学位申請 論文

Polymerization Process of Biopyribole in Metasomatism at the Akatani Ore Deposit, Japan

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Polymerization Process of Biopyriboles in Metasomatism at the Akatani Ore Deposit, Japan

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CONTENTS

I. Introduction

Ia. Historical review on the studies of the biopyriboles

The structural relationships between the pyroxenes and amphiboles have been discussed since the early stage of the crystal structure investigation of diopside and tremolite (Warren and Bragg,1928 ; Warren,1929). The replacement of the pyroxene by amphibole and vice versa has also been studied from the petrogenetic interests (Goldschmidt,1911 ; Kozu et al. 1927 ; Barnes,1930 ; Posnjak and Bowen,1931 ; Tomita 1965 ; Papike et al. 1969 ; Desnoyer, 1975 ; Smith,1977 ; Yamaguchi et al.,1978 ; Nakajima and Ribbe,1980,1981 etc.). The interests and progresses of the studies on the biopyriboles has been carried out on the extension of these previous mineralogical and petrological interests.

1. Structural relation ships among the biopyriboles and polysomatism

i) Biopyriboles and their nomenclature

Thompson (1970,1978) discussed the relationship between the structures of pyroxene , amphibole and mica, which had first been suggested by Jackson and West (1931). Thompson stated that amphiboles are factored by (010) cuts into layers that are alternately pyroxene and trioctahedral mica (or talc). This point of view contained the prediction that new structures due to various combinations of these pyroxene modules and mica modules may be present. He proposed the revival use of the term of biopyribole collectively for all these chain and sheet silicates which was first used by Johannsen (1911)

Various usages of biopyribole nomenclature are summarized as follows ;

Biopyribole nomenclatures

Biopyribole : collectively refers to a group name of all chain silicates and sheet silicates (from pyroxene to mica or talc), or, in recent usages, refers to any member of the series extending from pyroxene to mica (Thompson, 1978 , 1981) : cf. classical biopyriboles, non-classical biopyriboles, new biopyriboles.

Pyribole : refers to a group name of all chain silicates ,or, in recent usages, refers to any member of the chain silicates. cf. wide-chain (pyriboles), multiple chain; refers to silicate chain wider than double.

Hydrous pyriboles : refers to pyriboles excluding pyroxene. ; cf. anhydrous pyriboles (=pyroxenes).

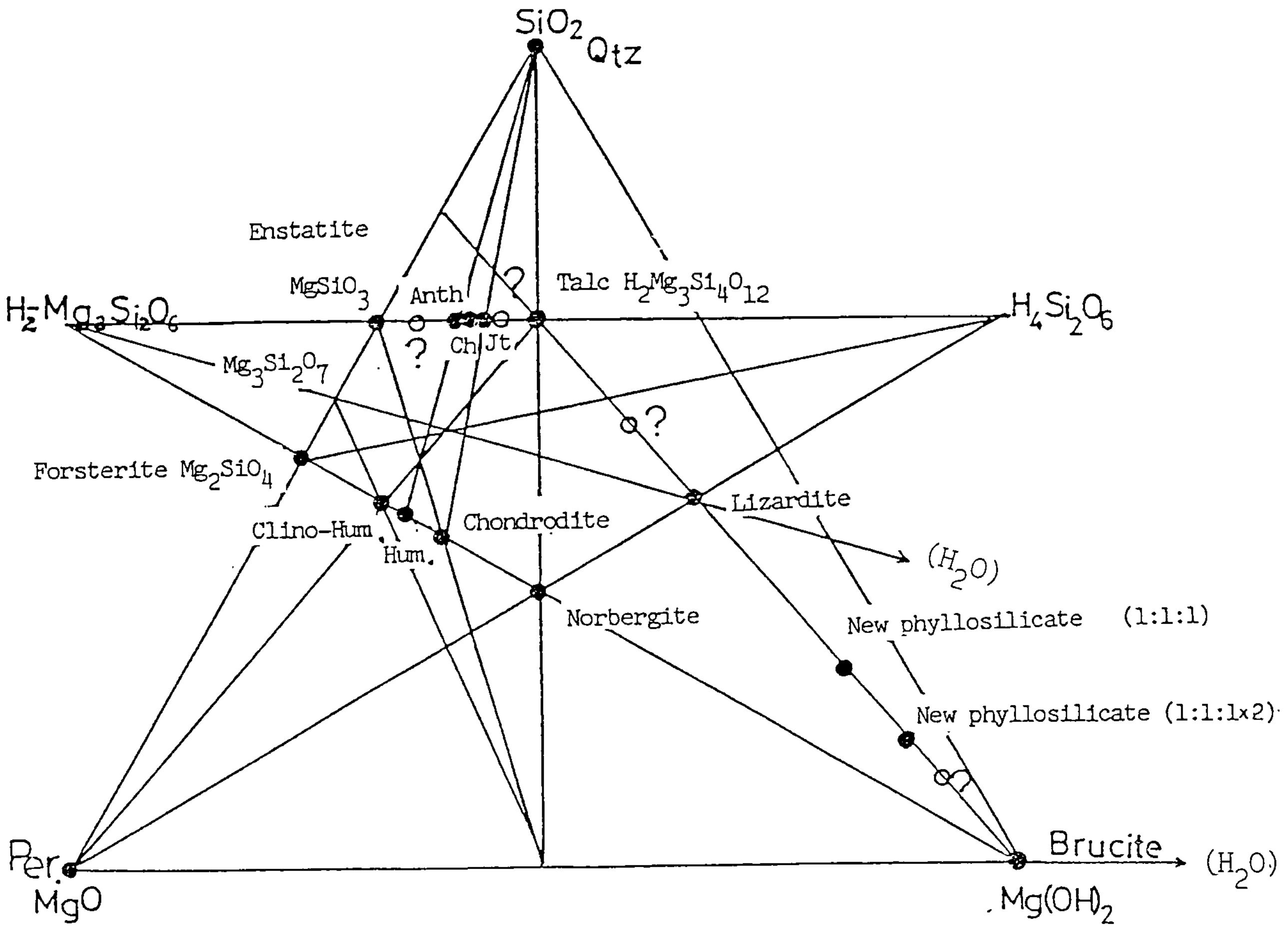
Clinopyribole, Orthopyribole, Protopyribole : collectively refer to all pyriboles having the stacking sequence found in clinoenstatite, enstatite and protoenstatite respectively (Veblen et al., 1977).

Mixed-chain pyriboles : refers to pyriboles having silicate chains of more than one width.

Chain-width disorder, chain-width error, chain-width defect, (structurally disordered) : refers to the states of disordered sequence of silicate chain widths.

ii) Polysomatic series and polysomatism

The concept of biopyribole was elaborated and generalized into the concept of polysomatism (Thompson, 1978,1981). This theoretical point of view by Thompson has been established, based on an extension of interests of the mutual relationships of crystal structures of pyroxene and amphibole, which were suggested by Warren (1929), and Jackson and West (1931). Polysomatic series (or polysomes) is a series composed of the crystals that may be regarded as made of interlayered chemically distinct modules taken from different crystals and such a phenomenon is called polysomatism. Thompson (1978) proposed these concepts instead of the confused and incorrect usages of many doncepts ; mixed-layer polytypism, heteropolytypism, homopolytypism and homologous series. Polysomatic relations can be found in many mineral groups. An example of polysomatic series containing biopyriboles is shown in the following figure. The figure is derived by modifying Fig 8 in Thompson (1978). New phyllosilicates (1:1:1x2), (1:1:1) (Akai, 1980 a, 1982 b) are also plotted in the figure.



: A portion of the composition plane $MgO-H_2O-SiO_2$. Some polysomatic serieses are found ; the humites, the biopyriboles and the phyllosilicate-hydroxide series Ch: Chesterite, Jt :Jimthompsonite, Anth: Anthophyllite, Hum:Humite.

Based on the concept of polysomatism, we can predict new polysomes which are structurally possible but are not found yet ; for example, dioctahedral amphiboles with dioctahedral mica modules , new biopyriboles such as quadruple chain silicate , mixed chain silicates composed of single and double chains , and so on (Thompson , 1970,1978,1981) These predictions , however, do not indicate their exact stabilities.

The structural changes among biopyriboles can be called as polysomatic reactions. Polysomatic reactions in biopyriboles are ,therefore,expressed as reactions that changes one polysome to another ; for example, pyroxene to amphibole, pyroxene to triple chain sillicate, amphibole to pyroxene ect..

Ordered pyriboles (new minerals) and their crystal chemistry

i) New minerals and their crystal chemistry

Four new minerals with triple chain structures (Jimthompsonite, clinojimthompsonite, chesterite, monoclinic analogue of chesterite) were first discovered by Veblen and Burnham (1975,1976,1978a,b). They occurred in the black wall zone of the Carleton talc quarry, a metamorphosed ultramafic body, near Chester, Vermont. Veblen and Burnham (1978a,b) described them in detail.

The crystal data of these new minerals are as follows (Veblen and Burnham,1978b) ;

Jimthompsonite	Clinojimthompsonite	Chesterite	Monoclinic analog of Chesterite
Orthorhombic	Monoclinic	Orthorhombic	Monoclinic
a = 18.6263 Å	a = 9.874	a = 18.614	a = 9.867
b = 27.2303	b = 27.24	b = 45.306	b = 45.31
c = 5.2970	c = 5.316	c = 5.2966	c = 5.292
	β = 109.47°		β = 109.7°
Pbca	C2/c	$A2_1ma$	A2/m, Am or A2
Z = 4[$(Mg,Fe)_{10}Si_{12}O_{32}$-$(OH)_4$]	Z=2[$(Mg,Fe)_{10}Si_{12}O_{34}$-$(OH)_4$]	Z=4[$(Mg,Fe)_{17}Si_{20}$-$O_{54}(OH)_6$]	

Veblen and Burnham (1978b) also solved and refined the crystal structure of these new minerals and characterized them crystalochemically. The new minerals share many of the crystal chemical attributes of the other low-calcium pyriboles (Veblen and Burnham ,1978b). According to Veblen and Burnham (1978b), and Veblen (1981) the crystal chemistry of the new pyriboles can be summarized as follows; (1) Two symmetrically distinct triple silicate chains are found in the jimthompsonite structure, called the A- and B-chains ; these are analogous to the A- and B-chains in orthopyroxenes and orthoamphiboles. The A-chains lie between (100) octahedral layers having opposite octahedral orientations (between + and - ,or between - and +), while B-chains lie between octahedral layers of like orientation (between + and +, and between - and -) (2) Each of these triple chains has three symmetrically distinct tetrahedra ; two inner tetrahedra, Si1 and Si2, analogous to the inner tetrahedra (T1) of amphiboles and the tetrahedra of sheet silicates, and one outermost tetrahedron, Si3, which is analogous to the tetrahedron of a pyroxene chain or the outer tetrahedron (T2) of amphiboles. Using the range of tetrahedral O-Si-O angles as a simple measure of distortion, it is found that the outermost , pyroxene-like tetrahedra in all of these structures are rather distorted compared with the other, mica-like tetrahedra. These distortions arise primarily because the outermost tetrahedra share O······O edges, or nearly share edges, with the outermost M cation polyhedra of the octahedral strips of the structures (M5 in triple chain silicates, M4 in amphiboles, and M2 in pyroxenes). (3) Triple chain structures contain wide strips of cation polyhedra. The coordination polyhedron of the outermost cation of the strip (M5) is quite distorted . The inner polyhedra (M1,M2,M3,M4) are , however, much more regular octahedra. The distorted outermost polyhedra are analogous to the distorted outermost sites of amphiboles (M4) and pyroxene (M2). Likewise, the regular inner octahedra of triple chain pyriboles are analogous to the regular octahedra of amphiboles (M3,M1,M2) and pyroxene (M1).

(4) New pyribole structures also possess A-sites, analogous to the A-sites of amphiboles and the interlayer sites of micas and talc. As in the amphiboles , the precise geometries of the A-sites depend on the rotations of tetrahedra in the chains and the displacement parallel to c between six-membered tetrahedral rings in the two chains that coordinate the A-site. Unlike the A-sites of most amphiboles, however, those of triple chain pyriboles do not have mirror symmetry. (5) Basal oxygen layers of all the chains in the Chester biopyriboles are"warped " out of the (100) plane. The same phenomenon also occurrs in pyroxenes and amphiboles. The chains of enstatite are not so warped (Morimoto and Koto 1969) as those of the the wider chain silicates , and the double B-chains of anthophyllite and chesterite are more warped than any of the single or triple B-chains.

(6) Refinement of M-site Mg-Fe occupancies for jimthompsonite, clinojimthompsonite, and chesterite reveals the same ordering pattern observed in the low calcium pyroxenes and amphiboles : Fe^{2+} is concentrated in the outer , distorted sites, while Mg prefers the inner, more regular sites.

ii) Occurrences of new minerals

The new minerals from Vermont all occur in the black wall zone (chlorite- or biotite-bearing metasomatic reaction zone) of metamorphosed ultramafic body. The generalized zoning sequence from country rock to ultramafic body is : (1) muscovite-quartz-garnet gneiss ; (2) altered gneiss ; (3) biotite and chlorite blackwall ; (4) actinolite ; (5) talc ; (6) talc, magnesite, and serpentinite. The simplified zoning sequence observed in the block containing the new pyriboles is : (1) chlorite ; (2) fibrous talc ;(3) fibrous talc, jimthompsonite, clinojimthompsonite,chesterite,the monoclinic analog of chesterite, anthophyllite and cummingtonite ;(4) anthophyllite ,cummingtonite, chesterite, the monoclinic analog of chesterite and actinolite ; (5) actinolite and massive talc. Actinolite and anthophyllite commonly occur as oriented intergrowth on planes near (100) , attaining length of 5 cm. The new minerals are part of a retrograde reaction sequence from anthophyllite to talc. This amphibole-to-mica reaction mechanism is not simple , but rather proceeds by reconstruction of double-chain I-beams to form mixed double and triple chains, pure triple chains, and finally continuous sheets of silicate tetrahedra. It is not yet clear whether or not other phases are also part of the reaction sequence.

Other two occurrences of the new minerals have been preliminarily reported by the author (Akai,1980b; Sato and Akai,1981). He found two specimens which gave adequate peak intensity to be identified as a triple chain silicate by X-ray diffractometry ; the one from Widgiemoolta , Australia (sampled by Kato and Matsubara, and kindly offered to the author) and the other from Takaragawa, Gumma Pref , Japan (Sato and Akai, 1981).

The characters found in the triple chain silicate which are valuable for the identification are listed in the following.

Identification table of the triple chain silicates (Jimthompsonite and clinojimthompsonite)

Under microscope

(similar to amphibole~fibrous amphibole)

lower cleavage angle ≒ 135°

(010) intergrowth of anthophyllite or other biopyribole

X-ray diffractometry

(useful only when the minerals are in large enough amounts)

(usually biopyribole mixtures)

low-angle peaks ($2\theta < 15°$) are especially useful.

210 peak of jimthompsonite can be separated from anthophyllite and tremolite.

Chemistry

(very close to anthophyllite or cummingtonite)

descrimination is often impossible

X-ray single crystal methods & ED techniques

(Identification is possible)

Mineral paragenesis in the three localities are compared in the following table (Veblen, 1975, 1976, 1978a,b, Akai, 1980b, Sato and Akai 1981.)

Mineral Paragenesis

	Takaragawa, Japan	Chester, Vermont** (Veblen&Burnham 1978b)	Widgiemooltha, Australia
Jimthompsonite	(?)	+	+
Clinojimthompsonite	+	+	?
Chesterite		+	
Anthophyllite	+	+	+
Actinolite(Trem.)	+	+	+
Cummingtonite		+ (as lamella)	?
Chlorite	+	(+)	+
Biotite (Muscovite)	+	(+)	
Talc	+	+ (fibr.& massive)	+
Quartz	+		
Magnetite		+	

All three cases are very similar in their occurrences ; probably formed in retrograde reactions. The similarity in their mineral paragesis is also characteristic although chesterite occur only in Chester.

iii) Short-range ordered pyriboles

Other short-range ordered pyriboles which are observable only by HREM have been reported. Most of them are reported by Veblen and his coworker (Veblen and Buseck, 1979) The new pyriboles observed are listed in the following table.

Chain sequence of observed ordered pyriboles

Sequence	Observed Repeats	Probability p	Site Composition	Repeat Length (Å)
From Chester				
(2233)	15	1.31×10^{-16}	M_3P_2	45
(233)	11	3.33×10^{-8}	M_5P_3	36
(232233)	4	2.06×10^{-5}	M_3P_2	67.5
(222333)	3	1.08×10^{-3}	M_3P_2	67.5
(2332323)	3	3.33×10^{-4}	M_3P_2	81
(2333)	45	1.62×10^{-42}	M_7P_4	49.5
(433323)	5	1.94×10^{-8}	M_2P	81
(43332343332423)	4	5.82×10^{-17}	M_2P	189
(2234)	4	5.41×10^{-5}	M_7P_4	49.5
From Akatani				
(223)	5	2.0×10^{-3}	M_4P_3	31.5

2= double chain, 3=triple chain, ····

$p=(n_A!\, n_B!\,)/(n_A+n_B)!$ where n_A and n_B represent the number of A's and B's in the sequence , after removing the first unit (Veblen and Buseck,1979).

M= mica module, P= pyroxene module

Chemical composition of these new pyriboles can also be derived by adding the compositions of pyroxene and mica modules ; for example, M_3P_2 = $3[(Mg,Fe)_3Si_4O_{10}(OH)_2] + 2[(Mg.Fe)_4Si_4O_{12}]$. The pyribole from Akatani can be derived by using the composition of pyroxene module of $Ca_2(Mg,Fe,Mn)_2Si_4O_{12}$.

3. Intergrowth of biopyriboles

i) Intergrowth of amphiboles and pyroxenes

The replacement of pyroxene with amphibole and vice versa had been a matter of petrogenetic interest. The most common phenomenon is known as uralitization, which was described petrographically and chemically by Goldschmidt (1911). Recently, there have also been some reports on pyroxenes which are partially replaced by hydrous pyribole lamellae (Bown and Gay, Yamaguchi and Tomita, 1968, Papike et al. 1969, and Desnoyers (1975) Smith 1977, Yamaguch et al. 1978, Veblen 1981). Amphibole intergrowths in pyroxene described are as follows ;

Intergrowth of pyroxene and amphibole in

Augites from basic intrustions such as
Skaergaad, Bushveld, Palisades Sill(Smith,1977)
Omphacites from Roberts Victor eclogite South Africa (Papike et al.,1969)
Jadeites from glaucophane schists of California (Papike et al.,1969)
Augite from Siera Nevada batholith and from Kaerusutite-bearing peridtite San Carlos Arizona (Papike et al.,1969)
Orthopyroxenes from Anorthosite (Smith,1977)
Augites from harzburgite (Smith, 1977)
Diopside from lherzolite from Alpe aArami Bellinzona(Yamaguchi, Akai, Tomita, 1978)
Augite from Salt Lake Crater, Hawaii (Veblen and Buseck,1981)
Augite in metamorphosed gabbro, Hokkaido Japan, (Yrmaguchi and Tomita, 1968 ; Nakajima and Ribbe, 1980,1981)

Papike et al (1969) considered four possible mechanisms of the intergrowths ; 1) amphibole as an alteration product of the pyroxene, 2) amphibole as a primary epitaxial intergrowth, 3) pyroxene could have formed from an amphibole precursor, 4) amphibole exsolution from pyroxene host. Desnoyer(1975) properly suggested the possibillity of exsolution of amphibole from pyroxene host besides alteration of pyroxene to amphibole. Smith (1977) reported an observation by EM of sub-microscopic amphibole lamellae in several pyroxenes and interpreted the amphibole lamellae to have been formed by exsolution from pyroxene. According to Yamaguchi et al. (1978), porphyroclastic diopside in garnet lherzolite from Alpe Arami Bellinzona, Switzerland includes optically visible clinoamphibole lammelae with a composition intermediate between pargasite and edenite. X-ray and electron microscopic observations show that the diopside crystal contains sub-microscopic thin clinoamphibole lamellae parallel to (010) which have coherent interfaces to the host. In HREM, the width of these thin amphibole lamellae ranges from 9Å to 900Å The chemical characteristics of element depletions near the amphibole lamellae and the textural relations of the development of such clinoamphiboles suggest that the chemical change required to form them is considred to have been caused principally by decreasing solubility of atoms such as Na, Al and Cr in clinopyroxene structure during the retrogressive reequilibration. Also, a possibility of finite solid solution of clinoamphibole in clinopyroxene was suggested.

Detailed historical review on these problems has been reported by Tomita and Yamaguchi (1980).

ii) Metasomatic alteration of pyriboles

Akai (1977,1979,1981,1982a) was the first to study and to report (1) the alteration microstructures of biopyribole (nucleation and growth of slab structures of triple and/or double chains in clinopyroxenes, etc), and (2) the alteration schems of clinopyroxenes (alteration by slab nucleation and alteration with iregular reaction front) with respect to a representative suite of specimens from a single ore body . Other investigations on pyroxene alteration by high resolution electron microscopy on single specimens from different localities (Buseck et al. 1980, Veblen and Buseck, 1981, Nakajima and Ribbe, 1980, 1981) were also carried out. Veblen and Buseck (1981) observed a varieties of intergrowth microstructures with HREM in pyroxene specimens that have been partially or wholly altered to other minerals. Textural considerations indicate that there are a number of different paths for pyroxene hydration reactions ; pyroxene to amphibole, pyroxene to clinojimthompsonite , and pyroxene to sheet silicate, as well as more complicated ,stepwise paths. The microstrucures indicate that there may be multiple mechanisms ; for example , replacement of pyroxene by amphibole or other hydrous pyriboles can take place either by the nucleation and growth of narrow lamellae of the product mineral,or by a bulk replacement mechanism along a broad reaction front. Nakajima and Ribbe (1981) observed augite specimens from metamorphosed gabbro from Hokkaido, Japan by a high resolution electron microscope and found that clinopyroxenes altered to double, triple and wider chain biopyriboles, with chlorite. They also proposed a structural model for the change from single to double and triple chain structures , which involves small movements of oxygen layers and tetrahedral atoms (Si,Al) with a minimum of bond breaking and re-forming, concommitant with hydroxylization of certain oxygens and the diffusion of Mg, Fe and/or Ca along the rift in the octahedral layer.

4. Chain-width disorders and termination defects in the pyribole structures

i) Chain-width disorder in the pyribole structures

Chisholm (1973) was the first to report the chain-width disorder in the chain silicates. He examined many amphibole asbestos specimens with electron diffraction methods and suggested that the streaks parallel to b^* are due to intercalation of single chains or silicate chains wider than double. Later on, his results were confirmed by many high resolution electron microscopic works (Akai et al. 1974; Hutchison et al. 1975; Jefferson et al. 1978, Veblen and Buseck, 1977). Many amphibole specimens have been examined by high resolution electron microscopy ;

amphibole asbestos ; Akai et al. (1974) ——cummingtonite,
Chisholm (1973, 1975) ——grunerite, amosite, crocidolite
Hutchison et al. (1975) —amosite tremolite anthophyllite
Alario Franco et al. (1977) —crocidolite
Veblen et al. (1977, 1979, 1980) —anthophyllite
Whittacker et al. (1981)
Dorling and Zussmann (1980) —tremolite actinolite asbestos.

Actinolite∼actinolite jade (nephrite)
: Hutchison et al. (1975)
: Jefferson et al. (1978)–nephrite jade
: Mallinson et al. (1977), Mallinson(1980)
: Dorling & Zussman (1980)

Amphiboles (massive ∼ ascilular)
: Chisholm (1973)
: Veblen et al. (1977)– anthophyllite
: Veblen (1980) – anthophyllite
: Cressey et al. (1981) – anthophyllite grunerite
: Champness et al. (1976)
: Veblen & Buseck (1979 b)
: Veblen (1980) — anthophyllite

It is suggested that almost all of the specimens of fibrous amphiboles have more or less chain width-disorder . It is found that the fibrous amphiboles formed at relatively low temperature are inclined to have many disorders The physico-chemical conditions of the formations of such disorder in chain width sequences are not known. It is not fully solved whether the disorders are formed in primary growth or during polysomatic reactions after growth. However, it is likly that at relatively low temperature and/or at relatively large growing rate they are apt to be formed.

Synthetic amphiboles were examined by high resolution electron microscopy (Velblen et al. 1977). These hydrothermally synthesized amphiboles also contains many chain width-defects ; many triple chains and minor amount of wider chains than triple.

2. Termination defects in pyribole structures

Veblen and Buseck (1980) made the detailed observations of termination defects of the double and triple chain structures in which one or more silicate chains terminate or turn into silicate chains of a different width. According to them, the types of chain terminations can be summarized as follows;

Chain terminations

- Termination at low-angle grain boundary (Incoherent)
- Cooperative chain termination (Two ore more zippers end together)
  - Coherent
  - Incoherent : with planar faults $\left\{ \begin{array}{l} \frac{1}{\pi}(010) \\ \frac{1}{\pi}(100) \end{array} \right.$
- Noncooperative chain termination
  - (termination of a (010) slab at a dislocation combined with readjustment parallel to a^*)
- Simple chain termination (A simple zipper terminate)
  - Coherent
  - Incoherent

They observed many examples of the termination defects by HREM (Veblen and Buseck,1981) and found that high resolution electron micrographs of such termination of wide-chain lamellae in narrow-chain host structures resemble zippers and hence they called them zipper termination. The simple rules for such chain termination which are essentially the same as those found in generation of new chain structure in host chain structure (Akai, 1979, 1981a) were suggested by Veblen and Buseck (1981) and Whittaker (1981). Veblen and Buseck (1981) derived two rules; (i) the " subchain rule" (" For strucutral coherence at a termination, there must be an equal number of subchains in a (010) pyribole slab and in the material it replaces ; a pyroxene chain contains one subchain, an amphibole chain has two and so on":Veblen and Buseck,1980) and ii) the "odd-even rule" (" For structural coherence at a termination, there must either be an even number of chains on both sides of the termination, or there must be an odd number on both sides " : Veblen and Buseck,1981).

Veblen and Buseck (1981) condsidered the kinetics of the polysomatic reactions with references to the defect structure such as chain terminations. Polysomatic reactions require chemical transport to occur together with structural reconstruction. The diffusion rates in most silicates are extremely sluggish at metamorphic temperatures. The answer to the question of how solid-state reaction involving chemical change occur to the degree that is observed probably lies in the mechanisms of diffusion (Veblen and Buseck,1981). They suggested that such the polysomatic reactions may not proceed by vacancy—hopping mechanism but by pipe diffusion mechanism which occurs by rapid motion of atoms or ions along structural tunnels (Dyson et al. 1967). In polysomatic reactions, the local structures at the terminations probably involve tunnels where I-beams are missing. They also proposed the term bulk reaction mechanism which is closely realted to massive polymorphic transformations (Christian, 1965). Veblen and Buseck(1981) suggested that some uralite may be formed by this bulk mechanism.

Ib. Purposes of this study

Polymerization of biopyribole

It is well known that pyroxene often alters to amphibole and/or talc maintaining topotactic relation. The structural changes in the process of of pyroxene alteration can be regarded to be a polymerization process. That is, silicate structures have been classified by the linkage of Si-O tetrahedra since the early stage of the determination of crystal structure (Warren,1929; Warren and Biscoe,1931; Warren and Bragg,1928 ; Warren and Model,1930a,b). Such a linkage can be interpreted as a series of polymerization of Si-O tetrahedra (or silicate chains) by analogy with the polymer science. Then, polymerization of the biopyriboles represents a structural change to produce the structure of wider-chain pyriboles from the structural units of single silicate chains , on the other hand, polysomatic reaction only represents the reaction from one polysome to another .

Depolymerization is the reverse process of polymerization and is, for example, found in the formation of oxyhornblende or in decomposition of hydrous pyriboles or sheet silicates by heating. The thermal change of amphibole to pyroxene has been studied by Kozu et al. (1927), Barnes (1930), and Posnjak and Bowen (1931). Ueda and Tomita (1964) and Tomita (1965) found a titaniferous oxyhornblende and an oxyhornblende made up of two different phases , a clinopyroxene and clinoamphibole, probably arranged as lamellae parallel to (010) in submicroscopic domains. High resolution electron microscopic investigations on the depolymerization of biopyriboles is preliminarily reported by Akai (1981 a).

The objectives of the study on polymerization of the biopyriboles in metasomatism at the Akatani ore deposit, Japan

As mentioned above, Veblen and Burnham (1975,1976,1978a,b) and Veblen et al. (1977) reported the occurrences of ferromagnesian triple chain silicate (jimthompsonite and clinojimthompsonite) in a metamorphosed ultramafic body at Chester, Vermont. Synthetic triple chain silicates containing Na were reported by Dritz et al.(1974,1976) and Tateyama et al. (1978). Other triple chain silicates with clearly different compositions have not yet been found.

The triple chain silicates formed in the amphibole-to-talc reaction sequence during metamorphism at Chester were investigated also from the viewpoint of genetic relation (Veblen and Buseck, 1979, 1980). However, any detailed genetic investigation of the triple chain silicates formed in the calciferous pyroxene-to-talc reaction sequence during the metasomatic alteration has not yet been made, although some investigations of a pyroxene alteration by HREM on specimens from various localities were carried out (Veblen and Buseck,1981 ; Nakajima and Ribbe,1981) . These specimens contained only a small amount of the triple chain silicates. However, any genetic investigation of the triple chain silicates in connection with the associated specimens with various degrees of alteration from a geologic field was not carried out.

The Akatani ore deposit in Niigata Prefecture, Japan is one of the typical localities where clinopyroxene altered to fibrous amphiboles and/or to talc during a metasomatism related to a specularite (hematite) ore formation (Imai,1952,1960; Suzuki,1970). Relatively a large amount of triple chain silicates were also found in the specimens from the Akatani ore deposit by HREM. This was preliminarily reported by Akai (1979,1981)

Then, perfect polymerization sequence from single to double, to triple chain, ... and to sheet structures was expected to be found in the metasomatic reaction. Furthermore, the studies of alteration microstructures with respect to a representative suite of specimens from a single ore body have never been carried out. This aspect of the study of microstructures in relation to a representative suite of specimens from a geologic field is essentially important not only for the consideration of the genesis of triple chain silicates, but also for understanding of the metasomatic alteration phenomenon.

In what follows, the polymerization process of the biopyriboles and the related microstructures in metamorphism at the Akatani ore deposit will be described in detail with special reference to the formation of calciferous triple chain silicates. The genetic relation of the biopyriboles cotaining the triple chain silicates will also be considered based on the concept of polymerization.

II Specimens examined

1. *Geology*

General geology and mineralogy of the Akatani ore deposit in Niigata Prefecture were described in detail by Imai (1952,1960) and Suzuki (1970). The Akatani ore deposit is associated with Paleozoic limestone which was metamorphosed by granitic intrusion at some time in pre-Miocene. Skarn minerals in the metamorphosed limestone are composed mainly of clinopyroxenes. The formation of the ore deposit is closely related to volcanic activity characterized by liparitic intrusion with introduction of hydrothermal solution. The useful data of the temperature at the metasomatism are not known except the one estimated by decrepitation method using quartz in the main ore body (Miyazawa and Nozaki ,1957). The temperature estimated is 278～281 °C.

The degree of metasomatic alteration is in general related to the distance from the ore body , although locally alteration conditions vary widely ; the degree of alteration becomes stronger as the sampling point approaches the ore body.

Specimens examined

On the basis of the microscopic observation, Imai (1952,1960) described the optical properties of the skarn minerals, hydrothermal alteration products of the skarns and the mineral paragenesis. The specimens of the fresh and altered clinopyroxenes were collected from the cutting in the mine (Bawarizawa- and Mizunashizawa-ore body). The sampling points of the specimens collected from the cutting in the Bawarizawa ore body are indicated in Fig.1. The degree of metasomatic alteration in these specimens is generally related to the distance from the ore body if ore vein or hydrothermal vein is not locally extending (Fig.1). The alteration of the specimens becomes stronger as the ore body is approached . Specimens of various degrees of alteration were examined by X-ray and optical microscope. As a result, the specimens were divided into seven classes according to the degree of alteration from fresh clinopyroxene through moderately altered specimens to talc. The degree of metasomatic alteration is roughly indicated here, by the ratio of primary clinopyroxene to altered "amphibole" and further altered talc (here, " amphibole" indicates the mineral of optically fibrous amphibole-like phase, which was revealed to be double and triple chain mixture). That is :

Degree I is represented by unaltered clinopyroxene;

Degree II , by slightly altered clinopyroxene with small amount of "amphibole" (Clinopyroxene>"Amphibole"); [7810-5,768-3,-7(390m level),7810-8,-10,766-I (410m level),7810-11(450m level)];

Degree III, by the mixture of altered "amphibole" and clinopyroxene ("Amphibole" $\simeq$ Clinopyroxene) ; [7810-4 (370m level)];

Degree IV, by the fact that almost all the specimens are composed of "Amphibole" ("Amphibole"), [768-1(350m level),7712-21(410m level)]

Degree V , by the mixture of "amphibole" and talc ("Amphibole" ≃ Talc),
[7810- 6, -7, -9 (410 m level0];

Degree VI, by the fact that the specimens are composed mainly of talc
(Talc > "Amphibole") , [7810-2 (360 m level)];

Degree VII, by the fact that talc is gradually replaced by dolomite
((Talc)), [7810-1 , 7911-1 (350 m level)].

Specimens* corresponding to each alteration Degree are listed above in brackets. Other specimens** from Mizunashizawa ore body also showed similar sequence of alteration containing utterly fresh specimens.

Optical micrographs of the specimens of some degrees of alteration are shown in Fig. 2. By microscopic observation of weakly altered specimens (Degree II), it has been found that alteration occurred mainly a) along cleavage, b) at the edge of columnar clinopyroxene crystals and c) along granular cracks (Figs.2a,b). Hematite and small rounded apatite grains are sometimes contained in the altered "amphibole" and talc (Fig.2-b). Further progress of alteration converts all clinopyroxene into fibrous "amphibole" (Fig.2c, Degree IV) and then into talc in the clinopyroxene pseudomorph (Fig. 2d, Degree VI). "Amphiboles" in the Degree IV are usually homogeneous in fibrous texture under microscopic observation. At the last stage talc is eventually replaced by dolomite still preserving clinopyroxene pseudomorph.

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* These specimens contain carbonate mineral, sphalerite and quartz with variable amounts of pyrite, specularite, lievrite, apatite and garnet (isotropic & anisotropic). (The detailed descriptions of the specimens are listed in the following table.)

** Specimens collected from Mizunashizawa ore body are as follows ; (Deg.I): 776-2,7712-1; (Deg.II): 766-III ;(Deg.III) : 766-II ; (Deg.IV): 23-5 ; (Deg.VI) : 776-4.
(The detailed descriptions of the specimens are listed in the following table.)

Degree of Alteration	Specimen Number	Alteration product of clinopyroxene	Paragenesis	Sampling position
I	776- 2	almost Cpx	carb. sph. pyr.	MIZUNASHIZAWA
	7712- 1	almost Cpx (Mo?)	qtz.	MIZUNASHIZAWA
II	7810- 5	Cpx ⩾ "Amph" (Mo)	gt(iso&aniso) carb. spec.	BAW. 390m level
	7810- 8	Cpx > "Amph" (Mo)	gt(iso&aniso) sph .	BAW. 410m Level
	7810-10	Cpx > Amph	gt(iso&aniso) ap. qtz. carb. sph. liev.	BAW. 410m level
	768- 3	Cpx ≫ "Amph	gt(iso&aniso) ap?	BAW. 390m level
	768- 7	Cpx ≫ "Amph" (Mo?)	gt(iso&aniso) carb. ap. liev.	BAW. 390m level
	766- I	Cpx > "Amph"	gt(iso&aniso) carb. ap. qtz. liev.	Baw. 410m level?
	766- III	Cpx > "Amph" (Mo)	gt(iso&aniso) ap. qtz. liev.	MIZUNASHIZAWA
III	7810- 4	Cpx > "Amph	gt(iso&aniso) carb. qtz. spec. sph .	BAW. 370m level
	766- II	Amph" ⩾ Cpx,Talc,Mo	gt carb. ap.? sph.	MIZUNASHIZAWA
IV	768- 1	"Amph" ≫ Talc	qtz. carb. ap. sph. spec.	BAW. 350m level
	7712-21	"Amph"	ap. carb. liev. spec. sph.	MIZUNASHIZAWA
	23- 5	Talc ≳ "Amph (Mo)	ap. qtz. carb. spe. sph.	MIZUNASHIZAWA
V	7810- 6	Talc + "Amph'	gt(iso&aniso) qtz. carb. liev.	BAW. 410m level
	7810- 7	Amph + Talc	gt(iso&aniso) spec.	BAW. 410m level
	7810- 9	Amph > Talc	gt(iso&aniso) qtz.	BAW. 410m level
VI	7810- 2	Talc ≫ "Amph"	ap. qtz. carb. sph. spec.	BAW. 360m Level
	768- V	Talc ≫ "Amph" (Mo)	gt(iso&aniso) qtz. ap. liev.	MIZUNASHIZAWA
	776- 4	Talc ≫ ("Amph")	gt(iso&aniso) qtz. ap. liev.	MIZUNASHIZAWA
VII	7810- 1	(Talc)	ap. qtz. carb. ispec. sph.	BAW. 350m level
	7911-1	(Talc)	ap. qtz. carb. spec. sph.	BAW. 350 m level

III. Experimental

Analysis by Electron probe microanalyzer (EPMA)

JXA-5A electron probe microanalyzer was used to determine the chemical compositions of the specimens, operationg at 15 kV and ca. 0.02 μA specimen current, and electron beam used was about 2∼3μm in diameter.

Analysis by analytical electron microscope (AEM)

Analytical electron microscope used was combined type of JEM 100 C equipped with energy dispersive X-ray detector. Semi-quantitative analysis of some elements was carried out by comparing the specimen with ion-thinned reference standard specimen (clinopyroxene) whose composition is known by EPMA analysis (CaO= 18.7∼22.5%). X-ray detecting angle used was 40°∼50° Accelerating voltage was 100 kV The time for counting X-ray was 200 sec.

Specimen preparation for electron microscopy

Specimens for electron microscopy were prepared in the following two ways. a) Powdered specimens were prepared both from polished thin sections and hand specimens. b) Specimens cut out of epoxy-impregnated petrographic polished thin sections were ion-thinned.

High resolution electron microscopy

For high resolution electron microscopy, top entry type JEM 100 C electron microscope with Cs= 1.4 mm was operated at 100 kV. Objective aperture of 60μm in diameter was used. The defocus value of -1000∼0∼1500 Å (positive value ; under focus, negative value ; over focus) was usually used, and through-focus images were also taken.

The details of the simulation of electron microscopic images based on kinematical approximation (Uyeda and Ishizuka 1974, Ishizuka and Uyeda 1975) will be given in an Appendix.

Results

Chemistry of biopyriboles at the Akatani ore deposit

The data concerning chemical compositions of clinopyroxene, "amphibole" and talc were obtained by electron probe microanalysis (Table 1). Unaltered clinopyroxene and "amphibole" show high content of Mn. Compositions of unaltered clinopyroxene in the specimens with degree of alteration I～III are variable from manganoan hedenbergite (or ferrosalite) to ferroan johannsenite in each specimen. Chemical compositions of the "amphibole" in the specimens with degree of alteration IV are usually almost uniform over a wide range in one thin section. Chemical compositions intermediate between those of amphibole and talc are sometimes obtained (sp.768-1 ; Table 1) , whereas the specimens are not pure triple chain silicate but mostly mixture of double chain silicate and talc. Talc in the specimen of Degree VI also contains a small amount of Mn.

Ca - Mg - Fe+Mn diagram of all biopyribole (clinopyroxene, "amphibole" and talc) is shown in Fig. 3. It is considered that the unaltered clinopyroxene has undergone a change to "amphibole" and further to talc by the reaction of hydrothermal solution. In this reaction, the chemical change is represented by the arrow in Fig. 3 , that is, Ca and Fe+Mn contents decrease and Mg content increases.

2-a "Amphibole "

"Amphibole" is an optically fibrous amphibole-like phase which replaces clinopyroxene. Under electron microscopic observation, it was ascertained that "amphibole" is a mixture mainly composed of (1) double chain silicates, (2) triple chain silicates and (3) disordered state of double and triple chain structures. Sometimes sheet structures are also associated. (1) Double chain silicates are volumes of double chain structure wider than several hundred Ångstroms in the b-direction. (2) Triple chain silicates are volumes of triple chain structure wider than several hundred Ångstroms in the b-direction. (3) Disordered double and triple chain structures are randomly mixed double and triple chain slabs of unit-cell-scale width. The intermediate states between (1) or (2), and (3) are also present.

X-ray powder pattern of "amphibole" is similar to that of C2/m amphibole, but sometimes accompanied by C2/c talc, according to the degree of alteration. Triple chain silicate was not completely confirmed by X-ray diffraction, except that faint diffraction of 13.5 Å peak and broad 9.0 Å peak which are assumed to be of the same 020 diffraction and superimposed 110 diffraction respectively as that of C2/c clinojimthompsonite were sometimes found. The electron diffraction pattern of b^*c^* reciprocal lattice plane which is the same as that of C2/c clinojimthompsonite was often obtained. However, jimthompsonite-like orthorhombic triple chain structure was not found.

2-b Frequency of occurrences of double and triple chain silicates in "amphibole"

With fine fibrous crystals, electron diffraction is the only method to obtain single crystal diffraction pattern. Fibrous "amphibole" is laid on microgrid with b- and c-axes lying nearly horizontal. Various electron diffraction patterns of fibrous "amphibole" from one hand specimen were obtained but each hand specimen has a tendency to show a characteristic predominance of one pattern among the various electron diffraction patterns. The statistic treatment of the frequency of double and triple chain silicates in fibrous "amphiboles" was carried out by using electron diffraction method Although electron diffraction method and electron microscopy are not essentially appropriate for obtaining the bulk average information of the mode of double and triple chain silicates in the "amphibole", they allow rough estimation of the relative predominance of double and triple chain silicates. Electron diffraction patterns were classified into the following four types.

1) Electron diffraction having 020 spot of I2/m amphibole on 0k0 lattice row of b^*c^* reciprocal lattice plane, 2) electron diffraction having the same 020 spot as C2/c clinojimthompsonite on 0k0 lattice row of b^*c^* reciprocal lattice plane, 3) electron diffraction having both 020 spots of the I2/m amphibole and the same 020 spots as C2/c clinojimthompsonite and 4) electron diffraction having streaks instead of the spots. Electron diffraction patterns containing b^* direction were observed till the total number of electron diffraction patterns from one hand specimen become one hundred. Typical specimens of each alteration degree were selected , dispersed on microgrid and examined. The results of the observations are shown in Table 2. The triple chains are rather dominant in the slightly altered specimens (Degree II). Relatively large quantities of triple chain silicates may be formed in the specimens from localities far distant from the ore body or in the specimens which suffered weak reactions.

2-c Calciferous double chain silicate and talc in "amphibole"

The bulk chemical composition of the "amphibole" which is composed mainly of double chain silicates is manganoan actinolite (Table 1). Semiquantitative analysis of single crystal of double chain silicate by AEM showed the same results. Low magnification electron micrograph of the ion-thinned "amphibole " is shown in Fig.4a. Fibrous aggregates mainly composed of double chain silicates are found with rough coincidence of lattice axes. The single fiber is long in c-direction ,about o.1 μ m wide in b-direction and very thin in a-direction (probably ⩽100 Å). Fig.4b shows the talc which is still preserving clinopyroxene pseudomorph. Talc also cotains cosiderable amount of Fe (Table 1).

2-d Calciferous triple chain silicate in "amphibole"

The chemical composition of the "amphibole" containing the triple chain silicates is shown in Table 1. Single fiber of triple chain silicate in "amphibole" was analyzed by AEM. The results showed the presence of appreciable amount of Ca, besides, Si, Mg, Fe, Mn. In order to clarify the chemical compositions of these triple chain silicates semiquantitatively, they were examined more closely Triple chain silicate aggregates adjacent to clinopyroxene in ion-thinned specimen were selected for semiquantitative. analysis of Ca content because the clinopyroxene can be used as reference standard specimen for Ca content which is already known by EPMA analysis (CaO = 18.7～22.5%). Fig.5 shows the chemical composition of the triple chain silicate adjacent to clinopyroxene semiquantitatively estimated by AEM.

The I_{Ca}/ I_{Si} value in triple chain structure region is reduced to about one third of calciferous clinopyroxene The C_{Ca}/ C_{Si} value in triple chain silicate is ideally one third of that of calciferous clinopyroxene. From these data, it was ascertained that the triple chain silicate is calciferous and has a nearly ideal composition of calciferous analogue of clinojimthompsonite. The calciferous analogue of clinojimthompsonite is derived from clinojimthompsonite by replacing Mg in M(5) site with Ca . The ideal composition is $Ca_2Mg_8Si_{12}O_{32}(OH)_4$. A part of Mg can be replaced with Fe and Mn Fig.6 shews triple chain silicate wider than 1000 Å in b-direction with only a small amount of disorder. High resolution electron micrograph of triple chain structure adjacent to double chain structure is shown in Fig. 7 It can be seen from Fig.7a that I-lattice of double chain structure is connected with C-lattice of triple chain structure. This is exactly what may be expected by the crystallographic relation of double and triple chain structures. Fig. 7a indicates that C2/c triple chain silicate has grown together with I2/m amphibole in such a way that its b- and c-direction are each parallel with those of amphibole. The mutual lattice relation is perfectly coherent By reference to the computor simulated image (Fig.7b & Appendix), the high resolution electron micrograph of Fig.7a is interpreted to be triple chain structure image at under focus of about 800 Å . These results are similar to those of nephrite by Mallinson et al.(1980) Previously the author (Akai 1977) preliminarily reported the presence of long-spacing diffraction spots in electron diffraction patterns of fibrous minerals from altered clinopyroxene in the Akatani mine. Later on, close examinations of these patterns revealed that they are not of mixed structure of single and double chains ,but of triple chain structure.

2-e Disordered state and locally ordered structure in "amphibole"

Structurally disordered states are often photographed in almost all of the "amphiboles"(Fig.8). Double ,triple and wider chains were identified in the high resolution electron micrographs, taking account of the electron diffraction , the computor simulation of electron microscopic images and the defocus value . The fibrous specimen which indicates heavy streaks or long-spacing spots in b^*-direction in the electron diffraction has disordered structures or locally ordered structures. These disordered structures are often composed of thin alternate slabs of double and triple chains. Wider chains , e.g. quadruple ,quintuple ,sextuple ·· chains are rarely inserted in double and triple chain structures (Fig.8). Fig.9 shows local ordered structure of 31.5 Å ,composed of regular stacking of two double chains and one triple chain to the extent of ca. 150 Å The probability of chain sequence p (Veblen and Buseck 1979) is 2×10^{-3} , and the periodicity may not be statistically so significant.

Slab structures of double and triple chains in "amphibole " appear to have no regularity in the disordered state, but when the lamellae widths are measured by taking many high resolution electron micrographs, the characteristic statistical frequence of slab width in b-direction is recognized (Fig.10). Slabs of two double chains and those of one triple chain are predominant, compared with other slabs having different widths.

2-f Other fine textures found in "amphiboles"

Low magnification electron micrograph of the ion-thinned "amphibole " is shown in Fig.4a. Fig.11 shows a single fiber separated from the aggregates. Talc (sheet structure) is almost always discriminated on both lateral sides of the single fiber The lattice relation between the chain structure and sheet structure of talc is also completely coherent. The interface between sheet structure and chain structure is found in Fig.12a,b The chain structure is surrounded by sheet structure. The boundary between talc and chain structure along (010) plane is straight, and that along (001) plane is slightly irregular.

3-a Fine textures found in the clinopyroxene

Various fine textures of biopyriboles from the Akatani ore deposit which suggest the progress of metasomatic alteration were found near the reaction front of the clinopyroxene, especially the clinopyroxene of Degree II. Electron micrographs of ion-thinned weakly altered clinopyroxene (Degree II, sp.766-I) are shown in Figs.13a,b , which indicate triple chain or double chain formation in clinopyroxene host. The slabs of triple and double chain structure in clinopyroxene host are constructed from one to several chains in b-direction and have a length of several hundred Ångstroms in c-direction. Both terminations of triple and double chain slabs are occasionally found in clinopyroxene. The lattice fringes of 13.5 Å of triple chain structure are resolved , coherently matching the (010) and (001) planes of the host clinopyroxene. There is no peculiar contrast due to severe lattice strain between these double or triple chain structures ,and the host single chain structure.

Figs. 13c,d indicate the growth of double and triple chains from short and narrow chains to longer and thicker ones. In these figures coherent relation is still maintained between clinopyroxene and the newly formed triple and double chain structures. Fig.13e shows further growth of double and triple chain structures separated from unaltered clinopyroxene and forming aggregate of triple and double chain silicates. The relation of crystal axes is still roughly maintained. In general, more irregular reaction front is also seen (Fig.13f).

3-b Statistics concerning slab width of double and triple chains in clinopyroxene host structure

The statistic treatment of the frequency of slab width of triple and double chain structures nucleated in host clinopyroxene was carried out to ascertain the character of topotactic transformation of clinopyroxene to triple and double chain structures. By high resolution electron microscopic study of biopyriboles, a great deal of heterogenieties are often found in the distribution of different chain widths even within a single specimen grid. This may result in a terrible sampling problem. A solution of this problem and a valid statistical analysis require counting as many chains as possible in each of many areas of a specimen. A large number of high resolution electron micrographs were taken of more than 10 different grains of the most typical specimen with alteration Degree II (766-I). The number of the double or triple chain slabs was then counted. The density of distribution of the thin slabs was generally low . Then,the total number of the slabs did not become so large. Histograms of the slab width measured by the number of triple or double chains sandwiched by single chain structures are shown in Figs.14a,b. The total number of slabs of triple chains in the host clinopyroxene is larger than that of double chains. This tendency was further confirmed by the fact that more electron diffraction patterns indicating the presence of triple chain slabs in clinopyroxene host were taken than those of double chain slabs. In the histogram of double chain slabs (Fig.14a), slabs of even number of double chains are predominant, while triple chain slabs show no such predominance ; but slabs of one triple chain are frequent (Fig.14b).

Discussions

Polymerization from the single chain structure to double and triple chain structure, and to talc

When the slab widths of double and triple chain structures in the weakly altered clinopyroxenes are represented by the number of double and triple chains, the frequency distribution of the widths exhibits characteristic features ; that is, the slabs of triple chain structure have various widths , while the slabs of double chain structure have widths of even number. In disordered double and triple chain structure slabs in "amphiboles", the frequency distribution of the slab widths of the double chain structure shows the maximum value at the two double chains (Fig.10a). On the other hand, the slab widths of triple chain structure vary somewhat widely, but relative predominance of slabs having one triple chain is seen (Fig.10b). In all the slab structures in the clinopyroxene consisting of triple and double chains, no special strain is found between the different structures. These facts can be interpreted as follows. When double or triple chains are formed in clinopyroxene structure, the displacement* of 1/2 (a+c) of one or two pyroxene slab units are needed for structural fit (The term pyroxene slab unit here used is essentially the same as the pyroxene module of Thompson (1978) although the method of choosing the unit structure is different from that of Thompson ;cf.Fig.15). To satisfy this structural relation the following topotactic relations which were preliminarily reported by Akai (1979) should be maintained . In the structural change from single chain structure to double chain structure, two among four pyroxene slab units must shift successively by 1/2 (a+c). As the result of the displacements , slab structures of two double chains are formed (Fig.15). One triple chain structure can be derived from three successive pyroxene slab units, their central unit shifting by 1/2 (a+c) without shifting of the chain structure on both sides (Fig. 15). If single and double chains are alternatively formed in C2/c clinopyroxene, three of the six slab units must shift . But such mixed structure of

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* The real atomic movement in polymerization ,however, may not necessarily represented by the displacement of 1/2 (a+c), but may be such movement as suggested by Nakajima and Ribbe (1981) or otherwise .

single and double (or wider) chains have not been observed so far in the specimens from the Akatani ore deposit.

This idea of the structural change of biopyribole maintaining topotactic relation which was preliminarily reported by Akai (1979,1981) can be called the polymerization of silicate chain structures. The polymerization can be ,in general, represented as follows. Supposing n pyroxene slab units shift among the m pyroxene slab units, in order to construct v-fold chain structure from u-fold chain structure ($P_{u,v}$: polymerization from u-fold to v-fold chain structure), the ratio of $\frac{n}{m}$ is assumed to represent the character of topotactic structural change among the biopyriboles The product $n \times m$ represents a kind of index indicating easiness of structural change from one to another biopyribole. The product $n \times m$; therefore, is here called topotaxy index of biopyribole. Table 3 shows the ratio $\frac{n}{m}$, the topotaxy index $n \times m$, and the number of newly formed chains p ($\doteqdot \frac{m}{v}$) This idea of topotaxy index of biopyribole contains the idea of " Rules for coherent zipper terminations " (Veblen and Buseck 1980). That is , Zipper Rule 1 is naturally the basis of topotaxy index of biopyribole in a condition where no stress is present. Zipper rule 2 is found in the relation where both p and $\frac{m}{u}$ are even or odd (Table 3). Furthermore , the topotaxy index expresses the topotactic relation concerning kinetics in the structural change. It forms the clue to the easiness of topotactic structural change only when geometrical structural relations are maintained. For example, the order of the decrease of easiness of the formation of new biopyribole structures from single chain structure are, triple , double, quintuple and quadruple ··· ··

Kinetics of the topotactic formation of triple and double cahins in clinopyroxene in metasomatism

It has not yet been ascertained whether all the triple chain silicates occur stable phases or not, because of the lack of phase equilibrium experiments. Taking into consideration,however, the mode of occurrences of biopyriboles at the Akatani ore deposit , it may be possible to estimate the kinetics in the formation processes of calciferous triple and double chain structures. On the basis of all the data concerning the frequency of occurrence of biopyriboles, schematic diagram representing the relative quantities of calciferous clinopyroxene, calciferous amphibole (double chain silicate), calciferous triple chain silicate and talc vs. distance from the ore body can be drawn as in Fig. 16 . The distance from the ore body may be regarded to be related to the quantities of hydrothermal solution. A knowledge of the mode of occurrence of all the triple and double chain slabs in the host clinopyroxene (Fig.14) is also essential for the characterization of biopyribole formation. The changes of the mode are continuous from the slab structures in clinopyroxene to fibrous aggregate ("amphibole") . The thinnest slabs, therefore, which are sandwiched between single chain structures and are composed of single or only a few chains may have been formed in the weakest stage of metasomatic alteration. The formation process of biopyriboles at the Akatani ore deposit will be discussed below. In the following discussions, metasomatic alteration model at the Akatani ore deposit is assumed to be as follows ; P,T- conditions may not significantly differ throughout the suite of the specimens. On the contrary, the quantities of hydrothermal solution differ greatly with the location in the field (i.e. distance from the ore body). It cannot be known whether these triple chain silicates are stably formed or not at these conditions, but it is clear that triple chain slabs are predominant in the weakly altered clinopyroxene. The kinetics therefore must also be taken into consideration in the discussion of the formation of biopyriboles.

i) Where the effect of hydrothermal solution was weak (far distant from the ore body), clinopyroxene partly altered to "amphibole " (alteration Degree II) In the clinopyroxene, thin slab structures of triple and double chains are formed near the reaction front, and slabs of triple chain structures nucleate more frequently than those of double chain structures (Fig. 14). Relatively large amounts of triple chain silicates are also contained in "amphibole " in the alteration Degree II (Table 2). When double and triple chain structures are formed in the C2/c pyroxene, these structures hold a topotactic relation with the C2/c Pyroxene structure as mentioned above. The details of the structural change in the clinopyroxene are considered as follows. Previous considerations have revealed that the topotactic minimum units of double and triple chain slab structures in the host clinopyroxene are constructed of two double chains and one triple chain respectively Metasomatic compositional change, however , from four single chains to two double chains implies $2Ca \rightleftharpoons Mg$ replacement and 2 H introduction per 4 $Ca(Fe,Mn,Mg)Si_2O_6$ Similarly, metasomatic compositional change from three single chains to one triple chain implies $2Ca \rightleftharpoons Mg$ replacement and 2 H addition per 3 $Ca(Fe,Mn,Mg)Si_2O_6$. The quantities of mass transfer in the slab formation with width of one triple chain may be nearly equal to that in slab formation with width of two double chains. However, the energy barrier protecting the structural change from three single chains to one triple chain is estimated to be lower than that from four single chains to two double chains, because the formation of one triple chain from three single chains requires only one single chain translation, while the formation of two double chains requires translation of two single chains (topotaxy indices of double and triple chains formation from single chain structure are 2 X 4 =8, 1 X 3 =3, respectively). This energy barrier may be related to an activation energy for the structural change.

Triple chain structure must be easily formed along the activation energy path.

If many of the above-mentioned processes proceed independently and simultaneously , thicker slabs of triple chain structure may be eventually formed, and will also become "amphibole". At least a part of the "amphiboles"in the alteration Degree II might therefore be formed in this process. The fact that double chain slabs with width composed of two double chains are predominant in locally ordered structure and disordered structures in "amphibole" may be explained by the above-mentioned process in which one triple and two double chains are assumed to be formed topotactically in the weakest stage of metasomatism in host clinopyroxenes.

Most of the triple chain silicates, however, may be formed from clinopyroxene as Ostwald steps although more detailed examinations are necessary to ascertain this point.

ii) The specimens from parts near to the ore body sufferred the stronger alteration. These specimens are composed mainly of "amphiboles" (alteration Degree IV). The "amphibole" of this alteration degree consists mainly of double chain silicates , with minor amount of triple chain silicates and talc. As mentioned above, the "amphiboles" in this alteration degree have homogeneous fibrous textures in appearance and show approximately homogeneous chemical compositions over a wide range of the thin section in EPMA analysis. Furtheremore, even in the specimens which show a composition nearer to that of triple chain silicte, they are composed not of triple chain silicates alone , but mainly of double chain silicates plus talc. It is therefore assumed that equilibrium mineral assenblage is double chain silicate (amphibole) plus talc in the metasomatic condition at the Akatani ore deposit.

iii) By summarizing the metasomatic reactions , the compositional changes of biopyribole can be represented by the following chemical reactions.

$$\underset{\text{single chain (Hd)}}{4\mathrm{Ca(Fe,Mn,Mg)Si_2O_6}} + \mathrm{Mg^{2+}} + 2\mathrm{H^+} \longrightarrow \underset{\text{double chain (Act)}}{\mathrm{Ca_2(Mg,Fe,Mn)_5Si_8O_{22}(OH)_2}} + 2\mathrm{Ca^{2+}}$$

$$\underset{\text{single chain (Hd)}}{6\mathrm{Ca(Fe,Mn,Mg)Si_2O_6}} + 2\mathrm{Mg^{2+}} + 4\mathrm{H^+} \longrightarrow \underset{\text{triple chain (Ca-cj)}}{\mathrm{Ca_2(Mg,Fe,Mn)_8Si_{12}O_{32}(OH)_4}} + 4\mathrm{Ca^{2+}}$$

$$Ca_2(Mg,Fe,Mn)_5Si_8O_{22}(OH)_2 + Mg^{2+} + 2H^+ \longrightarrow 2(Mg,Fe,Mn)_3Si_4O_{10}(OH)_2 + 2Ca^{2+}$$

double chain (Act) sheet (Tc)

$$Ca_2(Mg,Fe,Mn)_8Si_{12}O_{32}(OH)_4 + Mg^{2+} + 2H^+ \longrightarrow$$

triple chain (Ca-cj)

$$3(Mg,Fe,Mn)_3Si_4O_{10}(OH)_2 + 2Ca^{2+}$$

sheet (Tc)

These reactions represent chemical changes which occur by addition of hydrothermal solutions containing Mg^{2+} and removal of Fe^{2+} , Mn^{2+} and Ca^{2+} from the clinopyroxene. Calciferous triple chain silicate is naturally derived from the calciferous clinopyroxene. Other high resolution electron microscopic investigations revealed the presence of some narrow triple chain structure regions in fibrous amphiboles or in pyroxenes (Buseck et al.1980; Jefferson et al. 1978; Mallinson et al.1980; Nakajima and Ribbe 1980,1981; Veblen and Buseck 1981). Although they were not analyzed chemically ,they may also be calciferous. Calciferous analogue of clinojimthompsonite ,as a new mineral, may be found in some appropriate geological environments.

By summarizing the fine textures of biopyriboles observed , a proposed scheme for the propagation of metasomatism and the corresponding fine textures of biopyriboles can be drawn (Fig.18) It may be concluded therefore that the nucleation of biopyriboles is polymerization process and corresponds to the propagation of metasomatic reactions ,in the Akatani ore deposit.

VI. Conclusion

1) Clinopyroxene transforms to optically fibrous amphibole-like phase ("amphibole") and talc in the metasomatic process related to the formation of specularite at the Akatani ore deposit. It was ascertained that the "amphibole" was a mixture of double and triple chain silicates, and a disordered state of double and triple chain structures. The degree of metasomatic alteration was indicated by the relative quantities of the remaining clinopyroxene, "amphibole" and talc. The rough relation between this degree and the distance from the ore body was ascertained. In weakly altered specimens, relatively large amount of triple chain silicates is contained.

2) The triple chain silicate formed in the metasomatism at the Akatani ore deposit is of electron microscopic size of 1000 Å at maximum width in b-direction, and is a calciferous analogue of clinojimthompsonite.

3) In the weakest metasomatic alteration, a large amount of triple chains and minor amount of double chains are transformed from single chains in host clinopyroxene structure, maintaining topotactic relation. Fine textures of newly formed biopyriboles in the clinopyroxene could be analyzed by the topotactic relationship between biopyriboles (Fig. 13,14,15 ; Table 3).

4) Amphibole and/or talc may have been stably formed by the strongest reaction of the metasomatism at the Akatani ore deposit (near to the ore body). Where, however, the effect of hydrothermal solution was weak (far distant from the ore body), thin slabs of triple chain structures nucleated more frequently than those of double chain structures in host clinopyroxenes. Considering the kinetics, in clinopyroxene host the triple chain slab with one triple chain width may have been more easily formed than the double chain slab with two double chains width along the low activation energy path.

5) Various fine textures in clinopyroxene and "amphibole" were interpreted as corresponding to the propagation of metasomatic reaction processes.

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Abstract

Clinopyroxene transforms to triple chain silicate, double chain silicate (amphibole) and sheet silicate (talc) in the metasomatic process of the Akatani ore deposit. The triple chain silicate is contained in fibrous amphibole-like phase ("amphibole"). It is of electron microscopic size of 1000 Å at maximum width in b-direction, and is a calciferous analogue of clinojimthompsonite. Various kinds of fine textures formed in metasomatic reaction process were found in clinopyroxenes. A large amount of triple chains and a small amount of double chains were transformed from single chains in the host clinopyroxene, maintaining topotactic relation. The kinetics of the structural change of biopyriboles at the Akatani ore deposit was discussed from the viewpoint of the mode of occurrence of triple and double chain silicates. The nucleation of triple chain structure slab with one triple chain width is apt to occur rather than the nucleation of double chain structure slab with width of two double chains in clinopyroxene host. Various fine textures in clinopyroxenes and amphibole-like phase were interpreted as corresponding to the propagation of metasomatic reactions.

Fig.1 Sampling points of typical specimens from Bawarizawa ore district. The sampling points projected on WNW - ESE cross section of the Bawarizawa ore body (Shukosho) in the Akatani mine. The projected distances of sampling points from the ore body roughly correspond to the true distance from the ore body except for the sampling points of specimen number (sp.) 7810-5 ,768-3, 768-7 which are distant from the ore body by about 100 m and perpendicular to the cross section.

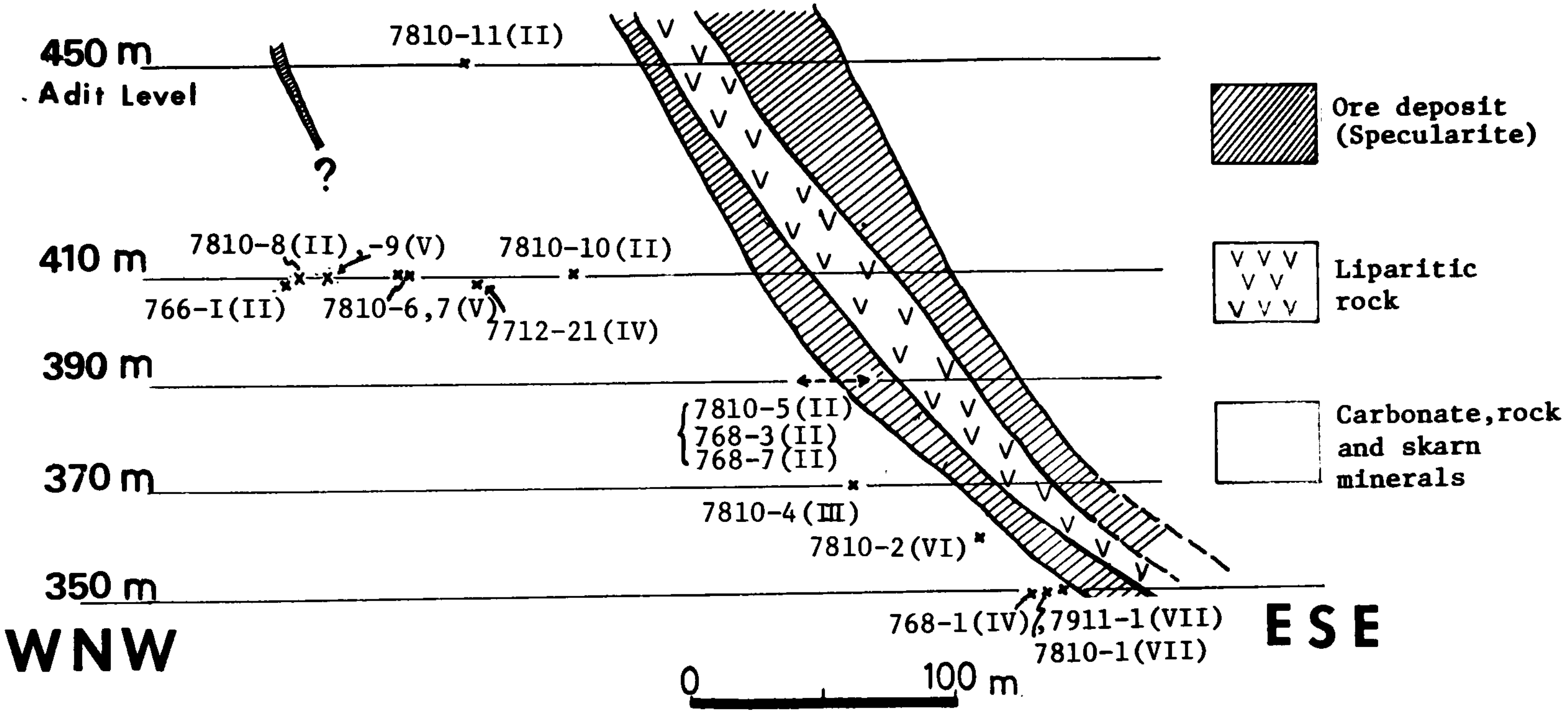

450 m
Adit Level
?
7810-11(II)
410 m
7810-8(II), -9(V)
7810-10(II)
766-I(II)
7810-6,7(V)
7712-21(IV)
390 m
7810-5(II)
768-3(II)
768-7(II)
370 m
7810-4(III)
7810-2(VI)
350 m
768-1(IV), 7911-1(VII)
7810-1(VII)
WNW
ESE
0
100 m
Ore deposit (Specularite)
Liparitic rock
Carbonate,rock and skarn minerals

Fig. 2 Photomicrographs of altered clinopyroxenes. (a),(b) : weakly altered specimens (sp.766-I , (a) : cross nicols ; (b) : open nicol).Reaction front is seen. (c) : Altered specimen composed of "amphibole " which is properly a mixture of double and triple chain silicates (sp. 768-1, open nicol). (d) : Talc pseudomorph after clinopyroxene (sp. 776-4 , open nicol) Cpx: clinopyroxene, 'Amph' : "Amphibole", Hem : Hematite (Specularite) , liev :lievrite , qtz.:quartz.

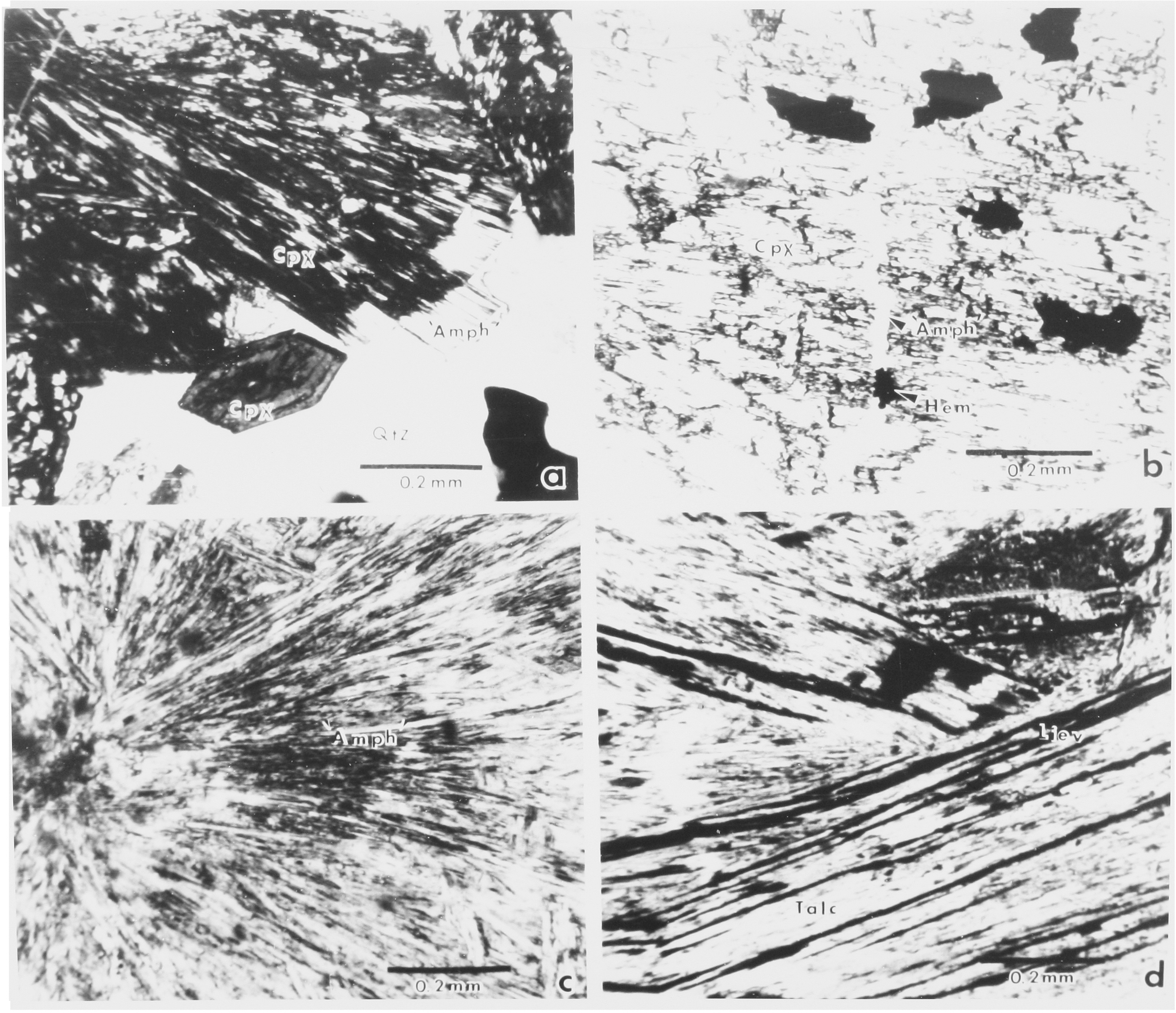

Cpx
Amph
Cpx
Qtz
0.2 mm
a
Cpx
Amph
Hem
0.2 mm
b
Amph
0.2 mm
c
Liev
Talc
0.2 mm
d

Fig.3 Ca- Mg- Fe+Mn diagram of biopyriboles in the Akatani ore deposit. Data of all biopyriboles are plotted in the same diagram (sp. 768-3,766-I, 766-II ,766-III, 768-1, 768-V) " o " represents composition of pyroxene, " • " , composition of " amphibole " (mixture of amphibole and triple chain silicates) " ▪ " , composition of talc respectively Arrow indicates the estimated direction of metasomatic change,

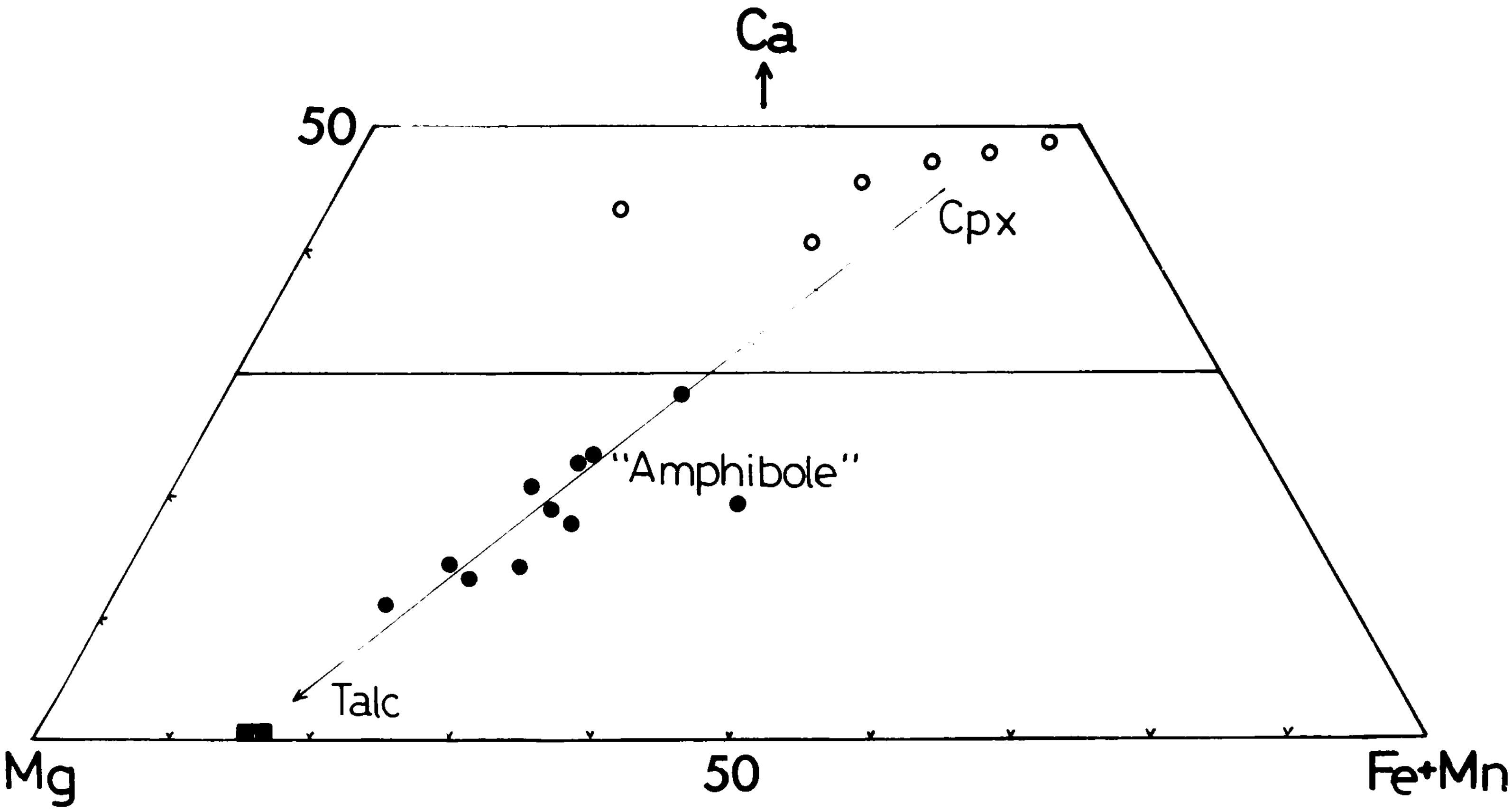
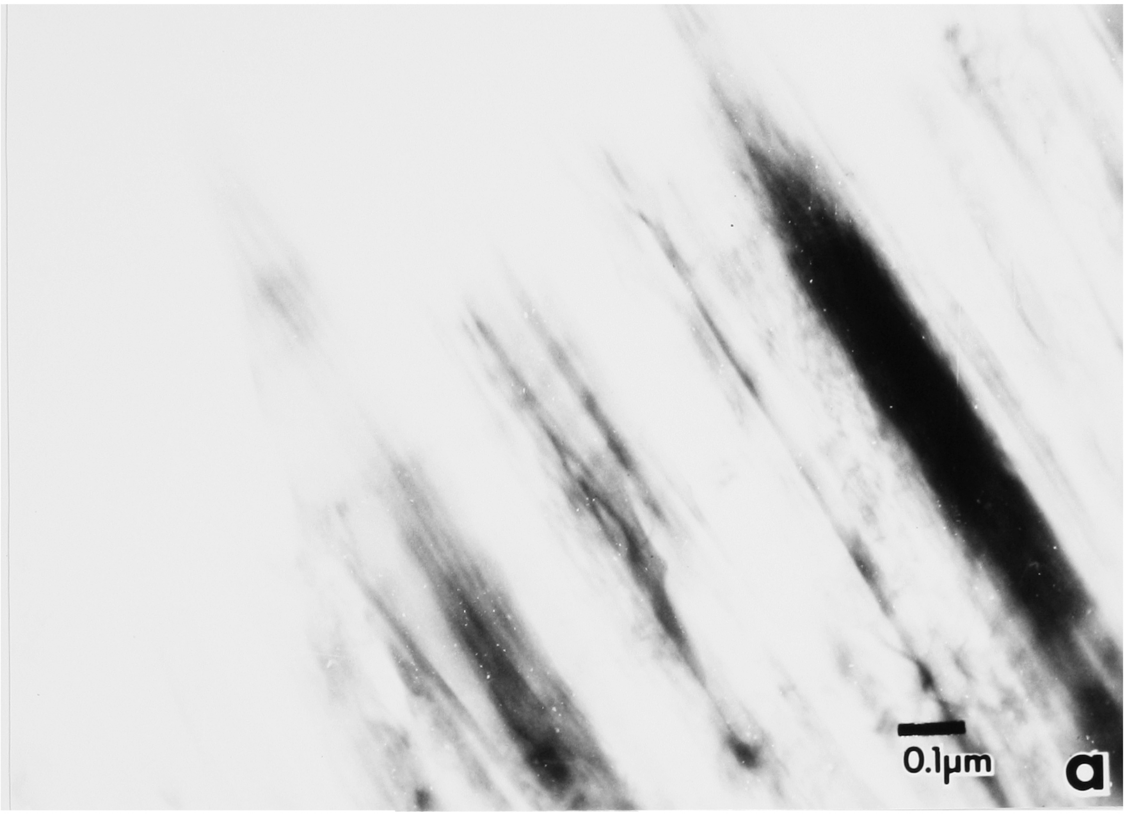
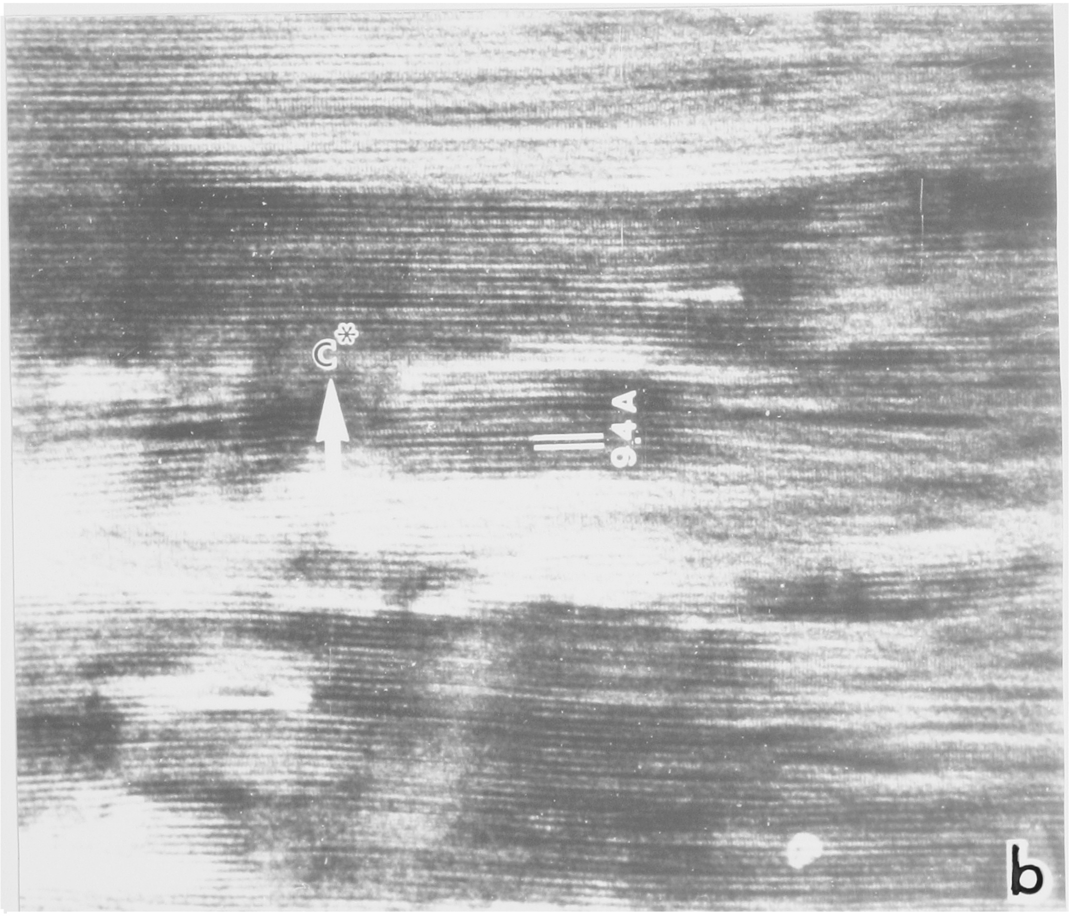

Ca
50
Cpx
"Amphibole"
Talc
Mg
50
Fe+Mn

Fig.4 (a) Electron micrograph of utterly fibrous aggregate of hydrous biopyriboles ("amphiboles"), (sp. 768-1) (b) Electron micrograph of (c) talc , the last product of metasomatism (sp.768-V)


0.1μm
a


c*
9.4 A
b

c

Fig.5 Semiquantitative composition estimate on triple chain structures by AEM (sp.766-I) (a) Electron micrograph of ion-thinned specimen edge. a,b, c and d indicate the positions analyzed (a : clinopyroxene ; b,c,d : portions mainly composed of triple chain structures) (b) Lattice fringes in the position b indicate triple chain structure of 13.5 Å (c) Electron diffraction pattern of the specimen containing triple chain structures. (d) The results of analysis shown as characteristic X-ray intensity ratios I_M/I_{Si} along analytical positions. I_M I_{Si} values were measured by peak height conventionally. Two different X-ray detecting angles of 40° and 48° were taken. X-ray counting time was 200 sec. I_{Ca}/I_{Si} value was reduced to about 1/3 in b,c,d compared with that of clinopyroxene.

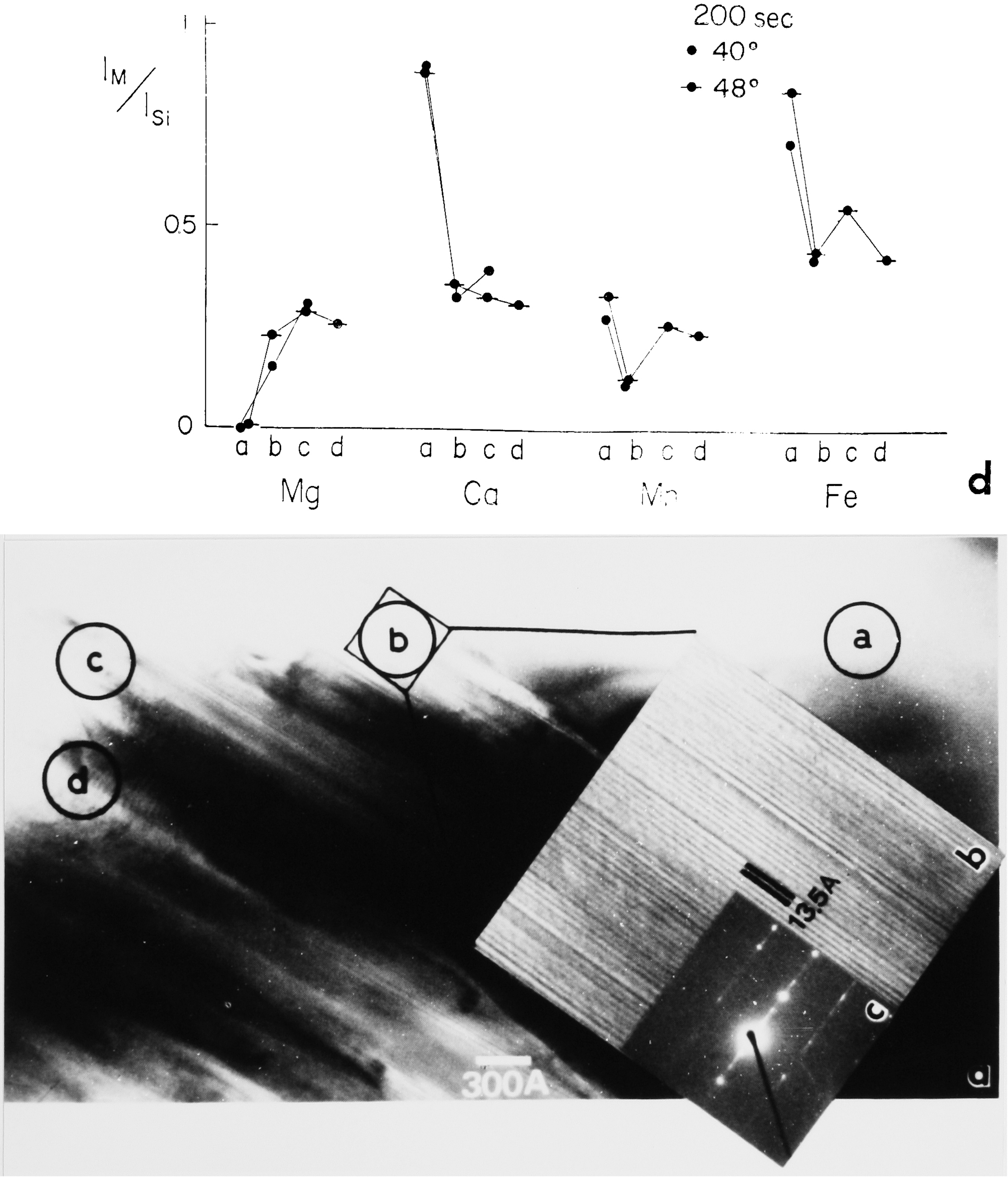

200 sec
● 40°
-●- 48°
I_M / I_{Si}
1
0.5
0
a b c d
Mg
a b c d
Ca
a b c d
Mn
a b c d
Fe
d
c
b
a
d
13.5A
300A
b
c
a

Fig.6 Electron micrograph of ordered area of calciferous triple chain structure with only small amount of disorder The sequence is wider than 1000 Å in b-direction (sp.766-I).

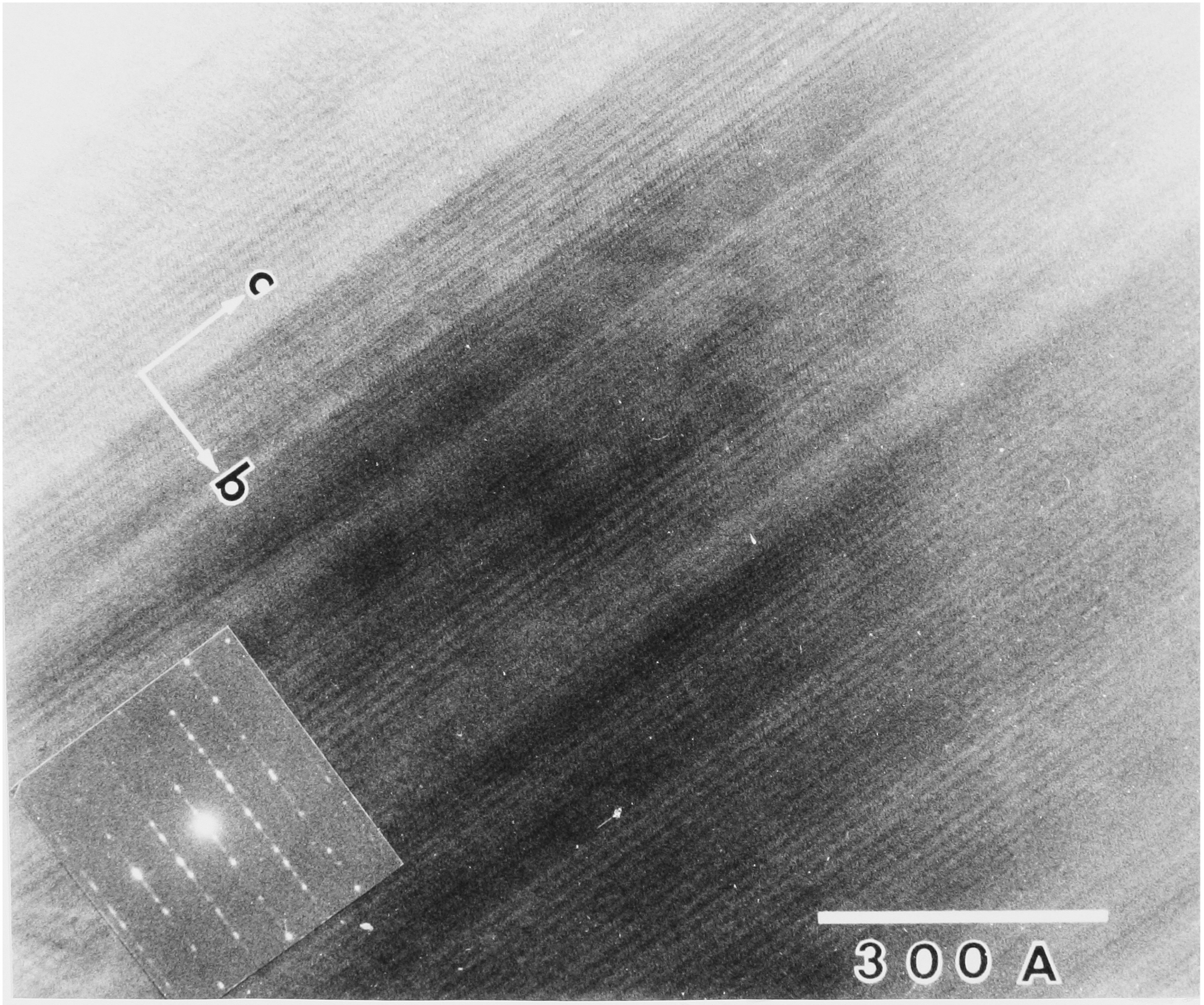
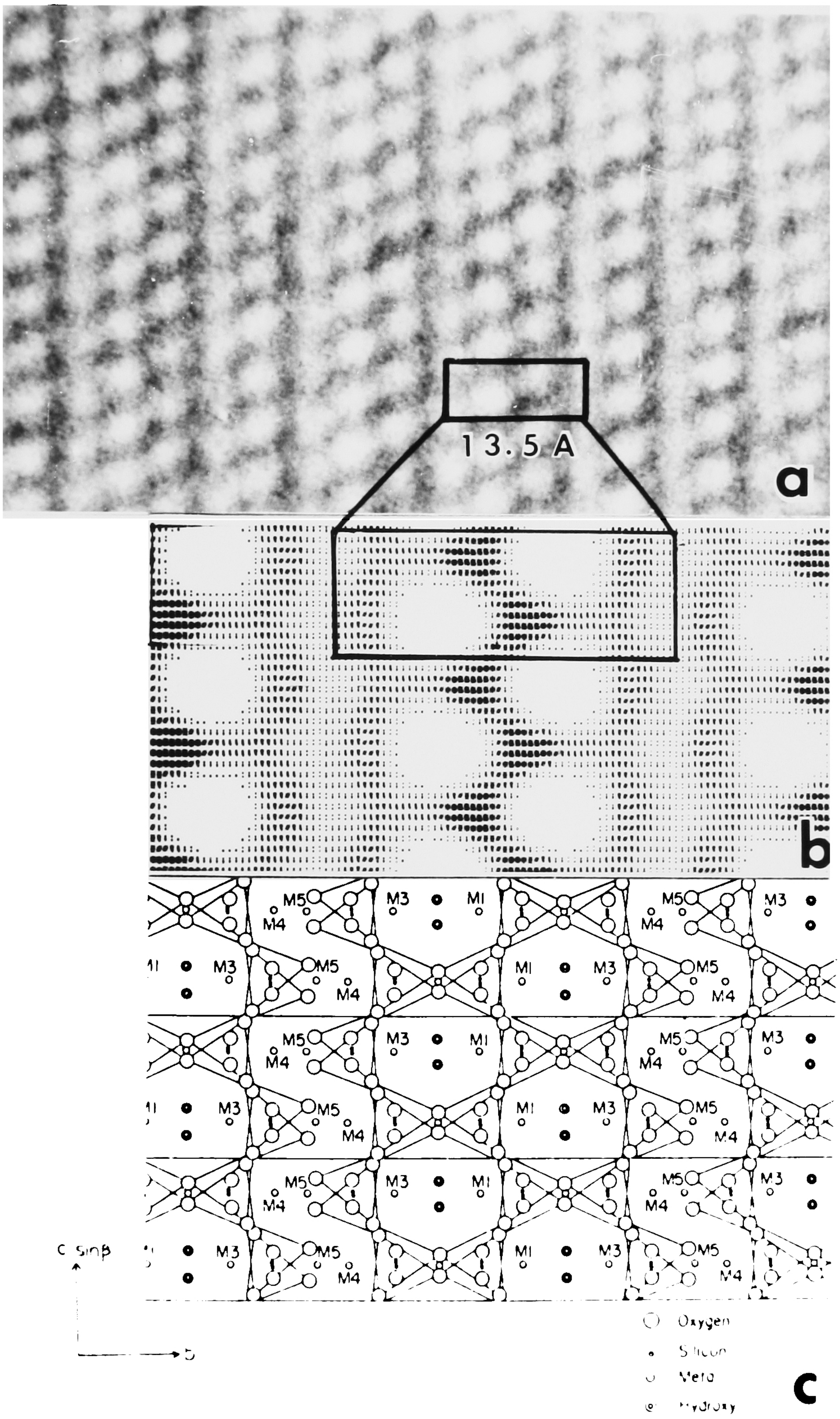

c
b
300 A

Fig.7 (a) High resolution electron micrograph of calciferous triple chain (a') structure adjacent to double chain structure (sp.768-3) (b) The corresponding (b') simulated electron microscopic image of calciferous triple chain structure under under-focussing condition of 800 Å (calculation was based on kinematical approximation) (c) The corresponding triple chain structure projected along a-axis which is based on Veblen and Burnham (1978b) M(5) site= Ca.


13.5 A
a
b
M1
M3
M4
M5
c sinβ
b
Oxygen
Silicon
Metal
Hydroxy
c

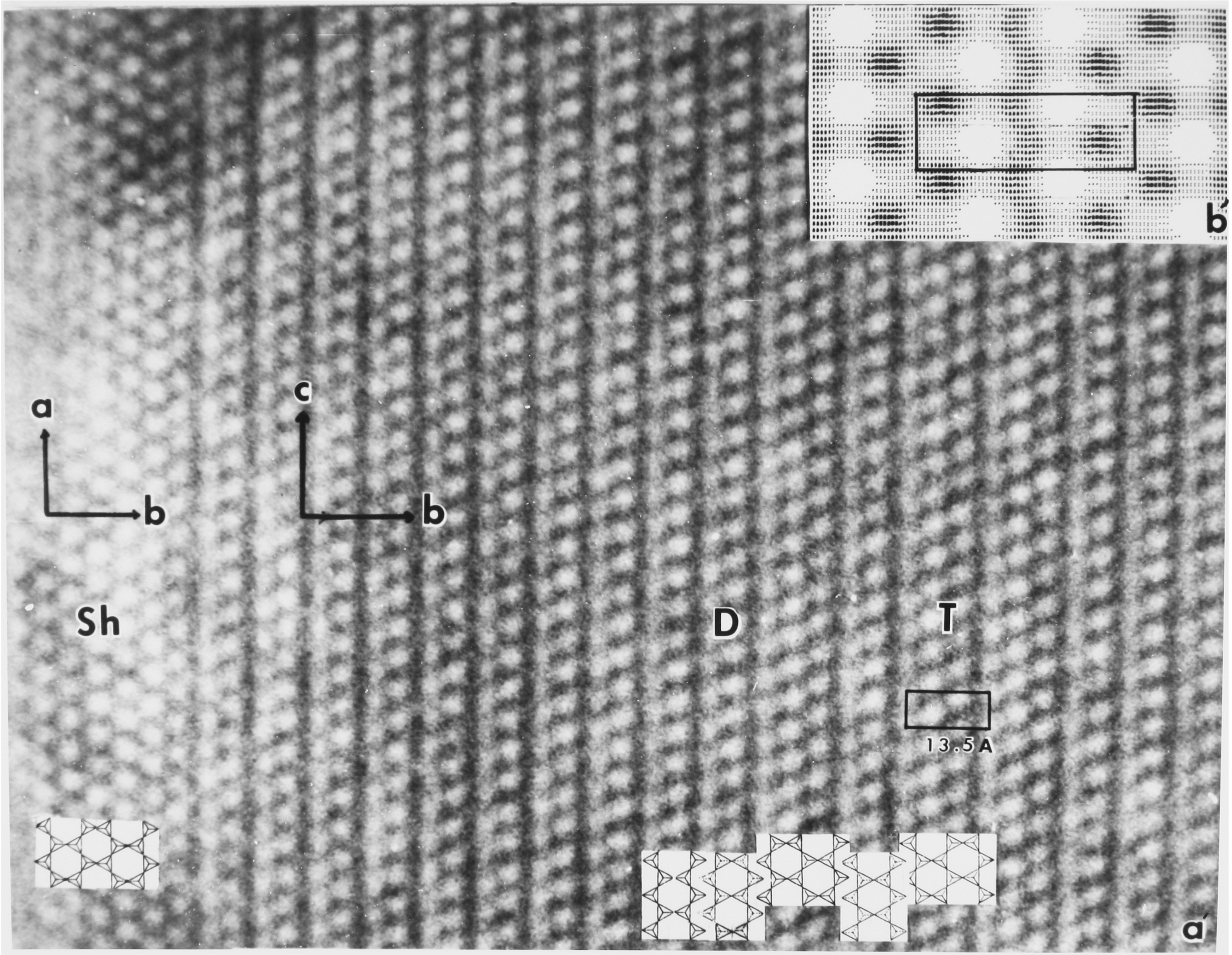
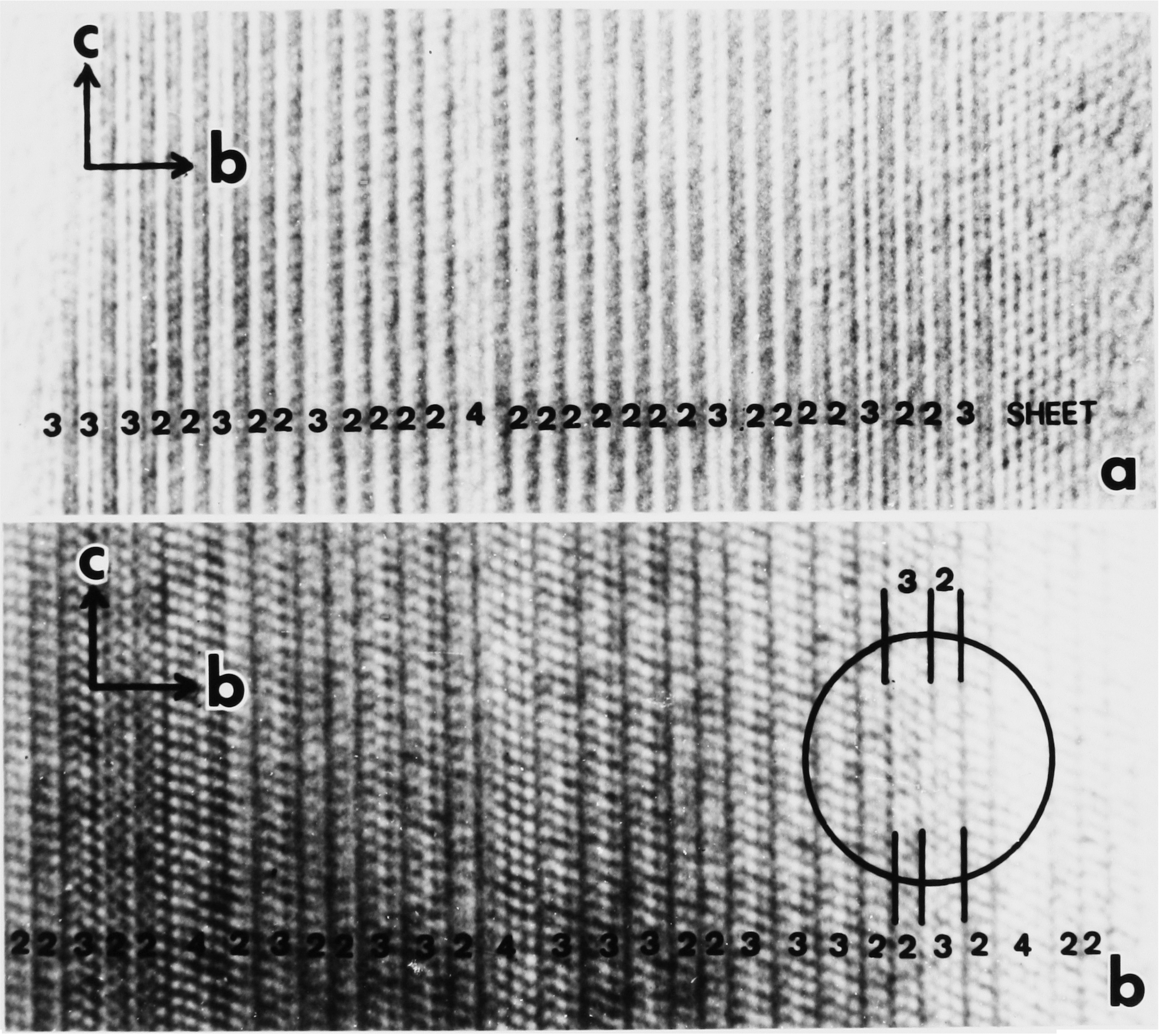
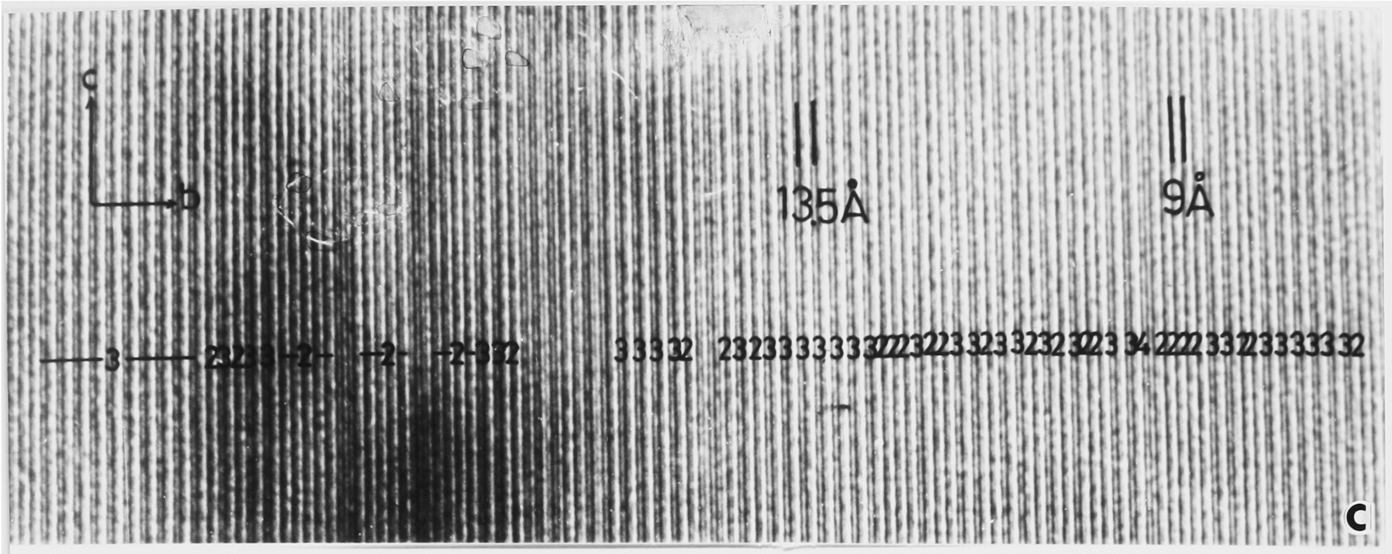

b'
a
b
c
b
Sh
D
T
13.5 A
a'

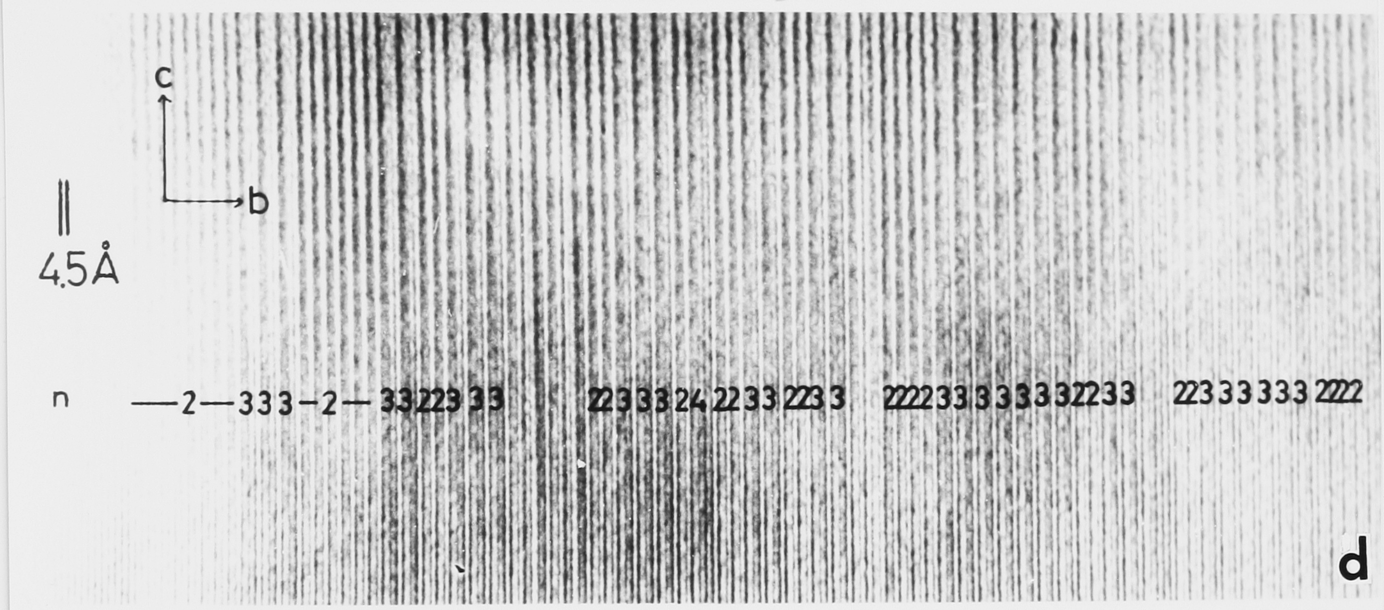
Fig.8 (a), (b) Two dimensional electron micrographs of fibrous specimens (" amphibole") indicating disordered state which is composed mainly of double (2) and triple (3) chain structure slabs (a: sp.766-I, b : 766-III)

The disordered state is not entirely random but is composed of slab structure with sequence of double and triple chains. Chain width exchange is seen in the circle in (b),. Double and triple chain structure (upper part in b) is replaced by triple and double chain respectively. The number in the photographs represents chain width , e.g. 2: double chain, 3: triple chain , 4 : quadruple chain

(c),(d),(e) One dimensional lattice images of disordered structures found in the fibrous specimens.


c
b
3 3 3 2 2 3 2 2 3 2 2 2 2 4 2 2 2 2 2 2 2 3 2 2 2 2 3 2 2 3 SHEET
a
c
b
3 2
2 2 3 2 2 4 2 3 2 2 3 3 2 4 3 3 3 2 2 3 3 3 2 2 3 2 4 2 2
b


c
b
13,5Å
9Å
——3—— 23233 -2- -2- -2-332
33332
23233333333222322332332323223 34 2222 3322333333 32
c


c
b
4,5Å
n
—2—333-2— 3322233 3
22333 24 2233 2233
2222333333322233
2233333332222
d

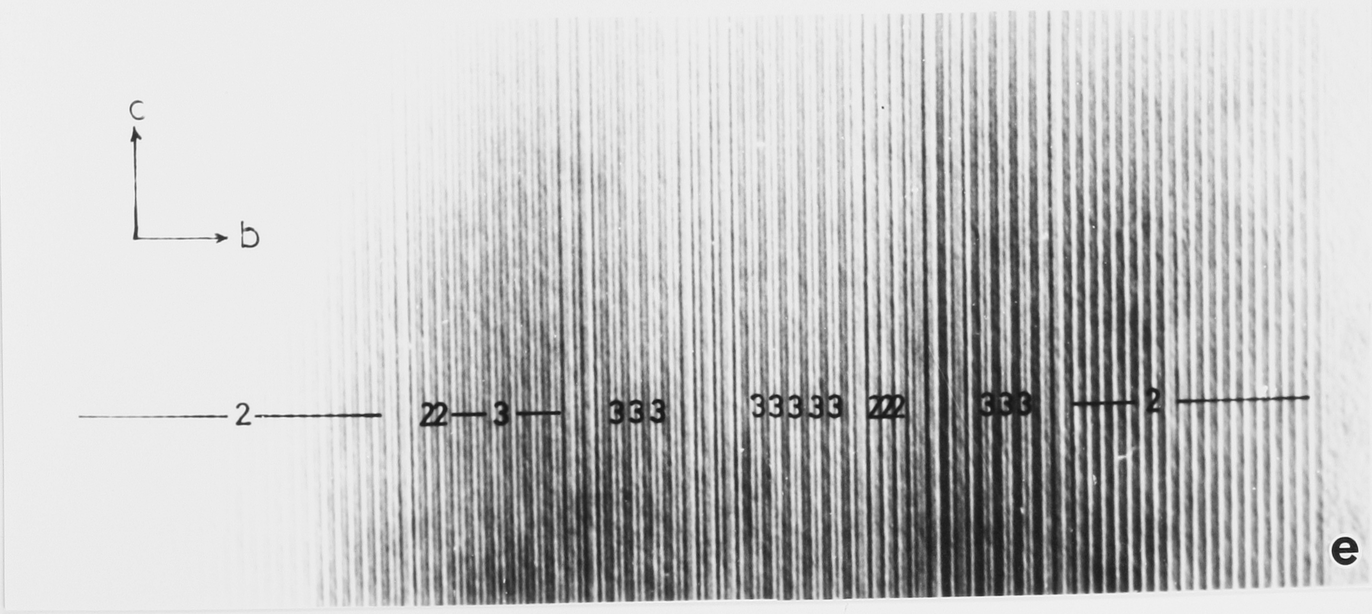

c
b
——2——
22—3—
333
33333
222
333
——2——
e

Fig.9 Electron micrograph of local superstructure of 31.5 Å composed of two double chains and one triple chain (322) with sequence of about 150 Å in b-direction (sp.766-I)

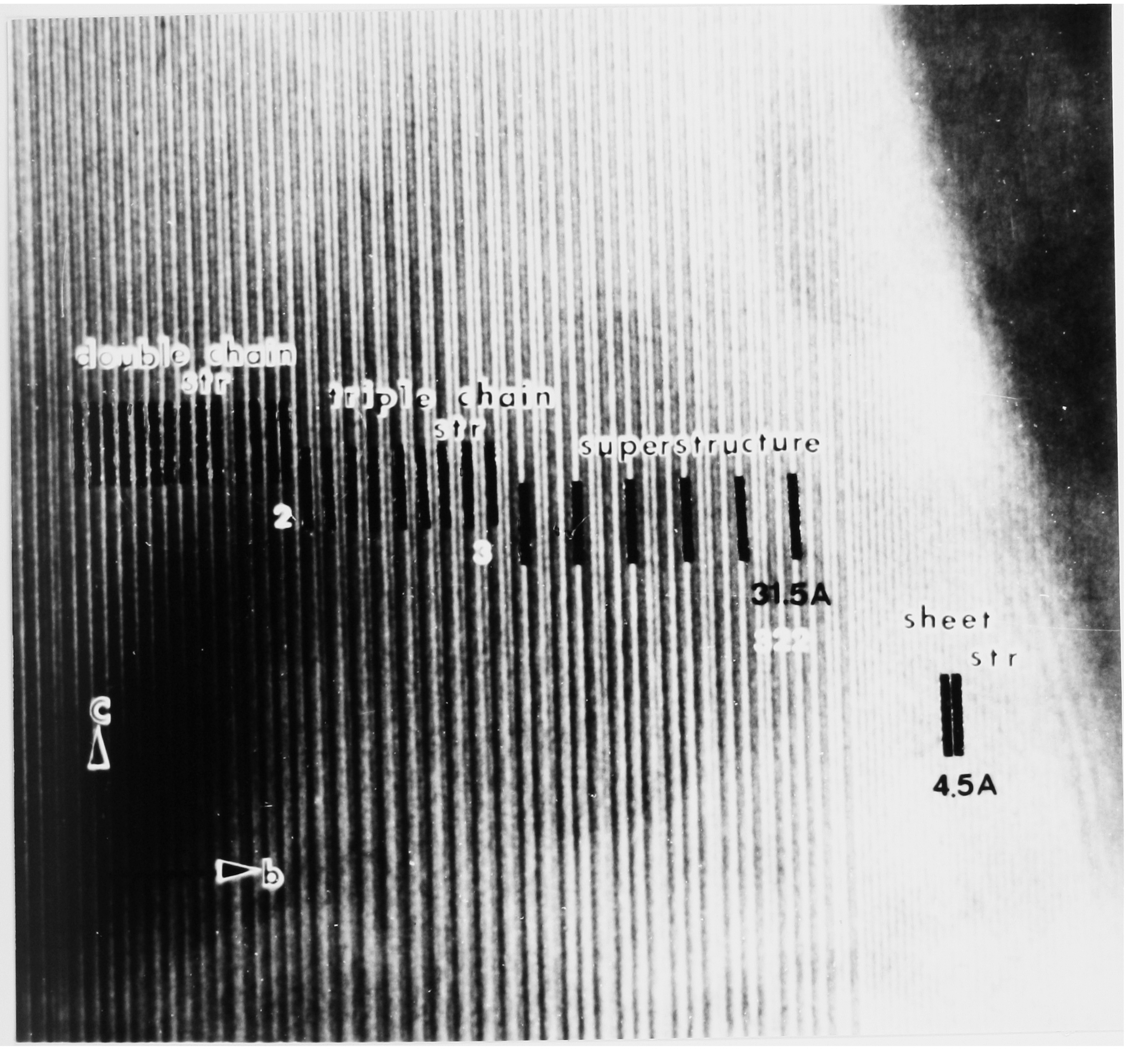

double chain
str
triple chain
str
superstructure
2
3
31.5A
822
sheet
str
4.5A
c
b

Fig.10 Histogram of the slab widths of double (a) and triple chains (b) sandwiched between the others in fibrous specimens (" amphiboles"). Slab width is measured by the number of double or triple chains in the b-direction. White columns represent the number of slabs and black columns represent the number of all the chains contained in the slabs.

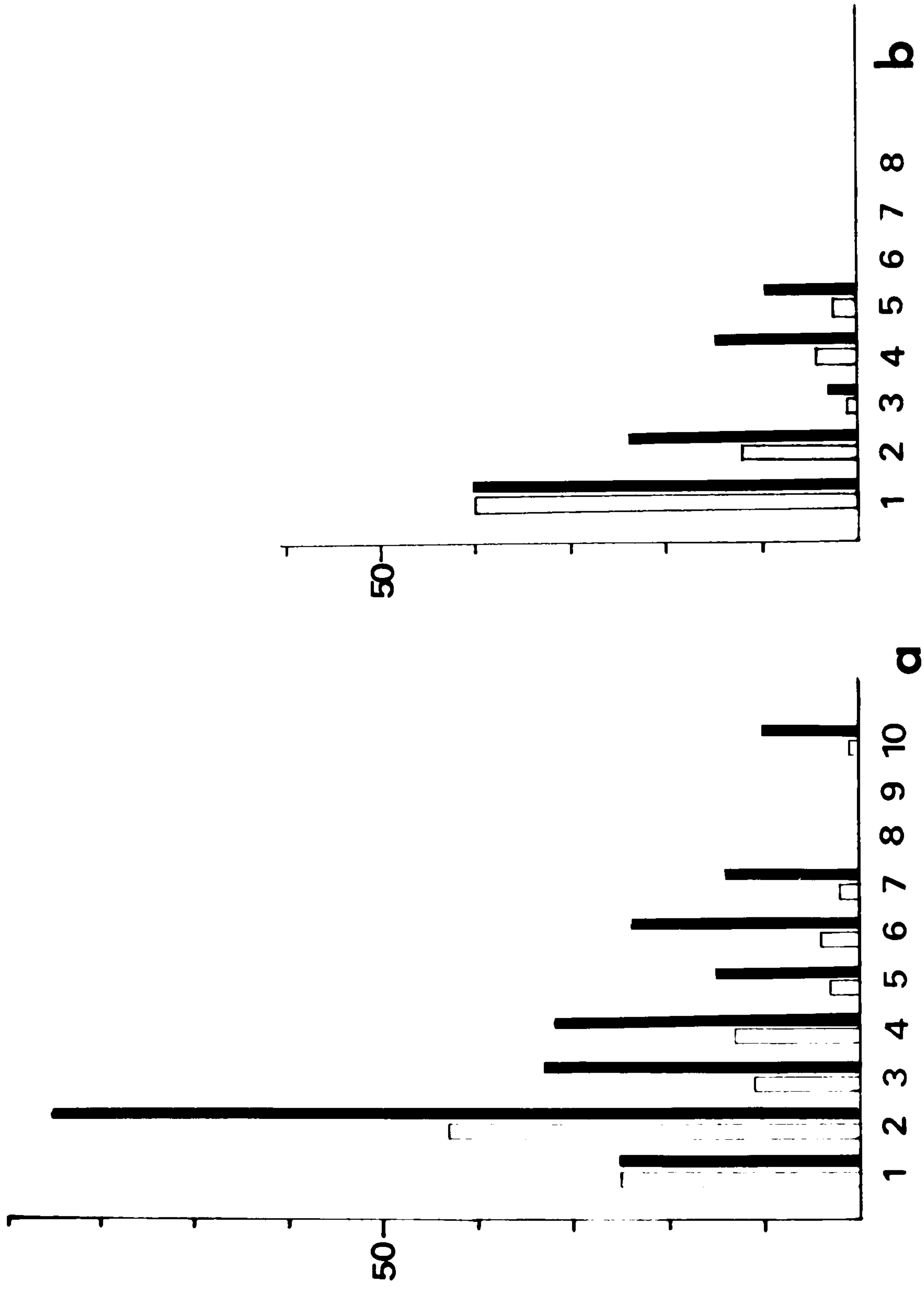

50
1
2
3
4
5
6
7
8
9
10
a
50
1
2
3
4
5
6
7
8
b

Fig.11 Electron micrograph of single hydrous biopyribole fiber derived from fibrous aggregate (sp.766-I). In the center of the fiber, pyribole (double and triple chains, and wider chains) structure is found. Sheet structure (talc) is growing on both lateral sides of the fiber

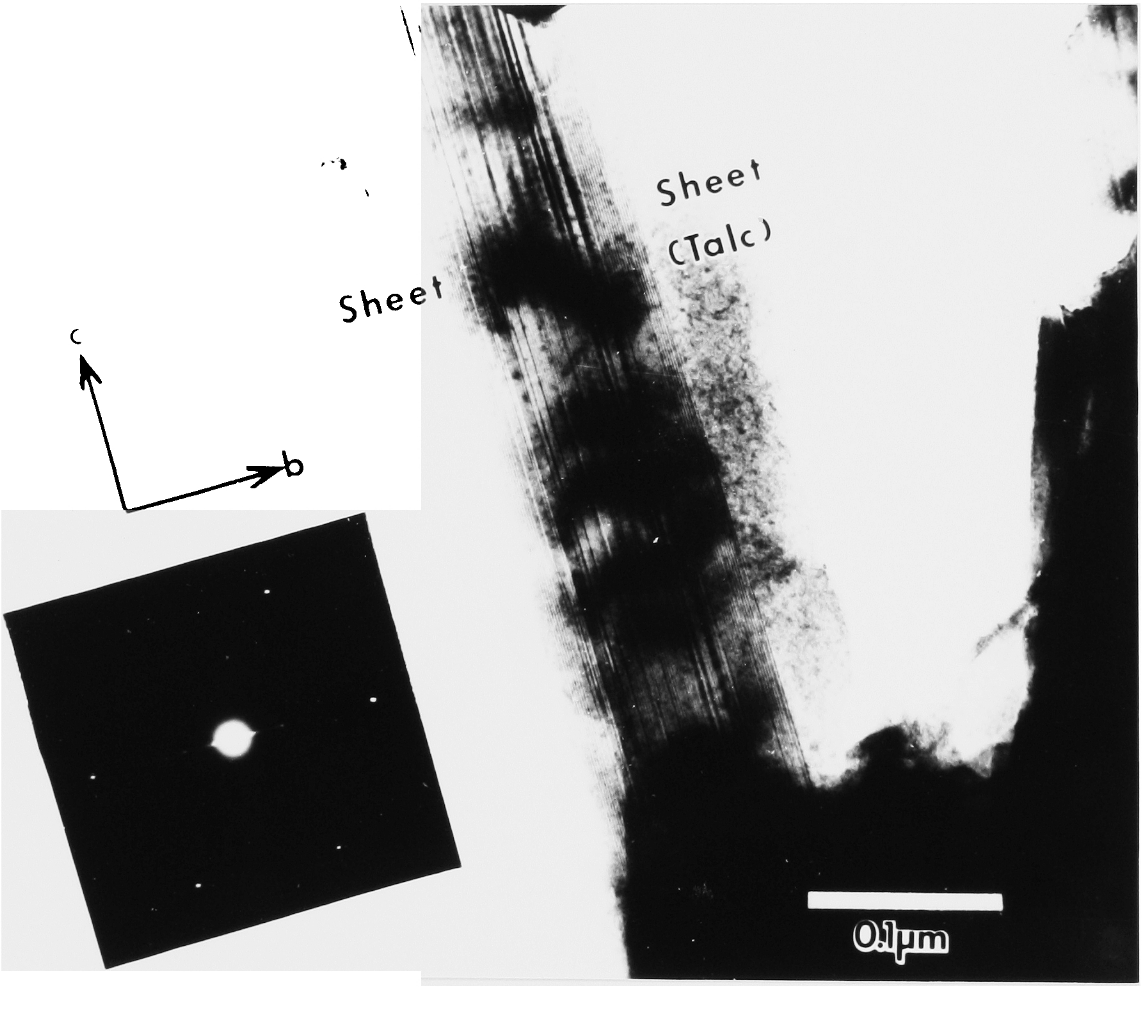
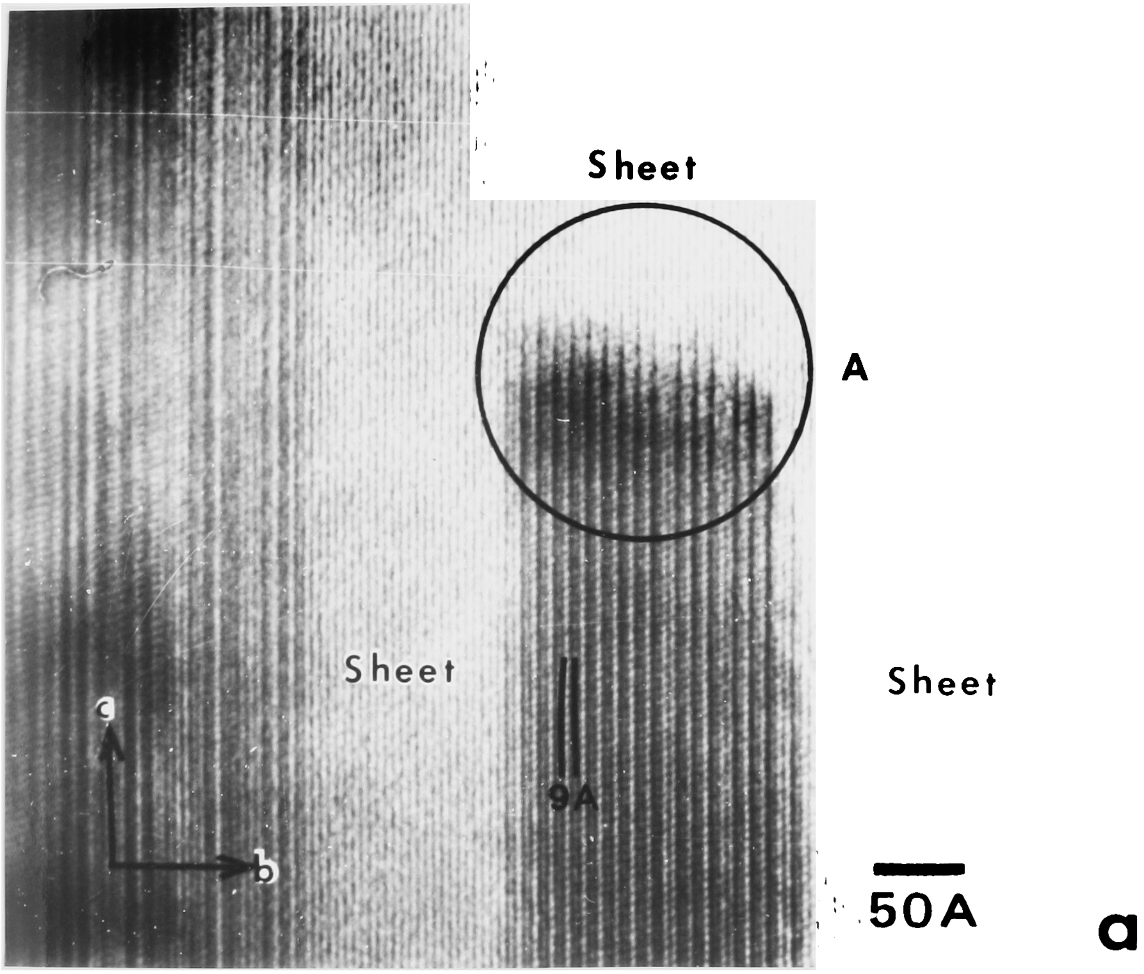

Sheet
(Talc)
Sheet
c
b
0.1μm

Fig. 12 (a) Electron micrograph indicating the interface between sheet structure (talc) and double and triple chain structure (sp.768-1) Position A is the boundary in [001] direction.

(b) Enlarged electron micrograph of (a) Coherent lattice fits between sheet structure, and double chain (B) or triple chain (C) parallel to (010) plane is found.


Sheet
A
Sheet
Sheet
c
b
9A
50A
a

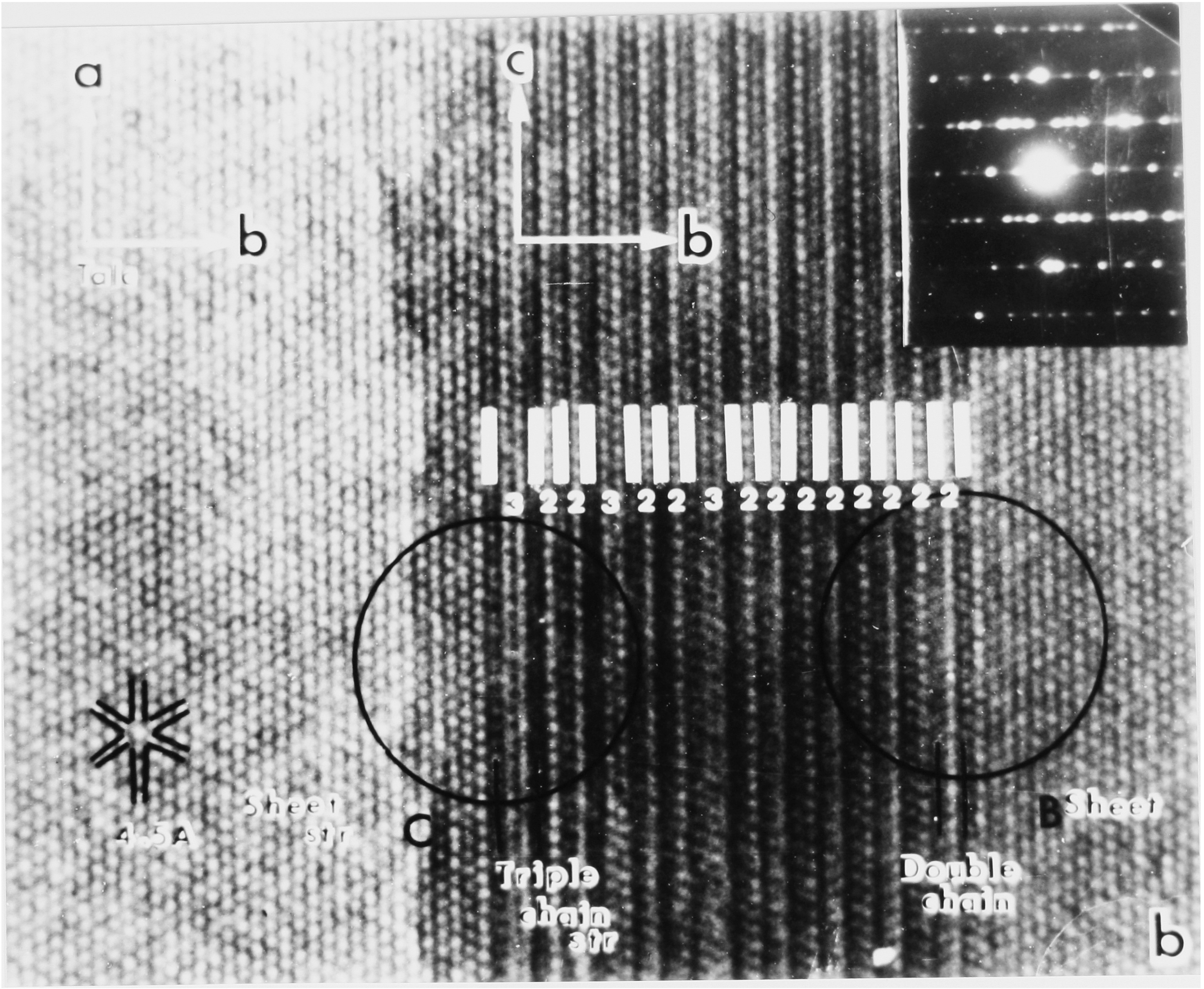
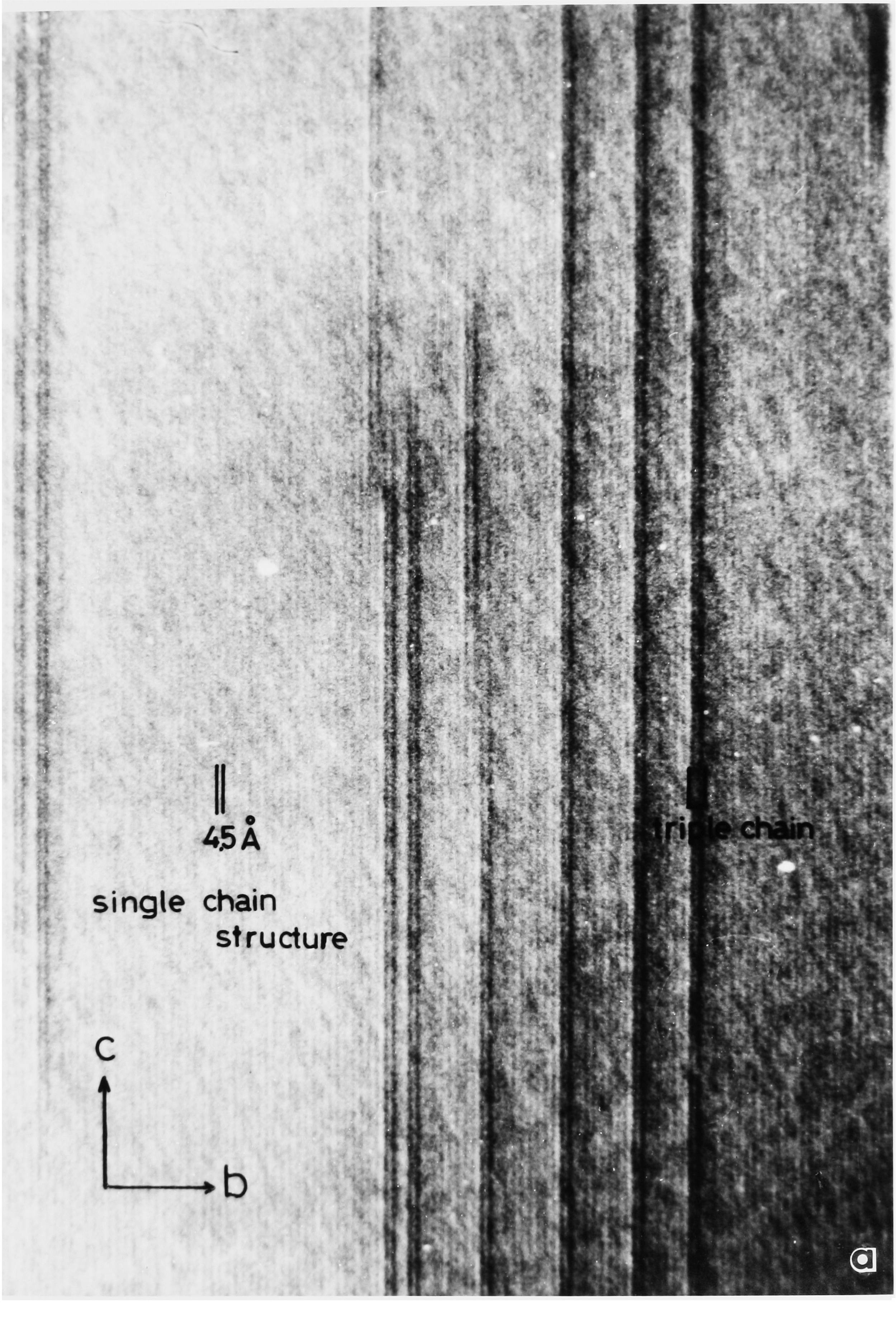

a
b
Talc
c
b
3 2 2 3 2 2 3 2 2 2 2 2 2 2 2
4.5A
Sheet
str
C
Triple
chain
3tr
Double
chain
B Sheet
b

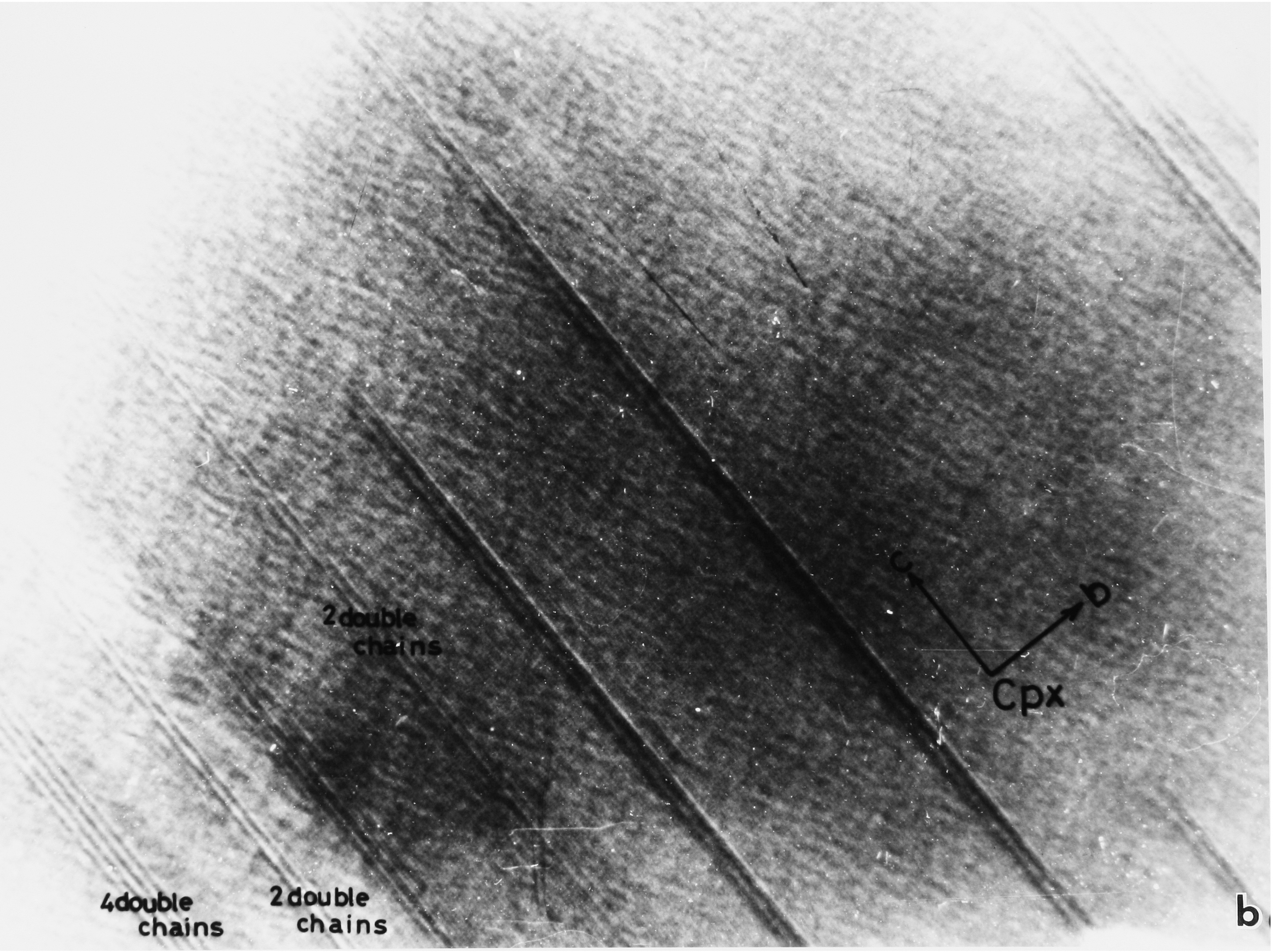
Fig.13 (a),(b) (b'), Electron micrographs indicating the formation of small triple and doubl chains in clinopyroxene host with width of one to several chains in the b-direction (a: sp.766-I, over focus image ; b: 766-III , under focus image). Some of these new chain structures apparently have both ends in c-direction. They are nucleated in clinopyroxene without any special strains.

(c),(d) (d') (d') Electron micrographs of ion-thinned weakly altered clinopyroxene, indicating the narrow and short chains growing longer and thicker, and gathering. Coherency between newly formed triple and double chains , and clinopyroxenes is held (sp.766-I , under focus images)

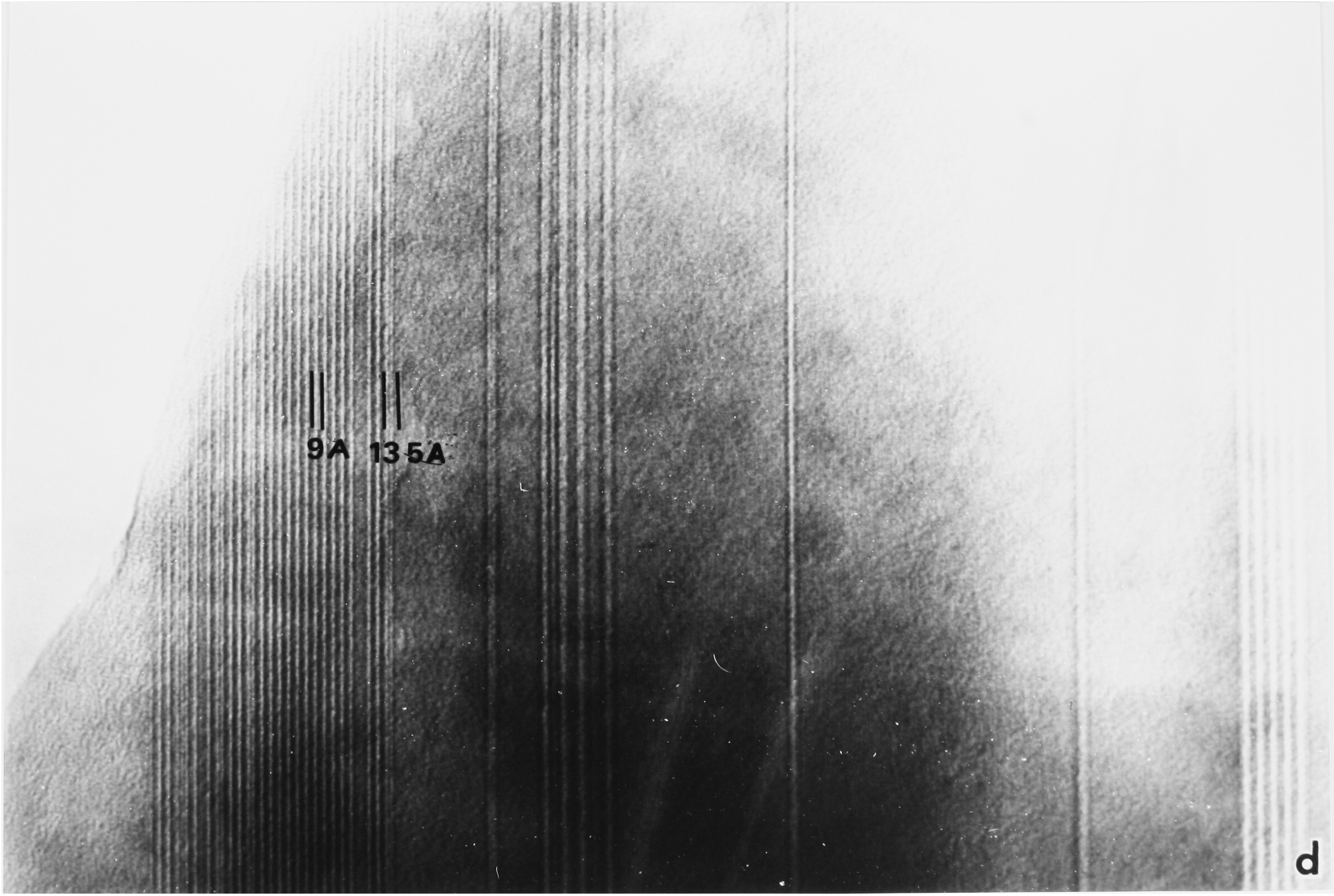
(e) Electron micrograph showing further growth of double and triple chains. They are separated from clinopyroxene and have become fibrous aggregates (sp.766-I, under focus image).

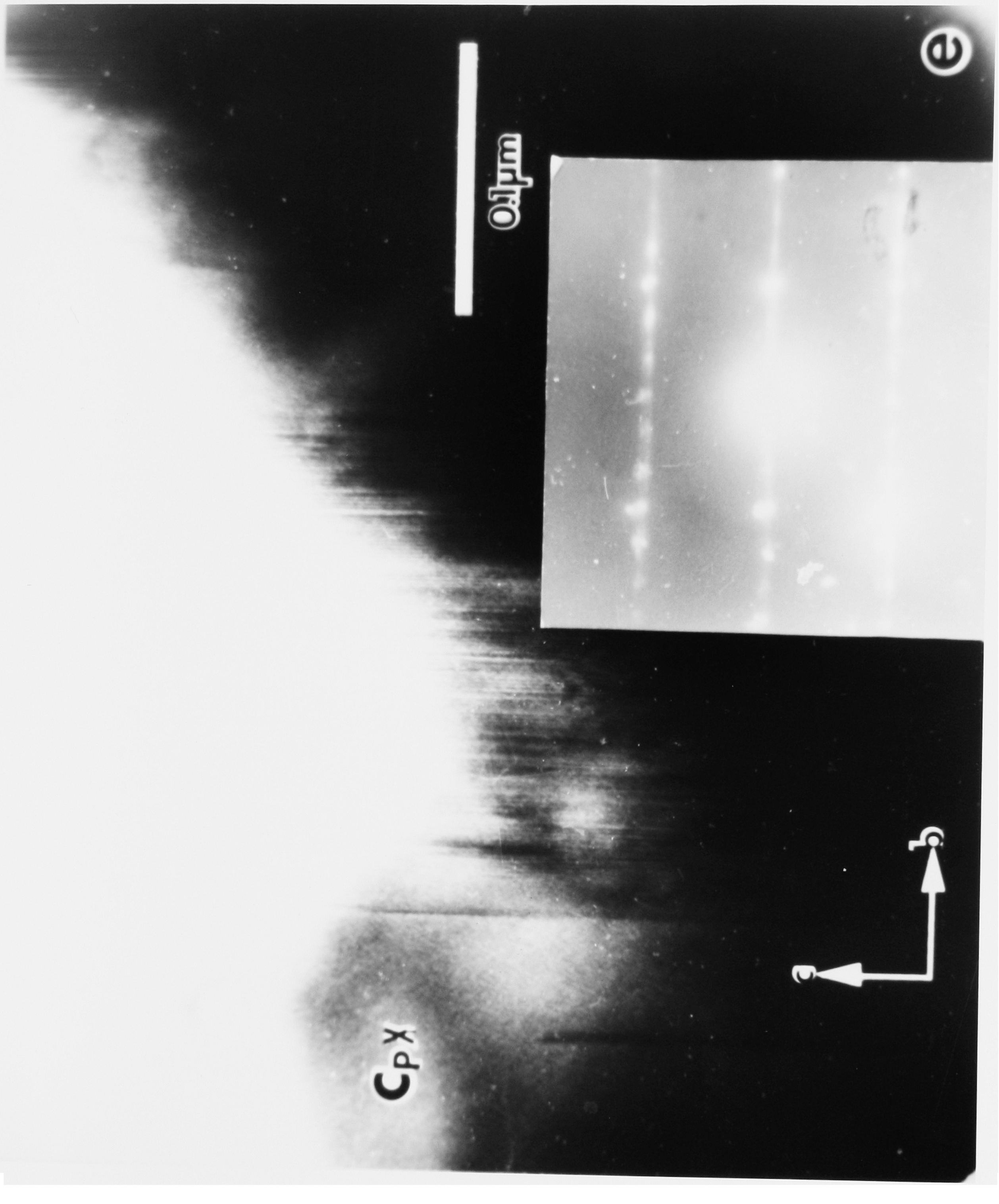
(f) (f') Irregular reaction front of alteration of clinopyroxene (sp.766-I, under focus image)

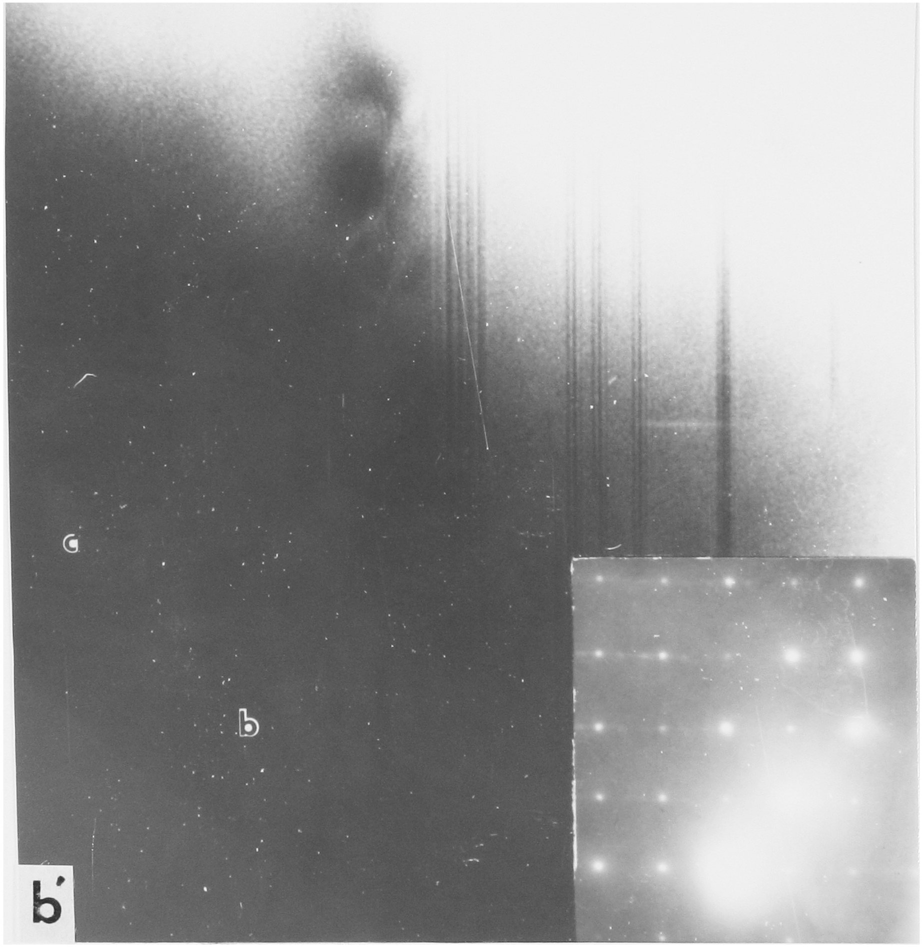

4,5 Å
single chain
structure
triple chain
c
b
a

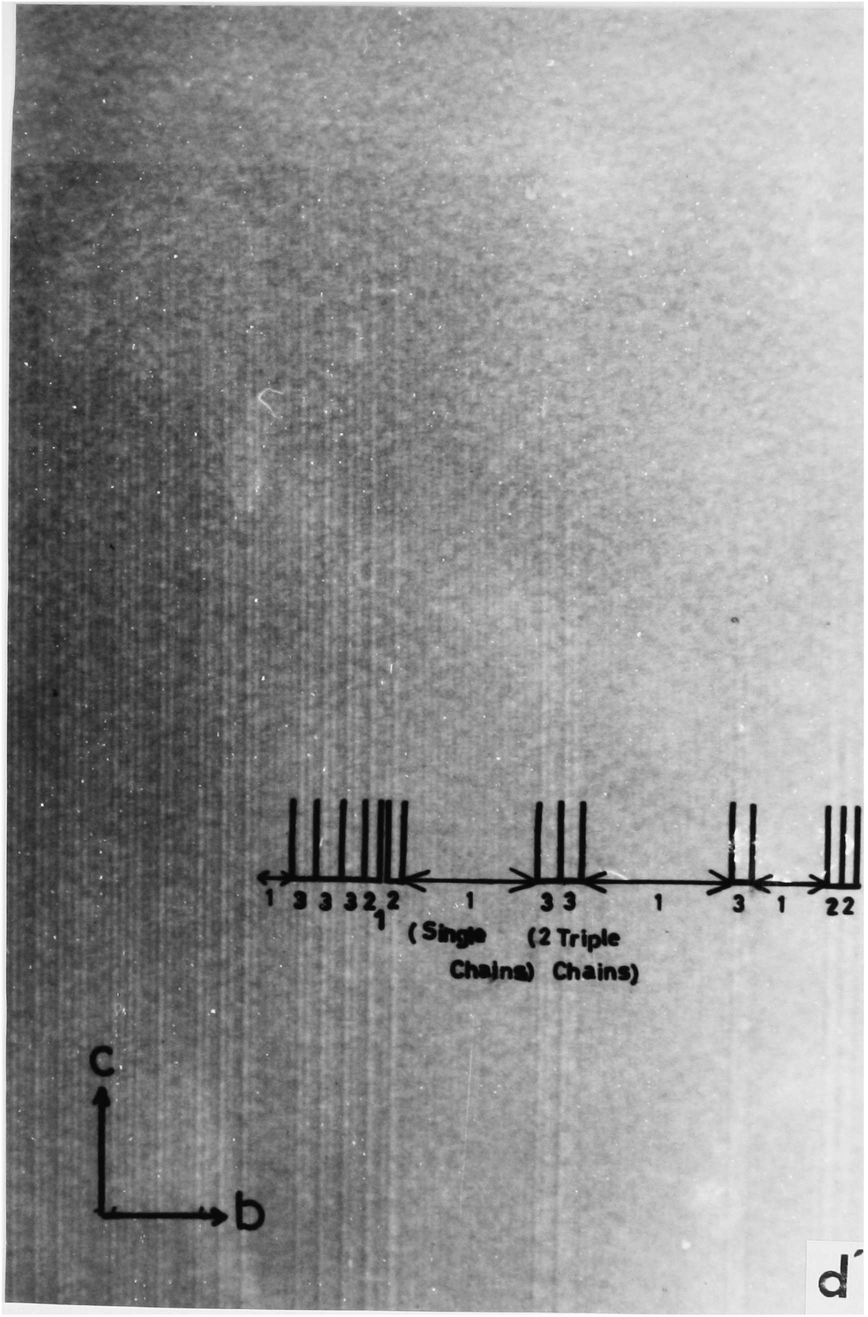

c
b
Cpx
2double chains
4double chains
2double chains
b

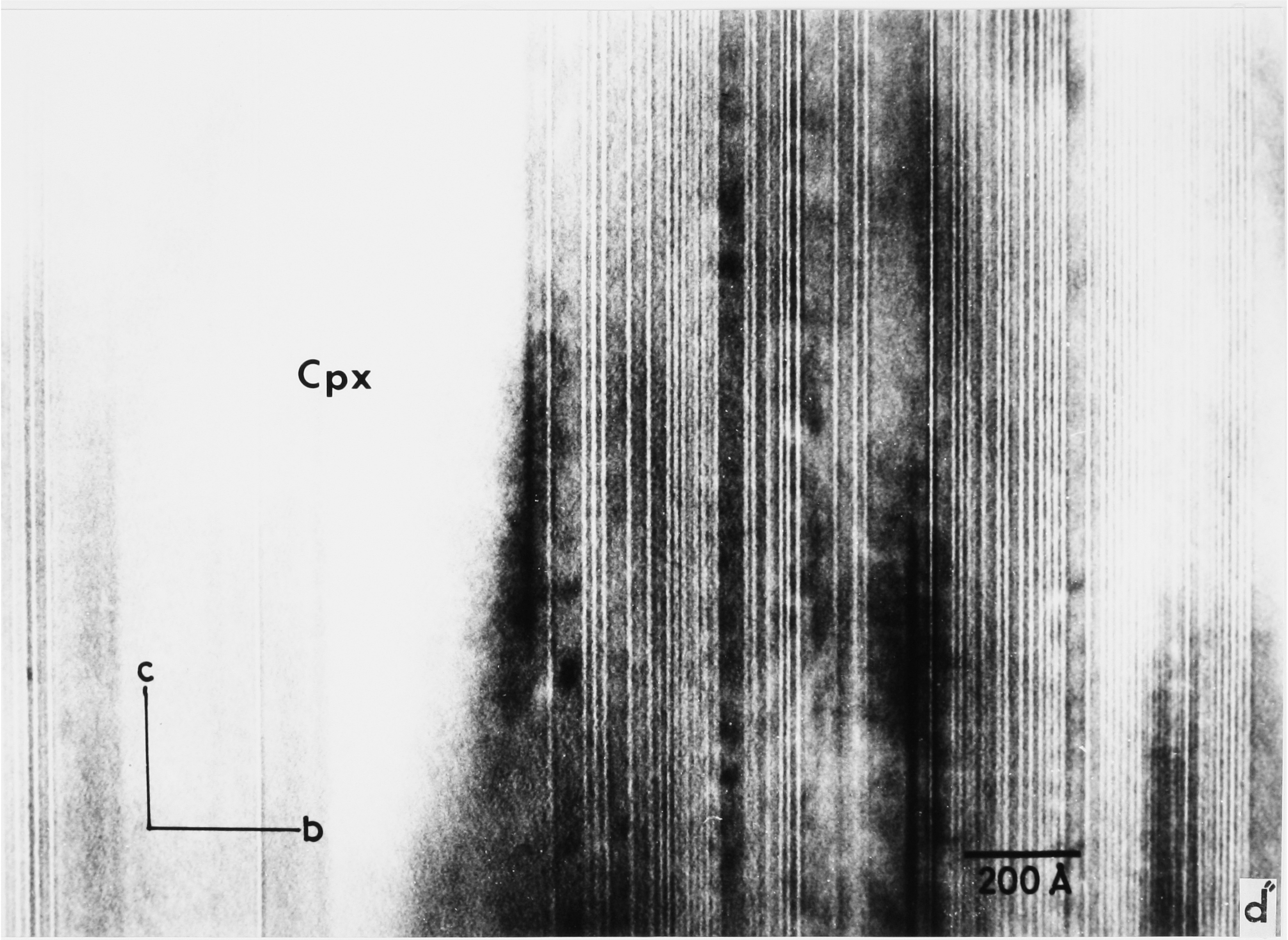

c

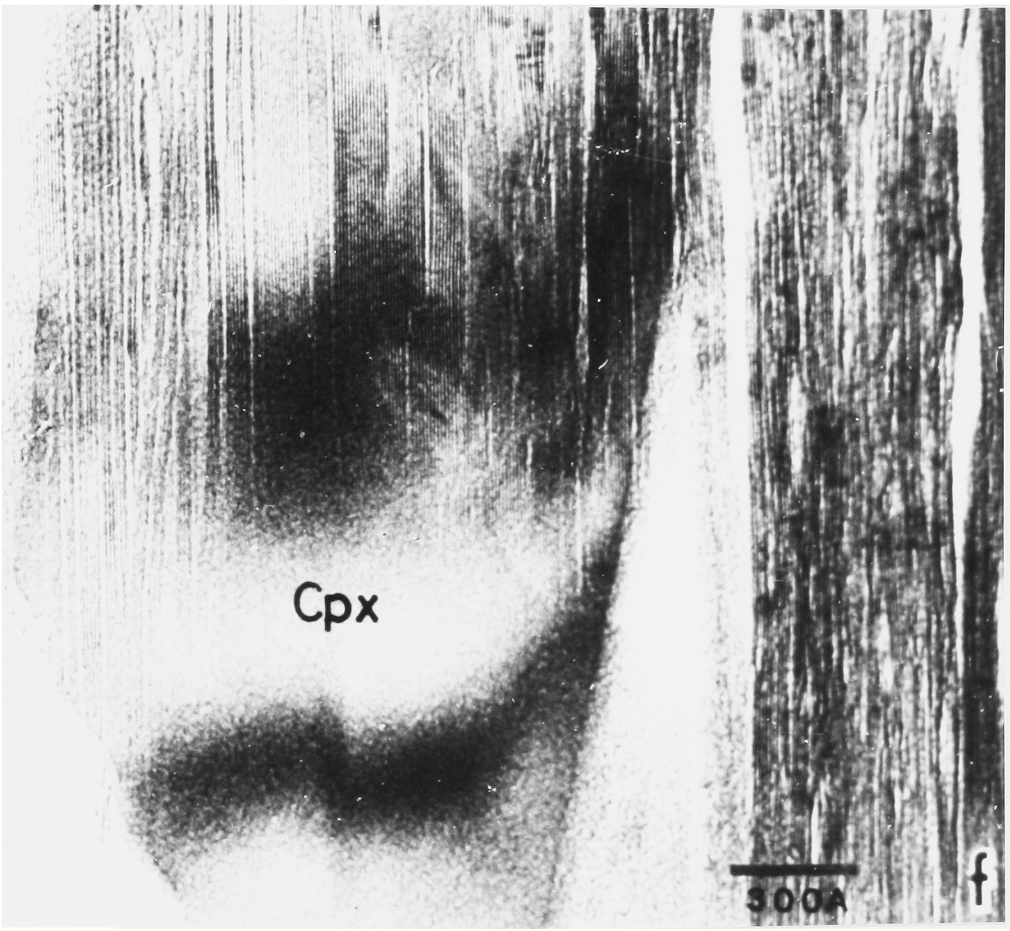

9A
13 5A
d


e
0.1µm
Cpx
a
b


b′
a
b


d′
1 3 3 3 2 1 2
1
3 3
1
3
1
2 2
(Single Chains)
(2 Triple Chains)
c
b


Cpx
c
b
200 Å
d″


Cpx
300A
f

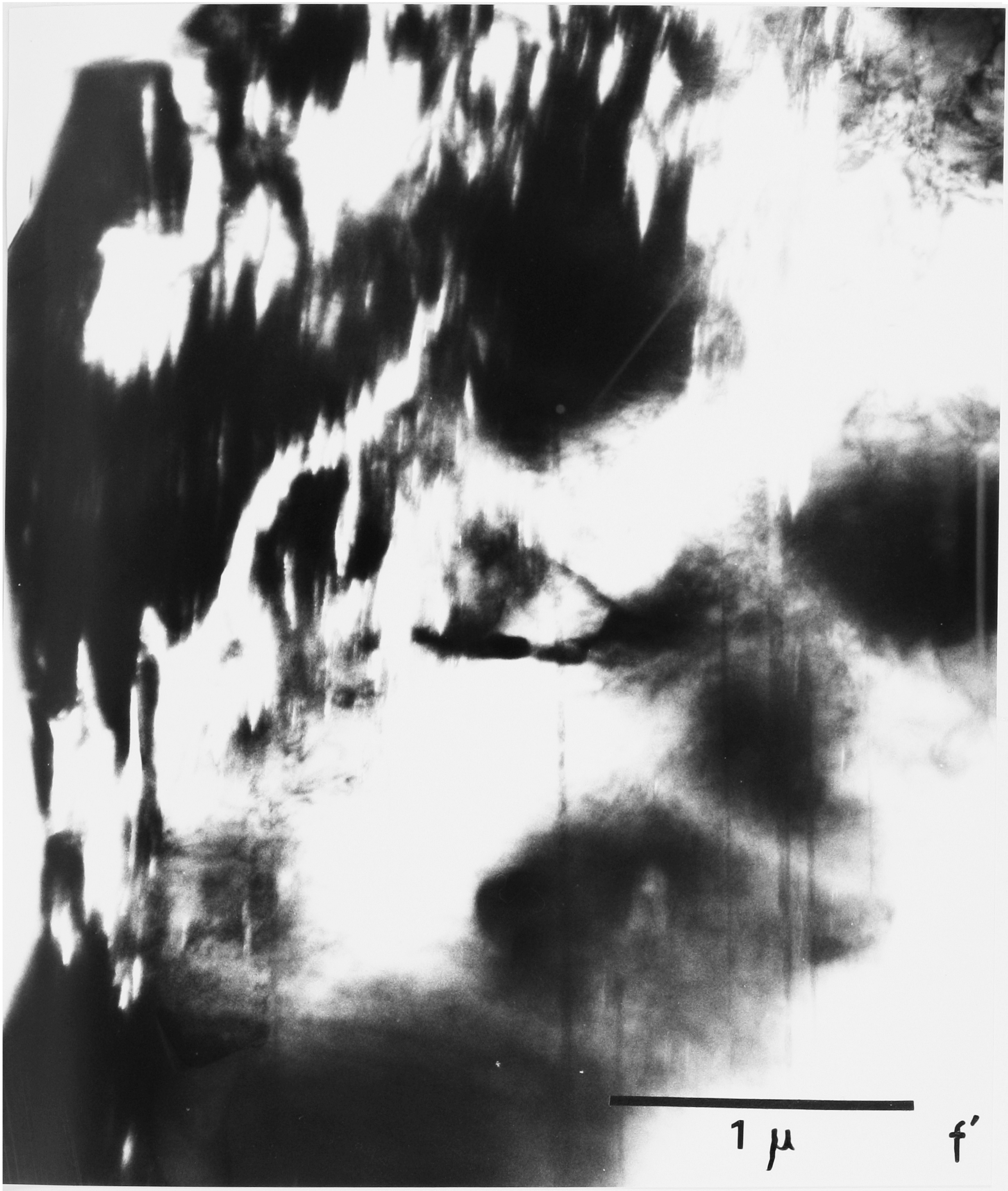
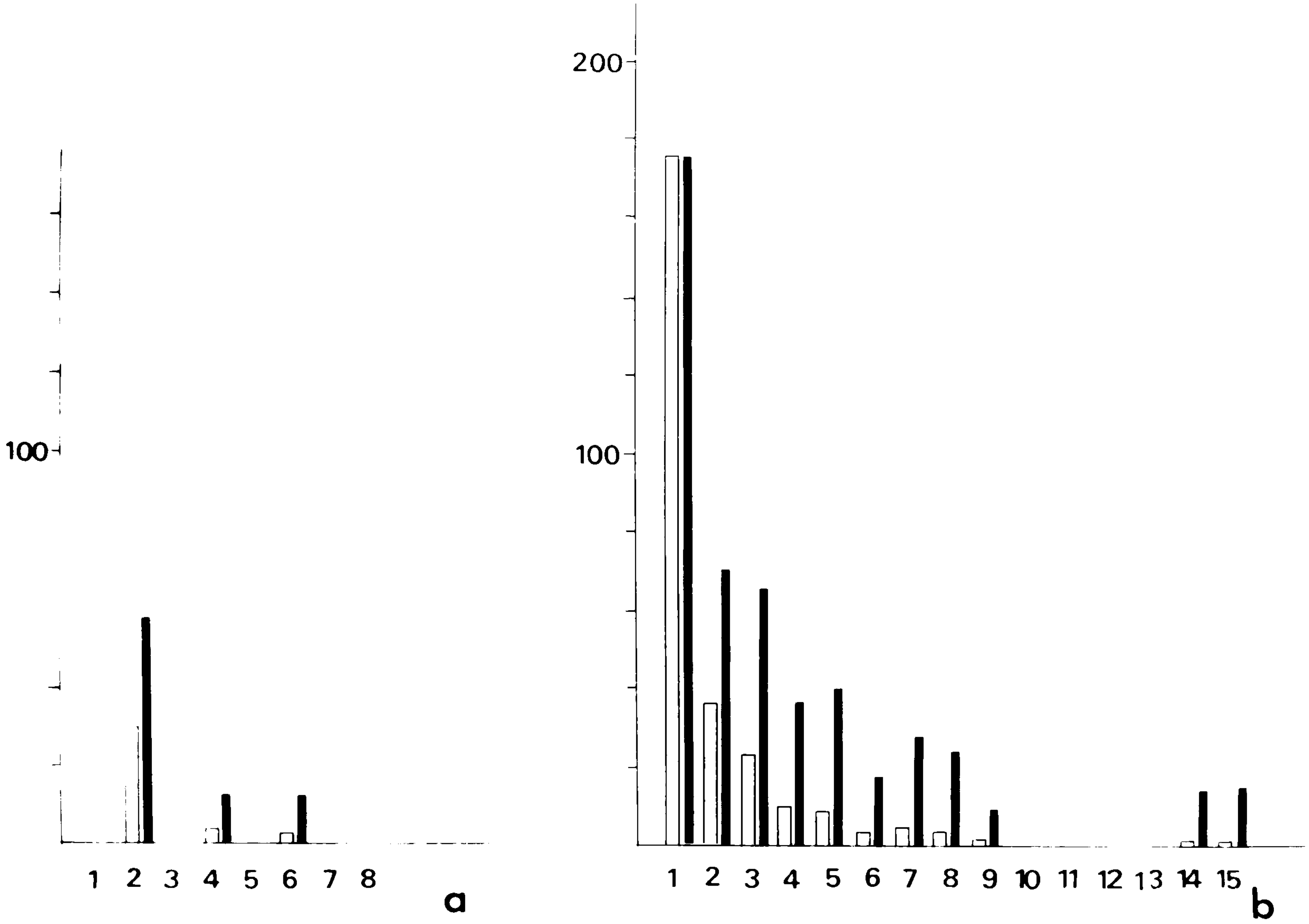
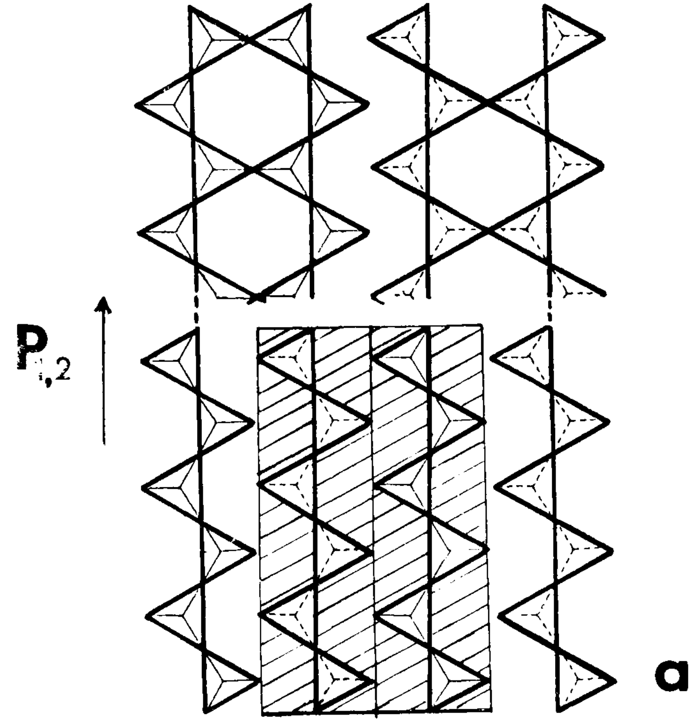

1 µ
f′

Fig.14 Histogram of the number of double (a) and triple (b) chains which are nucleated in the clinopyroxene host and sandwiched between single chain structures. The representation of white and black column is the same as in Fig. 10. Triple chains are more frequently nucleated than double chains.



100
1
2
3
4
5
6
7
8
a
200
100
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
b

Fig.15 Topotactic structural relations in polymerization. (a) Polymerization from 4 single chains (pyroxene slab units) to 2 double chains. (b) Polymerization from 3 single chains (pyroxene slab units) to 1 triple chain. The necessity to maintain topotactic relation with host structure controls the minimum structural unit (not minimum repeating unit) of newly formed biopyribole. $P_{u,v}$ represents polymerization from u-fold chain to v-fold chain. Shaded chains (pyroxene slab units) represent those to be shifted.


$P_{1,2}$
a

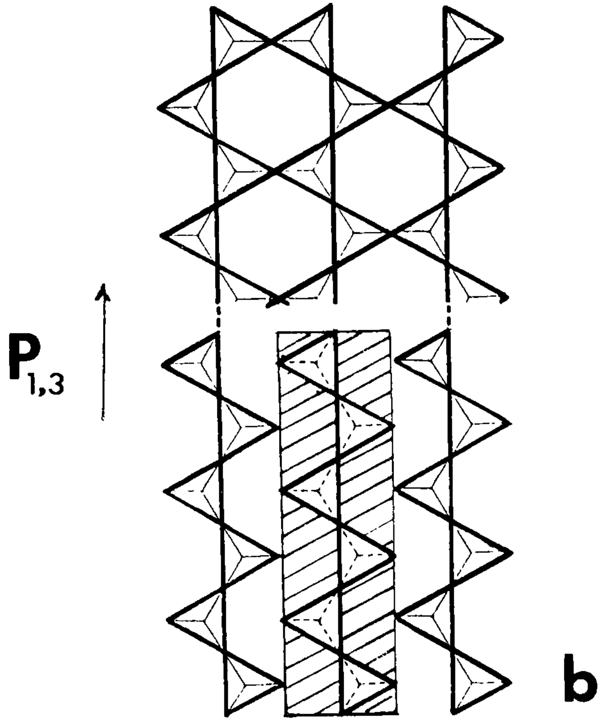

$P_{1,3}$
b

Fig. 16 Schematic diagram of relative quantities of biopyriboles vs. the distance from the ore body. The distance from the ore body may be regarded to be related to the quantities of hydrothermal soluion.

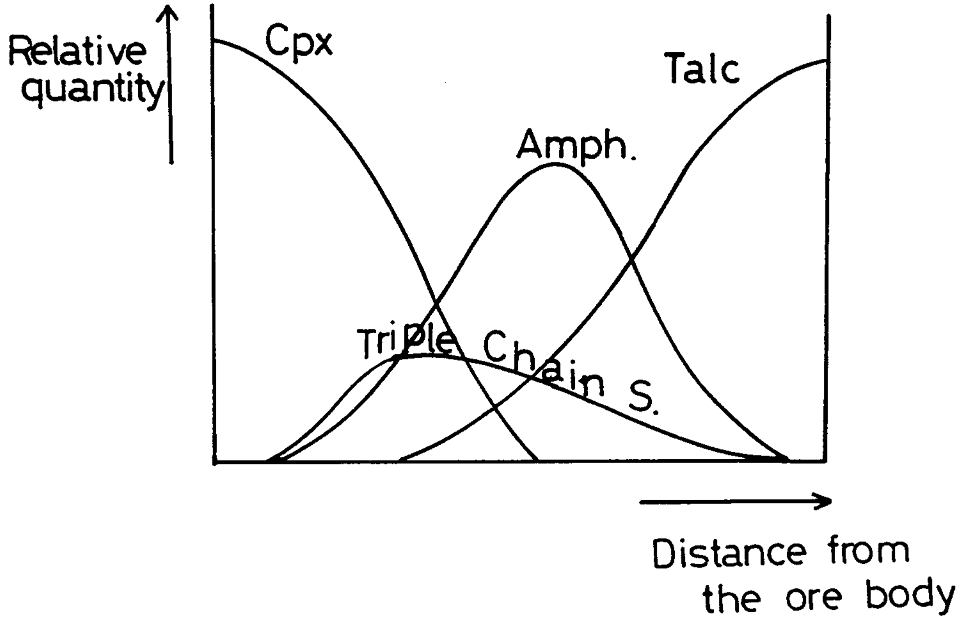

Relative quantity
Cpx
Talc
Amph.
Triple Chain S.
Distance from the ore body

Fig. 17 Proposed scheme for the propagation of metasomatism and the corresponding fine textures of biopyriboles.

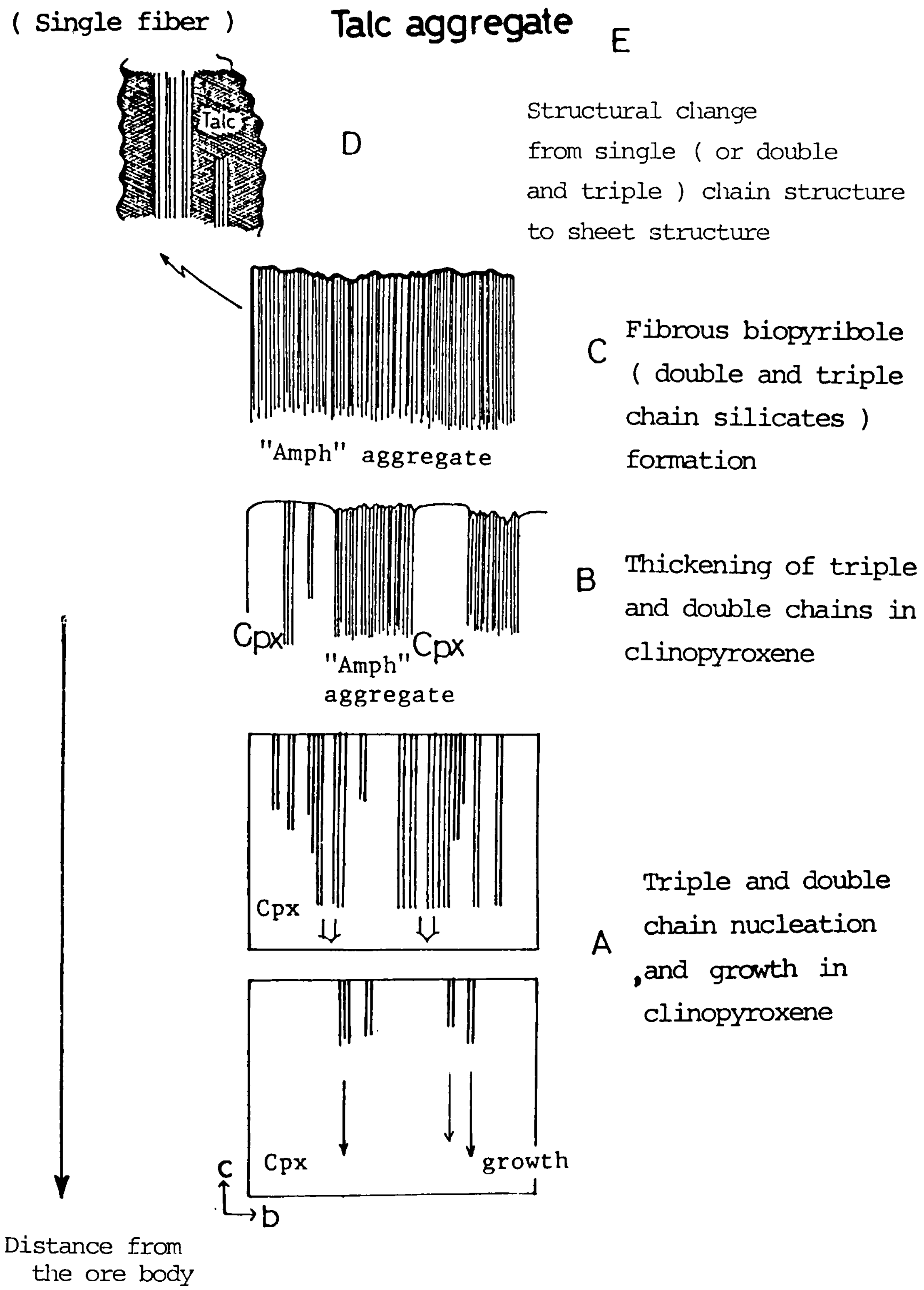

(Single fiber)
Talc aggregate
E
Talc
D
Structural change from single (or double and triple) chain structure to sheet structure
C
Fibrous biopyribole (double and triple chain silicates) formation
"Amph" aggregate
B
Thickening of triple and double chains in clinopyroxene
Cpx
"Amph" aggregate
Cpx
Cpx
A
Triple and double chain nucleation ,and growth in clinopyroxene
Cpx
growth
c
b
Distance from the ore body

Table 1 Typical compositions of biopyriboles formed in metasomatism at the Akatani ore deposit.

Specimen	Unaltered Cpx				"Amphibole"				Talc	
(specimen number)	7712-1	7712-1	766-I	766-II	766-II	768-1	766-II	768-1	768-1	768-V
SiO_2	49.2	50.0	50.5	52.0	55.3	55.5	54.1	56.9	60.0	60.1
Al_2O_3	0.1	-	-	-	-	0.1	-	-	-	-
FeO	17.4	10.2	13.6	14.7	10.7	7.9	11.3	8.6	8.0	8.8
MnO	8.8	17.3	8.5	7.5	6.7	5.4	7.5	4.0	2.7	0.9
MgO	1.9	0.4	5.8	10.6	17.0	18.0	12.7	18.9	22.9	25.2
CaO	22.5	22.2	21.6	15.0	7.9	7.2	12.7	6.2	4.1	0.2
Na_2O	0.2	0.1	0.2	0.1	0.1	0.3	0.1	0.2	-	0.1
Total	100.2%	100.3	100.2	99.9	97.7	94.4	98.4	94.8	97.7	95.4

Table 2 Estimation of the relative quantities of four types of electron diffraction patterns from "amphiboles" The four types are triple chain silicate (13.5Å), double chain silicate (9 Å), double and triple chain silicate (13.5 Å + 9 Å) and disordered structure (streaks) Total number of electron diffraction patterns counted in one specimen is 100 (see text)

Degree of alteration	Type of ED Specimen	13.5 Å (Triple)	9 Å (Double)	13.5Å + 9Å (Tri.+ Doub.)	Streaks (Disorder)
II	7810-8	34	42	8	16
	768-7	32	28	15	25
	766-I	44	35	10	11
III	766-II	4	90	3	3
IV	768-1	1	86	7	6
	23-5	13	62	14	11
V	7810-6	7	49	24	20
	7810-9	4	76	7	13
VI	7810-2	12	49	23	16
	768-V	7	73	14	6

Table 3

Host pyribole (u) Newly formed biopyribole (v)	Single chain (1) $(\frac{n}{m})$, n×m ,p $(=\frac{m}{v})$, $(\frac{m}{u})$	Double chain (2) $\frac{n}{m}$ n×m ,p ,$\frac{m}{u}$	Triple chain (3) $\frac{n}{m}$, n×m ,p , $\frac{m}{u}$	Quadruple chain (4) $\frac{n}{m}$, n×m , p , $\frac{m}{u}$	Quintuple chain (5) $\frac{n}{m}$, n×m , p , $\frac{m}{u}$	------- - -
Double chain (2)	$\frac{2}{4}$, 8 ,2 , 4					
Triple chain (3)	$\frac{1}{3}$, 3 , 1 , 3	$\frac{6}{12}$ 72 , 4 , 6				
Single + Double chain (1+2)	$\frac{3}{6}$, 18 , 2 6					
Quadruple chain (4)	$\frac{4}{8}$, 32 , 2 , 8	$\frac{4}{8}$, 32 , 2 , 4	$\frac{12}{24}$, 288 , 6 ,8			
Quintuple chain (5)	$\frac{2}{5}$, 10 , 1 5	$\frac{10}{20}$,200 , 4 , 10	$\frac{7}{15}$, 105 , 3 , 5	$\frac{20}{40}$ 800 , 8 , 10		
Double + Triple chain (2+3)	$\frac{5}{10}$, 50 , 2 , 10	$\frac{10}{20}$,200 4 10				

Sheet	$\frac{m}{2m}$ $2m^2$, 1 , 2 m	$\frac{2m}{4m}$, $8m^2$, 1 2m	$\frac{3m}{6m}$,$18m^2$, 1 , 2m	$\frac{4m}{8m}$, $32m^2$, 1, 2m	$\frac{5m}{10m}$, $50m^2$ 1 , 2m	

Appendix

Computer simulation of electron microscopic images

In order to interprete precisely the electron microscopic images , the computer simulation was carried out. Specimen thickness is estimated to be very thin from the electron micrograph of Al-shadowed specimens. It may be several hundred Angstromes at most, and less than 100 Å in specially thin portion. As a first approximation, images were calculated based on a kinematical theory which was previously applied to Cu-phtalocyanine (Uyeda et al. 1974; Ishizuka et al. 1975). The program written by Ishizuka et al. (1975) was used.

The following four models which are structurally possible and are inclined to be mutually confused in the lattice images were selected ;

A-1) Mg- triple chain silicate (:clinojimthompsonite) :[Veblen and Burnham (1978b)]

A-2) Ca-triple chain silicate : Ca in place of Mg in M(5) site in clinojimthompsonite

lattice parameters : $b=27.24$ Å
$c= 5.316$ Å ($c \sin\beta = 5.012$ Å)

B-1) Model structure of Ca-mixed chain silicate of single and double chain : derived from tremolite structure [Papike et al. (1969)]

B-2) Model structure of Mg-mixed chain silicate of single and double chain : Mg in place of Ca in the corresponding site, in above Ca-mixed chain silicate

lattice parameters : $b= 27.08$ Å
$c= 5.3$ Å ($c \sin\beta = 5.102$ Å)

Parameters used in the calculation of the two and one dimensional lattice images of pyriboles are as follows ;

Accelerating voltage	100 kV (λ=0.037 Å)
Spherical abberation constant	1.4 mm
Depth of focus	200 Å
Objective aperture diameter	60 in diameter which corresponds to $\sin\theta/\lambda = 0.2$
Envelope function used	: based on Wade R.H. and J. Frank (1977) a) defocus spread = 200 Å b) opening angle = 4.8×10^{-4} rad.

The through focus series of the simulated lattice images are shown in the appendix Figs. 1 and 2 .

Through focus series of one dimensional lattice images taken on the fibrous specimen from the Akatani ore deposit is shown in the appendix Fig. 3 .

References

Veblen DR, Burnham CW (1978b) New biopyriboles from Chester Vermont : II. The crystal chemistry of jimthompsonite, clinojimthompsonite,chesterite, and the amphibole-mica reaction. Amer Min , 63, 1000-1009.

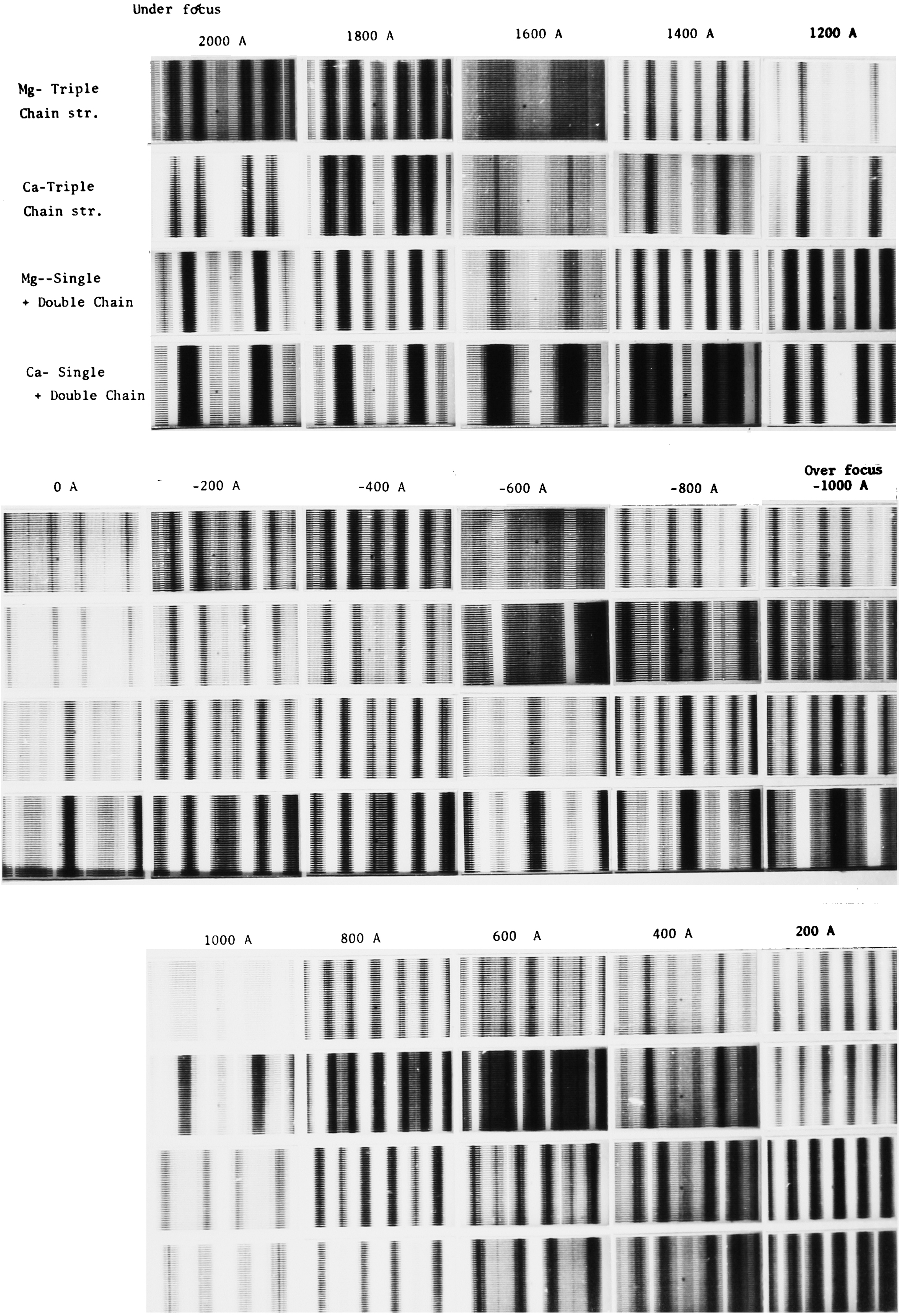
Ishizuka K, Uyeda N (1975) Effect of through-focussing on the bright and dark field molecular images in high resolution electron microscopy. Bull Inst Chem Res Kyoto Univ 53(2) : 200-215

Papike JJ, Ross M, Clark JR (1969) Crystal-chemical characterization of clino-amphiboles based on five new structure refinements. Min Soc Amer Spec pap, 2 : 117-136

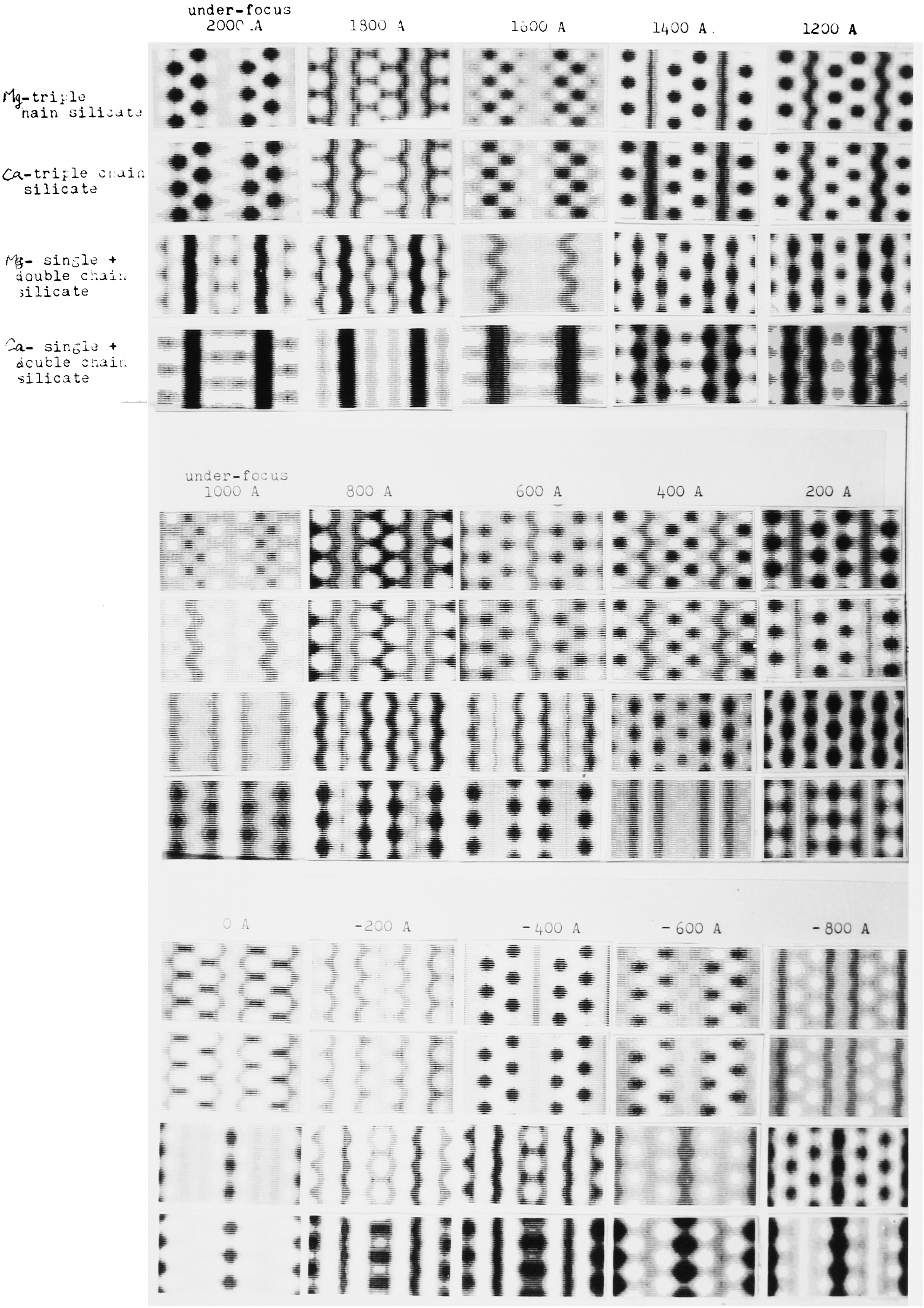
Uyeda N , Ishizuka K (1974) Effect of spherical aberration and accelarating voltage on atomic resolution in molecular images. J Electron Microscopy 23 : 79-88

Wade RH , Frank J (1977) Electron Microscopic transfer function for partialy coherent axial illumination and chromatic defocus spread. Optic, 47, 81-92.

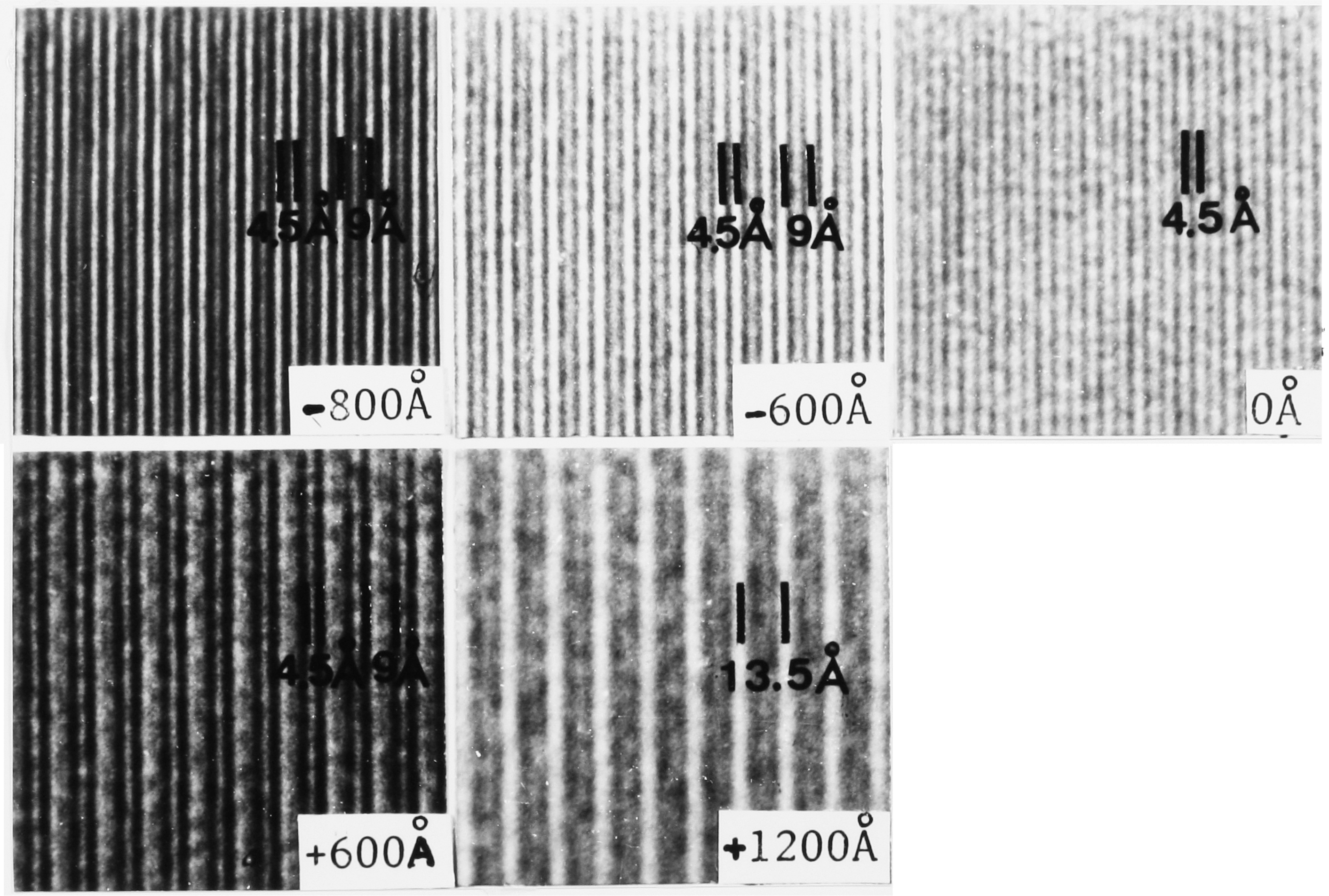
Appendix Fig. 1 Through focus series of simulated one dimensional lattice images of triple chain silicates.


Under focus
2000 A
1800 A
1600 A
1400 A
1200 A
Mg- Triple Chain str.
Ca-Triple Chain str.
Mg--Single + Double Chain
Ca- Single + Double Chain
0 A
-200 A
-400 A
-600 A
-800 A
Over focus -1000 A
1000 A
800 A
600 A
400 A
200 A

Appendix Fig. 2 Through focus series of simulated two dimensional lattice images of triple chain silicates.


under-focus 2000 A
1800 A
1600 A
1400 A
1200 A
Mg-triple nain silicate
Ca-triple chain silicate
Mg- single + double chain silicate
Ca- single + double chain silicate
under-focus 1000 A
800 A
600 A
400 A
200 A
0 A
-200 A
-400 A
-600 A
-800 A

Appendix Fig. 3 Through focus series of one dimensional lattice images taken on the specimen from Akatani ore deposit.


4.5Å 9Å
-800Å
4.5Å 9Å
-600Å
4.5Å
0Å
4.5Å 9Å
+600Å
13.5Å
+1200Å