548. 5 : 549. 324. 31

Surface Microtopographic Study of Pyrite Crystals

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Abstract

Pyrite is one of the representative minerals which exhibit wide variation of external forms depending on the difference of modes of occurrences. Since such variations of external forms of crystals (crystal habit) occur due to the difference in the environmental or growth conditions, and are the direct results of growth processes of individual crystals, the origin and the mechanism of habit variation should be understood on the basis of the knowledge of growth mechanisms of crystals.

Since crystals growing in dispersed phases (vapour or solution phases) are usually bounded by smooth solid-liquid interfaces, *i.e.* low index faces, information relating to growth process is marked on the crystal faces in forms of growth layers, spirals or pyramids, *i.e.* surface microtopographs. Detailed observations of surface microtopographs of crystal faces using sophisticated and sensitive microscopes will, therefore, provide useful information relating to crystal growth, and thus to crystal habit problem. It is the purpose of the present study to understand the origin and the mechanism of habit variation of natural pyrite crystals based on detailed observations of surface microtopographs of three major faces, {100}, {210} and {111} of the crystals collected from many localities in Japan and of a wide spectrum of modes of occurrences. Since the microscopic techniques applied in the present study can reveal steps of less than 10 Å, molecular information relating to growth processes of pyrite crystals is obtainable.

In Chapter 1, previous theoretical and experimental studies on the equilibrium and growth forms of crystals in general are critically reviewed. Then, crystal morphology, crystal chemistry and modes of occurrences of pyrite are described. Pyrite occurs in majority of cases in nature as euhedral bulky crystals bounded by low index faces; other forms such as dendrites, hoppers or whiskers being extremely rare. Even when pyrite occurs in forms of aggregation, such as framboidal, reniform and botryoidal, individual pyrite crystals composing such aggregations are bulky crystals. Although a large number of faces have been reported, {100}, {210} and {111} are overwhelmingly important faces and most pyrite crystals take habits consisting of either one or combination of two or three of these faces.

Previous studies on habit variation and surface microtopographs of pyrite crystals are also critically reviewed, and the problems to be solved are pointed out. Based on these, the purpose and the methods of the present study are explained.

Chapter 2 describes the localities and the modes of occurrences of the specimens studied in the present study, as well as the microscopic techniques applied. In addition to ordinary reflection type microscopy, Zernike type phase contrast microscopy, differential interference contrast microscopy of both Nomarski and Yamamoto-Françon types are applied for detailed observations of surface microtopographs, the latter three types of microscopy are capable of revealing steps of less than 10 Å. To measure the step height of growth layers, both Michelson type two-beam interferometry and Tolansky type multiple-beam interferometry are applied. Step heights of more than 300 Å, and of down to 10 Å can be precisely measured using these interferometric techniques respectively.

In Chapter 3, the results of observations on the surface microtopographs of three major faces which can be regarded as representing growth processes are described. The {100} faces are characterized by the free development of growth layers of elongated rectangular forms bounded by <001> only or truncated by <011> or <012> and sometimes of square

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form bounded by <011>. The morphology of growth layers varies considerably from crystal to crystal and from locality to locality. A close relation is noticed between the morphology of growth layers on the {100} faces and crystal habits, suggesting that the {100} faces are the most important and habit controlling crystal face among the three. In contrast, growth patterns observed on the {111} and {210} faces are very simple and uniform in most cases and their forms are strongly controlled by the neighbouring {100} faces. Freely developed growth layers are observed only exceptionally on some {111} and {210} faces, and when such layers are observed, crystals are usually simple octahedrons or simple pentagonal dodecahedrons, and the morphology of growth layers differs considerably from commonly observed simple patterns on {111} and {210} faces. Although growth spirals have been occassionally observed on the major three faces, it is concluded that spiral growth mechanism is not the principal growth mechanism in pyrite growth. The principal growth mechanism is concluded to be layer-by-layer growth originating either from two-dimensional nucleus or from epitaxially settled crystallites mainly on the {100} faces.

As to the origin of differences between positive and negative striations on the {210} faces, observations are made of surface microtopographs of {210} faces of both types of striations and of internal heterogeneities of negatively striated crystals. It is concluded that positive striations are formed by the pile up of edges of growth layers spreading on the neighbouring {100} faces, whereas negative striations are formed by free development of growth layers on the {210} faces. Negatively striated {210} faces occur only in limited modes of occurrence, which shows that growth layers can develop freely on the {210} faces only under specific conditions. Similar argument is also applicable to the {111} faces.

Based on these observations, growth mechanism of pyrite crystals, origin and mechanism of their habit variation are discussed in Chapter 4.

Equilibrium forms of pyrite which are deduced from Bravais-Friedel's Law, Donnay-Harker's Law, Hartman-Perdok's PBC analysis and Wolff's analysis do not agree with the observed growth forms in the present study, judging both from external forms (macro-morphology) and surface microtopographic characteristics of three major faces (micro-morphology). In growth forms, {100} is the most important face, followed by {210} and then {111}. The causes of this discrepancy between theory and experiment is explained in terms of actual growth mechanism of pyrite crystals; i.e. growth layers can develop freely only on {100} faces, but not on the other two faces. Origin and mechanism of habit variations in pyrite crystals are also explained with this growth mechanism. Pyrite crystals change their habits depending on the rate of two-dimensional nucleation of and that of lateral advancing of growth layers on the {100} faces, as well as impurity adsorption along the growth steps. Variations in these rates are caused by the difference in environmental or growth conditions. When pyrite crystals grow under favourable conditions, such as high sulfur fugacity or appropriate supersaturation, they tend to take octahedral or pentagonal dodecahedral habits, whereas when they grow under unfavourable conditions they have tendency to remain as simple cube. General relations between crystal habits of pyrite and the modes of occurrences also support this conclusion. Characteristics of crystal growth in hydrothermal solutions are also discussed on the basis of surface microtopographs.

In Chapter 5, surface microtopographs of three major faces which are formed by natural dissolution processes are described. The {111} is the face which receives dissolution most easily among the three major faces. This also indicates that {111} face is the least important face. Although etch pits at the outcrops of line defects are observed, it is found that the principal dissolution process is two-dimensional process starting from steps of growth layers.

The final Chapter 6 summarizes the results of observations and the understandings obtained as to the mechanisms of crystal growth and dissolution, origin and mechanism of habit variation of pyrite crystals. Future problems are also mentioned in this chapter.

Chapter 1. Introduction

1.1 Equilibrium Form of Crystals

Regular geometrical external forms bounded by mirror flat surfaces that many crystals exhibit have attracted ever-lasting interests of many people from the time of pre-science ages. Steno (1669) was the first scientist who made the earliest scientific work on this problem and drew a conclusion. He measured interfacial angles of corresponding faces on many quartz crystals of divergent external forms, and found that the interfacial angles were constant irrespective of external forms; *i.e.* "law of the constancy interfacial angles". This law implies two meanings. Firstly, that the interfacial angles are always constant in spite of different external forms suggests that the unit constituting a crystal should have a definite form and size. This brought forth the concept of primitive lattice, a sort of primordial idea of the present-day crystal structure, which was put forward by Häuy and R. Hook, and is the starting point of the recent structural crystallography. The other is the problem why external forms of a crystal species vary widely among crystals of different localities or occurrences, in spite of the same chemical composition and the same crystal structure, and of the constant interfacial angles. This is an ever-lasting problem in mineralogy.

The variation in external forms of crystals has two different implications. One is the variation of external forms due to combinations of different crystal faces, and the other is malformation of external forms due to anisotropic development of equivalent crystal faces. Depending on the rate of development of $\{100\}$ and $\{111\}$ faces, a cubic crystal changes its form from cube, via cubo-octahedron, to octahedron. This morphological change belongs to the former category. A cubic crystal bounded by six $\{100\}$ faces may vary from cube to needle or thin plate, depending on the anisotropic development of six $\{100\}$ faces, and such a variation belongs to the latter category. The main purpose of the present study is to understand the causes and mechanism of changes of external forms of the first category on crystals of natural pyrite. Since this variation of external forms is essentially caused by the factors involved in the environmental conditions, it is at first necessary to find out the external form of the crystal which is entirely free from such environmental factors *i.e.* equilibrium form.

The equilibrium form is the shape of a crystal which is expected to take when the crystal grows under the equilibrium condition, and corresponds to the shape with minimum surface energy summation. Gibbs appllied thermodynamical analysis for the shape of a liquid droplet which is in equilibrium with its vapour to the equilibrium form of a crystal, assuming that a crystal is a special case of a droplet whose surface energy is anisotropic. He considered that the external form of a crystal, when the crystal is in equilibrium with its vapour, will be defined by thermodynamics to be such a polygonal form as the sum of the surface energies of all faces appearing on the crystal is minimum, and will not be a sphere, since crystals have anisotropic surface energies. Similar concept was also put forward by Curie, who stated that the smaller is the surface energy of a face, the larger the face develops. Wulff (1901), based on these considerations, put forward a method of drawing equilibrium form from the polar diagram of surface energies.

Although the equilibrium form of a crystal may be determined thermodynamically since the

sum of surface energies is minimum, the problem is how to estimate the surface energies. Since there is no direct way to measure the surface energies of crystal faces, it is necessary to find alternative values which may replace the surface energies. Several approaches along this line have been made, using crystal geometry of lattice or structure to derive the equilibrium form.

The earliest approach to bridge between external morphology and internal structure was made by BRAVAIS (1848). He thought that the higher the reticular density per unit area of a face is, the larger the face will develop and the higher its frequency of appearance will be on actual crystals. This is called "The law of Bravais". Since only 14 translation lattices are considered in this law, many discrepancies have been noted between theoretically derived external forms and actual morphology. Taking the effect of glide planes and screw axes on the values of reticular densities into consideration, DONNAY and HARKER (1937) revised and extended the Bravais'law. DONNAY further developed the second law of Bravias-Donnay-Harker. These approaches, based on lattice geometry may be called "Bravais-Donnay-Harkers' law".

In the Bravais-Donnay-Harker's law, only lattice geometry is considered and no consideration is given to the interatomic bondings. Taking interatomic bondings into consideration, HARTMAN and PERDOK (1955) developed another method to deduce equilibrium forms of crystals. If stronger bonds in a structure are connected and the sum of all the partial bond vectors are chosen so as to fulfil the chemical composition, a set of periodic bond chains (P.B.C.) will be found running throughout the structure. Vectors of such P.B.C.s are called P.B.C. vectors, and crystal faces can be divided into the following three types, depending on the numbers of P.B.C.'s. Type F or flat faces, containing some coplanar P.B.C. vectors. Type S or stepped faces, containing one P.B.C. vector. Type K or kinked faces, containing no P.B.C. vector. F-faces are morphologically most important faces and will become the larger and persistent faces. K-faces are the least important faces and will not be observed on actual crystals, whereas S-faces are morphologically intermediate faces between the F- and K-faces. From the view point of crystal growth, it may be understood that F-faces develop through two-dimensional spreading and piling up of growth layers, S-faces by the attachment of molecular chains, and K-faces by the addition of molecules. It also follows from these differences that F-faces develop larger, followed by the appearance of S-faces, whereas K-faces are not observed on actual crystals. Based on this model HARTMAN (1953) has analysed equilibrium forms of many crystals.

WOLFF and GUALTIERI (1962) also put forward another method of deducing the equilibrium forms of crystals, in which factors of interatomic bond energy and the GIBBS' specific surface energy are correlated. Their basic idea is that the equilibrium form of a crystal is determined by the combination of various surface energy parameters at each possible surface site of the crystal, such as bonding, ionicity, surface configuration and adsorption.

The above descriptions summarize the important concepts on the equilibrium forms of crystals hiterto put forward.

1.2　Growth Form of Crystals

A great many works have also been accumulated, since the earliest work of l'ISLE in the 18th Century, on the causes of variations of external forms in actual crystals (we may call these "growth form" as contrasted with "equilibrium form"). In these studies, it has been aimed to find out the

most controlling factors to cause the variation of external forms among complicated environmental conditions. Among many factors, the effects of impurity adsorption upon external forms have been studied most extensively. Starting from the earlier works by l'ISLE, LEBLANC, GAUBERT, such studies have been continued to the recent works of BUNN, BUCKLEY, *etc.* The representative more recent works along this line may be the works by the group of KERN who prepared morphodroms on alkali halide crystals to express the relations between external forms of crystals and environmental conditions such as supersaturation and impurity concentration (*e.g.* BIENFAIT *et al.*, 1965). A large number of work has also been done on the effect of growth temperatures upon variation of external forms of crystals; *e.g.* works on snow crystals by NAKAYA (1949), KOBAYASHI (1965), MASON *et al.* (1963); on natural calcite crystals by SUNAGAWA (1953). Systematic changes of external forms of crystals as increase of grain sizes have also been reported on garnet crystals in metamorphic rocks (PABST, 1943), on magnetite crystals (RAMDOHR, 1955) and on pyrite crystals of various modes of occurrences (SUNAGAWA, 1957).

The theoretical and experimental works briefly reviewed above are on the morphology of bulky crystals bounded by flat low index crystal faces, and not on the morphology of dendritic or hopper crystals. In other words, in these studies main concern is on the morphology of crystals formed by steady state growth, where crystals grow by the layer by layer mechanism. In steady state growth, as can be expected from the layer growth model proposed by KOSSEL (1927, 1930) and STRANSKI (1928) or from the spiral growth model by FRANK (1947), crystals grow via the adsorption of adatoms at the kink and step sites on the smooth surface. Therefore, crystal faces are the only place where growth takes place, whose surface microtopographs reflect the process of growth in a form of step patterns. It is therefore possible to elucidate the growth process of a crystal through the observation of the surface microtopographs of its faces.

Since the external forms of crystals are the result of integration of growth on the crystal surfaces, the observation of surface microtopographs is a very useful method to study the problem of growth forms of crystals. However, not much work has been done so far to investigate the problem of growth forms of crystals, based on the surface microtopography of crystal faces.

It is intended in the present study to investigate the problem of crystal morphology of natural minerals by means of the surface microtopographic observations. Crystal morphology of natural pyrite has been studied extensively by SUNAGAWA (1957) in connection with their environmental conditions. However, detailed surface microtopographic studies have not been done so far. The surface microtopographs of three important faces {100}, {111} and {210} of natural pyrite in crystals collected from many localities of a wide variety of mode of occurrences have been studied detail in the present study. Based on these observations, the mechanisms of crystal growth of pyrite crystals as well as of natural etching have been analysed, and the processes and causes of morphological changes of pyrite crystals have been investigated.

1.3 Natural Pyrite Crystals, their Characteristics

1.3.1 Modes of Occurrences

Pyrite is one of the most persistent minerals in nature and occurs in a wide spectrum of occurrence, ranging from metallic ore deposits to recent sediments. It occurs as;

1. Accessory mineral in most igneous rocks, from ultra basic to acidic.

2. Porphyroblasts in basic metamorphic rocks.

3. Disseminated crystals or nodules in calcareous and pelitic sedimentary rocks.

4. Authigenic mineral in recent marine or lake sediments.

5. Euhedral crystals or aggregates of minute crystals in hydrothermal alteration zones around ore deposit or volcanic fumarole.

6. Major component mineral in most types of sulfide ore deposits.

Pyrite crystals have a strong tendency to grow with euhedral forms, and they occur in most of the above occurrences as bulky crystals bounded by flat faces. The modes of occurrences of pyrite crystals may be grouped in the following three types;

1. Isolated crystals: Isolated crystals typically occur in druses of vein type deposits, in massive sulfide deposits, as well as in hydrothermal alteration zones. These are bulky cubic, octahedral or pentagonal crystals. Even in sedimentary or igneous rocks, isolated crystals can be found frequently.

2. Aggregates of minute crystals: Pyrite crystals often occur as aggregates of minute crystals in forms of pisolite, reniform, colloform and framboid. Among these, framboidal aggregations have been most extensively studied. The so-called framboidal pyrite is a spherical aggregation of minute pyrite crystals of nearly equal size ($0.5 - 1.0\ \mu$m), the diameter of the sphere being less than $100\ \mu$m, and has been reported to occur commonly in syngenetic sulfide deposits or pelitic sediments. As to the origin of framboidal pyrites, two controversial opinions have been put forwards. SCHNEIDERHOEN (1926), RAMDOHR (1953) and others considered biogenic origins based on the studies of their natural occurrences, whereas BARNER (1969), SUNAGAWA et al. (1971) have recently synthesized framboidal pyrites under low temperature hydrothermal conditions, and suggested inorganic origin. Morphology of individual minute pyrite crystals consisting framboids has been also studied, and LOVE and AMSTUTZ (1969) described geometrical packing of minute crystals in framboids judged from their optical observation, though morphology of individual crystals was obscure. ENDO (1971) observed morphology of individual crystals for the first time, using the scanning electron microscope, and definitely proved that framboidal pyrite is a spherical aggregate of euhedral pyrite crystals, whose forms range from cube to octahedron, pyritehedron having been not observed so far.

Similar mode of aggregation of minute bulky crystals has been known in other types of aggregates, such as pisolite, though the modes of aggregation are not as regular as in the case of framboid.

3. Unusual morphology: pyrite crystals may occassionally occur as straight whiskers, ring or helical whiskers, slender prisms or dendrites. They also occur as iron-cross crystals, which are penetration twin of cubes with {110} composition plane (PABST, 1971). Needle and slender prismatic forms are malformed crystals, whereas ring like crystals are due to helical bending of a bundle of whiskers (WHITE, 1973). Rarely observed dendritic pyrite crystals are formed by the same mechanism as ordinary dendrite formation (ENDO, 1976). In any of these cases, pyrite crystals are always euhedral, being bounded by low index faces, though they are malformed along certain directions.

1.3.2 Crystal Chemistry of Pyrite

Chemical composition of pyrite is FeS_2 and its compositional variation is very small, though the existence of a limited non-stoichiometry has been reported. SMITH (1942) reported that electric conductivity and reflection color of pyrite crystals vary with a slight variation of chemical compositions, i.e. non-stoichiometry. Pyrite crystallizes in isometric system, m3; space group $Pa3$; its

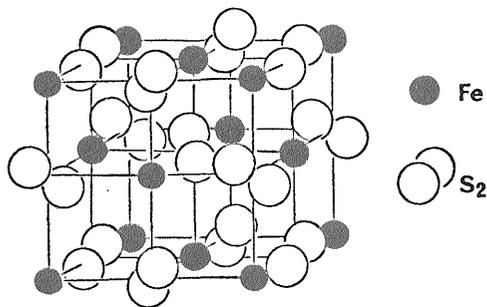Fig. 1 Crystal structure of pyrite.

lattice parameter is $a_o = 5.417$ Å; $Z = 4$. The crystal structure of pyrite is schematically shown in Fig. 1; two S atoms form dumb-bell like S_2 group and Fe atom is coordinated octahedrally by six S_2 groups. The distance between the two S atoms is 2.10 Å, much less than twice the radius of a S ion, suggesting the covalency in S_2 group. The Fe-S distance is 2.26 Å. The centers of S_2 groups may be regarded to constitute cubic closest packing, Fe atoms being situated at the center of octahedron of the c.c.p.

As can be seen in Fig. 1, the inclinations of the S_2 dumb-bell groups are oppositely oriented every half unit cell. In other words, if the pyrite structure is projected upon the neighbouring cube faces, e.g. (100) and (010), it has the appearance that the pairs of S atoms are perpendicular to each other on the two faces. The symmetry of pyrite is hemihedral, and the striations on pyrite cube faces display just the same feature of being perpendicular to each other on neighbouring faces. The structure is thus in accord with the external symmetry.

1.3.3 Crystal Morphology

Pyrite is a representative mineral to exhibit a wide variation of external forms and a large number of faces. In "Dana's System of Mineralogy (1962)", 17 major faces of high frequency of appearance are recorded, together with 223 rare faces summarized by TOKODY (1931) and WAKER (1933). In "Wada's Japanese Minerals; 3rd Ed." (ITO and SAKURAI, 1947), 27 faces are listed. Major crystal faces of pyrite listed in these two reference books are shown in Table 1. Although
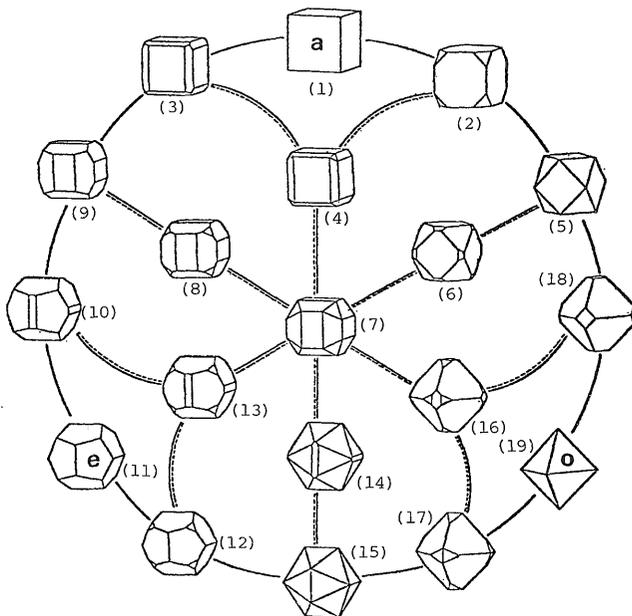

Fig. 2 Habit variation of pyrite crystals by the combination of three major faces
a, e and o (after SUNAGAWA, 1957).

Table 1 Crystal faces reported on pyrite.

a(100)	d(110)	δ(760)	D(540)	θ(430)	g(320)
e(210)	f(310)	γ(720)	h(410)	e_1(120)	B_1(180)
o(111)	o'(554)	r(332)	p(221)	β(332)	n(211)
μ(411)	E(511)	J(611)	s(321)	W(851)	Y(10.6.1.)
t(421)	x(721)	F(621)			

(Wada's Minerals of Japan, 3rd Ed., 1947)

Major faces

a(100)	h(410)	e(210)	$'v$(650)	p(221)	s(321)
d(110)	f(310)	g(320)	m(311)	v(531)	$'U$(532)
o(111)	e_1(120)	θ(430)	n(211)	$'t$(421)	

Rare faces (Indexing after Dana's System)

1·0·29	0·7·11	5·5·11	2·1·12	7·3·13	11·7·15
1·0·21	023	8·8·15	6·1·12	8·3·13	548
1·0·17	90·13	6·6·11	9·1·12	15·6·25	10·13·20
1·0·15	7·0·10	559	11·4·46	4·3·12	346
1·0·14	057	447	13·2·23	328	436
1·0·12	507	7·7·12	2·4·20	7·4·16	234
1·0·10	0·11·15	335	5·1·10	124	324
1·0·9	11·0·15	558	6·1·10	528	5·8·10
018	14·0·19	223	7·1·10	134	3·5·6
108	034	7·7·10	9·2·18	314	748
107	10·0·13	557	519	12·5·19	5·9·10
106	790	334	218	10·5·18	7·6·11
2·0·11	045	445	318	427	759
3·0·16	405	556	418	9·4·14	547
105	9·0·11	667	518	6·3·10	11·8·14
209	14·0·17	14·14·15	3·2·15	9·3·10	345
014	056	166	217	8·4·13	435
3·0·11	067	155	137	7·11·22	658
207	607	144	417	14·7·22	9·7·11
2·0·10	078	133	3·2·13	6·5·15	456
5·0·16	708	4·11·11	6·2·13	326	546
4·0·11	089	255	3·2·12	123	11·9·13
3·0·8	809	377	216	4·6·11	8·7·10
5·0·13	9·0·10	599	136	3·4·8	11·10·14
025	0·10·11	477	316	538	768
205	10·9·11	355	416	638	879
5·0·12	13·0·14	588	5·2·11	5·4·10	11·10·12
307	1·1·36	233	6·3·16	235	
409	119	577	5·4·20	10·6·15	
5·0·11	117	344	125	7·4·10	
7·0·13	116	455	215	425	
509	115	566	5·2·10	15·10·24	
047	114	4·1·20	415	437	
407	3·3·11	9·1·17	12·5·24	537	
7·0·12	227	8·1·16	9·3·14	649	
305	338	9·1·16	329	7·5·11	
0·8·13	225	1·6·14	429	8·5·11	
8·0·13	337	8·1·14	529	10·5·11	
508	449	7·1·13	629	9·6·13	

(Dana's System of Mineralogy, 7th Ed., 1962)

many faces have been reported, the most important faces of pyrite are a {100}, o {111} and e {210} faces, and the essential morphology of pyrite crystals is determined by the combination of these three faces (Fig. 2).

As to the causes of a wide variation of crystal morphology of pyrite, SUNAGAWA (1957) made a detailed and extensive work, based on the relation between crystal morphology and environmental conditions under which pyrite grew. He clarified that external forms of pyrite crystals grown under the same conditions change systematically as crystal grains become larger. He also summarized the relation between environmental conditions and external forms of pyrite, and showed that there are certain relations between the two. He gave an explanation based on the layer growth theory, to these relations. According to his explanation, pyrite crystals grow principally by layer-by-layer mechanism of the {100} faces, and the {210} or {111} faces appear as a result of piling up of steps of growth layers spreading on the {100} faces. He deduced this growth mechanism on the basis of surface microtopographic observations of three major faces of pyrite. From this it follows that pyrite crystals take on {210} or {111} dominant forms when they grow under favourable conditions for pyrite growth, whereas {100} dominant forms preferentially occur under unfavourable conditions.

1.4 Surface Microtopography of Pyrite

Surface microtopographic studies on pyrite crystals have been made by several workers, in addition to SUNAGAWA's work.

SEAGER (1953) observed surface microtopographs of some natural minerals including pyrite, and considered that the external forms of crystals have close relation with the ratio between two dimentional advancing rates of growth layers and their three dimensional piling up rate on the crystal surfaces, as well as with the positions of growth centers on the surface. As to pyrite crystals, he made observations of growth patterns on the {100} and {111} faces, and showed that the {100} faces are characterized by the development of four-, six- and eight-sided growth layers, and that forms of growth layers on the {100} faces vary considerably depending on the forms of the face. His observations also show that the {111} faces are characterized by the development of triangular vicinal hillocks, whose orientations are often oblique to the triangle of the {111} face. He also reported, prior to the above observations, growth spirals on the {100} face of a pyrite crystal (SEAGER, 1952), but these are not ideal mono-molecular growth spirals judged from his photomicrograph and his method of observation. He himself did not mention this observation in his later paper (SEAGER, 1953).

AMSTUTZ et al. (1958) and SUNAGAWA (1955) suggested a possibility to utilize external forms of pyrite crystals as a key of prospecting new ore deposites. Later, AMSTUTZ (1963) proposed to observe surface microtopographs of crystal faces to identify external forms of crystals when they show only a part of faces, and tried to classify surface patterns characteristic to the {100}, {111} and {210} faces of pyrite.

FONT-ALTABA (1963) observed irregular growth layers and dislocation lines on the {100} faces of pyrite from Spain and discussed their relation.

All of the above observations have been done using the ordinary reflection type optical microscopes, none of the more sophisticated and sensitive methods such as phase contrast microscopy and

multiple beam interferometry having been applied in these studies. It is therefore badly needed to have detailed observation of surface microtopographs of pyrite crystals, using these sophisticated and sensitive methods, and to clarify the mechanism of crystal growth of pyrite based on such observations. Through such studies, the followings are expected to be clarified in connection with crystal growth.

1. Process of change of external forms during growth: Since morphology of crystals is the result of growth process, it is necessary to study such a problem principally based on actual growth mechanism of crystals.

2. Growth mechanism in hydrothermal solution: The so-called FRANK's "spiral growth theory", which has been the most fundamental theory on crystal growth, was originally put forward for the growth from low supersaturated vapor phases. Later, it was found on various artificial crystals, that the theory is also applicable to the growth from solution phase of low supersaturation. However, there are many natural crystals which are formed from hydrothermal solutions, yet do not exhibit any growth spirals. From detailed investigations of surface microtopographs of pyrite crystals which are one of the most persistent minerals in nature, it is expected to understand characteristics of crystal growth taking place in natural hydrothermal solutions.

3. Order of importance of crystal faces: Growth of crystals in vapour or solution phases takes place via two-dimensional advancing and piling up of growth layers on low index crystal faces. From the standpoint of crystal growth, the P.B.C. concept (HARTMAN and PERDOK, 1955) may be understood in the following way: the F-face develops larger since growth layers on this face can develop freely. According to HARTMAN's analysis of pyrite morphology based on the P.B.C. concept, pyrite has three important F-faces, {100}, {111} and {210}, in this order of decreasing importance. It is important in understanding crystal morphology how these theoretically expected surface characteristics are in good accordance with or different from the actually observed surface microtopographs of these faces.

Based on the above points of view, surface microtopographs of many pyrite crystals have been observed in the present study, focusing on the following points;

1. Whether ideal growth spirals can be observed universally on natural pyrite surfaces or not.

2. What kinds of growth patterns are observed on the three F-faces? Is there any relation between the morphology of growth layers and bulk morphology of crystals?

3. On which face among the three faces growth layers can develop most freely?

This paper consists of the following chapters. Chapter 2 describes the mode of occurrences and localities of pyrite crystals used in the present study as specimens, and an outline of experimental methods. In Chapter 3, surface microtopographs representing growth processes observed on the three important F-faces will be described in detail. In Chapter 4, discussion will be made on the relation between the mechanism of crystal growth and the process of changes of external forms. Chapter 5 describes surface microtopographs formed by dissolution, and discussions will be made on the relation between growth and dissolution. In the final Chapter 6, the result of the present works will be summarized and the problems to be solved in future will be pointed out.

Chapter 2. Specimens and the Methods of Observation

2.1 Specimens Observed

It was intended in the present observation to cover pyrite crystals of as many localities and from as wide spectrum of modes of occurrences as possible. Some of the crystals studied were collected by the author himself, together with field observations of their occurrences and others were borrowed from the museum of the Geological Survey of Japan and personal collections. Localities of the specimens studied are shown in Table 2.

Table 2   Localities of samples.

Locality	Location
Shimokawa*	Shimokawa, Kamikawa-gun, Hokkaido
Kamikita	Temmabayashi, Kamikita-gun, Aomori Pref.
Oppu	Nishimeya, Naka-Tsugaru-gun, Aomori Pref.
Taro*	Taro, Shimoheii-gun, Iwate Pref.
Washiaimori*	Yuda, Waka-gun, Iwate Pref.
Tsunatori	Waka, Waka-gun, Iwate Pref.
Iwasawa	Waka, Waka-gun, Iwate Pref.
Akyu*	Akyu, Miyagi-gun, Miyagi Pref.
Namariyama*	Kosaka, Kazuno-gun, Akita Pref.
Furutobe*	Kosaka, Kazuno-gun, Akita Pref.
Ainai*	Kosaka, Kazuno-gun, Akita Pref.
Kosaka*	Kosaka, Kazuno-gun, Akita Pref.
Osarizawa*	Osarizawa, Kazuno-gun, Akita Pref.
Shakanai*	Hanaya, Kita-Akita-gun, Akita Pref.
Hanaoka*	Hanaya, Kita-Akita-gun, Akita Pref.
Matsumine*	Hanaya, Kita-Akita-gun, Akita Pref.
Ani*	Ani, Kita-Akita-gun, Akita Pref.
Mizusawa	Sawame, Yamamoto-gun, Akita Pref.
Arakawa	Kyowa, Sempoku-gun, Akita Pref.
Oizumi	Asahi, Higashi-Tagawa-gun, Yamagata Pref.
Hitachi*	Hitachi-shi, Ibaragi Pref.
Ashio*	Ashio, Kamitsuga-gun, Tochigi Pref.
Komatsu	Akagi, Tone-gun, Gunma Pref.
Chichibu	Otaki, Chichibu-gun, Saitama Pref.
Ogasawara	Ogasawara Islands, Tokyo
Ogoya	Nishio, Nomi-gun, Ishikawa Pref.
Kamioka*	Kamioka, Yoshiki-gun, Gifu Pref.
Kambe	Ouda, Uda-gun, Nara Pref.
Udo	Taisha, Hikawa-gun, Shimane Pref.
Yanahara*	Yanahara, Kume-gun, Okayama Pref.
Sazare*	Iyo-Mishima-Shi, Ehime Pref.
Besshi*	Kadono, Nii-gun, Ehime Pref.
Okuki*	Ikazaki, Kita-gun, Ehime Pref.
Shirataki	Okawa, Tosa-gun, Kochi Pref.

* refers to the localities surveyed by the author

2.2　Methods of Observation

Crystals were cleaned with cotton wool saturated with about 10% H_2O_2 solution (for very dirty crystals, dilute HCl solution is sometimes used), followed by similar cleaning with detergent solution, and finally dried by rubbing with dry cotton wool. By these treatments, oxidized film or organic adsorption on the surface are entirely cleaned. Ultrasonic cleaner is also used in cases.

After cleaning the surface, morphology of the crystal is recorded, and the general surface microtopographs of each face is observed and photographed by the reflection type projector with magnification of 10–50 times. Such macro-photography is essential to make correlation between macro- and micro-morphology.

Details of surface microtopographs of crystal faces are observed using several types of optical microscopes with high resolution in vertical direction; *i.e.* phase contrast and interference contrast microscopes. For the measurement of step height of growth layers both two-beam and multiple-beam interferometry are applied. Table 3 summarizes the microscopes and interferometric methods applied in this study, as well as their methods of observations.

Table 3　Optical microscopes used in the present study and the methods of observations.

Microscope \ Method	Low power reflection	Reflection phase contrast	Differencial interference contrast	Interferometry	
Nikon Universal Projector	A				
Olympus PMF		B		E	
Reichert MeF	A	B	C	E	F
Nikon PF			D		
Union MEIC			C		
Olympus TO-MI				F	

Symbols;
A: Ordinary reflection type
B: Zernike type phase contrast
C: Normarski type interference contrast
D: Françon-Yamamoto type interference contrast
E: Tolansky type multiple-beam interferometry
F: Michelson type two-beam interferometry

Chapter 3. Surface Microtopographs to Show Growth Processes

3.1　The {100} Face

The {100} faces exhibit a wide variety of surface microtopographs, ranging from heavily striated faces to mirror flat faces. It is however the characteristic of the {100} faces that on every {100} faces, distinct growth layers are observed under the reflection type microscope, and this makes a prominent contrast with the other two faces.

As an example is seen in Plate 27-1, the surfaces of heavily striated {100} faces are rugged, but show a large number of rectangular growth islands elongated parallel to the <001> direc-

tion, when they are observed under the reflection type microscope. Detailed observation of these islands reveals that they consist of densely piled up steps of relatively thick growth layers. Characteristic striations of cubic faces appear due to the development of these elongated growth islands. If differences in the roughness of the surfaces and the density of growth islands are neglected, it is regarded that the morphology of growth patterns on cubic faces is almost uniform, no noticeable difference being observed among different crystal individuals of this type.

In contrast to the heavily striated cubic faces, growth layers appearing on relatively flat cubic faces show remarkable changes in their morphology. Although there are cases that elongated growth islands, similar to those on the striated faces, are observed near the edges of some of such cubic faces (Plate 27-2), relatively flat cubic faces generally exhibit thin growth layers with wide step separation which originate from a single or a small number of growth centres on the surface. At the growth centre, growth layers invariably take rectangular form elongated parallel to the <001>, but as they advance outwards, they change their forms considerably. When growth layers have straight steps, crystallographic orientations of such steps are principally <001>, <011> and <012>. As a result, the following morphologies are generally observed forms of growth layers on cubic faces; simple elongated rectangle parallel to the <001> (Plate 27-3), <001> rectangle truncated by the <011> (Plate 28-1), <001> rectangle truncated by the <012> (Plate 28-2) and combination of these three directions (Plate 28-3). There are also cases that growth layers take almost square form bounded by <011> directions only (Plate 29-1). In this case, growth layers originate from square growth pyramids, which is quite different from the other cases in which most growth centers appear as tables with flat top surfaces.

In addition to the above, there are also crystals on which curved or irregular growth layers develop. Plate 29-2 shows growth layers observed on the surface of a mirror flat {100} face of a beautiful single cubic crystal from the Chichibu mine. Although growth layers appear as a whole rectangular, their steps are very irregular and their heights are very small. Plate 29-3 shows the {100} face of a crystal bounded by {100}, {111}, and {210} faces from the Iwasawa mine. It is observed in this photograph that the growth layers at the centres take eye-like form, and as they advance outerwards they become boat-like form elongated to the <001> and eventually square form bounded by the <011> directions. On the {100} faces of crystals from the Arakawa mine, boat-like growth islands develop densely, and relatively high growth hillocks resembling boats placed up-side-down are observed. Growth layers appearing apart from the growth hillocks are also characterized by the wavy irregular steps (Plate 30-1). It is also observed that the morphology of growth layers change gradually with a certain tendency from the centre towards the outer parts (Plate 30-2). In this case, growth layers near the centre take unusual rhombic form with longer axis parallel to the <001>, and this itself is an unusual feature. Moreover, as going outwards, growth layers become more curved and the advancing ratio of the <001> direction to the <010> direction gradually decreases.

The observations of the {100} faces under the low magnification reflection type microscope may be summarized as follows. The surface microtopographs of the {100} faces are macroscopically characterized by the development of several different types of growth patterns such as, elongated rectrangular growth islands, growth layers with straight steps of three directions, <001>, <011> and <012>, curved or irregular growth layers. It is expected that the difference of details of

surface microtopographic characteristics among different types, or the characteristics of micro-structures may be clarified through detailed observations under higher magnification and with more sensitive microscopes. In the following sections, the result of detailed observations of each type of cubic faces by means of more sensitive phase contrast microscopy and interferometry will be described.

The surfaces of striated {100} faces, on which elongated rectangular growth islands develop as an example being shown in Plate 27-1, are very uneven and jaggy, and the average height of growth islands is in the order of 10^4 Å. These growth islands consist of growth steps of the order of 10^3 Å in the average step height and exhibit flat, not pyramidal top surfaces. It is also often observed that the side faces of these growth islands are not stepwise but flat and smooth. If, however, these flat side faces are observed under the phase contrast microscope, straight lines parallel to the edge between the flat top face and the side face are observed, showing the same nature as stepwise side faces. When goniometry is applied to these side faces, slit images from the reflection of the side faces vary from sharp spots to a series of contineous spots in a form of band. Interfacial angles between the side faces giving sharp images and the top (100) face were measured to be 26.3°, 28.9° and 29.7°, corresponding to (210), (950) and (740), respectively.

The step heights of growth layers on the {100} surfaces characterized by the development of straight growth steps such as shown in Plates 27-3, 28-1, 2, 3 are in general much thinner than the average step heights observed on the striated {100} faces, in the order of 10^2 Å, and the step separations are also much wider. The growth centres as well as terraces of these layers appear mirror flat, on which any step patterns are not detected under the ordinary reflection microscope or two-beam interferometer. However, when such mirror flat surfaces are observed under the phase contrast microscope, extremely thin growth layers are observed. They are in most cases straight, though irregular layers are in cases observed and their morphology is essentially similar as thicker layers, only the heights being different. Although thin straight growth layers are observed on the surface of mirror flat growth centers, they are always closed loops, spiral patterns being not observed (Plate 30-3). Small local growth centers are also observed on the surface of thicker growth layers, but they are always closed loops, not spirals.

The summits of square form growth pyramids parallel to the <011> shown in Plate 29-1 exhibit spiral forms as shown in Plate 31-1 under the phase contrast microscope. Although these are spirals, they are not ideal spirals and consist of fairly thick growth layers which have jagged steps parallel to the <011> directions. They appear as if a large number of small pieces of square paper are pasted along spiral staircases. It is often observed that the summits of these pyramids align along a line (Plate 31-2). Such a line may correspond to the outcrop of microscopic internal misfit of the crystal (such as grain-, tilt-, twist-boundaries). Examples of outcrops of internal misfit on the surfaces have been known on many crystals with flat faces. Irregular growth layers usually originate from, or small growth islands align along such portions. They are usually composed of thick growth layers and their centres are flat, spirals being not observed (Plate 31-3).

There are also examples in which a large number of tiny growth islands develop uniformly on one surface (Plate 32-1). Growth islands in these cases are not localized but occur uniformly all over the surface. Much thinner growth layers are observed under the phase contrast microscope on the surface of these growth islands, and they often exhibit spiral patterns (Plate 32-2).

When the {100} faces are characterized by the development of irregular thin growth layers such as the crystal shown in Plate 29-2, the growth layers originate from a group of screw dislocations as shown in Plates 32-3 and 33-1. Thin spiral layers originate from independent screw dislocations outcroping in a very narrow area, *i.e.* from a cluster of screw dislocations, and as advance outerwards they soon bunch together to form thicker layers with step heights of n × 10 Å.

Now let us next investigate the relations between the growth patterns on the {100} faces observed under the ordinary reflection microscope and phase contrast microscope as well as interferometry and the external forms of pyrite crystals. In the followings, characteristics of growth patterns on the {100} faces will be summarized in relation to the external forms of crystals. Table 4 summarizes the relation.

When pyrite takes simple cubic habit, the most commonly observed growth patterns on the {100} faces are striations, which appear due to the development of elongated rectangular growth islands, typical example being shown in Plate 27-1. Next comes elongated rectangular growth layers, including those truncated rectangular layers in the directions of <011> and <012>. This morphology has been observed mainly on simple cubic habit. In addition, growth layers with irregular form and growth spirals, Plates 29-2, 32-3 and 33-1 being examples, have been observed only on pyrite crystals of simple cubic habit, and not on the {100} faces of other habits. When pyrite crystals take habit of {100}—{210} combination, the {100} faces most commonly exhibit striations, similarly as the above case. However, it is observed as a general tendency that the density of rectangular growth islands increases as {210} faces develop. Although growth layers as seen in Plates 27-3 and 28-1 are observed on crystals with predominant {100} faces, growth layers of such morphology, especially <011> steps, gradually diminishes as {210} faces develop.

Table 4 Relation between crystal habits of pyrite and the morphology of growth layers on the {100} faces.

Morphology of growth layers	Crystal habits				Examples
	simple {100}	combination of			
		{100} -{210}	{100} -{111}	{100} -{111} -{210}	
Elongated rectangular //<001>	◉	◎			Plrte 27-1 27-3
Elongated rectangular //<001> truncated by <011>	○		◎	○	28-1
Elongated rectangular //<001> truncated by <012>		○			28-2
Elongated rectangular //<001> truncated by <011> and <012>				○	28-3
Square // <011>			○		29-1
Irregular form	○			○	29-2

Symbols:
◉ very common
◎ common
○ often

When pyrite crystals take habit of {100} — {111} combination, the most commonly observed morphology of growth layers is rectangular truncated by the <011>, typical example being seen in Plate 28-1. As the {111} faces develop, the ratio of <011> to <001> of these growth layers gradually increases, and eventually growth layers become square form bounded by the <011> steps only on the crystals of {111} dominant or cubo-octahedral habit as shown in Plate 29-1. It should also be pointed out that striation type growth patterns have not been observed on the crystals of this habit, except in the case that only small {111} faces appear.

When pyrite crystals take habit of {100} — {111} — {210} combination, growth layers usually take complex pattern bounded by three directions <001>, <011> and <012>, as can be seen in Plate 28-3. Complicated morphology such as eye-form or boat shaped growth islands (Plate 29-3) are also observed on crystals of this type of habit.

3.2 The {111} Face

The most characteristic growth patterns commonly observed on the {111} faces, when they are investigated with low power of 10 to 50 times under the reflection type microscope, are regular triangular patterns. The edges of the triangles are parallel to the edges between the {111} and the neighbouring {100} faces, namely the triangle has opposit orientation to the triangle of the {111} face. Such triangular patterns have been observed universally on almost all {111} faces investigated, except in a few cases, irrespective of the habits of crystals. They consist of narrowly spaced concentric triangular steps, with their centre at a point on the face whose typical example is shown in Plate 33-2. Occassionally there are cases in which triangular patterns have no centre on the face.

Although the {111} faces show in most cases uniform surface microtopographs characterized by the development of regular triangular patterns consisting of straight steps parallel to the edges between {111} and {100} faces, the {111} faces which exhibit different surface characteristics have been also observed exceptionally.

Plate 34-1 shows a (111) face on a simple octahedral crystal from the Ani mine, on which a large number of nearly regular triangles are observed. Although this face has similar characteristics with the common {111} faces in a sense that both show regular triangular patterns, it is noticed on the photograph that there are many triangles on one face, and the triangles incline at about $20°$ against the triangle of the (111) face, both of which make a good contrast with the feature of commonly observed {111} faces. The edges of these triangles correspond to the $<\bar{1}2\bar{1}>$, i.e. the edges between {111} and {210} faces. It is also noticed that the steps consisting of these triangles are more irregular than the straight steps consisting of commonly observed triangular patterns.

Plate 34-2 shows another example of unusual surface patterns observed on the crystals from the Akyu mine, in which it is seen that at the central part only of the triangular pattern, triangular form is inclined but as going outerward the pattern becomes ordinary triangular form. Additional two examples of irregular growth patterns observed on the {111} faces are shown in Plate 34-3 (Mizusawa mine) and in Plate 35-1 (Hanaoka mine), both are observed on simple octahedral crystals. Although triangular patterns observed on these faces are essentially similar as commonly observed triangular pattern, the steps are much irregular in these cases than ordinary straight patterns.

The growth patterns observed on the {111} faces under low magnification may be roughly classified into the following three types.

1. Triangular patterns with straight steps which are oppositely oriented to the triangle of the {111} face.

2. Triangles inclined at about $20°$ to the ordinary triangular pattern, *i.e.* with edges parallel to the $<\bar{1}2\bar{1}>$.

3. Irregular steps.

The first type has been observed on almost all {111} faces, whereas the second and the third types have been observed only exceptionaly and only on the {111} faces of simple octahedral crystals.

Under the phase contrast microscope, it is observed that the {111} faces showing the most commonly observed first type consist of densely piled up straight steps, the centers of the triangular pattern being the summits. Their step heights range from $n \times 10^2$ to $n \times 10^3$ Å, and the surfaces between the neighbouring steps are flat. The central parts of the triangular pattern form triangular plateau on which thinner steps are difficult to detect due to halation from high steps (Plate 35-2). On the flat surfaces between the neighbouring steps, saw-tooth or somewhat irregular growth layers with step heights of the order of 10^2 Å are observed. In most cases, they originate from the steps of thicker layers and do not originate from centers on the surface. Occassionaly thinner growth layers originate from points on the surface, in which case they are not spirals but triangular closed loops whose orientations incline to the ordinary triangular layers. Thus, phase contrast microscopic observations of the {111} faces showing the first type surface microtopograph under low magnification have revealed that growth patterns of the second and third types also appear on their surfaces in addition to the general growth patterns of the first type. However, it should be pointed out that spiral growth layers have never been observed on these faces, either at the center of the triangles or on the flat surface between the successive steps.

In contrast to the above, growth spirals of several different types have been observed under the phase contrast microscope on the {111} faces of the third types. From Plates 35-3 to 37-1 several examples are shown. Plate 35-3 is an example of such spirals observed on a crystal from the Mizusawa mine, and shows composite spirals originating from a cluster of screw dislocations. It is seen that a large number of thin spiral layers originate from many screw dislocations, and bunch together to form thicker layers as soon as they advance short distances. Bunched thick layers are relatively straight and consist triangular patterns, whose orientations are the same as that of the commonly observed triangles, *i.e.* of the first type. It is observed that growth layers seen on this face all originate from this centre. Plate 36-1 shows a typical example of composite spirals observed on a crystal from the Hanaoka mine. On the {111} faces of this crystal, several triangular plateaus of the first type are seen on one face, and on the surfaces of such plateaus growth spirals of Plate 36-1 are seen. It is interesting to note that the basal triangular plateaus are of the first type, yet the triangular growth spirals occurring on the former rotated at about $20°$ against the basal triangles, the angle corresponding to the $<\bar{1}2\bar{1}>$, *i.e.* parallel to the edge between (111) and (210). In other words the triangular spirals have morphology of the second type. Plate 36-2 demonstrates this relation. On the other portions of the same (111) face, triangular growth pyramids as shown in Plate 36-3 are observed. Due to surface damages or dissolution, individual layers consisting these pyramids are difficult to resolve even under the phase contrast microscope of high magnification

(Plate 37-1). However, similar growth pyramids have been observed on the surfaces of a wide variety of natural and synthetic crystals and have been confirmed to consist of spiral layers with narrow spacings between successive layers. It is therefore safe to assume that the growth pyramids in Plate 36-3 are also formed by spiral growth mechanism.

As already described, regular triangular patterns of the first type have been observed on the {111} faces of different habits, ranging from simple octahedral habit to the habits with small {111} faces. They appear on the {111} faces, irrespective of crystal habits. In contrast, growth patterns of the second and the third types, *i.e.* triangular layers with $<\bar{1}2\bar{1}>$ edges or irregular growth layers, as well as growth spirals have been observed only on the {111} faces of simple octahedral crystals. These relations are summarized in Table 5.

3.3 The {210} Face

The most commonly observed patterns on the {hk0} faces including {210} are striations parallel to the direction of the edge between the neighbouring {100} and {210} faces, *i.e.* $<001>$. Although these striations resemble in appearance to the striations on the {100} faces, they are essentially different each other. The striations on the {100} faces are due to the development of elongated rectangular growth islands as can be seen in Plate 27-1, whereas those on the {210} faces are simple striations parallel to the $<001>$, neither growth layers nor growth islands being observed (Plate 37-2). This is true even under the sensitive phase contrast microscope at higher magnification, which reveals only parallel and densely populated straight lines. Any evidence suggesting the existence of growth layers or growth islands has not been observed on these striated {hk0} faces.

This type of striations observed on the {210} or {hk0} faces may be called "positive stria-

Table 5 Relation between crystal habits of pyrite and the morphology of growth patterns on the {111} and {210} faces.

| Morphology of growth patterns on the {111} faces | Crystal habits | | | | Examples |
| | simple {111} | combination of | | | |
		{100} {111}	{111} –{210}	{100} –{111} –{210}	
Regular triangular	○	◉	○	○	Plate 33-2
Triangular tilted from regular orientation	○		○		34-1 34-2
Composite spirals	○				35-3 36-1
Mono-molecular spirals	○				36-3

| On the {210} faces | | combination of | | | |
	simple {210}	{100} –{210}	{111} –{210}	{100} –{111} –{210}	
Positive striations	○	◉	○	○	Plate 37-2
Negative striations	○	○			38-1 38-2
Trapizoidal growth hillocks	◎		○	○	39-1

tions". There are also pyrite crystals of pentagonal dodecahedral habit, which occur only exceptionally and in limited modes of occurrences, and whose {210} faces show striations perpendicular to the edge, *i.e.* parallel to the $<\bar{1}20>$. Such striations may be called "negative striations". Differing from the nature of positive striations, the surface microtopographs of the {210} faces with negative striations may be classified into two types, *i.e.* striations consisting of very straight lines (Plate 38-1) and of relatively irregular lines (Plate 38-2). Phase contrast microscopic observations of the latter type reveal that the striations are due to the development of growth layers elongated parallel to the striations (Plate 38-3), suggesting that negative striations appear due to growth steps freely developed on the {210} face, which is of similar origin as the striations on the {100} faces, and different from the positive striations in their origin. Detailed observations and discus-,sions on the origins of positive and negative striations will be described in the next section.

Pyrite crystals with mirror flat {210} faces are also seldom observed. On the surface of these flat {210} faces, growth hillocks with pointed summits and smooth side faces are observed under low magnification. These growth hillocks usually have trapezoidal form though occassionally exhibit malformed morphology (Plate 39-1). Under the phase contrast microscope, these pyramids consist of growth layers with very narrow spacings between the successive layers (Plate 39-2). Due to the narrow spacings between successive layers, it is practically impossible to detect single layers, but judging from the morphology, it is safe to assume that these growth hillocks are spirals consisting of almost mono-molecular layers and originating from single screw dislocation, as similarly as the case of growth pyramids in Plate 36-3. It is interesting to note that a hole is found at the summit of these growth pyramids (Plate 39-3), which may suggest the existence of a screw dislocation outcroping at the summit.

The characteristics of the growth patterns on the {210} faces may be summarized as follows;
1. $<001>$ striations (positive striation).
2. Striations perpendicular to the edge between the neighbouring {210} faces (negative striation).
3. Growth pyramids of trapezoidal form (probably spirals).

Among these, the first type, *i.e.* positive striation, is the most commonly observed growth patterns on the {210} and {hk0} faces, whereas the other two types are found only exceptionally. It should be stressed that on the {210} faces showing positive striations growth layers do not develop at all, whereas on the {210} faces of the second and third types growth layers develop freely, some originating from screw dislocations.

The growth patterns of the second and the third types have been observed only on the {210} faces of simple pentagonal dodecahedral crystals, whereas those of the first type on the {210} surfaces of crystals of any habits, *i.e.* irrespective of crystal habits. The above relations are summarized in Table 5.

3.4 Positive and Negative Striations on the {210} Face

3.4.1 Introduction

As already mentioned in the preceding section, two different types of striations are observed on the {210} faces. One is parallel to the edge between the (100) and the (210), *i.e.* parallel to the $<001>$, the other perpendicular to the edge between the neighbouring {210} faces, *i.e.* parallel
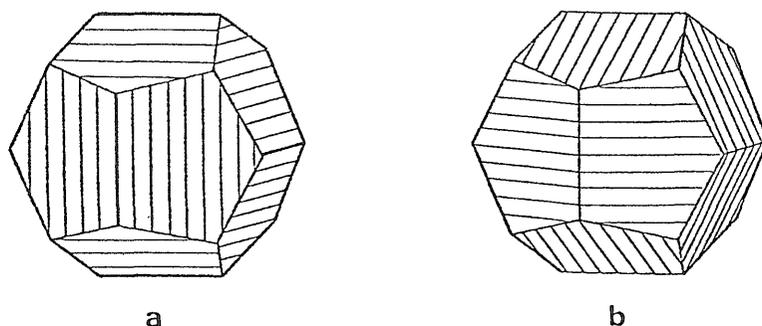
Fig. 3   Positive (a) and negative (b) striations on {210} faces.

to the $<\bar{1}20>$. The former striations are called "positive", and the latter "negative". Crystals show-ing positive striations and those with negative striations are shown schematically in Fig. 3.

Previous work by SUNAGAWA (1957) has established that when crystals with negative striations occur, such crystals are predominant, and crystals with positive striations are rarely seen. Interest-ingly, if pyrite crystals occur in an ore body as pentagonal forms with negative striations, the crystals occurring in its wall rock always show the same external forms. In contrast, in the case of crystals with positive striations, pyrite crystals in the wall rock are always cubic, irrespective of the crystal habits of pyrite in the ore body. It is therefore conjectured that crystals with negative striations must have been formed under a specific growth condition.

It has been widely believed that the striations on the {100} and {210} faces are composed of an oscillatory combination of cubic and pentagonal faces. However, this is not the case. As described in sections 3.1 and 3.4, the striations on the {100} faces are truly steps of growth layers developing on the {100} faces, whereas those on the {210} faces are formed by the pile up of edges. SUNA-GAWA (1957) observed that many pentagonal faces on pyrite crystals belong not only to the {210} form but to several other {hk0} forms, whose indices vary from crystal to crystal.

For crystals with positive striations, growth layers seem to develop on {100} but not on {210} faces. Consequently, it is believed that the growth of pyrite crystals takes place on the {100} faces by two-dimensional layer spreading and stacking, with the {210} faces formed initially by the pile up of edges of growth layers on the {100} faces, about which detailed discussions will be made in the later chapters. This growth mechanism, however, does not adequately explain the forma-tion of negative striations on the {210} faces, though it satisfactorily accounts for the positive striations. Therefore, to determine the origin of negative striations, the author studied the mode of occurrence of pyrite crystals with negative striations, the surface microtopographies of their {100} and {210} faces, and their internal heterogeneity. The specimens mainly used in the present study are those obtained at the Shakanai mine, Akita Prefecture. Crystals with negative striations from a few other localities in Japan were also studied for reference.

3.4.2   Crystals with Negative Striations from the Shakanai Mine

Pyrite crystals from the Shakanai mine exhibit a wide variety of crystal habits, from cubic to pentagonal and octahedral, but all {hk0} faces show positive striations. However, pyrite crystals impregnated in a pumice tuff with brecciated ferruginous chert overlying the black-ore body
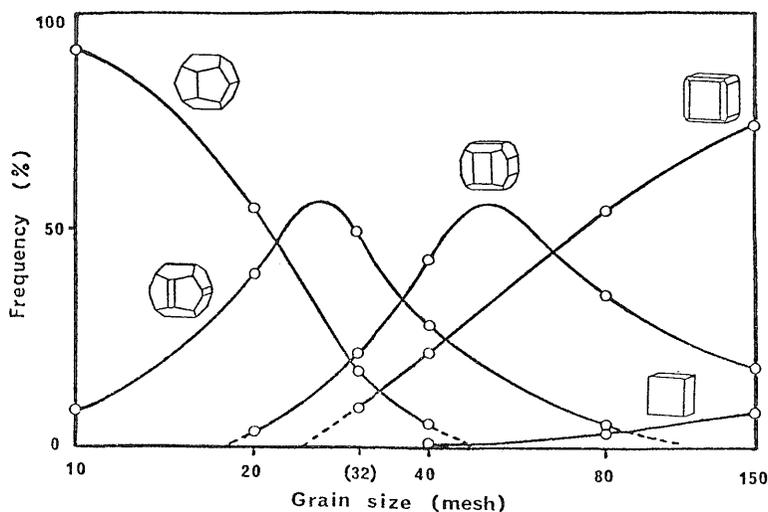
Fig. 4   Habit variation depending on grain sizes of crystals (Shakanai mine).

at the No. 1 deposit, show negative striations on {210} faces. Pyrite crystals with negative stria-
tions are found only in this pumice tuff, and never in ore bodies or in other country rocks.

Pyrite crystals within a single hand specimen of pumice tuff vary widely in grain size, from
less than 100μ to over 15 mm in diameter. They exhibit nearly perfect holohedral, pentagonal
dodecahedrons with negative striations.

Because the pumice tuff containing pyrite crystals is soft enough to crush in one's hands, crystals
can be easily separated from the host rock, and concentrated by water decantation. Crystals were
sieved into the 5, 10, 20, 40, 80, 150 and 200 mesh size-fractions respectively, and the frequency
of occurrence of different types of habit was counted under the binocular microscope. Identification
of different habits was made semiquantitatively. The result (Fig. 4) clearly shows that frequency of
occurrence of different habits collected in a small hand size specimen changes gradually with crystal
size. Among smaller crystals the cubic habit predominates, whereas almost all of the larger crystals
show pentagonal habit. This change of crystal habit with grain size substantiated results obtained
previously by SUNAGAWA (1957) on a great number of pyrite crystals from other Japanese localities.
The results suggest that the pyrite crystals assumed the cubic habit at the earliest stage of growth.
Thereafter {210} faces started to develop gradually, and finally a pentagonal habit appeared. In
other words, pyrite crystals changed from cubic to pentagonal habit as they grew larger.

Surface microtopographies of both {100} and {210} faces were observed on crystals for each
grain size category using the phase contrast microscope. The {100} faces, which appear only on
smaller crystals, exhibit rectangular growth layers (Plate 40-1) elongated parallel to the <001>.
This results in the appearance of striations on the {100} faces and confirms the observations in
section 3.1. Surface microtopographs of the smaller {210} faces that appear on small- to medium-
size cubes (up to 40 mesh) exhibit positive striations only. They are essentially similar to those of
ordinary {210} faces with positive striations described in section 3.3. These striations can be as-
sociated with the edges of growth layers on the {100} faces. No free development of growth layers

is noticed on these {210} faces. This definitely shows that at least up to this stage, the {210} faces are formed by the pile up of the edges of growth layers spreading on the {100} faces. Goniometric measurements of the {210} faces revealed that these faces actually consisted of not only {210} but also narrow strips of {310}, {520}, {830}, *etc.*

In contrast, the {210} faces which are dominant on the medium-to-larger (40 to 20 mesh) crystals exhibit quite different surface characteristics. On the {210} faces of medium size crystals, areas showing positive striations coexist with areas having fairly flat surfaces. On the flat surface thin growth layers develop freely; they are elongated in the direction of negative striation $<\bar{1}20>$. In the areas of positive striations, small patches of flat areas containing short negative striations occur (Plate 40-2). These areas of negative striations become wider as crystals become larger and, on crystals larger than 20 mesh, entirely cover the {210} faces (Plate 38-2). This indicates clearly that the origin of the negative striations differs from that of the positive striations, and that they have been formed by the steps of growth layers freely developed on the {210} faces.

The above observations suggest at least two distinct stages in the formation of {210} faces. In the earlier stage the {210} faces are formed by the pile up of the edges of growth layers spreading on the {100} faces, and are characterized by the development of positive striations. In this stage, growth layers cannot develop freely on the {210} faces. The {210} faces are considered to have been formed by the attachment of chains; thus the faces have the characteristics of HARTMAN's (1963) S-faces. In the later stage, growth layers develop freely on the {210} faces to form negative striations. In this stage, therefore, the {210} faces are formed by the attachment of slices, *i.e.*, through a layer-by-layer process; thus they are F-faces. In other words, the {210} faces change character from S-face to F-face, from earlier to later stages. It is thus conjectured that a somewhat abrupt change of conditions occurred during the growth of these crystals. This is supported by studies of the internal heterogeneity of these crystals, as described below.

Pyrite crystals of each grain size were sectioned and polished, then etched in concentrated HNO_3 for about 30 seconds at room temperature. After the treatment, any internal heterogeneity became visible under the ordinary reflection microscope.

Crystals smaller than 80 mesh exhibit more or less uniform internal structures, except for the occurrence of a number of smaller inclusions (Plate 40-3). In contrast, crystals larger than 40 mesh show internal heterogeneity consisting of a polygonal core and a surrounding mantle (Plate 41-1), the core having been more heavily attacked by the etchant than the mantle. In general, the core occupies the larger volume and shows either pentagonal or cubo-pentagonal forms. The mantle enveloping the polygonal core is generally thin and uniform in thickness and sometimes displays thin zonal bands after electric etching.

This internal heterogeneity clearly discloses an abrupt discontinuity in growth process between core and mantle. The fact that the mantle appears only among larger crystals corresponds well to the fact that negative striations appear only on larger crystals.

3.4.3 Negatively Striated Crystals from Other Localities

Pyrite crystals from the Ani mine, Akita Prefecture, epithermal chalcopyrite-pyrite-chlorite vein deposits, show a simple pentagonal habit. The {210} faces exhibit negative striations, which are quite clear and straighter than those observed on the crystals from the Shakanai mine. It is interesting to note that in the Ani mine, even pyrite crystals in the wall rocks exhibit a simple pentagonal

habit with negative striations. This is especially noteworthy because, according to previous observations (SUNAGAWA, 1957), pyrite crystals in wall rock are in most cases simple cubes, irrespective of the habit of pyrite crystals in the ore bodies. Two types of negative striations exist. One is essentially the same as the previous case and consists of a large number of small growth pyramids. The other is characterized by the development of extremely straight parallel lines. In the former case, the growth pyramids are trapezoidal in form and aligned in rows parallel to the negative direction (Plate 41-2). In the latter case, the straight-line striations are inferred to be elongated rectangular growth layers (Plate 41-3). Therefore, in both cases the negative striations are associated with the growth layers freely developed on the {210} faces.

The internal heterogeneity of the crystals from the Ani mine was studied by the same method and under the same conditions as those from the Shakanai mine. In contrast to the Shakanai crystals, all were practically homogeneous from the center to the surface, core and mantle being indistinguishable. This homogeneity suggests that there was no stage of formation of positive striations in the Ani crystals and that they may have grown in pentagonal habit from their very beginning.

Pyrite crystals showing negative striations are also found in vein-type deposits at the Osarizawa mine, Akita Prefecture, and at the Washiaimori mine, Iwate Prefecture. Surface microtopographies of their {210} faces resemble those of the second type observed in the crystals from the Ani mine (Plate 41-3).

3.4.4 Conclusion

Observations of the surface microtopography and of internal heterogeneity of pyrite crystals with negative striations collected from four localities in Japan lead to the following conclusions:

(1) Positive and negative striations have different origins. The positive striations are associated with the pile up of edges of growth layers developed on the {100} faces. No free development of growth layers is noticed on the {210} faces with positive striations, conveying the impression that such {210} faces may be S-faces. The negative striations may be closely associated with the free development of growth layers on the {210} faces, suggesting that such {210} faces are F-faces.

(2) There is apparently an abrupt change in the growth process between the stages of formation of positive striations and negative striations, respectively. In the case of crystals from the Shakanai mine, positive striations may have possibly been formed at an early stage, whereas negative striations may have been formed only at a later stage. In the case of crystals from the Ani mine, it is considered possible that there was no stage of formation of positive striations.

(3) From the above observations and the fact that crystals with negative striations occur only occasionally and, when they do occur, most pyrite crystals embedded in the neighbouring country rock also show negative striations, it is conjectured that only under certain conditions do growth layers develop freely on the {210} faces, which in turn results in the appearance of negative striations.

The specific conditions required for the formation of negative striations are not yet clear. However, the most reasonable explanation may be impurity adsorption. Although electron probe microanalysis and laser spectroscopic analysis were applied to find the chemical difference between the mantle and core portions of the Shakanai specimens, the results were inconclusive in that no shignificant differences were detected. Colorimetric analyses were kindly made of Co contents in bulk crystals

Table 6   Variation of Co content vs. grain size in pyrite crystals from the Shakanai mine.

Grain size (mesh)	5	10	20	40	80
Co content (ppm)	1.5	2.5	3.0	4.4	6.4

of different sizes by Professor H. SAKAI of Okayama University, as shown in Table 6. A clear decrease in Co contents was noticed as crystals become larger. However, this again does not provide conclusive correlation, except that the mantle portion may contain less Co than the core portion. What impurities one might suspect to be responsible for their genesis, therefore, remains to be solved in future studies.

3.5   Discussion

Since essential information relating to external forms (macro-morphology) of pyrite crystals and surface microtopographs of three major faces has been gathered as described in the preceding sections, the mechanism of crystal growth of pyrite will be discussed in this section.

3.5.1   Comparison of Growth Patterns among the Three Major Faces

It is established that the {100} faces, irrespective of crystal habits, are formed by free advancement of growth layers on the face and that morphology of growth layers on the {100} faces varies considerably depending upon crystal habits and localities. This shows that growth layers can advance freely on the {100} faces and are not controlled by the appearance of other faces.

In contrast to this, growth patterns on the {111} and {210} faces are very simple in most cases; the {111} faces show regular triangular patterns of <110> directions and the {210} faces striations parallel to the <001> (positive striations).

Regular triangular patterns commonly observed on the {111} faces are composed of piled up thick straight steps, forming a summit at the center of the triangle. On the flat surfaces between the successive steps, thin growth layers develop freely, which may give an impression that thick straight steps are formed by bunching of these thin growth layers. However, this is not so judged from the following observations; i.e. 1) the heights of straight steps and of thinner growth layers are remarkably different and steps of intermediate heights are not observed, 2) thick steps are very straight, whereas thin layers are irregular, 3) triangular growth layers developed freely on the {111} faces show different orientations from that of straight steps. From these it is safe to assume that the regular straight triangular patterns on the {111} faces are not formed by bunching of thinner growth layers but are due to that the growth on the {111} faces is strongly controlled by the growth on the neighbouring {100} faces.

On the {210} faces with positive striations, any evidence to suggest free development of growth layers has not been observed. As already mentioned in section 3.4, the {210} faces with positive striations are formed by piling up of steps of growth layers advancing on the neighbouring {100} faces and not by the free development of growth layers on the faces.

These observations show that the growth patterns on both {111} and {210} faces show, in most cases, morphology strongly controlled by the neighbouring {100} faces. There are, however, crystals, though exceptionally, whose {111} or {210} faces exhibit free development of growth layers, but these crystals are invariably simple octahedral or pentagonal dodecahedral in habit. Freely developed growth layers have never been observed on the {111} or {210} faces of crystals with habits of combined {100}, {111} or {210} faces. Only when the {111} and {210}

faces develop predominantly or when crystals grow under exceptional environmental conditions, growth layers can develop freely on these faces.

3.5.2 Mechanism of Crystal Growth of Pyrite

It is concluded from the above summary that growth of pyrite crystals takes place mainly by two dimensional layer growth on the {100} faces. Thus, the mechanism of crystal growth of pyrite in nature will be considered mainly based on the analyses of surface microtopographs of {100} faces.

As described in section 3.1, growth patterns on the {100} faces exhibit a wide variety of forms, ranging from relatively rough surfaces with many growth hillocks to mirror flat surfaces on which thin growth layers develop. Among these, typical growth spirals have never been observed on the striated {100} faces which show a large number of elongated rectangular growth islands. The step heights of growth layers on such striated {100} faces are very high, in the order of 10^3 Å. These characteristics suggest that such striated {100} faces are formed under the condition in which two dimensional nucleation rate on the {100} faces is high. In other words, these crystals are formed under relatively high supersaturation conditions by layer growth mechanism originating from two dimensional nucleus. It may also be plausible in some cases that such crystals are formed through auto-epitaxial settlement of minute cubic crystallites already formed in the solution onto the {100} faces, and growth layers originate from epitaxially settled crystallites. In this case, impurity ions in the solution may play an important role as heterogeneous nucleation sites, in addition to the factor of high supersaturation. Growth layers on the mirror flat {100} faces are much thinner, less than 10^2 Å in height and the step separations much wider than those on the striated {100} faces. They show a wide variation of morphology. Although growth layers on these faces are thin and widely spaced, no growth spirals have been observed on these faces. These faces are thus not formed by the spiral mechanism but by the two dimensional layer growth mechanism. Judging from the density of growth centers and the heights of growth layers it is conjectured that these crystals grew under lower supersaturation or higher temperature conditions than the crystals with striated {100} faces.

Although the {100} faces of pyrite crystals do not exhibit growth spirals in most cases, some show spirals as an example is seen in Plate 31-1. The spirals appear only on the summits of growth pyramids alignning on dislocation lines outcropped on the surface, and the growth layers originating from them cover only small areas on the surface, not covering the whole surface, showing that they play a role of local growth centers only. Most thin growth layers seen on the same surface originate from two-dimensional islands, not from screw dislocations. When crystals grow from vapour phase, it is generally observed that growth layers originating from isolated screw dislocations, clusters of screw dislocations or from alignment of screw dislocations cover the whole surface, showing that screw dislocations play dominant roles in crystal growth, the surfaces of the type seen in Plate 31-1 being not observed. On pyrite crystals, growth spirals have been observed only exceptionally, and even when they appear on the {100} faces, they play a role of local growth centers only.

Plate 32-2 is an example of spiral layers observed on the surface of tiny growth islands appearing on flat {100} surfaces. These tiny growth islands, judging from the mode of their appearance, are most probably formed by auto-epitaxial settlements of crystallites which are formed in the solution. Therefore, it is considered that the screw dislocations at the centers of these spirals are not

inherited from the host crystal but are induced in the crystallites while they are growing. Other growth layers observed on the same {100} faces, except these local spirals, are formed by ordinary layer growth process originating from two-dimensional nucleus. Throughout the present study, there was only one exceptional case in which spiral growth plays dominant role in crystal growth, *i.e.* crystals from the Chichibu mine, whose {100} face is shown in Plate 29-2. As can be seen in this photograph, all growth centers on the {100} face exhibit distinct spiral patterns, though these spirals are not ideal spirals originating from isolated dislocation and having uniform step separation. The spiral layers originate from a small number of dislocations and after only a few turns they soon bunch together, forming closed loops.

Summarizing the observations on the growth patterns of the {100} faces of pyrite crystals from many localities, we arrive at a conclusion that two-dimensional nucleation and layer growth are the controlling mechanism in the growth of pyrite crystals and spiral growth plays only a minor role.

Since most {111} and {210} faces exhibit surface microtopographs strongly controlled by the {100} faces and growth spirals are observed only on exceptional {111} and {210} faces on which growth layers develop freely, similar mechanism as for the {100} faces may be applied for pyrite crystals as a whole. Namely, pyrite crystals grow mainly by the two-dimensional nucleation and layer growth; spiral growth mechanism playing only subsidiary role. In the followings, we shall consider why this is so.

The spiral growth model was originally put forward as a possible mechanism of crystal growth from low supersaturated vapour phase, and is based on the growth on the smooth surface and the existence of surface diffusion process. Since interaction of solute with solvent can be neglected in vapour growth, adatoms arriving on the crystal surface will be incorporated via surface diffusion, into the crystal at kinks and steps on the surface provided by screw dislocations. In such a case, ideal growth spirals may be easily formed. For vapour growth, this simple process is expected, and in fact, according to SUNAGAWA (1968) ideal growth spirals have been observed universally on the surfaces of almost all kinds of crystals grown from the vapour phase.

In contrast to vapour phase growth, situations will be more complicated when crystals grow from solution phases, especially from aqueous solution phases in which stronger interactions between solute and solvent and thus dehydration processes are involved. It is expected that due to these interactions and processes critical supersaturation of transition from dislocation controlled growth to nucleation controlled growth may be lowered remarkably as compared to the case of vapour growth. Namely, the critical supersaturation above which growth is controlled by two-dimensional nucleation and below which spiral growth is the controlling mechanism is expected to be much lower in aqueous solution growth than in vapour growth for the same material. Indeed, the critical supersaturation is as low as 0.5% in the case of NaCl and KCl growing from the aqueous solution phase. All pyrite crystals studied in this work are formed in the aqueous solutions. It probably reflects the above situations that spiral growth mechanism has been observed only exceptionally in the pyrite crystals studied. The facts that nucleation controlled growth is universally observed in the growth of natural pyrite crystals do not, therefore, automatically suggest very high supersaturation conditions for pyrite growth in nature.

Let us next make a qualitative estimation of growth temperatures of pyrite crystals. It depends

on the roughness of the growth step, *i.e.* density of kink sites along the steps whether a growth layer takes circular or polygonal forms. Densities of kink sites vary depending on the crystallographic orientations and the temperature. For the same crystallographic orientations, the growth temperature defines the roughness. When kink density is high, the growth layer is not affected by the anisotropy of the face and takes circular form, whereas when it is low a polygonal form is expected. JACKSON's theory on the roughness of solid-liquid interface (1958) may be applied, after slight modification, to estimate the roughness of a growth step. JACKSON's theory says that the structure of solid-liquid interface changes depending upon the α value, it is rough for $\alpha < 2$, and smooth for $\alpha > 2$. Since JACKSON's α is written as $\alpha = \xi L/kT$, where ξ is orientational factor, L binding energy, k Boltzman constant and T growth temperature in K°, so α is proportional to $1/T$ for the same crystallographic orientation. Therefore, for the same crystal and the same crystallographic orientation, rough interface is expected at higher temperature, smooth interface at lower temperature. Similar argument may be applied to the morphology of growth layers, *i.e.* to the two-dimensional interfaces, and it is expected that circular growth layers appear at high temperature conditions and polygonal at lower temperatures.

On natural pyrite crystals studied, circular growth layers have not been observed at all, all growth layers being polygonal. Only the crystals from the Chichibu mine show irregular, more or less circular, growth layers. This suggests that natural pyrite crystals grew under considerably lower temperature conditions than the dissolution temperature (Factor L in JACKSON's equation of α may be modified to dissolution energy for the case of solution growth). Pyrite crystals from the Chichibu mine may be regarded to have grown under higher temperature conditions than pyrite crystals from other localities. This is in accordance with their modes of occurrences, *i.e.* Chichibu mine is the only example of contact metasomatic ore deposits, other crystals being from hydrothermal ore deposits.

Chapter 4. Crystal Growth and Habit Variation

As to the origins of habit variation of pyrite crystals, SUNAGAWA (1957) made a detailed and extensive study. In addition to his work, the surface microtopographs and the growth mechanism of pyrite crystals have been clarified in the present work as discussed in the preceding chapters. We shall now compare the theoretically deduced equilibrium forms and actually observed growth forms of pyrite crystals so as to find whether there are any discrepancies between them and if there are any what will be the reason for that.

4.1 Equilibrium Forms of Pyrite Crystals

Table 7 summarizes the reticular densities and the order of morphological importance of crystal faces of pyrite calculated on the basis of Bravais-Friedel's law which considers only 14 translation lattices and of Donnay-Harker's law in which both glide plane and screw axis are taken into consideration. According to the Bravais-Friedel's law, the order of morphological importance is {100}, {110}, {111}, {210}, ······, which differs strikingly from the actual morphological importance of pyrite crystals, in that only rarely observed {110} face occupies the second position. This is due to that the effect of glide plane is neglected. In the Donnay-Harker's law in which glide plane

Table 7 The order of morphological importance of pyrite deduced from Bravais-Friedel and Donnay-Harker laws.

Bravais-Friedel Lattice P	Donnay-Harker Aspect $Pa3$
001	111
011	002
111	021
012 = 021	112
112	022
122	122

(after DONNAY and HARKER, 1933)

is taken into consideration, both (001) and (110) are calculated as (002) and (220), respectively, and thus the order of morphological importance changes to {111}, {100}, {210}, {211} ……, DONNAY and HARKER (1937) emphasized that the higher three faces are the most important faces and there is a big gap in morphological importance between these three and the other lower faces. Therefore, the equilibrium form of pyrite expected on the basis of Donnay-Harker's law should be octahedral with well developed {111} faces, together with smaller {100} and {210} faces.

According to the P.B.C. analysis by HARTMAN (1953), the P.B.C.s of pyrite are <100>, <110>, <121>, <$\bar{1}$20> and <021>, thus F-faces of pyrite are {100}, {111} and {210}. This order is in the order of increasing surface energies, and so is regarded as decreasing morphological impotance. The equilibrium form of pyrite derived from the Hartman's law is therefore cubic with well developed {100} faces, together with medium {111} and smaller {210} faces. This is different from the equilibrium form derived by the Bravais-Donnay-Harker's law. Although surface microtopographic characteristics of each face are not infered in the Bravais-Donnay-Harker's law, the Hartman analysis can tell these characteristics. Since the above three faces are F-faces, growth layers should develop freely on any of these three faces.

In addition to the above three theories, WOLFF and BRODER (1965) proposed a new theory on equilibrium form of crystals based on the bonding energy differences. This model includes the concepts of surface energy and P.B.C. According to the analysis of WOLFF and BRODER, the equilibrium form of pyrite type crystals changes their forms depending on the bonding energy ratio between Fe–S and S–S ($\gamma = \phi_{S-S}/\phi_{Fe-S}$) in the case of pyrite (Fig. 5). The equilibrium forms of pyrite type crystals analysed by them are shown in Fig. 5 which indicates that the equilibrium form is composed of only {100 }and {111} faces, {210} faces do not appear.

$\delta \geq 3$ $3 > \delta \geq 1$ $1 > \delta > 0$ $\delta = 0$ $\longrightarrow$ CaF₂–type

Fig. 5 The equilibrium forms of pyrite-type crystals depending on the γ values (after WOLFF and BRODER, 1965).

4.2 Growth Forms of Pyrite Crystals

Most natural pyrite crystals show external forms consisting of combination of {100}, {111}

Table 8 Frequency of appearance of three major faces of pyrite.

Form	F	H
100	92.6	76
111	84.5	67
210	85.9	75

F: Fundortspersistenzen
H: Haufigkeitspersistenzen
(after HARTMAN, 1953)

and {210} faces. Frequencies of appearance in nature of these faces calculated from the morphological data given by TOKODY (1931) (F, Fundortspersistenzen) and by WACKER (1933) (H, Häufigkeitspersistenzen), both are listed in HARTMAN (1953), are shown in Table 8. Both data show that the {100} face gives the highest frequency of appearance, but it should be noted that the frequency of appearance of this face is much higher than these values, since both F and H values were calculated from the data reported in literatures where rarely observed forms are apt to be reported more frequently. According to the studies by SUNAGAWA (1957), the most commonly observed crystal habit of pyrite is cubic with dominant {100} faces in a wide spectrum of modes of occurrences, ranging from metallic ore deposits, their alteration zones to igneous and sedimentary rocks, except for special cases. The {210} faces come to the next, and the {111} faces appear only in limited occurrences. For instance, it is often observed in vein type deposits that even if crystals with well developed {111} or {210} faces appear in the inner portion of the vein, crystals occurring at the marginal part of the vein or in the surrounding wall rocks usually take cubic habit with well developed {100} faces (SUNAGAWA, 1957). SUNAGAWA also reported, and this was confirmed in the present study as well, that pyrite crystals in black-ore deposits or impregnated in hydrothermal alteration zones show systematic changes of habits from {100} to {210} as grain sizes become larger (Fig. 6), and that similar changes are also found for the combinations of {100}-{111} and {100}-{210}-{111}.

Based on these observations SUNAGAWA (1957) considered that the {100} faces can develop when pyrite crystals grow under the conditions unfavourable for pyrite growth, whereas the {210} or {111} faces can appear when crystals grow under much favourable conditions. In other words, the {100} face may be regarded as the most persistent crystal face among three major faces of pyrite. He applied the layer growth mechanism to explain this, and considered that the face on which growth layers can always develop is the {100} faces, thus the external form of crystals is determined by the ratio between the advancing rate and the rate of piling up of growth layers on the {100} faces, and that when crystals grow under fabourable conditions, the piling up rate increases, resulting in the development of {210} or {111} faces, whereas under unfavourable conditions cubic habit develops since the

Fig. 6 An example of habit variation depending on grain size of crystals (Wanibuchi mine, after SUNAGAWA, 1957).

advancing rate is much higher compared to the rate of piling up. He presented the results of observations on the surface microtopographs of three major faces to support his explanation.

Although SUNAGAWA made observations on the surface microtopographs of pyrite crystals using only low magnification reflection microscope, more sensitive methods of observation and measurement such as phase contrast microscopy and multiplebeam interferometry have been used in the present study. The result obtained in the present study may be summarized as follows.

1.　Distinct growth layers are always observed on the {100} faces. Morphology of growth layers varies, depending on crystal habits and also from crystal to crystal (Fig. 7).

2.　Roughly, a constant relation is noticed, between the step heights of growth layers and the density of growth islands on the {100} faces and crystal habits. When crystals grow large yet show simple cubic habit bounded by the {100} faces only, their growth layers are always thin and the density of growth islands is low, whereas growth layers on the {100} faces of crystals with well developed {111} or {210} faces are usually thick and the density of growth islands is high.

3.　In contrast to this, {111} and {210} faces show in most cases uniform surface microtopographs, i.e. straight triangular patterns parallel to the edges between the three neighbouring {100} faces on the {111} faces (Fig. 8-a), and positive striations parallel to the edges between the {100} and {210} faces on the {210} faces (Fig. 8-b). On these faces, free development of growth layers are not observed in most cases.

a　　　　　　　　　　　　　b
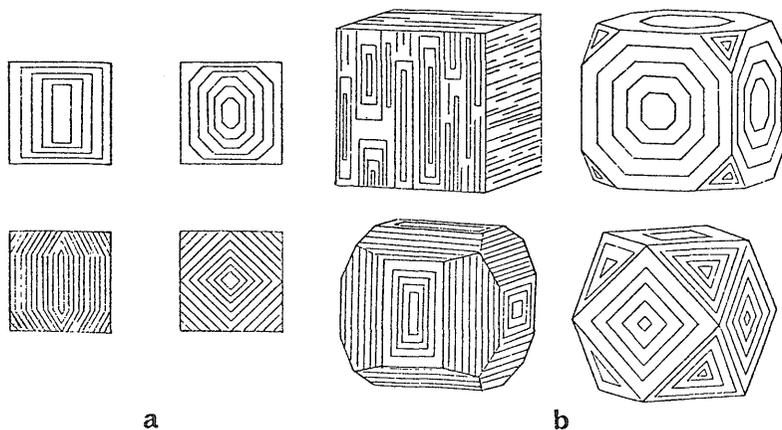
Fig. 7　Morphological variation of growth layers on (100) faces (a) and the relations to crystal habits (b).

a　　　　　　　　　　　b
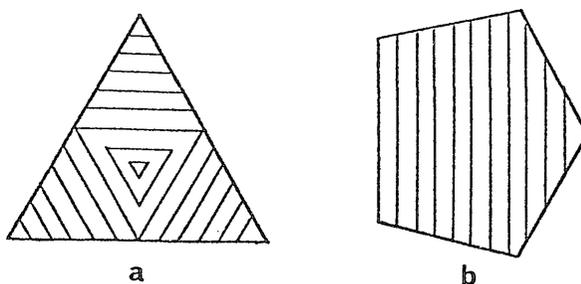
Fig. 8　Growth patterns commonly observed on {111} (a) and {210} (b) faces.
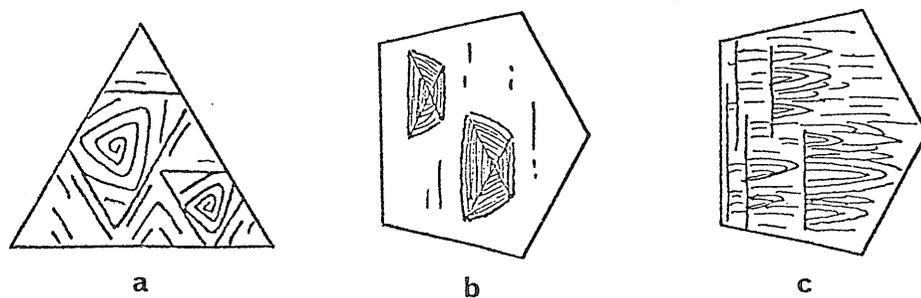
Fig. 9   Growth layers developing freely on {111} (a) and {210} (b and c) faces.

4.   However, free development of growth layers are observed on the {111} and {210} faces in rare cases. In these cases, triangular growth spirals with $<\bar{1}2\bar{1}>$ edges (Fig. 9-a), which are different in orientation from the commonly observed triangular patterns, are observed on the {111} faces, and trapezoidal growth pyramids (Fig. 9-b) or elongated growth layers perpendicular to the direction of positive striations on the {210} faces (Fig. 9-c).

5.   Growth pyramids on the {210} faces have been observed only on simple pentagonal dodecahedral crystals with mirror flat {210} faces, and elongated growth layers on the {210} faces only on the pentagonal dodecahedral crystals with negative striations. On the {210} faces of most pyrite crystals whose {210} faces show positive striations, development of growth layers have never been observed. It is also only on simple octahedral crystals that growth layers can develop freely on the {111} faces.

From the above observations, it is concluded that the {100} faces are the only faces in pyrite crystals on which growth layers can always develop freely, whereas the {111} and {210} faces are the faces on which growth layers can develop freely only when crystals grow under specific conditions and the advancement of growth layers on these faces are in most cases strongly controlled by the development of growth layers on the {100} faces. In other words, the {210} and {111} faces may be regarded as subsidiary faces which are initially formed by piling up of edges of growth layers on the {100} faces. Therefore, it is concluded that the {100} face is the most important face in natural pyrite crystals. It has been also observed that there is a close relation between crystal habits and the morphology and step heights of growth layers as well as the density of growth islands (growth centers) on the {100} faces. When crystals grow large yet have simple cubic habit, growth layers on the {100} faces are thin and the density of growth centers is low, whereas when crystals take habit with {210} or {111} faces, thicker growth layers and higher density of growth centers are commonly observed characteristics. It is also noticed that as the morphology of growth layers on the {100} faces changes, crystal habits transform from simple cubic to those {210} or {111} faces and eventually to simple pentagonal dodecahedral or octahedral habits.

4.3   Discussion and Conclusion

Major crystal faces appearing on natural pyrite crystals are {100}, {210} and {111} faces. This agrees well with both Bravais-Donnay-Harker's law and Hartman's P.B.C. analysis in that these three faces are major faces consisting of equilibrium form, but disagrees with Wolff's equilibrium

form on which {210} face does not appear. As to the order of morphological importance of the three faces, the order according to the Bravais' law is {111}, {100} and {210} and according to both Donnay-Harker and Hartman {100}, {111} and {210} in the decreasing order of importance, all theoretical order being not in accordance with the order of importance in growth forms which is {100}, {210} and {111}.

According to HARTMAN (1953), the {100}, {111} and {210} faces are all F-faces, thus they must be faces formed by the spreading and piling up of growth layers which develop freely on respective faces. However, on actual crystals, the {100} face is the only face on which growth layers can develop freely, the {210} and {111} faces do not exhibit free spreading of growth layers in most cases. Especially most {210} faces consist of only positive striations. It is only in exceptional cases that growth layers can develop freely on {210} and {111} faces. Therefore, it is considered that the {210} and {111} faces have characteristics similar to the first order S-faces in Hartman's definition. Summarizing the present observations, we see a considerable discrepancy between the theoretically deduced equilibrium form (mainly from the structure) and the the growth forms observed on actual crystals, both in macro-morphology (crystal habits) and micro-morphology (surface microtopography).

Considering the mechanism of habit variation of pyrite crystals on the basis of the characteristics of macro- and micromorphology observed in the present study, a basically similar conclusion as the one by SUNAGAWA (1957) is obtained. That is, growth of pyrite crystals mainly takes place by the spreading and piling up of growth layers on the {100} faces and the {210} and {111} faces appear initially in most cases by piling up of edges of growth layers spreading on the {100} face. It is due to this fact that most commonly observed habit of pyrite crystals in nature is simple cubic. If growth layers spring out very actively on the {100} faces and/or their step heights are relatively high, the {210} or {111} faces will appear gradually resulting in pentagonal dodecahedral or octahedral habits, but if they do not, crystals will not change their habit and maintain simple cubic habit even if crystals grow larger.

This explanation, however, is applicable when most growth layers on a {100} face can advance up to the edges of the face, *i.e.* when numbers of growth centers are small, or in other words when crystals grow under steady state growth conditions. If many growth centers are formed on one face, and growth layers originating from them can cover only local areas, a large number of growth pyramids or growth plateaus with side faces of {210} or {111} faces will appear on the {100} face, and the crystal will remain a simple cube as a whole, instead of changing its habit from simple cube to pentagonal dodecahedron or octahedron.

It is thus explained why pentagonal dodecahedral or octahedral habits are dominant in the center of ore body whereas cubic habit appears mainly in the marginal part and in wall rocks of ore deposits. The phenomenon that pyrite crystals in alteration zones surrounding ore deposits and in hydrothermal alteration zones change their habits depending on grain size is also explained satisfactorily by this mechanism.

It has been observed in the present study that which faces, {210} or {111} faces, appear by piling up of growth layers on the {100} faces is closely related to the morphology of growth layers on the {100} faces. It is, therefore, assumed that the morphology of growth layers on the {100} faces controls the habits of pyrite crystals. The morphology of growth layers is de-

fined by the α values of growth steps and P.B.C. It is expected that growth layers will take circular form when α value is low (*i.e.* high temperature) and polygonal form when α value is high (low temperature) for the growth steps with the same P.B.C. Since in the case of polygonal growth layers, their morphology is defined by the closest packed directions, it is directly related to P.B.C. The α value here is essentially the JACKSON's (1958) α value, but generalized to apply for the steps of growth layers, and is related to P.B.C.

$$\alpha = \xi \cdot L/kT$$
$$\xi = E^{sl}/E^{cr}$$

where L: dissolution heat (in the case of solution growth)

  k: Boltzman constant

  T: growth temperature (K°)

  E^{sl}: bonding energy of growth unit in a slice defined by HARTMAN

  E^{cr}: crystallization energy

Circular growth layers have not been observed at all on natural pyrite crystals. The fact that most pyrite crystals exhibit polygonal growth layers bounded by the $<100>$ suggests that natural pyrite crystals grow with high α values, *i.e.* under considerably lower temperature conditions than the dissolution temperature. When growth layers show polygonal form and have high α values, growth steps are defined by the closest packed directions. After HARTMAN (1953), the P.B.C.s of pyrite are $<100>$, $<110>$, $<\bar{1}21>$, $<\bar{1}20>$ and $<021>$. Among these, only $<100>$ has bonding energy, or attachment energy, (2a + b) per one molecule and the others have less bonding energy (2a). That is, the $<100>$ is the strongest P.B.C. among these P.B.C.s. The energy differences among the other four are not known and the difference between the two $<100>$ directions is also not analysed. Assuming there is a difference in bonding energies between the two $<100>$ directions, judged from the symmetry of pyrite, it is expected that growth layers on the {100} faces will take elongated rectangular form bounded by $<100>$, when crystals grow with high α values. This agrees well with the observations that elongated rectangular growth layers are the most commonly observed form. If impurity adsorption occurs along steps of growth layers under higher temperature conditions, the possibility of appearing growth steps with different directions in addition to the $<100>$ increases and the growth layers with $<110>$ and $<210>$ start to appear. Thus, various forms of growth layers appear depending on the growth conditions, resulting in various crystal habits.

Table 9 summarizes the present observations on the surface microtopographs of {100} faces, in relation to the modes of occurrences, mineral, assemblages, crystal habits and sizes of pyrite crystals. The localities are arranged roughly in the order of decreasing temperatures and are broadly divided into categories. Kieslarger deposits are grouped separately from contact, vein and Kuroko type deposits, since pyrite crystals in Kieslager deposits seem to have experienced recrystallization, whereas in the latter types of deposits they are precipitated directly from hydrothermal solutions and have not experienced recrystallization. The column of mineral assemblages is divided into two, ore minerals and gangue minerals, both are mineral assemblages of the deposits, not of pyrite itself, though such assemblages may indicate environmental conditions of pyrite formation. Surface microtopographs of {100} faces only are described in respect to the roughness of the face, step heights of growth layers and the densities of growth centers. Since the {100} faces are the most

Table 9   Crystal habit and surface microtopographs of

Locality	Type of ore deposit	Mineral assemblage	
		Ore minerals	Gangue minerals
Kamioka	Contact metasomatic	Sp Gn Cc Cp Py	Qz Cal skarn
Chichibu	Ibid with hydrothermal stage	Cp Sp Gn Py Aspy Po	Cal skarn
Ashio	Xenothermal vein	Cp Bo Py Po Sp Cass	Qz
Ogoya	Epithermal vein	Cp Bo Py Cc Sp	Qz
Osarizawa	〃	Cp Bo Py	Chl Qz
Arakawa	〃	Cp Py Sp Gn Bo	Chl Qz
Washiaimori	〃	Cp Py Sp Gn	Chl Qz
Ani	〃	Cp Gn Sp Bo Py	Chl Qz
Akyu	〃	Cp Sp Gn Py	Qz
Komatsu	〃	Cp Bo Py	Qz
Namariyama	〃	Cp Cc Bo Gn Py	Qz Chl
Oppu	〃	Cp Py Sp Gn	Qz Cal carb.
Oizumi	〃	Cp Sp Gn Py	Qz Cal carb.
Kambe	〃	Py Stb	sericite
Mizusawa	Network with Kuroko	Cp Cc Sp Gn Py	Qz Ba
Tsunatori	〃	Cp Py Bo Sp Gn Hm	Qz Chl Ba
Kamikita	Kuroko (network)	Tet Eng Sp Cp Py Dig	Ba Gps
Furutobe	〃 （ 〃 ）	Cp Gn Sp Py	Ba Qz
Kosaka	〃 （yellow ore）	Py Cp Sp Gn Cc Bo Cv	Ba Gps Qz clay
Ainai	〃 （ 〃 ）	Cp Py Sp Gn	Gps
Shakanai	〃 （ 〃 ）	Cp Py Sp Gn	Gps Ba
Matsumine	〃 （ 〃 ）	Cp Py Gn Sp	Qz
Iwasawa	〃 （gypsum ore）	Cp Py	Gps
Hanaoka	〃 （ 〃 ）	Cp Py Sp Gn Tet	Ba Gps
Udo	〃 （ 〃 ）	Cp Cc Cv Py Sp	Gps
Hitachi	Kieslager*	Py Cp Sp Po Mt Gn	Chl Qz Ba Cd
Taro	〃 ＊	Py Cp Gn Sp Po	Qz Ba
Shimokawa	〃	Cp Py Po Pn	Qz Chl
Yanahara	〃	Py Cp Po	Qz
Besshi	〃	Py Cp Po Mt Bo Tet	Qz
Shirataki	〃	Py Cp Sp Mt Bo	Qz Ga
Sazare	〃	Py Cp Po	Qz Tm
Okuki	〃 （low grade）	Py Cp Sp Tet Bo	
Ogasawara	Druses in basalt	Py	

Remarks, *: received later contact metamorphism
　　Aspy: arsenopyrite, Bo: bornite, Cass: cassiterite, Cc: chalcocite, Cp: chalcopyrite, Cv: covelline,
　　Dig: digenite, Eng: enargite, Gn: galena, Hm: hematite, Mt: magnetite, Pn: pentlandite, Po:
　　pyrrhotite, Py: pyrite, Sp: sphalerite, Stb: stibnite; Ba: barite, Cal: calcite, Cd: cordierite, Chl:
　　chlorite, Ga: garnet, Gps: gypsum, Qz: quartz, Tm: tourmaline, carb.: carbonates

important face among the three major faces and they control the morphology of crystals, their surface microtopographs only are tabulated. The descriptions on the surface microtopographs are only of the crystals investigated in the present study and may not be generalized for the locality, yet they may give some idea.

In Table 9, the first point to be noted is that simple cubic habit or habits with well developed

{100} faces in relation to the modes of occurrences.

Locality	Crystal habit		Surface characteristics of {100} faces***			Crystal size (mm)
	In ores	In wall rocks	Rough-ness	Step heights	Density of growth centers	
Kamioka	a	a	I	H	H	<10
Chichibu	a ≃ e > o	a	F	L	H	<30
Ashio	a ≃ e > o	a	I	M	H	<10
Ogoya	e ≃ o	?				<10
Osarizawa	e > o ≃ a	a	R	H	M	<20
Arakawa	a	a	I	H	M	<30
Washiaimori	e > a	a	I	M	M	<20
Ani	e > a**	e > a**	I	L	M	<30
Akyu	e ≃ a > o	a	I	M	M	<15
Komatsu	o > a	a	I	M	M	<20
Namariyama	a > o	a	I	H	M	<15
Oppu	e > a	a	I	H	M	<15
Oizumi	a	?	R	H	M	<15
Kambe	o	a	R			<10
Mizusawa	o	?				<10
Tsunatori	a > o	a	F	L	L	<15
Kamikita	a	a	R	H	H	<10
Furutobe	a	a	I	M	M	<10
Kosaka	a > e > o	a > e	I	M	L	<20
Ainai	a > e > o	a	I	M	L	<10
Shakanai	a ≃ e > o	a ≫ e ≃ o	I	M	L	<10
Matsumine	a ≃ e > o	a ≫ e ≃ o	I	M	L	<10
Iwasawa	a ≃ e ≃ o	?	I	M	M	<20
Hanaoka	a ≃ e ≃ o	a ≫ e ≃ o	I	M	L	<20
Udo	a > e	a	I	M	L	<15
Hitachi	a > e	a	I	M	H	<20
Taro	a	a	R	H	H	< 1
Shimokawa	a	a	R	H	H	< 1
Yanahara	a	a	R	H	H	< 1
Besshi	a	a	R	H	H	< 1
Shirataki	a	a	R	H	H	< 1
Sazare	a	a	R	H	H	< 1
Okuki	a	a	R	H	H	< 1
Ogasawara	a		F	L	H	<10

Remarks, **: negatively striated {210} crystals
***: crystals in ores, where,
roughness; R: rough, I: intermediate, F: mirror flat,
step heights(Å); H > 100, 100 > M > 50, 50 > L
density(number/cm²); H > 10^2, 10^2 > M > 10, 10 > L

{100} faces are most predominant, followed by habit with combination of {100} and {210}, and then by those with {111} faces. Octahedral habit is the least predominant habit.

Another striking tendency that can be noticed in this table is that pyrite crystals in Kieslager deposits almost exclusively show simple cubic habit, whereas those in vein types as well as Kuroko type deposits show variable habits. Most pyrite crystals in Kieslager deposits are much smaller in size than

those in other types of deposits. Their sizes are almost comparable to those of pyrite crystals occurring in wall rocks of contact, vein or Kuroko type deposits, which again almost exclusively show simple cubic habit. There is a close similarity, both in crystal sizes and crystal habits, between pyrite crystals of Kieslager deposits and those in wall rocks of ore deposits of other types.

Although it is not certain whether pyrite crystals in Kieslager deposits took the present habit before they experienced recrystallization, it is definitely true that they exclusively take simple cubic habit. Even pyrite crystals in Kieslager deposits, which received contact metamorphism, $e.g.$ in the Hitachi mine, and attained larger sizes, show cubic habit associated with minor {210} faces, not with {111} faces. There is no evidence whatsoever to suggest that original habits differing from simple cubic habit have transformed to the present simple cubic habit due to recrystallization. It is therefore conjectured that pyrite crystals both in Kieslager and wall rocks of vein, Kuroko or contact type deposits grew under unfavourable conditions for pyrite formation, such as the conditions of low supersaturation, low sulfur fugacity or either much higher or lower temperatures than appropriate temperatures for pyrite formation.

Comparing crystal habits of pyrite among vein type deposits, it is noted that pyrite crystals in sulfide-quartz-chlorite veins generally take pentagonal dodecahedral or octahedral habits, or cubic habit with well developed {210} and/or {111} faces, whereas those in sulfide-carbonate veins simple cubic habit or habits with well developed {100} faces. This again may be related to sulfur fugacity difference. Crystals in the Kambe mine, stibnite-sericite veins, are an exception and take simple octahedral habits, but the origin of this unusual octahedral habit has been interpreted as due to impurity adsorption of arsenic on {111} faces by SUNAGAWA and TAKAHASHI (1955).

It is also noticed in the table that pyrite crystals in black-ores, yellow-ores and gypsum-ores of Kuroko type deposits take habits of combination of three major faces and not simple cubic habit, whereas those in net work zone of Kuroko type deposits almost exclusively show simple cubic habit, in spite of the fact that they attain fairly large sizes. Such differences may also be related to the difference in environmental conditions.

Final point to be noted is that the roughness, step heights and densities of growth centres are markedly different between crystals in Kieslager deposits and those in deposits of other types. Although there are exceptions, it is noticed as a general tendency that crystals in Kieslager deposits and in wall rocks exhibit rough surfaces, high step heights and high densities of growth centres, whereas those in contact metasomatic deposits, vein type deposits and Kuroko type deposits much smoother surfaces, lower step heights and lower densities of growth centres. This difference should be related to the difference in environmental and growth conditions. If crystals grow under steady state growth conditions, in other words under favourable conditions, their crystal surface will be flat, the step heights of growth layers low and the densities of growth centers also low, whereas if they grow under the conditions apart from the steady state growth conditions, they will show opposite characteristics due to inclusion of foreign particles and other complicated factors. Furthermore, if crystals grow in confined environments, they will show much rough surface than those grown in free space. The observed difference of surface microtopographs of {100} faces between crystals in Kieslager type deposits as well as in wall rocks and those in deposits of other types may be due to such differences in environmental and growth conditions.

Chapter 5. Dissolution Patterns

5.1 Introduction

In addition to growth patterns described in chapter 3, dissolution patterns due to natural etching are often observed on pyrite crystals.

It is well known that dissolution of crystals, in general, preferentially progresses at edges and corners of crystals, resulting in external forms bounded by curved edges and faces. Natural diamond crystals which invariably exhibit curved edges and faces are typical examples of dissolution forms. There are crystals, on the other hand, which exhibit perfect polygonal external forms with flat faces, yet their surface microtopographs show features formed by dissolution process.

Since dissolution takes place, due to the changes in environmental conditions, on the crystal surfaces which are formed through growth process and have kinks and steps as surface micro-topographs, it is expected that similar, but in reverse direction, process as growth process will take place.

Dissolution (etching) patterns observed on crystal faces have been studied widely in the field of metallurgy and crystallography and a great number of results have been obtained. Most of the previous studies on dissolution patterns have been done with the purpose of clarifing crystal structure or lattice imperfections, by studying symmetry, density and alignment *etc.* of etch pits produced artificially on as-grown crystal faces, bisected and polished surfaces or cleavage surfaces by chemical, thermal, mechanical and electrolytic etching. In these investigations, etch pits are artificially forced to be formed so as to see their symmetries or densities, and thus enough attention has not been paid to the mechanism itself, as a result people simply thought that etching process is a three dimensional digging process at line defects out cropping on the surfaces.

It is clear, however, that growth of crystals takes place by two dimensional spreading and piling up of growth layers on the crystal surfaces, and so if dissolution takes place on the as-grown crystal faces and in reverse direction of growth, evidence to show two dimensional dissolution process should also be expected on weakly dissolved surfaces. Among the works based on such point of view, the theoretical consideration by FRANK (1958) and observations on hematite crystals by SUNAGAWA (1962) gave significant answers to the two-dimensional nature of dissolution process, both from theory and experiment.

Observations on natural etching patterns on pyrite crystals have been done by several workers such as ICHIKAWA (1929), WACKER (1933) and KOMATSU (1964). Especially ICHIKAWA observed in detail etching patterns of natural pyrite crystals from many localities in Japan and described their morphological characters and symmetries on each face. He observed both etch pits and etch hillocks. However, as his observations were mainly made by the un-aided eyes or low power reflection microscopes, some of his results seem to need reexamination using modern high sensitive observation methods. In fact, it is conjectured that many of the etch hillocks in his observations are not hillocks formed by dissolution but growth hillocks. There is also indication that he apparently misjudged elevations as depressions and identified them as pits. KOMATSU (1964) observed dissolution patterns on the {100} faces of pyrite crystals from the Tsunatori mine using the phase contrast

microscope and reported evidence to show two dimensional dissolution process, similar one as SUNAGAWA's observation on hematite crystals. He observed such features only on one kind of faces of pyrite crystals from only one locality, and thenceforth no works have been done to observe details of dissolution patterns on different crystal faces of pyrite crystals from many localities using high sensitive methods.

5.2 Observations

5.2.1 The {100} Face

Among the major three faces of pyrite crystals, {100} faces are the faces on which dissolution patterns are most difficult to find. Although ICHIKAWA (1929) reported eye-form etch pits with square centers on {100} faces, any features which can be clearly regarded as etch pits have not been observed on any crystals investigated in the present study. It is plausible that ICHIKAWA mis-judged eye-form growth hillocks such as shown in Plate 29·3 as etch pits. The dissolution patterns observed in the present study on the {100} faces of a large number of pyrite crystals from various modes of occurrences and many localities may be classified into the following three categories.

1.   Point-form depressions
2.   Linear etch trenches
3.   Dissolution along growth steps

Among these three, the first and the second types are observed most remarkably on the crystals from the Tsunatori mine and their morphological characteristics are exactly the same as those reported by KOMATSU (1964). That is, most of dissolution patterns appear as depression spots or lines. On mirror flat {100} faces on which any growth layers are hardly observed even under the phase contrast microscope, point- or linear-form depressions are observed in a form of worm-eaten spots. Point-form depressions appear as if they are distributed randomly, but they align along certain crystallographic directions if their general distribution is observed macroscopically. Most linear-form depressions are also straight parallel to the <001> and <011> directions (Plate 42-1, 2). KOMATSU (1964) considered that the linear depressions are formed by preferential dissolution along the steps of thin growth layers, and the point-form depressions at vacancies or impurity sites on the surface, both representing the patterns formed by two dimensional dissolution. Judging from the visibility of the phase contrast microscope, the depths of these depressions are estimated to be in the order of n × 10 Å. KOMATSU's conclusion is therefore acceptable. However, the linear depressions must possibly have been formed by trenching along crystallographically weak directions, starting from point form depressions. The third type dissolution patterns have been observed on crystals from several localities. Corners of growth layers are curved or become irregular due to dissolution of this type, two remarkable examples are shown in Plate 29-3 and Plate 28-3, observed on the crystals from the Iwasawa mine and the Akyu mine, respectively. Due to dissolution, original rectangular growth hillocks are transformed to eye-form hillocks. These crystals have curved edges which also show that they have experienced dissolution.

5.2.2 The {111} Face

The {111} faces are the faces which are affected comparatively easily by dissolution. It is often observed on one crystal that {111} faces alone give dull luster due to mottled surface by dissolution, while other faces show metallic luster. The rates of dissolution on the {111} faces vary

considerably from crystal to crystal, some show deep triangular etch pits, or a large number of tiny etch pits, others show heavily etched surface on which original growth patterns are hardly observed. It is almost exceptional to find {111} faces entirely free from dissolution.

A good example of well-developed deep etch pits is found on the crystals from the Kambe mine. The crystals are simple octahedral, and deep triangular etch pits which are parallel to the triangle of the (111) face are found on their {111} faces. Smaller triangular etch pits to be described later have the same orientation as the above, and it should be noted that the triangular patterns formed by etching have opposite orientation to the triangular growth patterns described in section 4.3. The depth of the triangular etch pits are in the order of microns, and they are point-bottomed. These crystals also exhibit dissolution ditches along the steps of growth layers and their surfaces appear very rough (Plate 42-3).

Although crystals from the Kambe mine exhibit the heaviest dissolution patterns like the remarkable development of etch pits, there are also many crystals whose {111} faces are heavily etched. There is a general tendency that the {111} faces on the crystals with {111} and {100} faces are more heavily etched than on simple octahedral crystals. For instance, in the case of crystals from the Tsunatori mine as already described, the dissolution patterns on the {100} faces are observed only under the phase contrast microscope, whereas those on the {111} faces of the same crystal can be easily seen under the ordinary reflection microscope at low magnification (Plate 43-1).

The dissolution patterns described above are easily observed under the ordinary reflection microscopes, but there are also weak dissolution patterns on the {111} faces which are detectable only under the phase contrast microscope. As already described in section 3. 2, growth patterns commonly observed on the {111} faces are triangular steps. If such steps are observed carefully, dissolution patterns of several types are observed. On the crystals from the Ogoya mine, a large number of tiny triangular pits are seen, and the corners of these triangular pits are slightly rounded off, their depths range from n × 10 to 200 Å. These pits usually coagulate together to form larger triangles or align along certain directions, but there are also cases that they appear isolately. On the side surfaces of these pits, concentric steps are observed and their slopes are much shallower than those of larger etch pits. Together with etch pits, thin steps of complicated forms are also seen on the same surface. These relations may be seen in Plates 43–2 and 43–3. It is considered that these thin steps are formed by dissolution along steps of thin growth layers, which suggests two dimensional nature of dissolution process. In addition to these, {111} faces exhibit tiny etch pits or depressions in a form of negative crystals which appeared due to dissolution of smaller foreign crystals adhered on the surface.

5.2.3 The {210} Face

The {210} faces have a similar nature as the {100} faces, in that dissolution patterns are hardly observed. One reason for this is that most {210} faces are heavily striated (positive), thus it is difficult to detect delicate patterns on those faces. However, distinct dissolution patterns are observed only rarely even on mirror flat {210} faces. The most distinct dissolution patterns observed on the {210} faces are etch pits at the summits of growth hillocks, which are regarded as ordinary etch pits formed at line imperfections outcropped on the surface such as dislocations which played a role of growth centres. When such surfaces are heavily etched, etch pits of this type change their

form to take a falling droplet form elongated parallel to the direction of negative striations (Plate 44–1). Growth layers of such growth hillocks become more irregular in form as advancing outer-wards. It is not certain whether such a change in form is due to growth process or dissolution process along growth layers of regular form. In addition to these patterns, random distribution of small etch pits or etch trenches of irregular form are also observed. These are considered to have been formed by preferential dissolution at point imperfections on the surfaces similarly as in the case of {100} faces. ICHIKAWA (1929) reported triangular, trapezoidal and pentagonal pits on the {210} faces. Such etch patterns have not been observed in the present study, except etch pits observed at the summits of growth hillocks (Plate 44-2).

5.3 Discussion

The dissolution patterns of pyrite crystals observed in the present study may be summarized as follows:

1. Among the three major faces of pyrite, the {111} face receives the heaviest dissolution, and the {100} and {210} faces much less dissolution.

2. In the present study, distinct etch pits have not been observed on the {100} faces. The weak dissolution patterns observed on the crystals from the Tsunatori mine are in accordance with the observations by KOMATSU (1964).

3. Triangular etch pits are observed on the {111} faces. They have the same orientation as the triangle of {111} faces, and reverse orientation to the triangle of growth layers. The depths of triangular etch pits vary from crystal to crystal as well as locality. Features to show two dimensional dissolution process have been observed on the {111} faces of octahedral crystals from the Ogoya mine.

4. No distinct dissolution patterns have been observed on the {210} faces, except etch pits at the summits of growth hillocks.

Based on the above results, some comments as to the dissolution (etch) process of pyrite will be made in the followings.

Firstly, why various dissolution patterns observed by ICHIKAWA (1929) were not found in the present observations? One of the reasons may be that he was confused and did not make clear distinction between growth and dissolution patterns, but more important reason is sample selec-tion. Since the present study has mainly focussed on the growth process, crystals with the least etched surfaces have been selected. However, it should be pointed out that because such crystals have been selected, it was possible to investigate initial stage of dissolution process.

Secondly, why different faces received different degree of dissolution on one crystal? It is especially interesting that the {111} faces are much heavily dissolved compared to the other two faces on the same crystal. The {111} face has the highest reticular density among the three major faces ac-cording to the Bravais-Donnay-Harker's law and occupies higher position than the {210} face in the order of morphological importance derived from P.B.C. analysis, yet it receives much heavier dissolution than the {100} and {210} faces. The increasing order of dissolvability is {100}, {210} and {111}. This order agrees well with the order of predominancy of crystal faces ob-served in actual crystals. Therefore, it is considered that the {210} faces are more important face than the {111} faces, judging both from growth and dissolution features.

Chapter 6. Conclusion

Based on the observations of surface microtopographs of pyrite crystals, the mechanisms of crystal growth, dissolution and the origin of variation of crystal habits of pyrite are discussed in the preceding chapters. To conclude this thesis, the results of the present study will be summarized in this chapter.

Although external forms of pyrite crystals in nature vary considerably from crystal to crystal and depending on the modes of occurrences and localities, crystals mainly consist of three major faces, a {100}, o {111} and e {210}. Although a large number of faces are also reported in addition to these three major faces, they are subsidiary large only in rare cases.

The three major faces are F-faces according to HARTMAN's definition and P.B.C. analysis, but {100} faces are the only real F-faces on which growth layers can develop freely. The other two faces have a nature of S-faces in most cases, since growth layers can not develop freely on these faces and their advancing is strongly controlled by the {100} faces. Only when crystals are nearly simple octahedral or pentagonal dodecahedral in habit, free development of growth layers are observed on these faces. It is therefore concluded that pyrite crystals grow in most cases by a layer-by-layer growth mechanism on the {100} faces.

The above conclusion on the growth mechanism of pyrite crystals implies significant meaning in considering the problem of their habit variations. The equilibrium forms of pyrite crystals theoretically derived on the basis of geometry of the lattice, crystal structure and the bonding energies, are quite different from the actual growth forms both in macro- and micro-morphology, i.e. in the frequency of appearance of each habit as well in the surface microtopographs of three major faces. In the present study, the causes of such discrepancies are investigated, and the origins of habit variations are analysed on the basis of crystal growth mechanism of pyrite. It is concluded that external forms of pyrite crystals vary depending on the ratio between the rate of lateral advancing of growth layers on the {100} faces and the rate of their piling up, as well as on the variation of morphology of these growth layers. Based on this conclusion, the previous works on the relation between crystal habits and the modes of occurrences reported mainly by SUNAGAWA (1957) are analysed and it was possible to give a satisfactorily explanation to the relations.

The differences and origins of two types of striations on the {210} faces, i.e. positive and negative striations, which have hitherto been obscure are also well understood in the present study. Based on the observations of habit variations depending on grain sizes and on the internal inhomogeneities in negatively striated crystals, it is concluded that positive striations are formed by the piling up of the edges of growth layers on the {100} faces, and not by the free development of growth layers on the {210} faces, whereas negative striations are due to free development of growth layers on the {210} faces.

Finally, natural dissolution patterns on the three major faces are also observed in detail and the relation between growth and dissolution is investigated. It was found that 1) the {111} is the face which receives dissolution most easily among the three major faces, 2) dissolution process is fundamentally a two dimensional process, and 3) triangular etch pits on the {111} faces are reversely oriented to the triangular growth patterns.

The following conclusions may be derived from the surface microtopographic observations of pyrite crystals and several informations obtained from them. Most natural pyrite crystals are regarded to have grown from aqueous solution phase judging from their modes of occurrences and their surface microtopographs. Although growth spirals are observed on pyrite crystals in this study for the first time, it is concluded that the spiral growth mechanism is not the major growth mechanism of pyrite crystals, and that pyrite crystals grow in a majority of cases by the layer-by-layer growth mechanism originating from two dimensional nucleation. It is considered that this reflects the characteristics of crystal growth in aqueous solution phase.

As to the reasons that pyrite crystals exhibit a wide variation of habits, it should be pointed out that there are differences among the three major faces in their importances in crystal growth and morphological aspects. If the three major faces are equally important, crystals will always take more or less similar form in which three faces develop nearly equally, unless crystals grow under certain specific conditions such as condition where impurity adsorption is expected. The fact that the {100} faces are stronger than the other two faces in the importance in crystal growth and in morphological aspects is the main reason for the variation of crystal habit of pyrite depending on the environmental conditions.

The reason why pyrite crystals with negative striations occur far rarely than those with positive striations and when they occur all pyrite crystals are negatively striated would not have been understood unless the surface microtopographic characteristics of the {210} faces with both negative and positive striations were understood.

Several problems relating to the morphology of pyrite crystals have been clarified as discussed in this thesis through the study of growth mechanism of pyrite crystals based on the surface micro-topographic studies. Although the present study may have offered some new understandings as to the growth and dissolution mechanism, and the origin of habit variation of natural pyrite crystals, there still remain problems to be solved in future.

Problems awaiting future studies are such as follows;

1. Relation between morphological changes during growth and impurity concentration among different growth sectors.

2. Relation between impurity adsorptions and the morphology of growth layers on the {100} faces.

3. Detailed P.B.C. analysis of expected morphology of growth layers on the {100} faces, as well as those on the {210} and {111} faces when growth layers can develop freely on the latter two faces.

4. Search for specific conditions under which growth layers can develop freely on the {210} or {111} faces; *i.e.* conditions to form negatively striated {210} faces or $<\bar{1}2\bar{1}>$ triangular growth layers on {111} faces.

Acknowledgements

sity, a former staff of the Survey, who suggested this topic and contineously guided the author throughout this study.

A part of the samples used in this study owes to personal collections especially of the late Professor Shuzo Hasegawa, Dr. Kin-ichi Sakurai and Mr. Isao Takatori, to whom the author's thanks are also due.

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地 名 英 和 対 応 表

(c.f. Table 2)

Ainai	相 内	Akyu	秋 保	Ani	阿 仁
Arakawa	荒 川	Ashio	足 尾	Besshi	別 子
Chichibu	秩 父	Furutobe	古遠部	Hanaoka	花 岡
Hitachi	日 立	Iwasawa	岩 沢	Kambe	神 戸
Kamikita	上 北	Kamioka	神 岡	Komatsu	小 松
Kosaka	小 坂	Matsumine	松 峰	Mizusawa	水 沢
Namariyama	鉛 山	Ogasawara	小笠原	Ogoya	尾小屋
Oizumi	大 泉	Okuki	大久喜	Oppu	尾 太
Osarizawa	尾去沢	Sazare	佐々連	Shakanai	釈迦内
Shimokawa	下 川	Shirataki	白 滝	Taro	田 老
Tsunatori	綱 取	Udo	鵜 峠	Washiaimori	鷲合森
Yanahara	柵 原				

黄 鉄 鉱 の 表 面 マ イ ク ロ ト ポ グ ラ フ

遠 藤 祐 二

要　　旨

本邦各地から種々の産状を持つ黄鉄鉱の結晶を集め，その主要な結晶面である {100}，{111} および {210} の３面上の表面マイクロトポグラフを，最も精鋭な手法を駆使して詳細に観察し，それを もと

に，黄鉄鉱の結晶成長機構，晶相変化の原因と過程，産状の差による形態的特色等について検討した．

　主要3面の表面マイクロトポグラフの観察から，{100}面上には常に成長層の自由な発達がみられ，その形態は産地や結晶個体の差による変化に富み，晶相と密接な関係を持っている；対照的に，{111}および{210}面上の成長模様は，大部分の場合，極めて単純かつ画一的であり，その形態は隣接して発達する{100}面の消長に強く影響されている；3者の面のいずれにも渦巻成長層が存在することが初めて確認されたが，黄鉄鉱の成長では二次元核形成による層成長が主役で，渦巻成長は副次的な役割しか果していない；などの事実が明らかになった．

　以上の事実は，黄鉄鉱の結晶成長は主として{100}面上での層成長機構によって推進されることを示している．したがって，黄鉄鉱の晶相変化は，基本的には{100}面上における二次元核の形成速度と成長層の拡がり速度の比，および成長層沿いの不純物効果等によって決定されるといえる．この結論は，理論的に導かれた黄鉄鉱の平衡形と現実にみられる成長形との間の喰い違いの理由をよく説明することができるし，天然における黄鉄鉱の晶相と産状との間の一般的な関係からも支持される．

　また，黄鉄鉱の表面マイクロポトグラフに基づいて，熱水溶液中での結晶成長の一般的な特徴についても論議し，成長の逆過程である天然での溶解作用を示すトポグラフについても検討を試みた．

Plate 27

3 Typical example of rectangular growth layers bounded by <001>, (100) face, Hanaoka mine. impregnated in gypsum ore of Kuroko type deposit.
simple {100}

2 Mirror flat (100) face with growth islands occurring only along edges of the face, Tsunatori mine. in network vein.
simple {100}

1 Low magnification photomicrograph of (100) face with heavily striated appearance, Oizumi mine. in druse of epithermal vein.
simple {100}
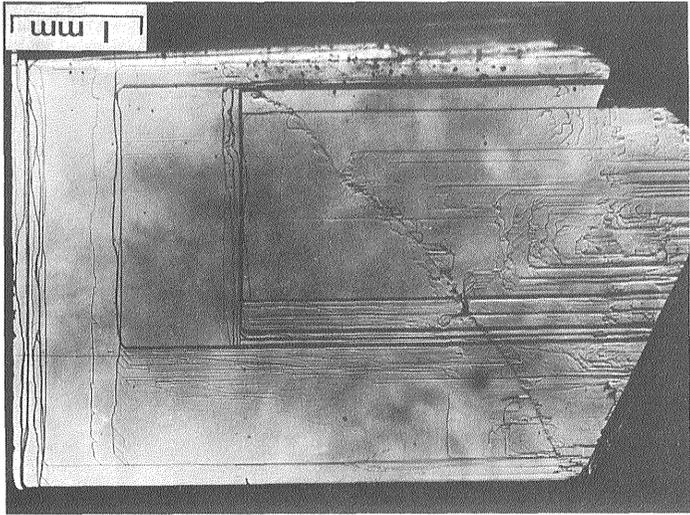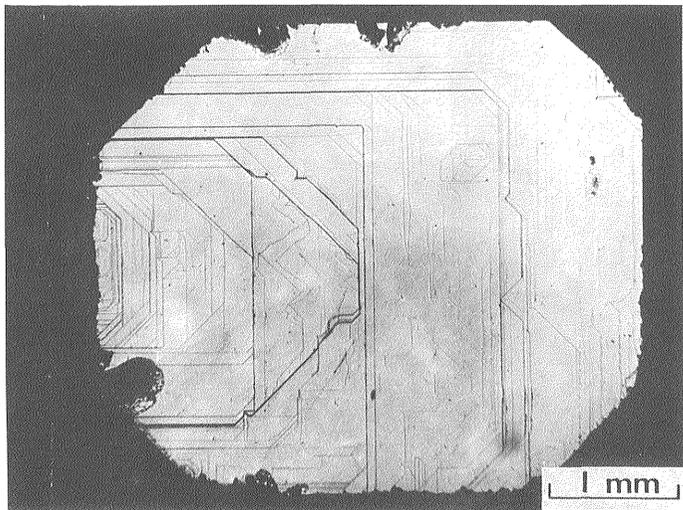
1   An example of rectangular growth layers bounded by <001> and <011>, (100) face, Hanaoka mine. impregnated in gypsum ore of Kuroko type deposit.
simple {100}

2   An example of growth layers bounded by <001> and <012>, (100) face, Chichibu mine.
impregnated in contact metamorphosed limestone.
simple {100}
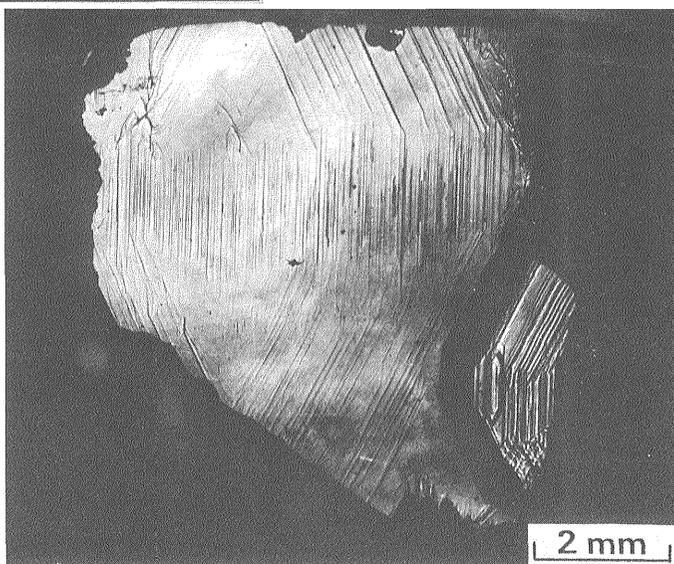
3   Growth layers bounded by <001>, <011> and <012>, (100) face, Akyu mine.
in epithermal vein.
{100} ≃ {111} ≃ {210}
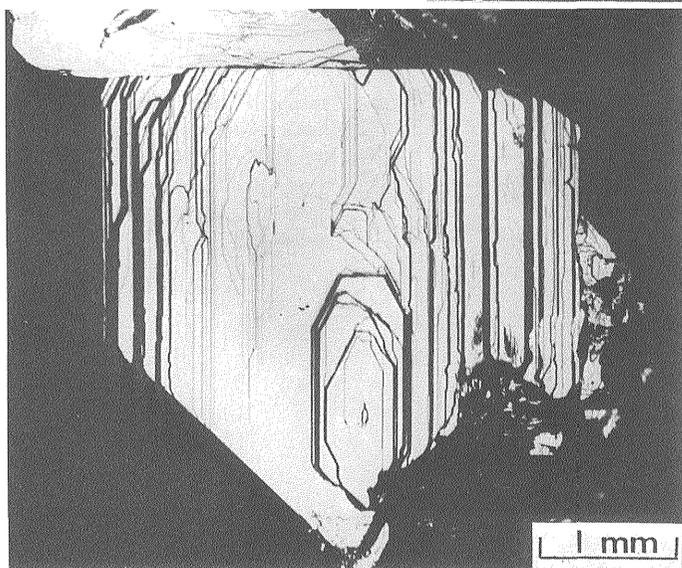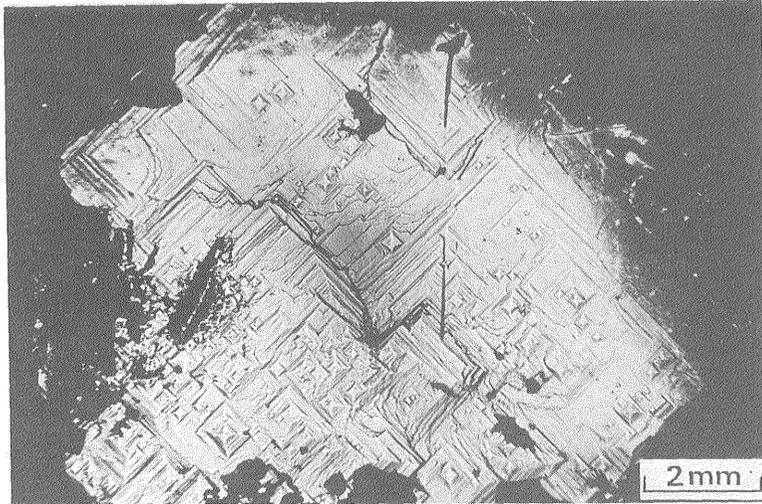
1 An example of square form growth layers bounded by <011> only, (100) face, Ashio mine.
in network vein.
{100} ≃ {111}

2 Elongated rectangular growth layers with irregular steps, (100) face, Chichibu mine.
in druse of vein.
simple {100}
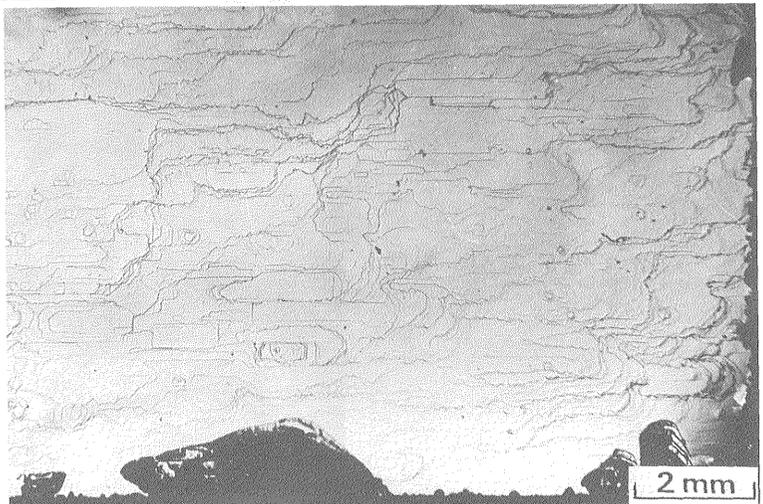
3 Irregular growth layers originating from eye-form growth islands, (100) face, Iwasawa mine.
in epithermal vein.
{100} ≃ {111} ≃ {210}
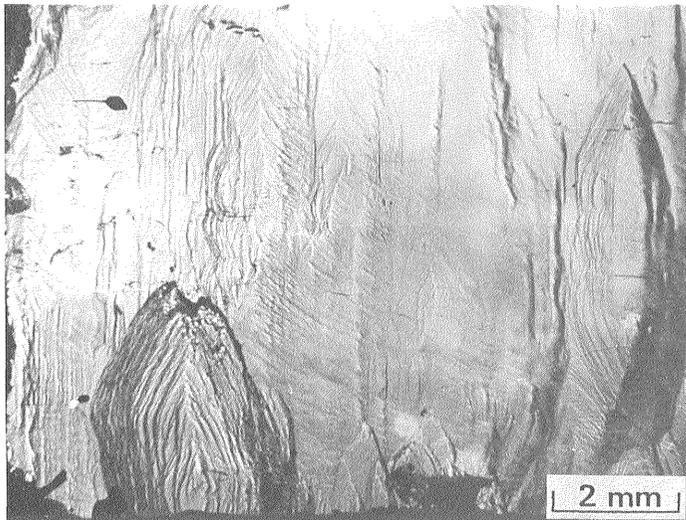
1 Typical example of irregular growth layers, (100) face, Arakawa mine. impregnated in gangue chlorite. {100} ≃ {111} ≃ {210}

2 Growth layers of unusual morphology, (100) face, Komatsu mine. in epithermal vein. {100} with {111}
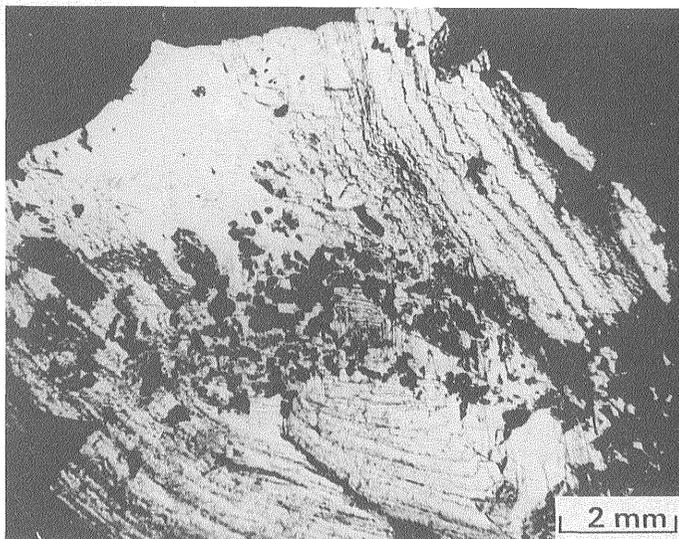
3 The surface of growth centers on (100) face, Hanaoka mine, positive phase contrast (p.p.c.). impregnated in gypsum ore of Kuroko type deposit. simple {100}
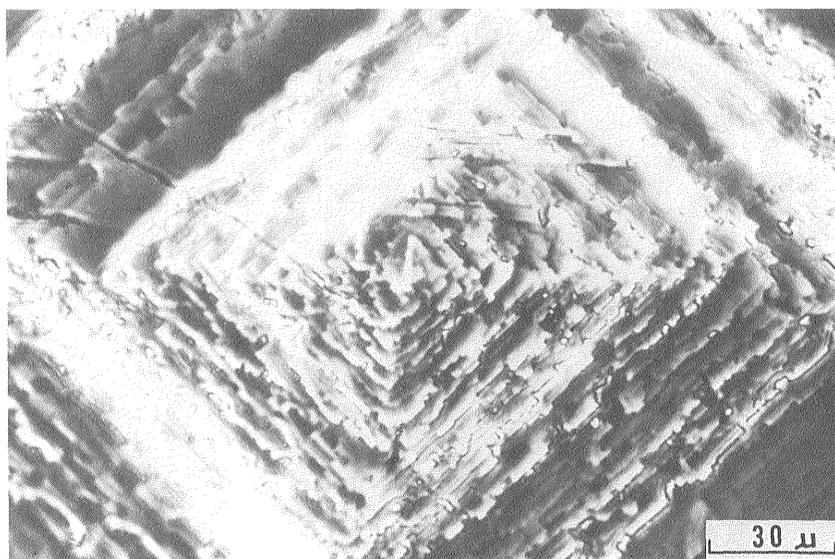
1 The summit of growth pyramid in Plate 29-1, p.p.c.
   Ashio mine.
   the same crystal of Plate 29-1.
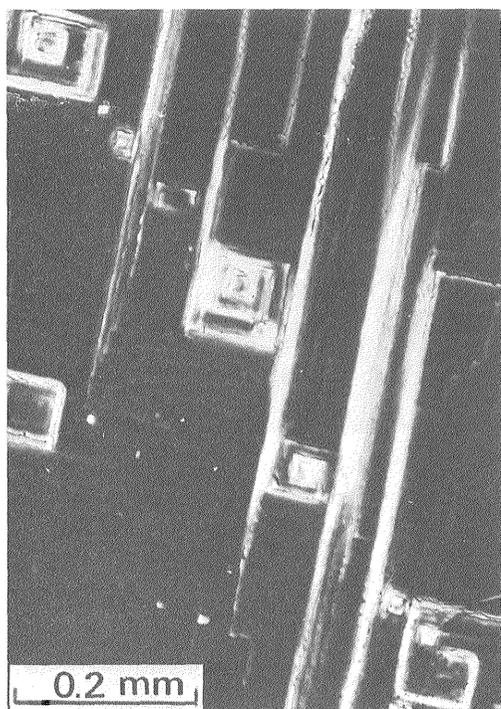
2 Growth pyramids aligning along a line in Plate
   29-1, p.p.c.
   Ashio mine.
   the same crystal of Plate 29-1.

3 Another example of growth islands aligning along
   a line, p.p.c.
   Hanaoka mine.
   impregnated in gypsum ore of Kuroko type
   deposit.
   simple {100}
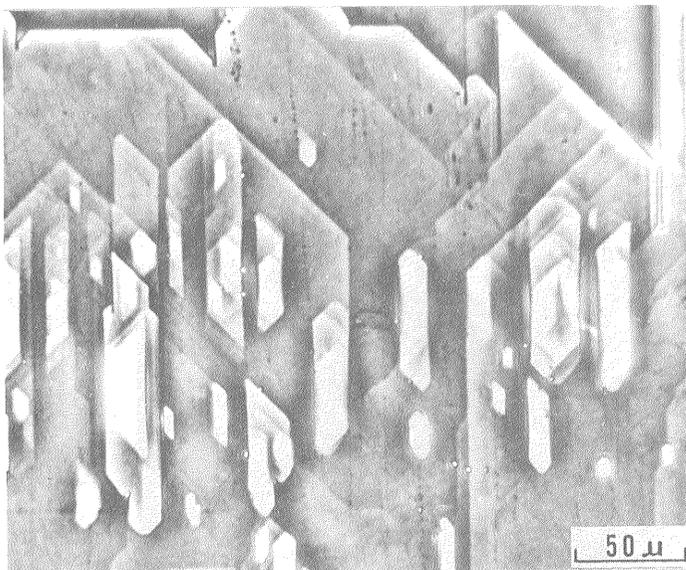
1 Tiny growth islands auto-epitaxially settled on (100) face, Ogasawara islands, p.p.c.
in druse of basail.
simple {100}

2 Spiral layers on growth islands in Plate 32–1, p.p.c.
Ogasawaralands.
the same crystal of Plate 32-1.
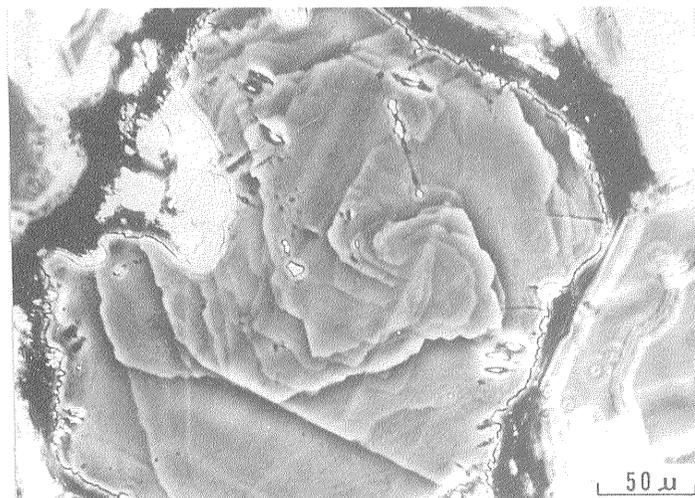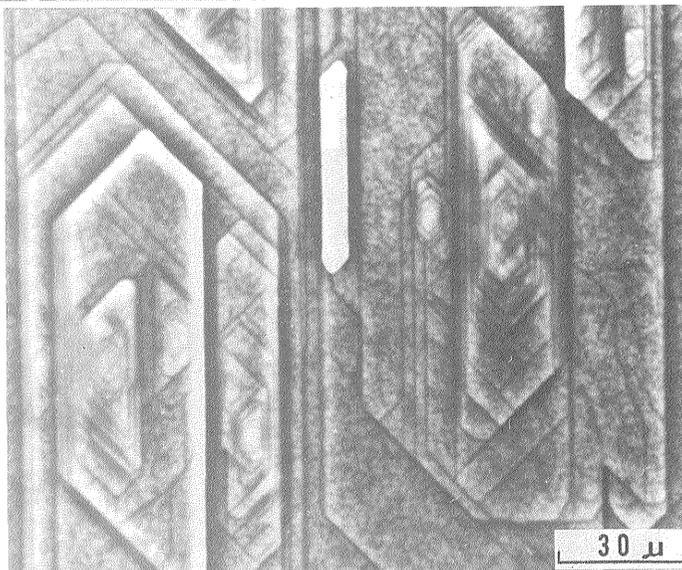
3 Spiral growth layers on (100) face, Chichibu mine p.p.c.
the same crystal of Plate 29–2.
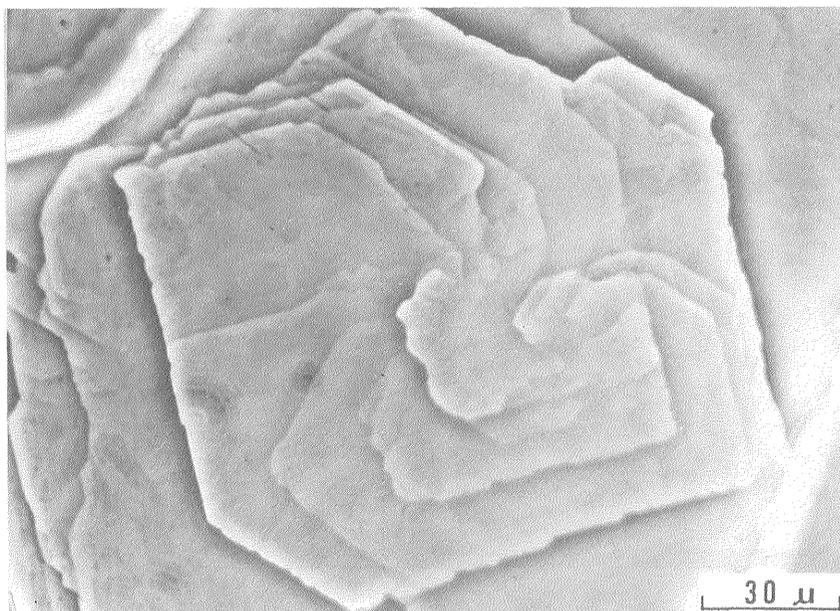
1   Same as Plate 32-3, higher magnificatino, p.p.c.
    Chichibu mine.
    the same crystal of Plate 29-2.
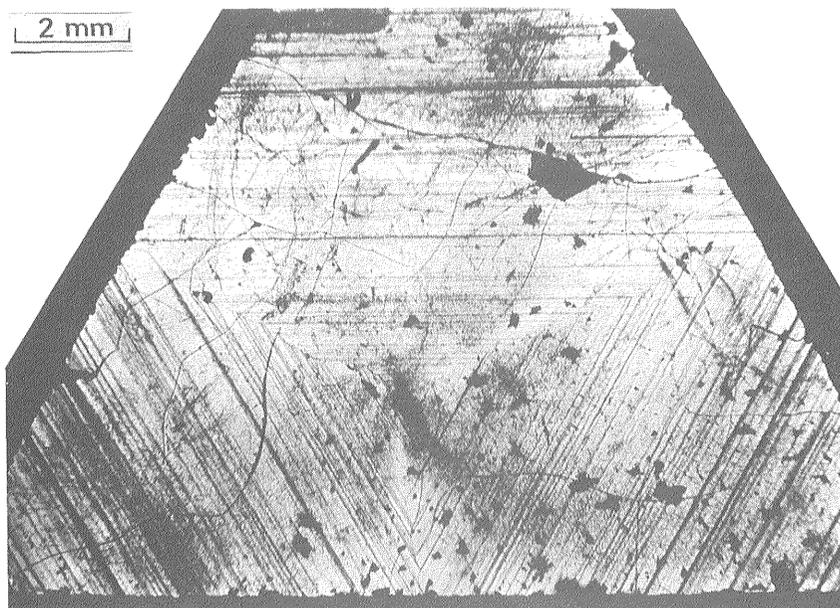
2 Typical example of regular triangular patterns commonly observed on (111) faces,
   Komatsu mine.
   in epithermal vein.
   simple {111}
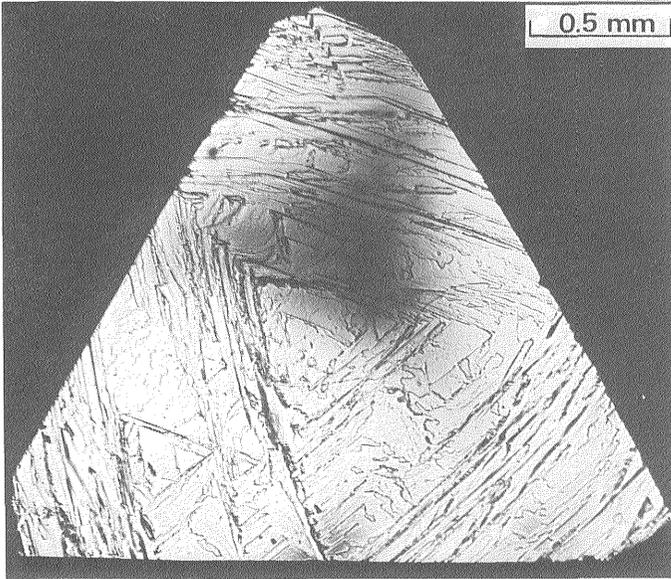
1   Another triangular patterns on (111)
    face, note the orientation of triangles
    to the edges, Ani mine.
    in epithermal vein.
    simple {111}

2   Another triangular patterns on (111)
    face, note inclined orientation of
    triangles only at the central part,
    Akyu mine.
    in epithermal vein.
    {111} with {100}
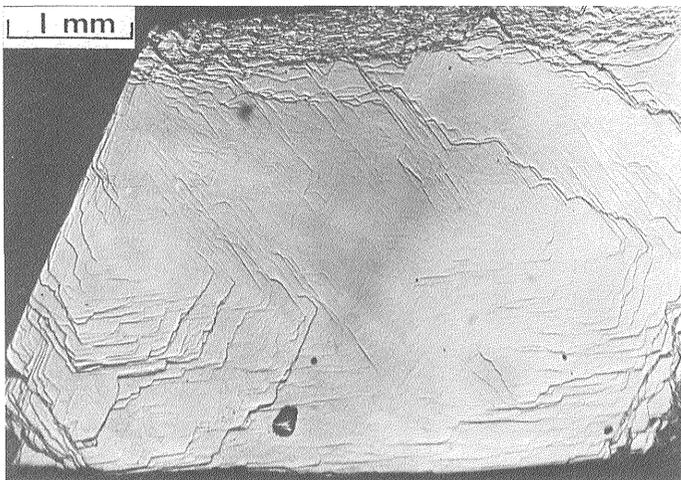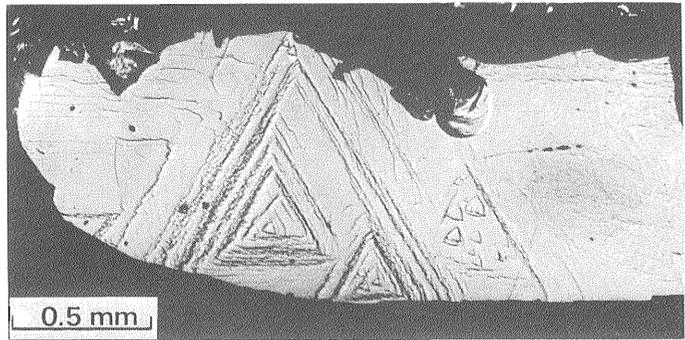
3   An example of irregular growth
    layers on (111) face, Mizusawa mine.
    in network vein.
    malformed simple {111}
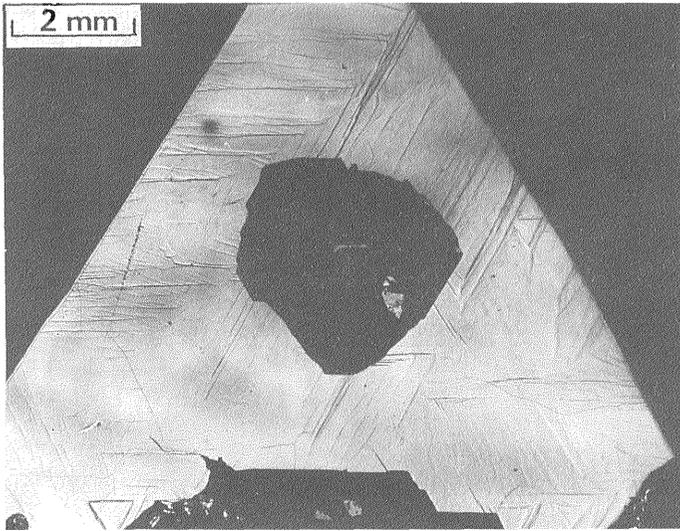
1 Another example of irregular growth layers on (111) face, Hanaoka mine. in druse of massive yellow ore of Kuroko type deposit.
simple {111} with smaller faces

2 Central portion of triangular pattern on (111) face, Ogoya mine, p.p.c. embeded in chalcopyrite ore.
{111} ≃ {210}
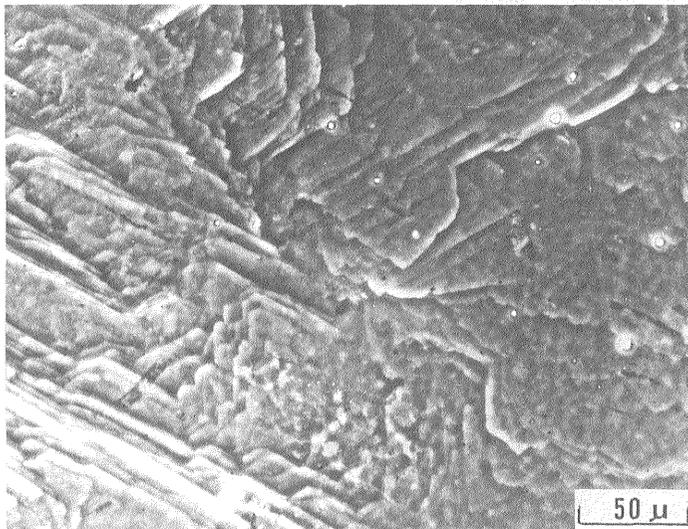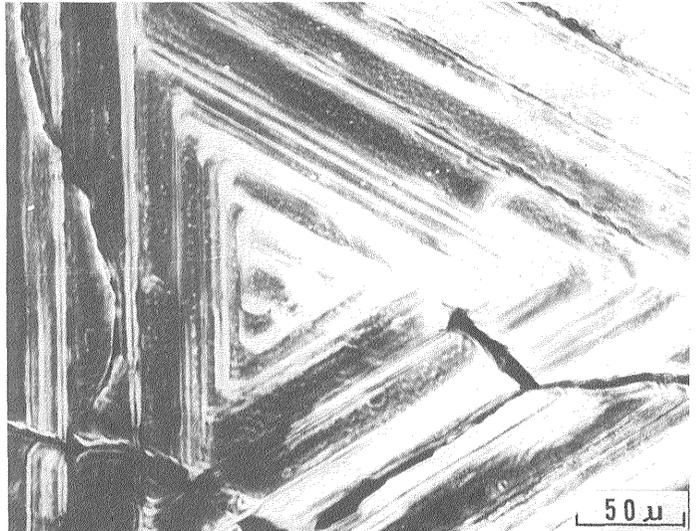
3 One of the growth centers in Plate 34-3, p.p.c.
Mizusawa mine.
the same crystal of Plate 34-3.

1　Composite growth spiral observed on the face shown in Plate 35-1, p.p.c.
Hanaoka mine.
the same crystal of Plate 35-1.

2　Relation between growth spiral and basal triangular layer in Plate 35-1, p.p.c.
Hanaoka mine.
the same crystal of Plate 35-1.
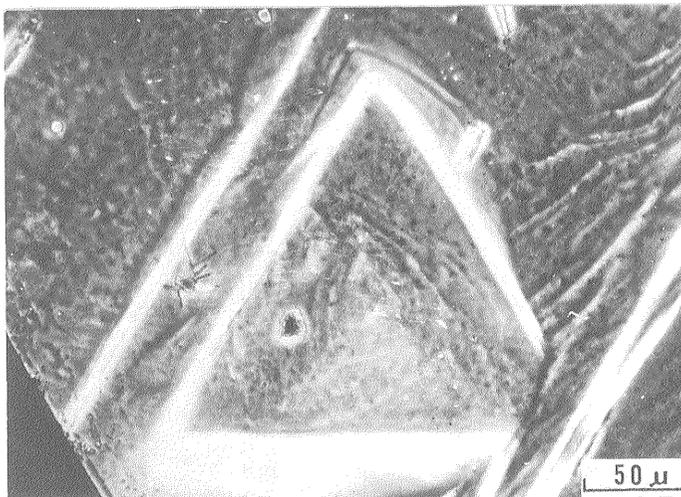
3　Triangular growth pyramids found in Plate 35-1, p.p.c.
Hanaoka mine.
the same crystal of Plate 35-1.
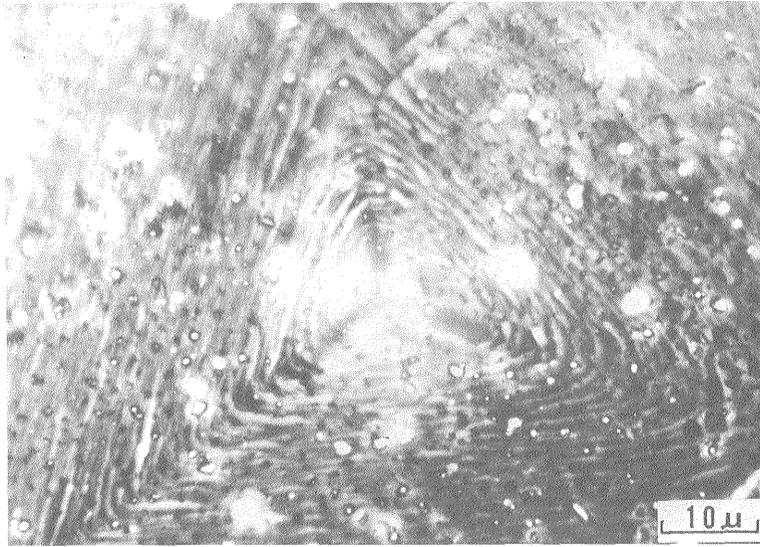
1   One of the summit of growth pyramids appeared in Plate 36-3, n.p.c.
    Hanaoka mine.
    the same crystal of Plate 35-1.
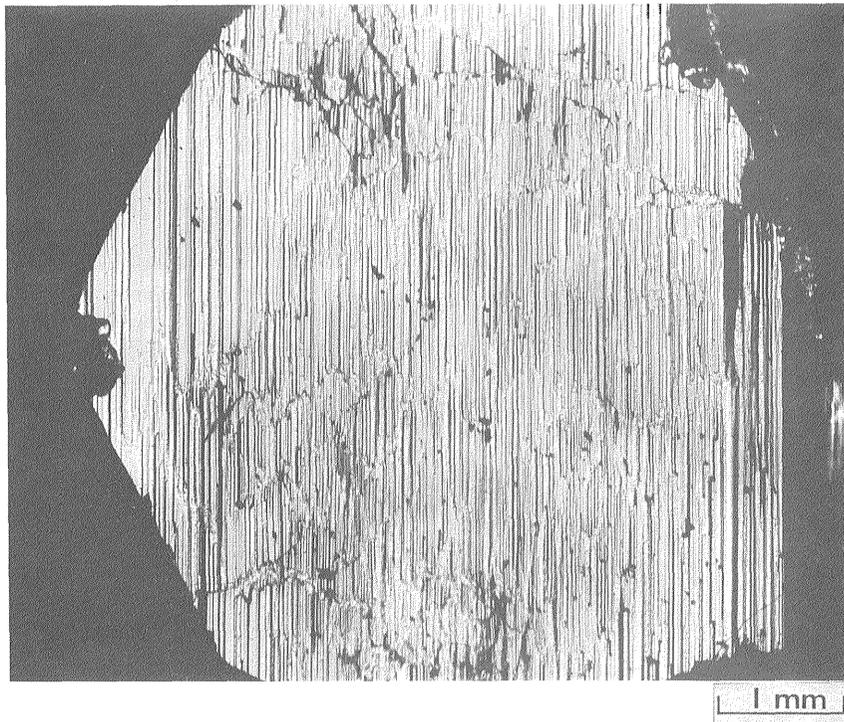
2   Positive striations on (210) face, Oppu mine.
    in epithermal vein.
    simple {210}
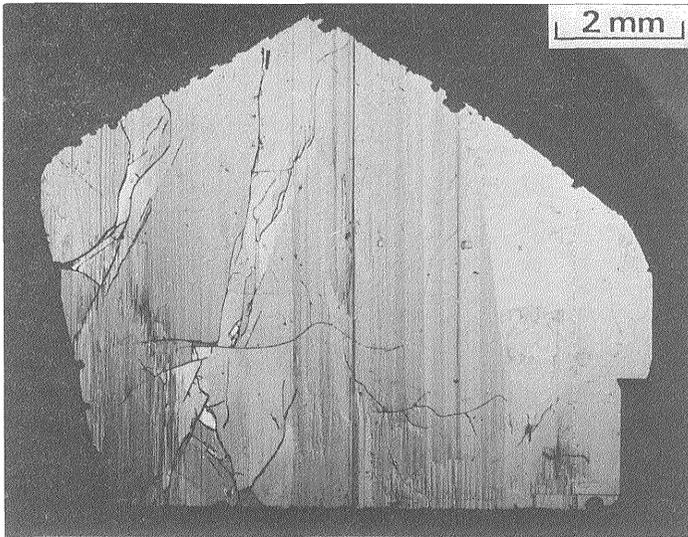
1 Negative striations on (210) face,
Osarizawa mine.
in epithermal vein.
simple {210}

2 Another type of negative striations
on (210) face, Shakanai mine.
impregnated in tuff breccia over-
laying Kuroko deposit.
simple {210}
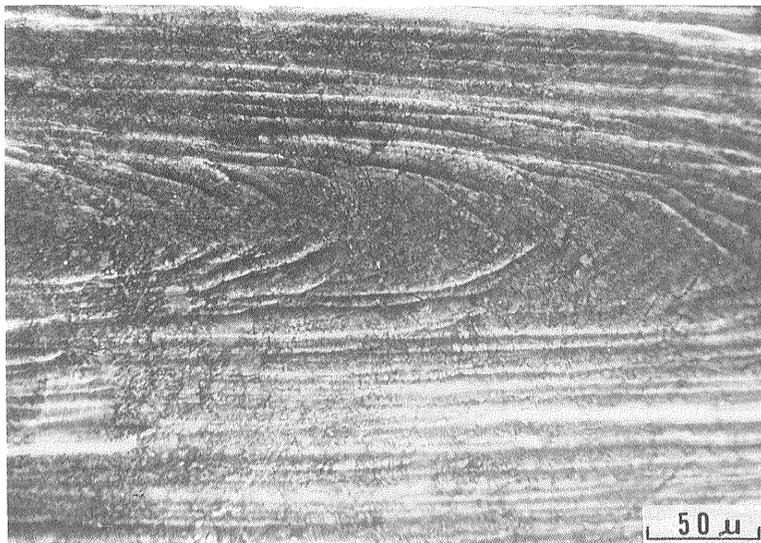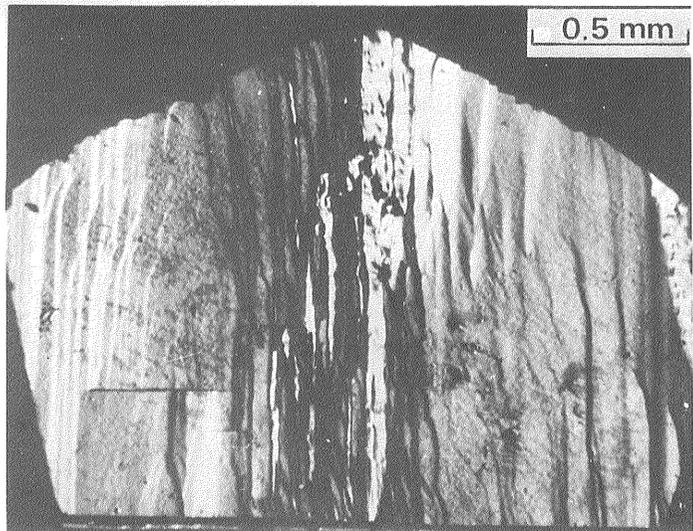
3 Growth layers observed on
negatively striated (210) face
of Plate 38-2, p.p.c.
Shakanai mine.
the same kind of crystal of
Plate 38-2.
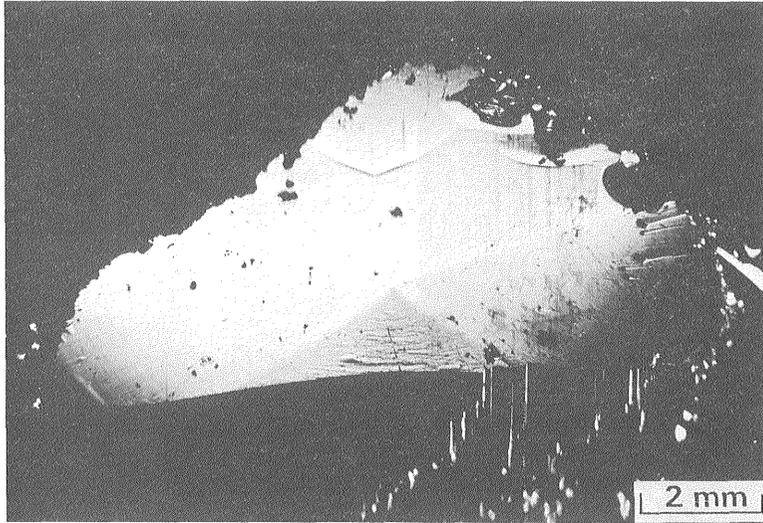
1 Growth pyramids on (210) face, Hanaoka mine. impregnated in gypsum ore of Kuroko type deposit. {210} with {*hk*0}

2 The summit of growth pyramid in Plate 39-1, p.p.c. Hanaoka mine. the same kind of crystal of Plate 39-1.
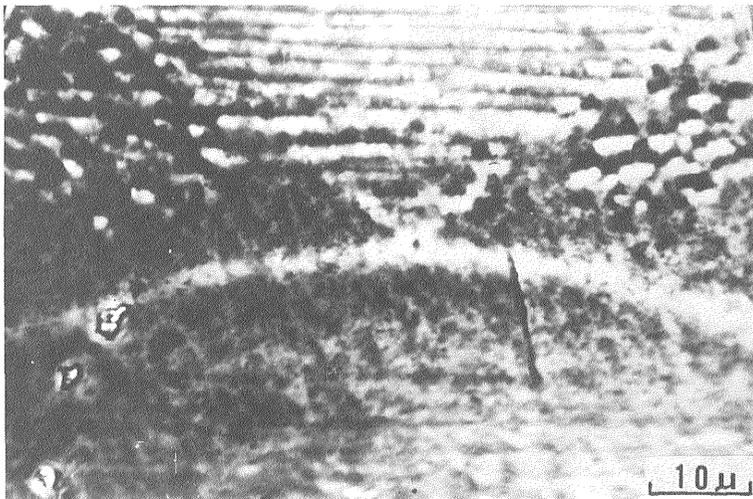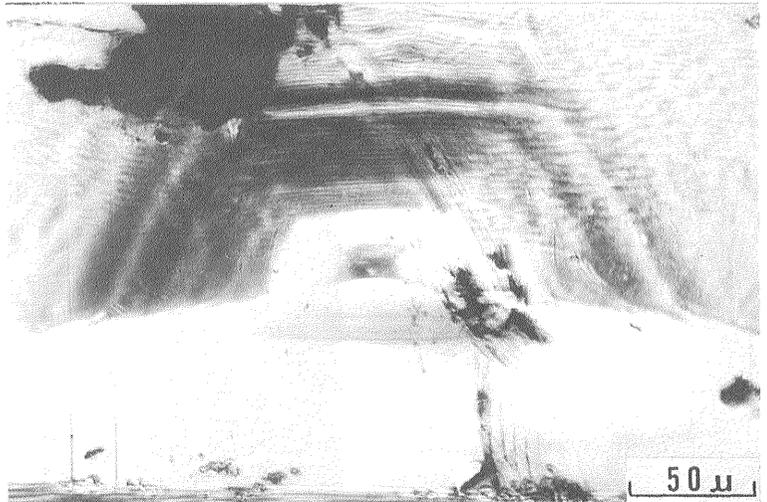
3 Higher magnification photomicrograph of Plate 39-2, note the hole at the summit, p.p.c. Hanaoka mine. the same crystal of Plate 39-2.
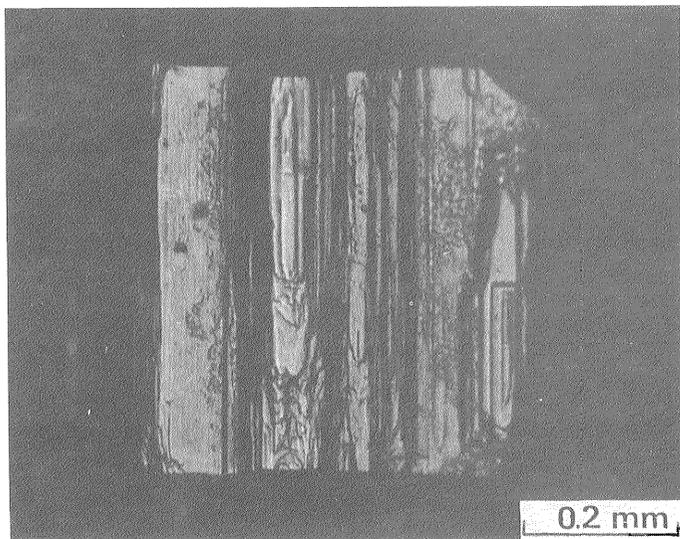
1 (100) face of a smaller crystal, Shakanai mine differencial interference contrast (d.i.c.).

2 (210) face of a medium size crystal, Shakanai mine, d.i.c.
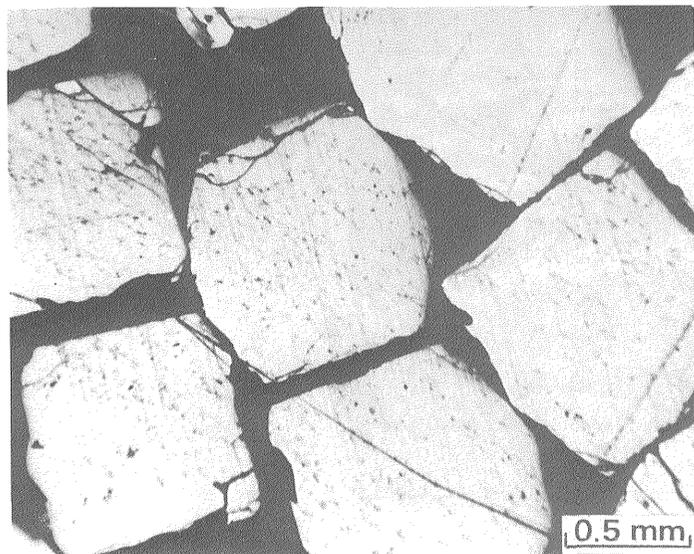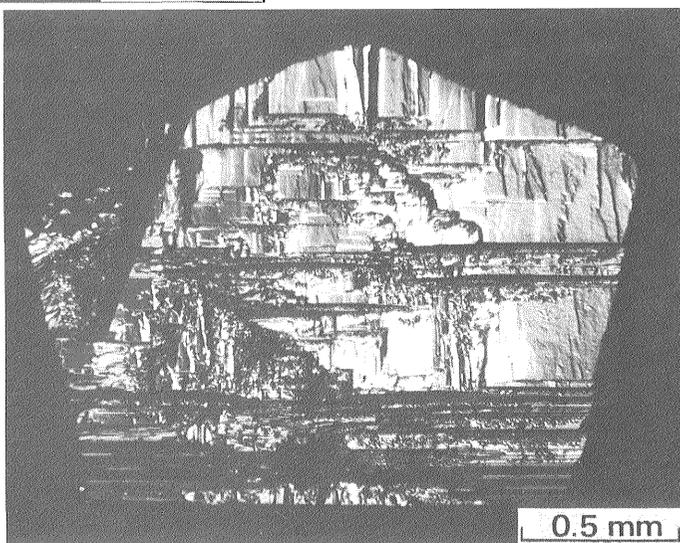
3 Internal feature of smaller crystals, note the homogeneity, Shakanai mine.
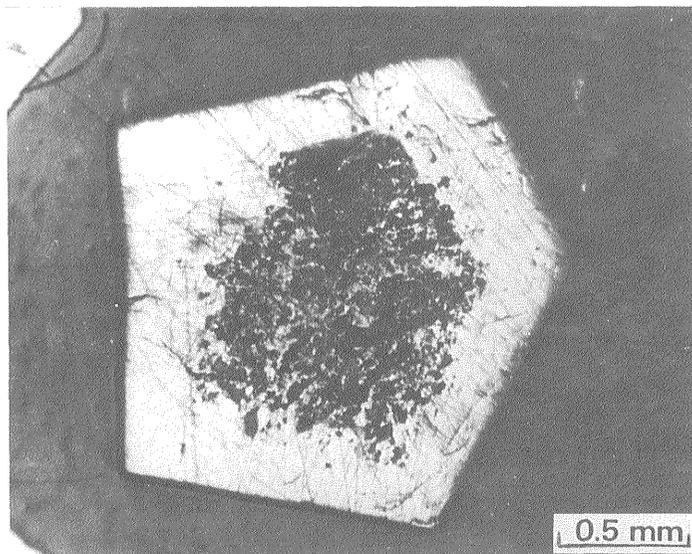
1   Internal feature of medium size crystals, note the two distinct zones, Shakanai mine.

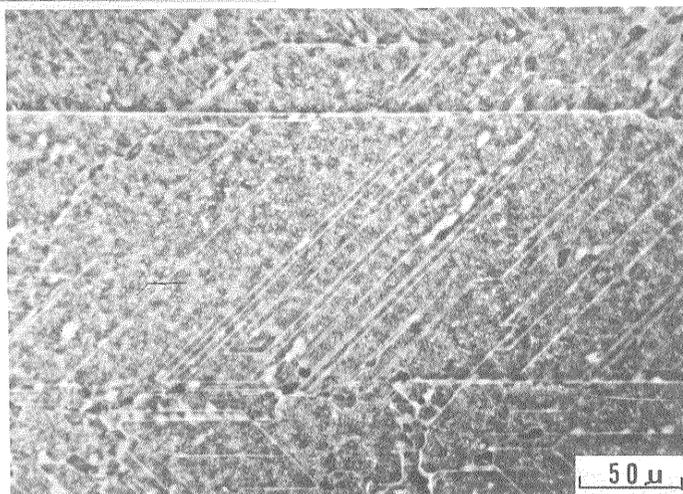2   One type of negatively striated (210) face from Ani mine, p.p.c.
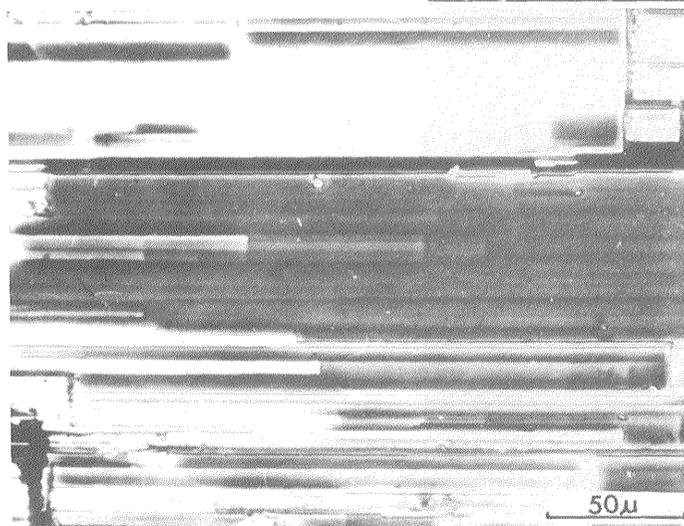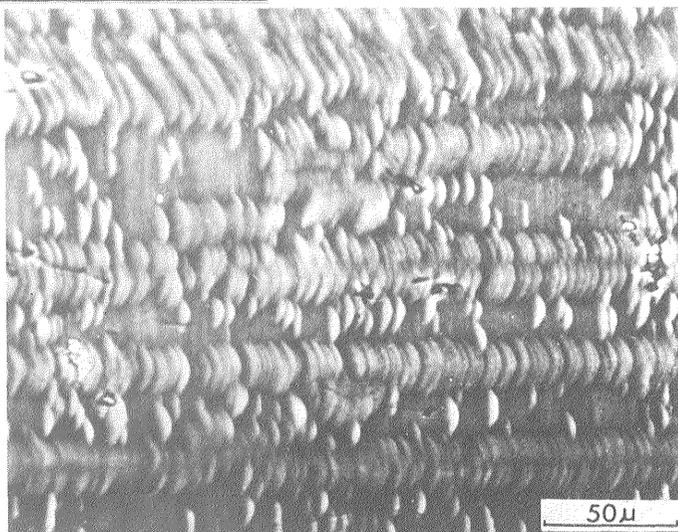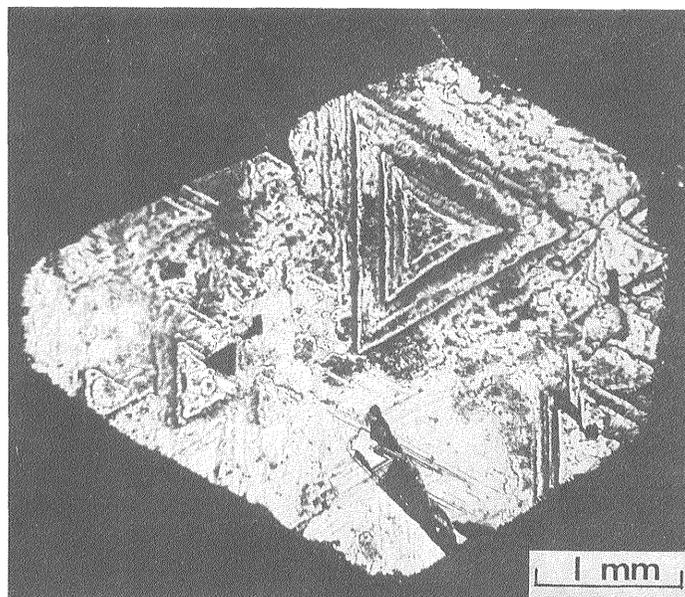

3   Another type of negatively striated (210) face from Ani mine, p.p.c.
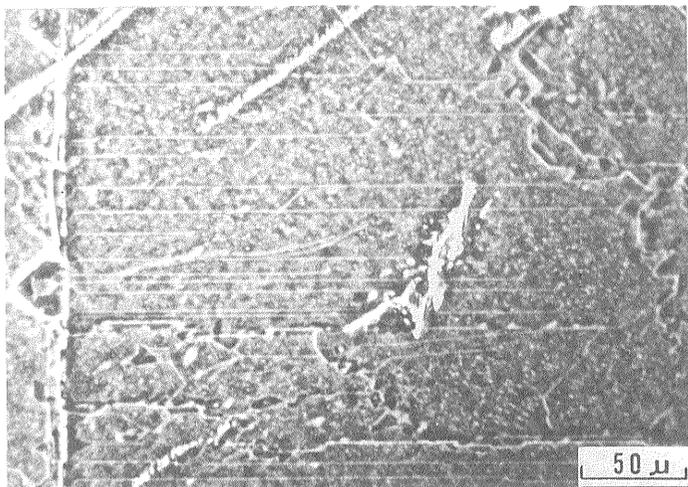
1 Linear dissolution ditches mainly parallel to <001> direction observed on (100) face, Tsunatori mine, n.p.c.

2 Linear dissolution ditches parallel to both <001> and <011> directions on (100) face, Tsunatori mine, n.p.c.
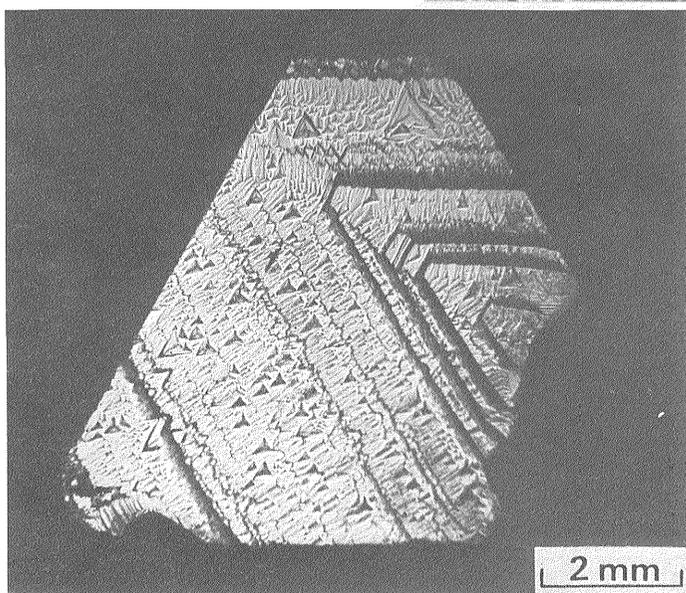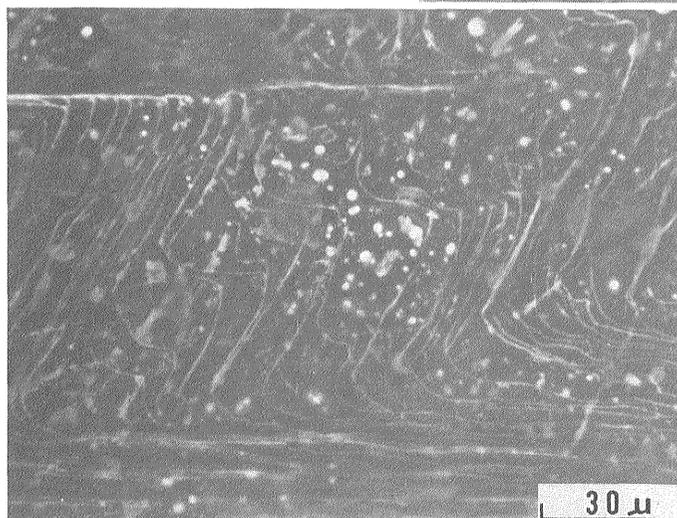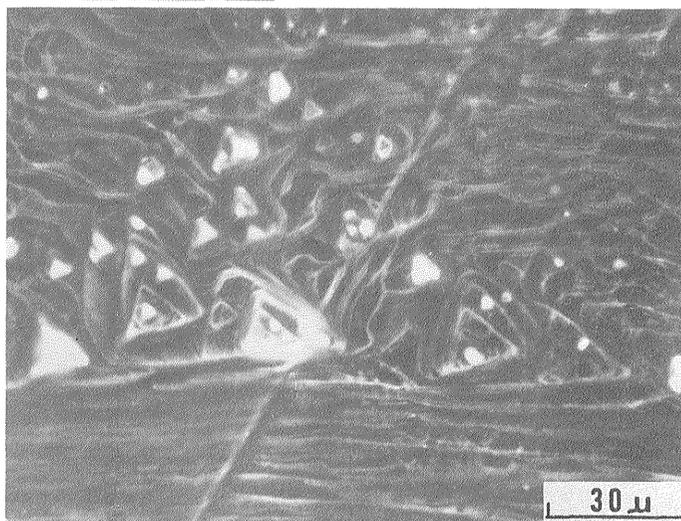

3 Large dissolution triangular pits on (111) face, Kambe mine.

1　Heavily dissolved (111) face, Tsuna-
　tori mine.

2　Minute dissolution triangles on (111)
　face, Ogoya mine, n.p.c.

3　Linear dissolution ditches on (111)
　face, Ogoya mine n.p.c.

1 Etch pits formed at the summits of growth pyramids on (210) face, Hanaoka mine, p.p.c.

2 Higher magnification photomicrograph of the etch pits appeared in Plate 44-1, p.p.c.