahedral habits is not yet been clarified. Octahedral habit seems to be crystallized under a relatively higher temperature than pentagonal as it is in the case of the pyrophyllite-diaspore deposits. Octahedral habit results from a low temperature and weak alkalic solution containing a large amount of As.

These relations can be satisfactorily explained by the idea of layer growth, exactly as it was considered in the case of the replacement pyrites. Namely, when pyrites grow under conditions not so suitable for crystallization, i.e., under low or high temperature or under condition of unsufficient supply of solution, the layers on *(100)* will mainly spread and the rate of piling will become slow, consequently, cubic habit appears. Contrary to this, if pyrites do grow under a condition of moderate temperature or sufficient supply of solution, etc., the ratio of piling of the layers to the two dimensional spreading of the layers will increase and result in the formation of octahedral or pentagonal habit. Furthermore, if the impurity particles adsorb on the surface of crystal under some special condition, the spreading of the layers will cease as the result of formation of a stable two-dimensional complex of the impurities and crystal structure. Then, the rate of the piling of the layers will increase, consequently, crystal habit will change to octahedral when the impurities are arsenic.

Here, a question arises on why the rate of the piling of the layers varies according to the different conditions.

According to Bunn, the factor necessary for the spreading of the layers is the existence of high index faces. Either an island of a new layer or nucleus on the surface or successional kinks which are exposed on the surface by the presence of the dislocations must exist in order to pile the layers. In the former case, very high supersaturation is needed. As a result of theoretical calculation, the rate of supersaturation, which is necessary for nucleation under laboratorial condition, is at least from 25 to 50%[8]. This supersaturation is not a normal laboratorial condition but is normally within the range of possibility under the conditions of high temperature and pressure in nature. Therefore, the fact that the rate of variation according to grain size is very large under the condition of a sufficient supply of ore solution is considered as a result of an abundant formation of new layers or nuclei resulting from high concentration. No result has been obtained experimentally on the relation between frequency of the dislocations and crystallization condition. However, the fact that vein pyrites which crystallize under suitable conditions show octahedral or pentagonal habit, it is assumed as the results of the chances of spontaneous nucleation on the surface of the layers increase due to sufficient supply of solution, or due to increase of frequency of dislocation, or due to the attachment of the foreign particles. If ore solution is not supplied sufficiently or is cooled rapidly, the frequency of nucleation on the surface of the layers will decrease, and the supplied molecules will adhere mainly at the kinks of the layer edges, and cubic habit results. The reason is that the probabilities of adhesion of the molecules at the kinks (the continuity of spreading of the two dimensional layers) are much higher than that of formation of new nuclei of the monolayer islands on the surface of the layers. If the impurity molecules exist in ore solution, they combine with the structures of pyrite and form stable two-dimensional complex, consequently, the spreading of the layers cease, and piling of the layers mainly takes place, and as a result octahedral habit appears. Under the condition in which the impurities do not form a stable two-dimensional complex, the impurity molecules such as As have no influence on habit variation. That is, the effectiveness of the impurities varies according to the conditions of the environment such as temperature or cooling rate etc., and therefore, the selective adsorption is considered as a secondary factor of habit variation.

IX. Conclusion

The writer has made systematical observations and statistics on habit variations of pyrites from the various occurrences and localities. He also discussed and considered the fundamental causes of habit variation from the standpoint of crystal growth.

From these observations, discussions, and considerations, he obtained the following conclusion.

The fundamental cause, controlling the habit variations of pyrites, is the difference of the conditions of crystallization environments. Crystal habit is controlled by whether pyrites grow under suitable conditions and sufficient supply of solution or not. The suitable conditions for crystallization are such as moderate temperature, slow cooling, sufficient supply of solution, etc. In this case, pyrites appear as octahedral or pentagonal habit. Unsuitable conditions for crystallization are the extreme temperatures of high and low, rapid cooling, insufficient supply of solution, etc. In this case, pyrites take cubic habit. Influence of the impurities upon habit change is recognized only under some limited conditions, thus, their effectiveness is controlled by the conditions of environment. Therefore, this is considered as a minor factor than the factors above.

These relations can be explained from the standpoint of the idea of layer growth.

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要　約

黄鉄鉱の晶相変化

砂川一郎

黄鉄鉱は天然の鉱物のうちでも最もpersistentな鉱物の1つであり，かつ晶相の種類もはなはだ豊富である。この結晶の晶相変化の実態と晶出環境との関係を明らかにすることができれば，晶相変化の原因が究明されるとともに，晶相によつて晶出時の物理化学的条件の推定も可能となるであろう。

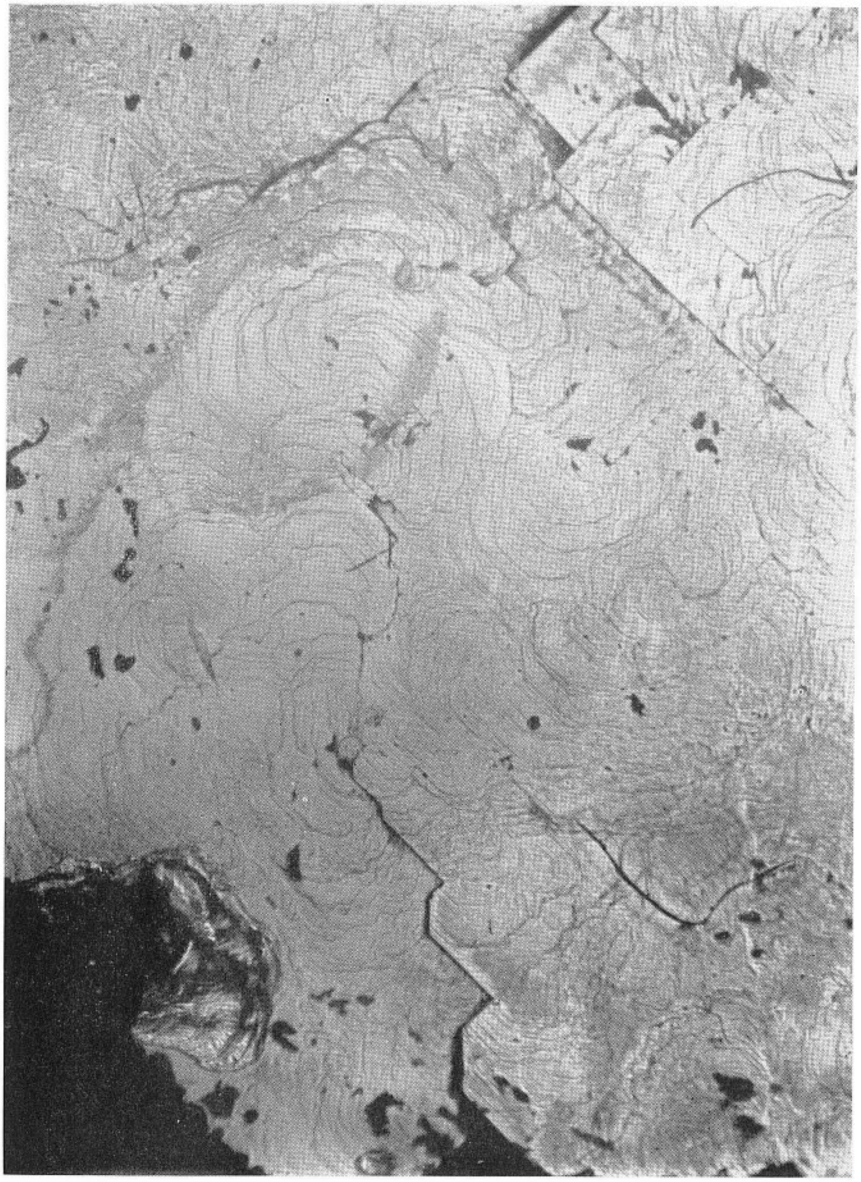
本論文は上記の目的をもつて著者が従来行つて来た研究結果を系統的に記述し，新しい結晶生長説の立場から解釈を行つたものである。

著者の観察結果は，従来結晶化学者たちによつて提唱され，晶相変化の原因についての解釈の主流となつていた“異種物質の吸著による変化”という考え方では，解釈し得ない多くの点をもつている。これらは，結晶生長が主として2次元的な生長層のひろがりによつて行われるという生長説の立場に立つて考察したとき，はじめて統一的な解釈が与えられる。

著者の観察の結果から，黄鉄鉱の晶相の差が生ずる主原因は，結晶が充分な鉱液の供給下で，生長に適当な条件の下で，晶出したか否かであると結論される。好適な条件で晶出した場合pentagonalないしoctahedral habitをとり，逆の場合にはcubic habitとして晶出する。異種物質の吸著による変化は，特定な条件下においてのみ現われ，他の条件下では晶相を変化させる力をもたない。したがつて，これはむしろ副次的な原因と考えるべきである。

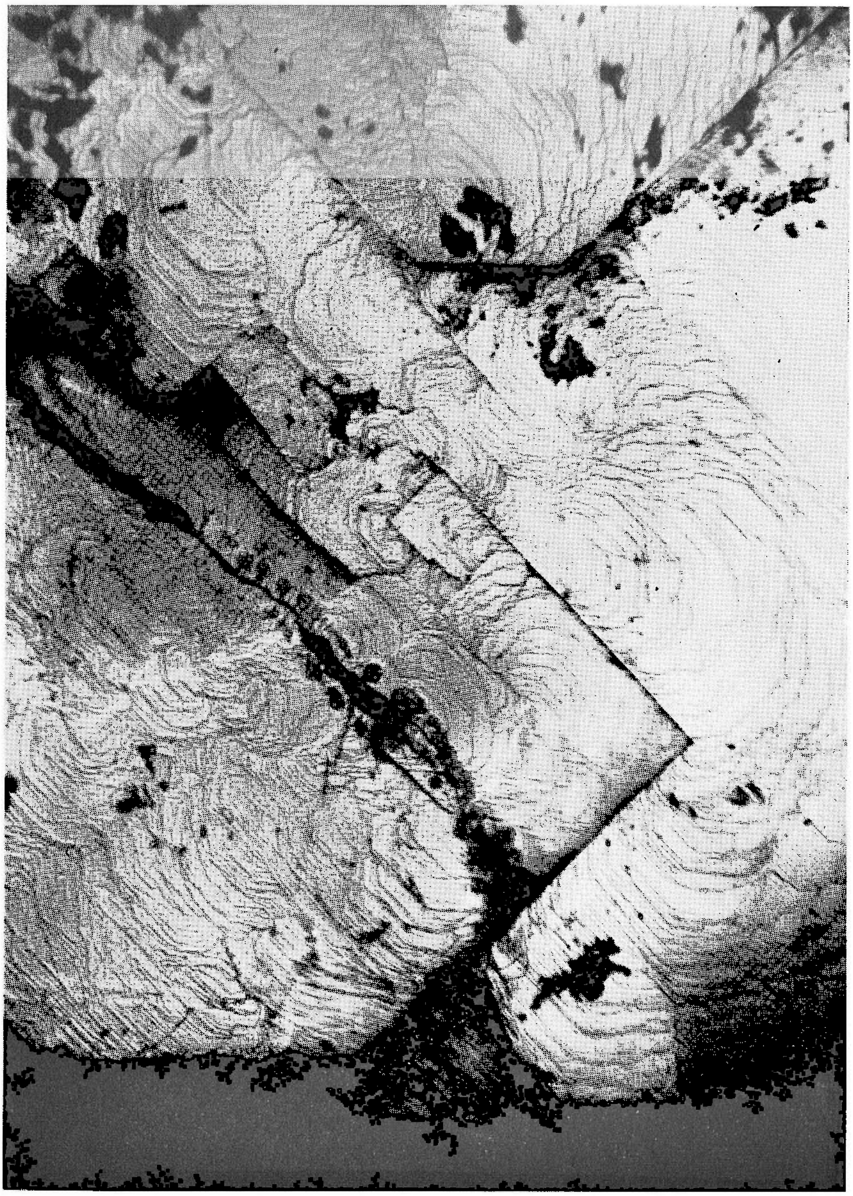
PLATES
AND
EXPLANATIONS

(with 10 Plates)



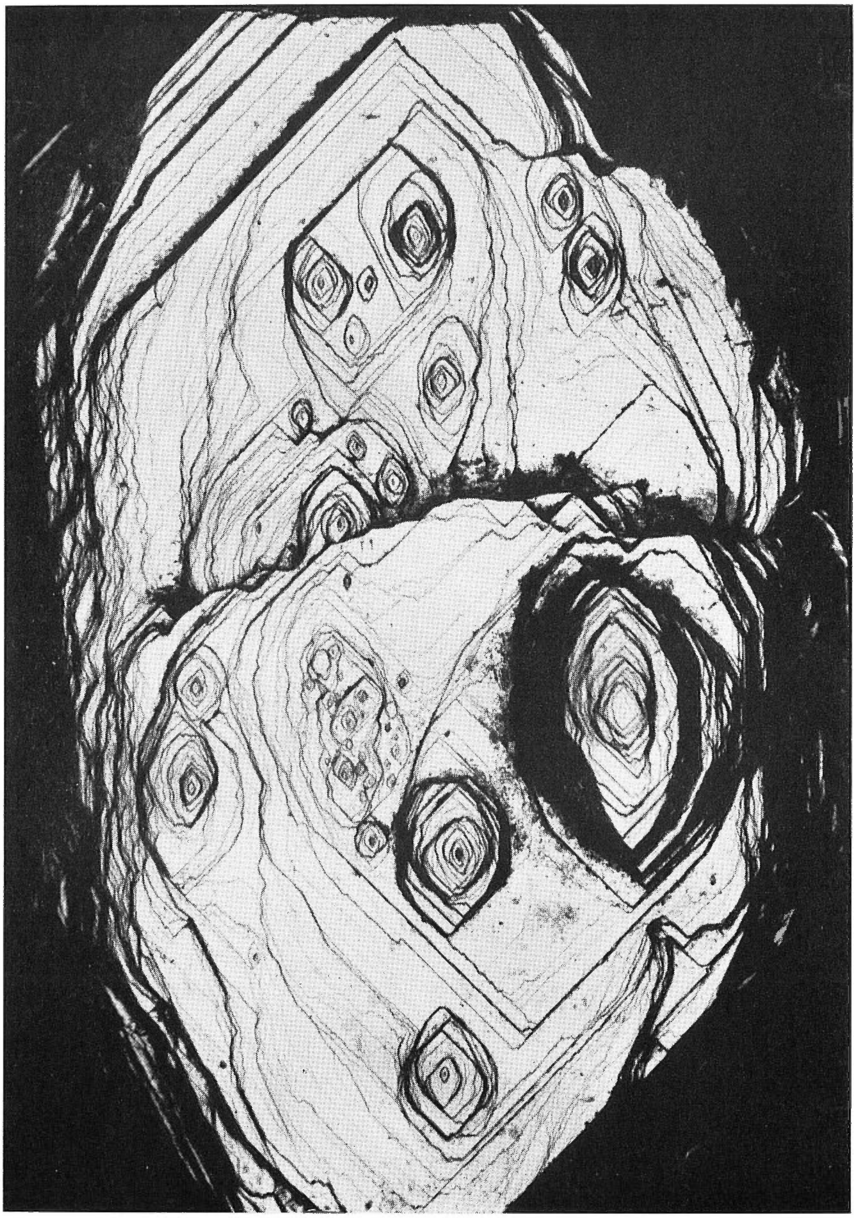
Growth layer on *a(100)* face of pyrite from the Obira mine, Oita Pref., Japan

Cubo-octahedral habit ×20



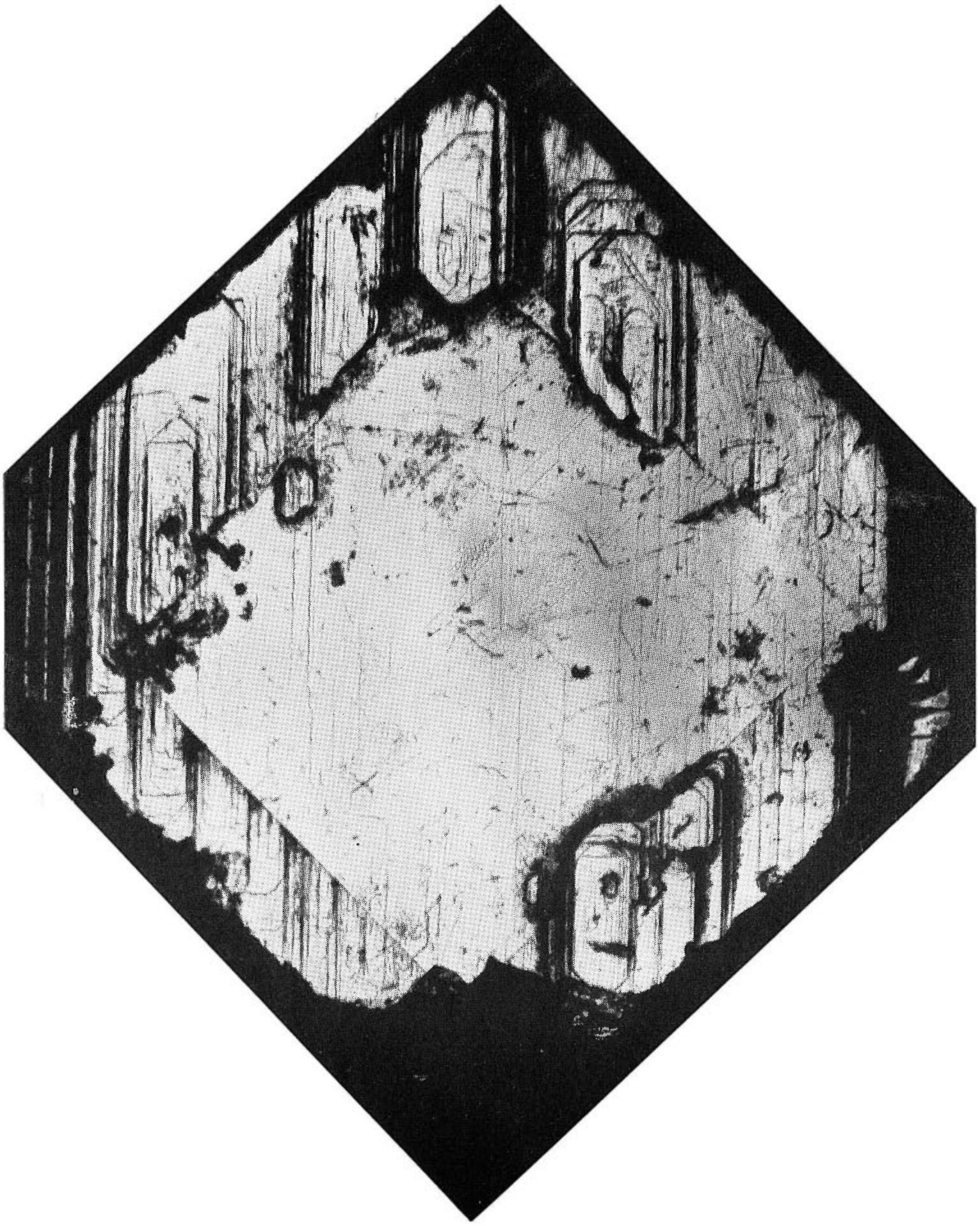
Growth layer on *a*(*100*) face of pyrite from the Obira mine, Oita Pref., Japan

Cubo-octahedral habit ×20



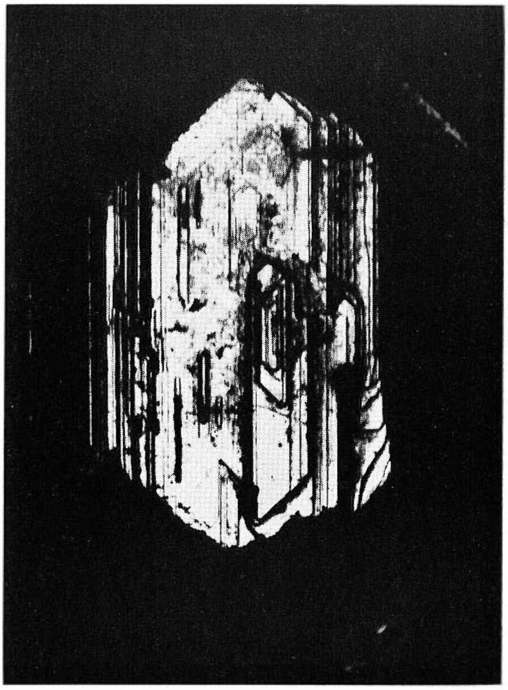
Growth layer on *a*(*100*) face of pyrite from the Iwasawa mine, Iwate Pref., Japan

Cubo-octahedral habit+middle *e*(*210*) ×20



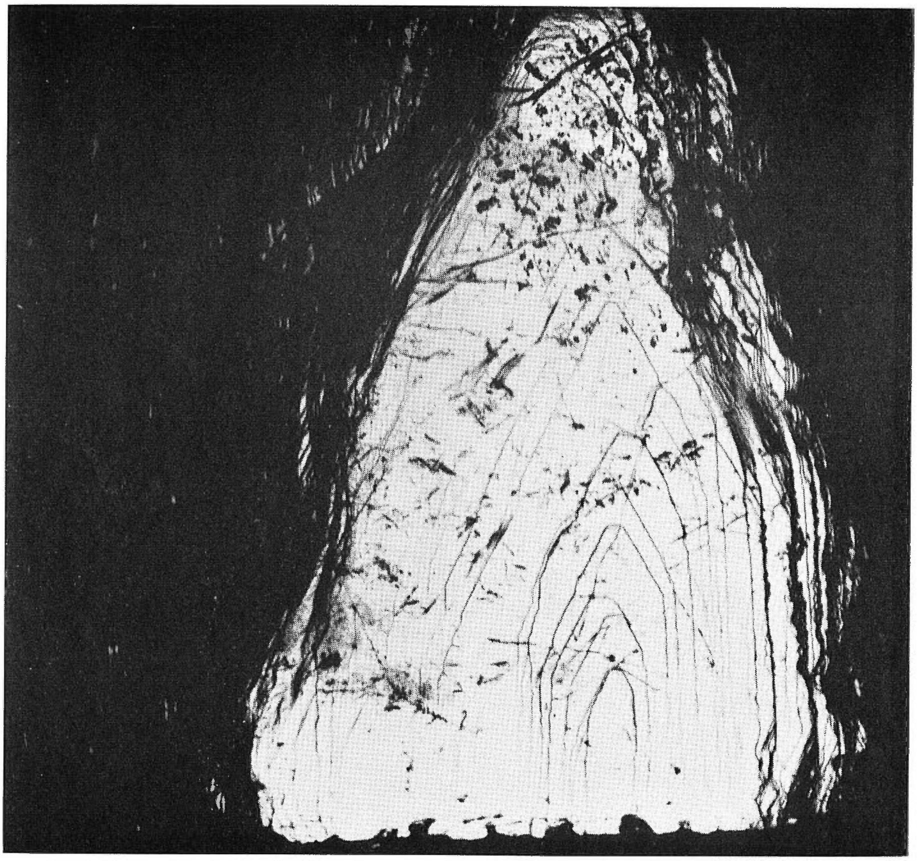
Growth layer on $a(100)$ face of pyrite from the Nagaki mine, Akita Pref., Japan

Octahedral+middle $a(100)$ ×20



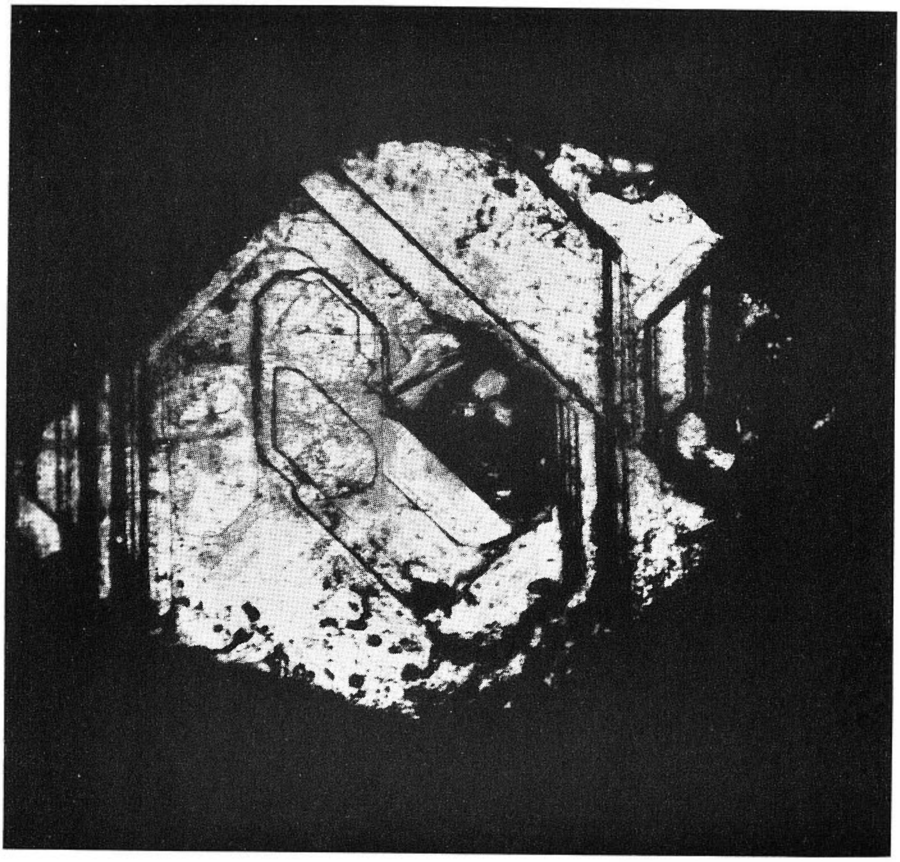
Growth layer on *a*(*100*) face of pyrite from the Sagi mine, Shimane Pref., Japan

Octahedral+middle *a*(*100*) and *e*(*210*) ×10



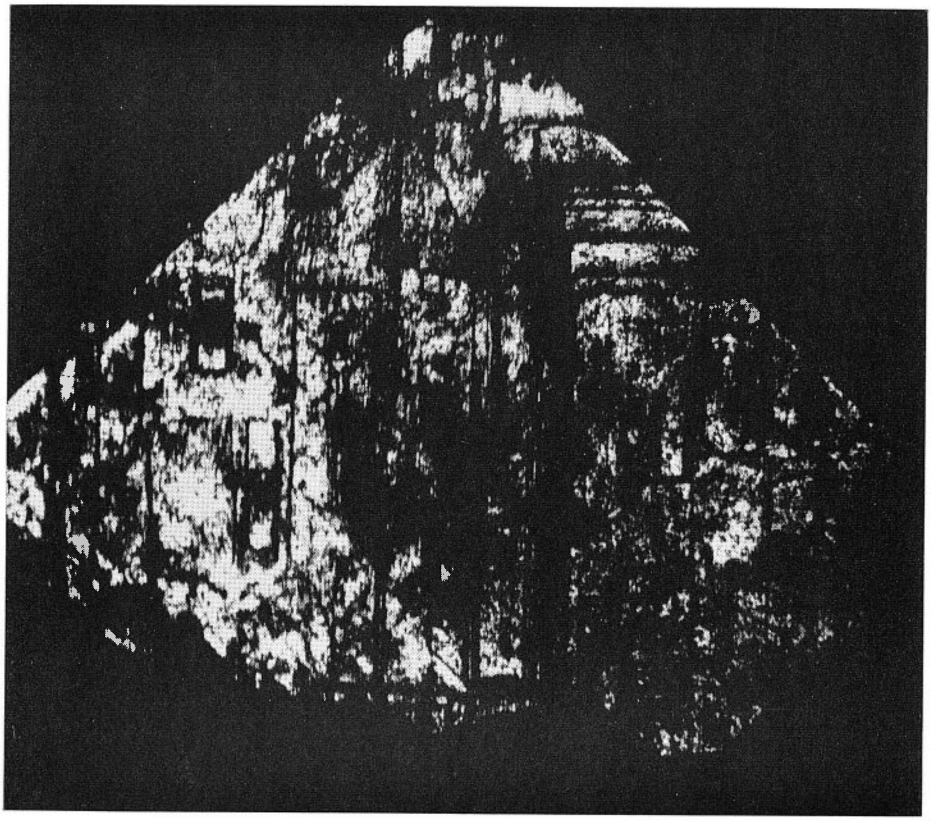
Growth layer on *a*(*100*) face of pyrite from the Komaki mine, Niigata Pref., Japan

Deformed rhombohedral habit composed of *e*(*210*) and *a*(*100*).
e(*210*) face consists of the edges of layers ×10



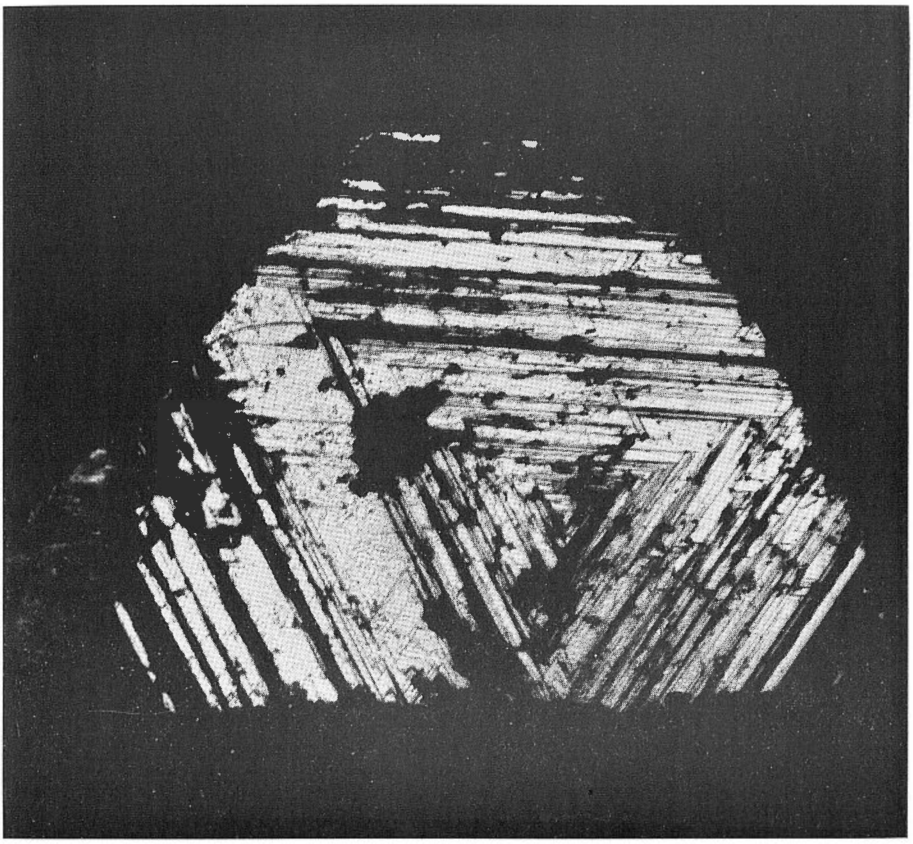
Growth layer on *a*(*100*) face of pyrite from the Ogoya mine, Ishikawa Pref., Japan

Cubo-octahedral habit ×20



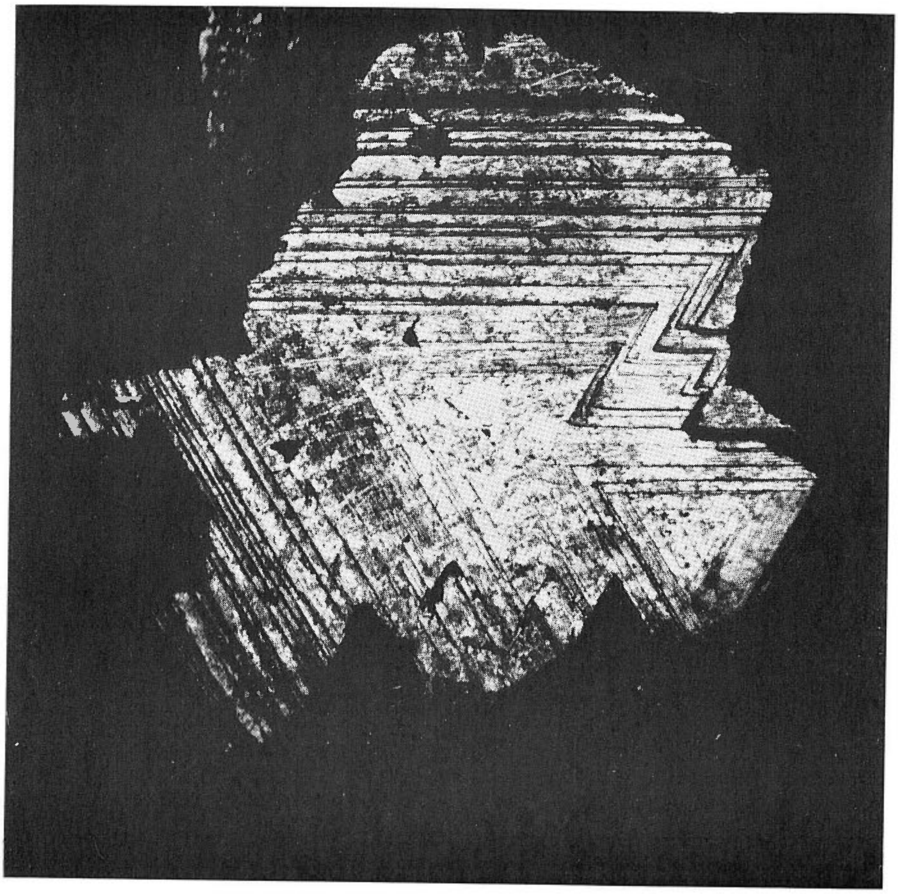
Growth layer on $a(100)$ face of pyrite from the Udo mine, Shimane Pref., Japan

Cubo-octahedral habit ×10



Surface structure on $o(111)$ face of pyrite from the Sen'nin mine, Iwate Pref., Japan

Octahedral habit ×10



Surface structure on $o(111)$ face of pyrite from the Sagi mine, Shimane Pref., Japan

Octahedral+$a(100)$ and $e(210)$ ×10

The Geological Survey of Japan has published in the past several kinds of reports such as the Memoirs, the Bulletin, and the Report of the Geological Survey.

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  - f. Geochemistry
- B. Applied geology
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  - b. Coal
  - c. Petroleum and Natural gas
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  - f. 地球化學
- B. 應用地質に関するもの
  - a. 鉱　床
  - b. 石　炭
  - c. 石油・天然ガス
  - d. 地下水
  - e. 農林地質・土木地質
  - f. 物理探鉱・化學探鉱および試錐
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- D. 事業報告

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