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Citation	Journal of science of the Hiroshima University. Series C, Earth and planetary sciences , 11 (1) : 41 - 53
Issue Date	1998-03-30
DOI	
Self DOI	10.15027/53161
URL	https://ir.lib.hiroshima-u.ac.jp/00053161
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Jour. Sci. Hiroshima Univ., Ser. C, Vol. 11, No. 1, 41-53 (1998)

Surface Microtopographs of Clay Minerals

By

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with, 8 plates

(Received, February 27, 1998)

Abstract: By means of transmission electron microscopy (TEM) and the gold-decoration technique, the surface microtopography of clay minerals collected from various mode of occurrence were investigated. The clay minerals investigated exclusively exhibit many kinds of patterns on their crystal surfaces, such as growth, cleavage, aggregation patterns and so on.

Contents

I. Introduction

The microtopography of the surfaces of layer silicates such as kaolinite, mica, pyrophyllite, chlorite and rectorite has been studied by many investigators for the purpose of elucidating the growth mechanisms of the crystals (Baronnet, 1972; 1980; Sunagawa et al., 1975; Tomura et al., 1979; Kitagawa, 1994; 1997). The growth step-patterns, a few nanometers in height, were revealed by gold-decoration technique employed with TEM, which was developed by Bassett (1958) and Gritsaenko & Samotoyin (1966). These examinations revealed spiral and parallel step patterns on the (001) crystal surfaces of various layer silicates, and their growth mechanisms and growth conditions were inferred (Sunagawa, et al., 1975; Tomura et al., 1979).

Using the Au-decoration technique, Sunagawa et al. (1975) and Tomura et al., (1979) demonstrated that 1) in hydrothermal solution, coalescence of crystals is common, 2) in a metasomatic environment, rocks are dissolved to form a low (weakly) supersaturated aqueous solution, in which crystals grow by the spiral-growth mechanism, and 3) in regional metamorphic environment, Ostwald ripening plays an essential role in the growth of layer silicates, and the spiral growth is absent. These results demonstrate that the observations on the surface microtopographs can provide important information as to the genesis of layer silicates. Thus we have applied the decoration technique to the (001) surfaces of clay mineral crystals collected from various localities, such as hydrothermal clay deposits, veins, faults and druses. In this paper, the results of observation are described.

II. Specimens and method

1. Characteristics of the specimens

Clay minerals investigated in the present study come from more than 30 localities in southwest Japan. Specimens were collected from hydrothermal clay deposits, veins, replacement products of vein form, faults, alteration zone of ore deposits and druses in rocks.

Morphology of the observed crystals under TEM are full of variety such as hexagonal, lath shaped and irregular plates.

2. Method of observation

For the Au-decoration technique, the specimen was dispersed in distilled water and collected on a thin cover-glass. After drying, the cover-glass with specimen was heated in a vacuum of 10-4 torr at ~400-500° C for 2-3 hours. Heating the specimen gives a clearer surface without impurity and a higher mobility of Au, enabling selective nucleation of Au along the growth steps (Bassett, 1958; Tomura et al., 1979). Gold was flash-evaporated from a tungsten coil heater. After a carbon coating was applied, the specimen was removed and immersed in a solution of HF for 3-4 days, in order to completely dissolve the specimen. After soaking the remainder in distilled water, the thin carbon films with gold grains were collected on copper mesh grids and were then ready for observation with a TEM.

III. Observation results

Spiral patterns are observed on a few crystals investigated, though some kinds of patterns are found on all the crystals, as seen in Plate I. The separation between the neighboring steps is variable. On a few crystals circular or polygonal steps which corresponds to growth patterns are observed. The other patterns correspond to features of the cleavage.

The electron micrographs on illite crystals in Plates II and III show that gold grains preferentially nucleated along the steps of spirals, thus exhibiting the step patterns of crystal surfaces. These step patterns represent not cleavage but growth steps, and the heights of single steps are assumed to be of unit cell-layer height size (10Å, refer to Sunagawa et al., 1975; Tomura et al., 1979; Sato, 1970). As shown in Plates II and III, a few specimens are characterized by circular and polygonal growth-spirals with varying separation of steps.

Illite crystals of 2M polytype are characterized by the interlacing of polygonal spiral steps (Plate III) or paired steps with circular or malformed spirals (Plate II). 1M crystals exhibit polygonal (Plate V) or malformed circular spirals with a single step (Plate VI). However 1Md illite shows complexed step pattern as exhibited in Plate VII.

Crystals of clay minerals such as illite and rectrite exhibit hexagonal, lath-shaped or irregular morphologies. The hexagonal or lath shaped crystals are characterized by polygonal spirals (Plates III, IV and V), whereas irregular crystals show circular or malformed circular growth-spirals (Plates II, VI and VII).

The aggregation patterns are often observed on the surfaces as indicated in Plate VIII.

IV. Discussion

Morphologies of growth spirals are classified into polygonal and circular or malformed circular, with various ranges of step separation.

According to Sunagawa et al. (1975) and Tomura et al. (1979), illite that is assumed to have been directly precipitated from hydrothermal solutions in open fractures such as druses (higher porosity) are characterized by the development of polygonal spirals. In contrast, illite crystals formed in massive metasomatic rocks (lower porosity) by hydrothermal activity exhibit a circular or malformed circular outline. Their step separations vary from locality to locality. It is noted that circular or malformed circular spirals have, in general, a narrower separation of steps compared with polygonal spirals. It is natural to assume higher the temperaturse and/or supersaturation, growth spirals becoms more circular.

Almost all hexagonal and lath shaped crystals are characterized by polygonal spirals. In general, irregular plates are characterized by circular or malformed circular patterns.

Crystals belonging to 2M polytype always exhibit either interlaced patterns (Plates III and IV) or paired steps (Plate IV-B), whereas those belonging to 1M and 1Md do not show such step patterns (Plate V). As has demonstrated on clay minerals by Sunagawa, et al.(1975) and Sunagawa (1984), when a structure contains zigzag stacking, interlaced pattern or paired steps appear by a spiral-growth process. Interlacing and pairing will appear, depending upon the symmetries of the elemental sheet and their mode and number of stacking, due to the difference of advancing rates in the same direction among the successive elemental sheets.

According to Sunagawa (1982) and Sunagawa and Bennema (1982), whether a spiral takes a polygonal or a circular form is determined by the roughness of the spiral step, and thus related to the α-factor and the chemical potential difference, $\Delta\mu$. Here, α is expressed, in general form, as $\alpha = \xi[\Phi sf - 1/2(\Phi ss + \Phi ff)]/\kappa T$, where Φss is the bond energy in solid, Φsf the interaction energy between solid and fluid components, Φff the interaction energy between the neighboring fluid-fluid components. ξ is orientational factor and T is (absolute) temperature, and κ is Boltzmann's constant. As the α-value becomes

smaller, the step becomes rougher, as it contains a higher density of kinks. The step, then, advances isotropically, i.e., with the same rate in all directions in that plane, resulting in a circular spiral. On the other hand, if the α-value becomes larger, the step becomes smoother, containing a lower density of kinks, and the rate of advance is now strongly controlled by the crystallographic anisotropy, resulting in a polygonal spiral. Therefore, polygonal spirals are expected under lower temperature at constant supersaturation or at lower supersaturation (chemical potential difference) under isothermal conditions than for circular spirals. This may be valid if crystals grow from the same phase (e.g., hydrothermal solution) and if the impurity effect is neglected. According to the same authors, the step separation (λo) of a spiral is related to the radius of the two dimensional critical nucleus $\gamma *$, which is defined by the edge free energy per elemental sheet γ, the chemical potential difference $\Delta\mu$ and the molar volume Ω:
$\lambda o = 19\gamma * = 19\gamma\ \Omega / \Delta\mu$. Since γ is assumed to be equal when crystals grow from similar phase, if T is assumed constant, and if the effect of impurities is neglected, we may expect a narrower separation of steps for crystals grown from higher supersaturation.

The circular or malformed circular spiral patterns have a narrower separation of steps than polygonal spiral patterns.

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EXPLANATION OF PLATES

Plate I. Gold grains are preferentially nucleated on the crystal surfaces.
A, B and C: Hydrothermal illite, D: Rectrite

Plate II. Circular spiral growth patterns with growth center.
A, B, C and D: Hydrothermal illit

Plate III. Polygonal spiral patterns with interlacing on crystal surface .
A, B, C and D: Hydrothermal illite

Plate IV. Interlacing and paired patterns are observed on 2M crystal surface on which the spiral growth is not recognized.
A, B, C and D: Hydrothermal illite

Plate V. Single polygonal growth steps are observed on 1M crystal surfaces.
A, B and C: Hydrothermal illite, D: Dickite

Plate VI. Single circular growth steps on 1M crystal surfaces.
A and B: Hydrothermal illite, C and D: crystals in kaolin deposits (kaolinite ?).

Plate VII. Complex patterns developed on 1Md crystal surfaces.
A, B, C and D: Hydrothermal illite

Plate VIII. TEM image indicating aggregation crystals. Gold grains are preferentially nucleated along crystals edges.
A, B. C and D: Hydrothermal illite

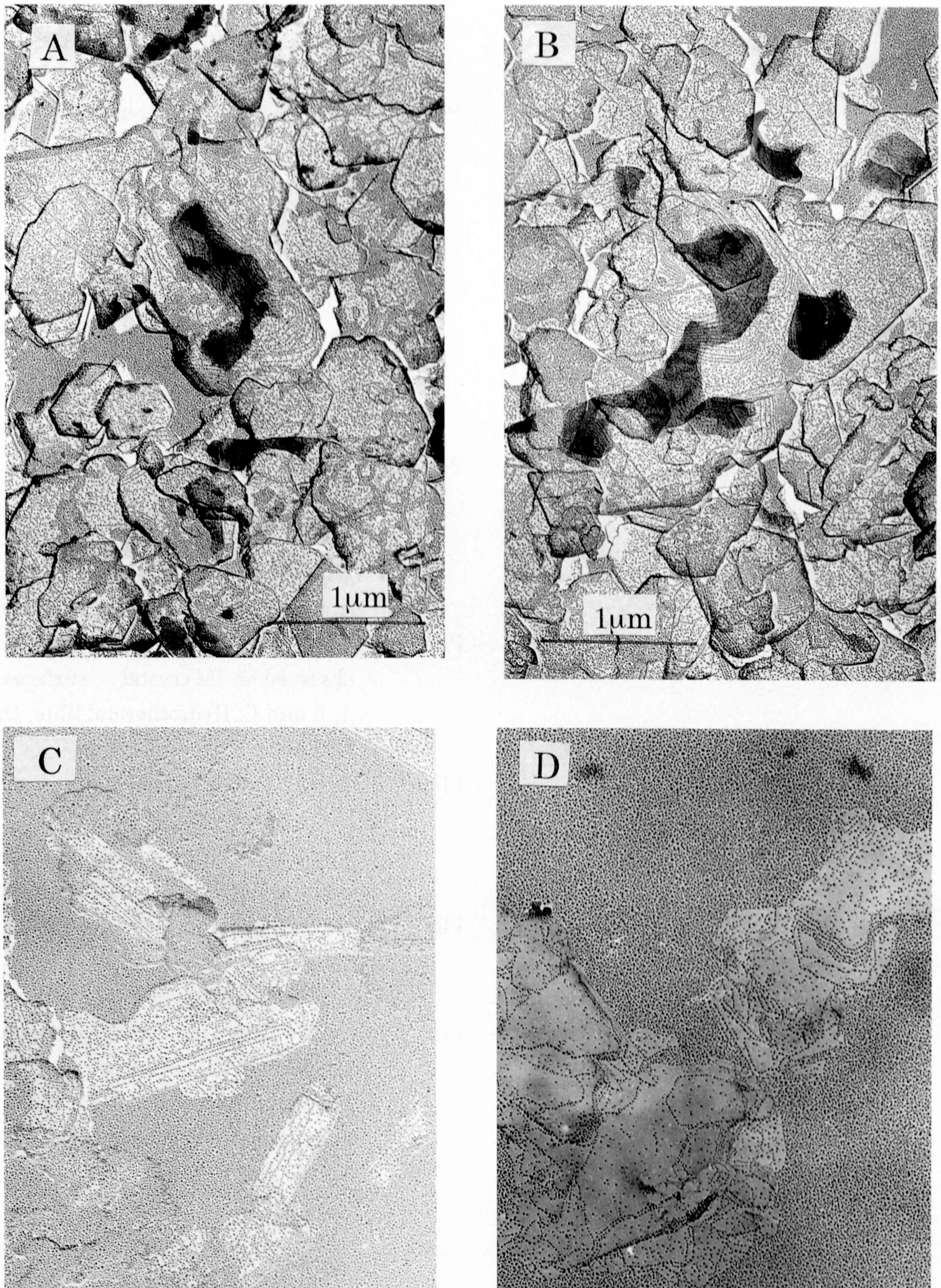
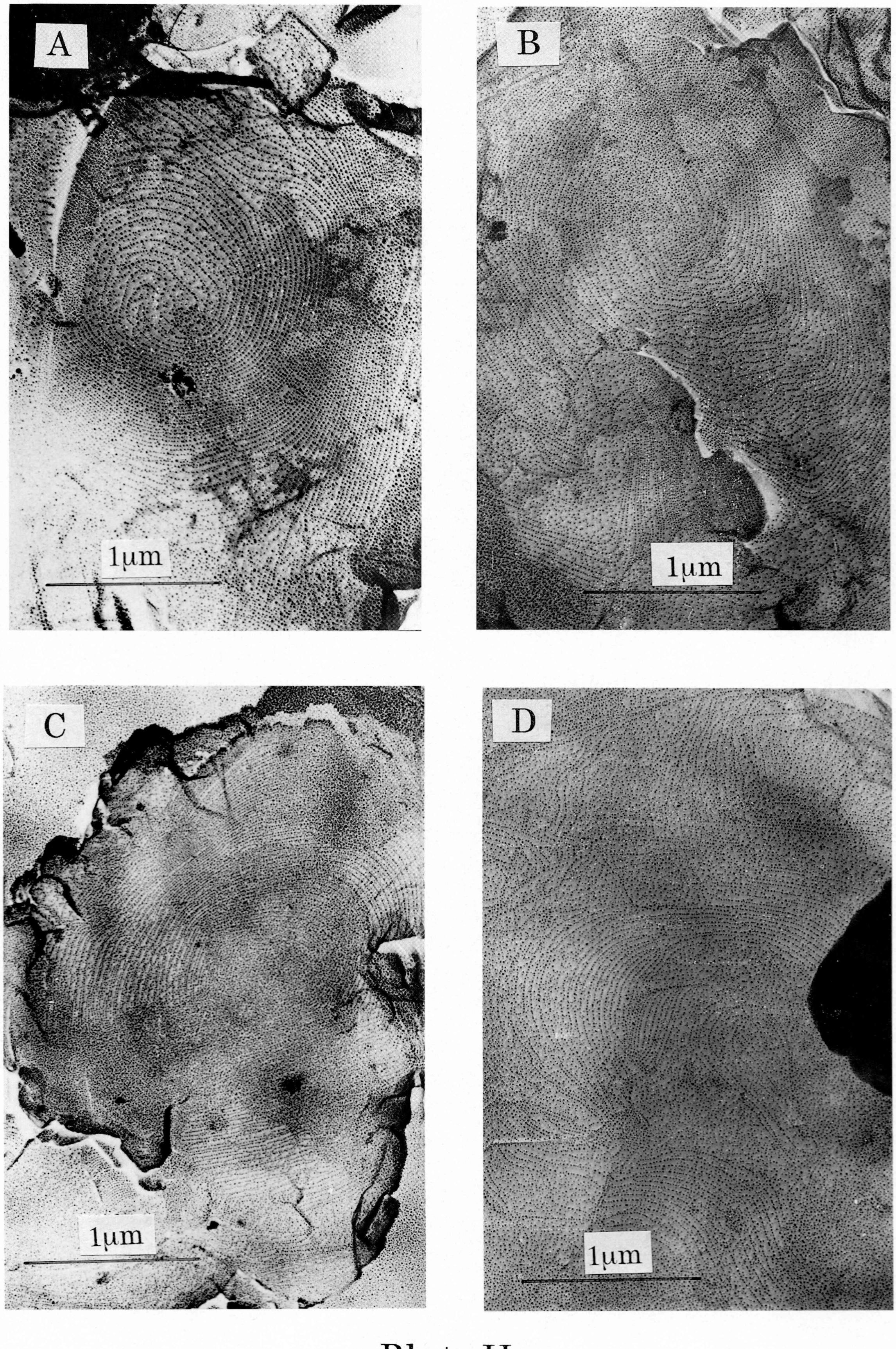


Plate I



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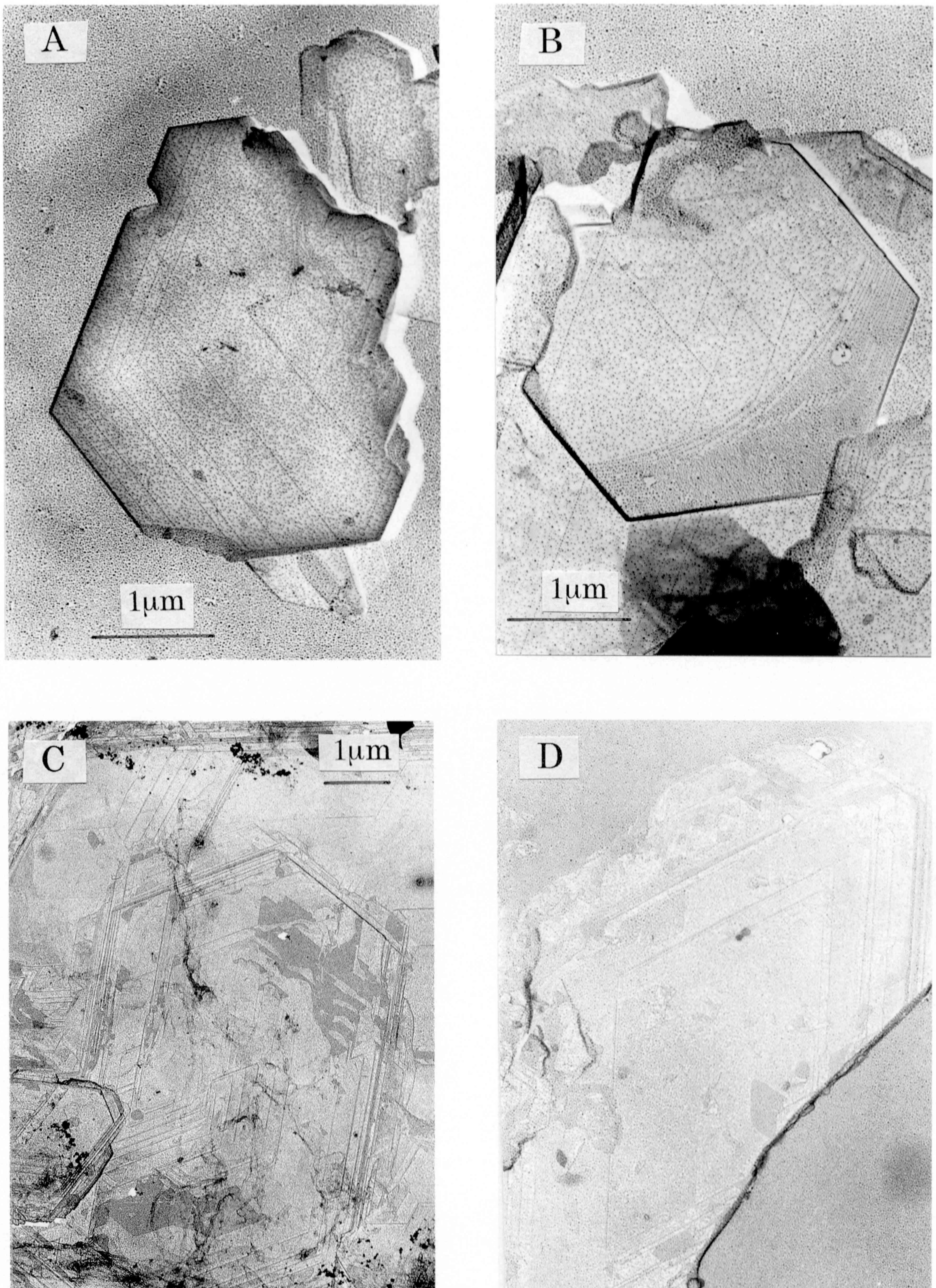

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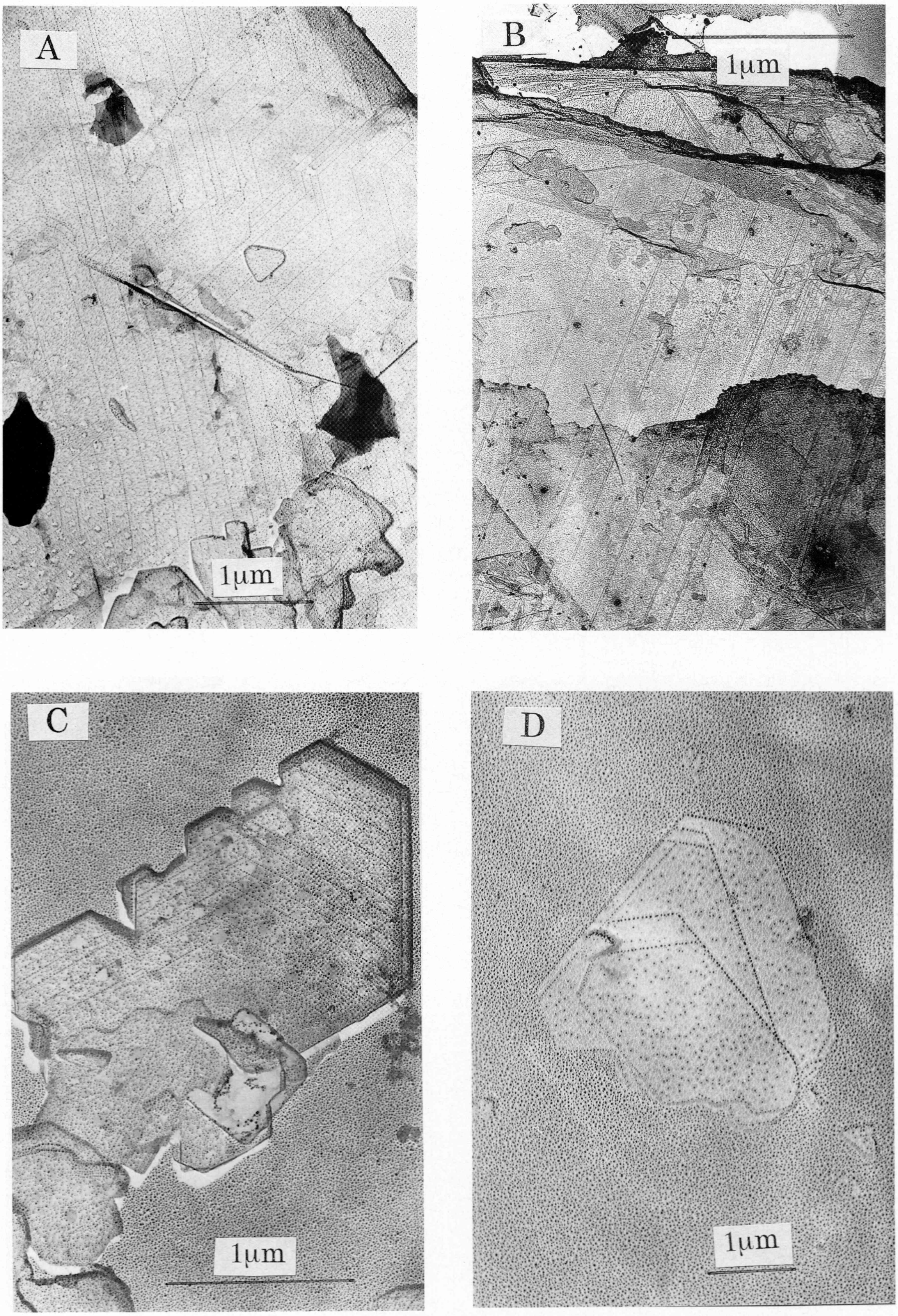

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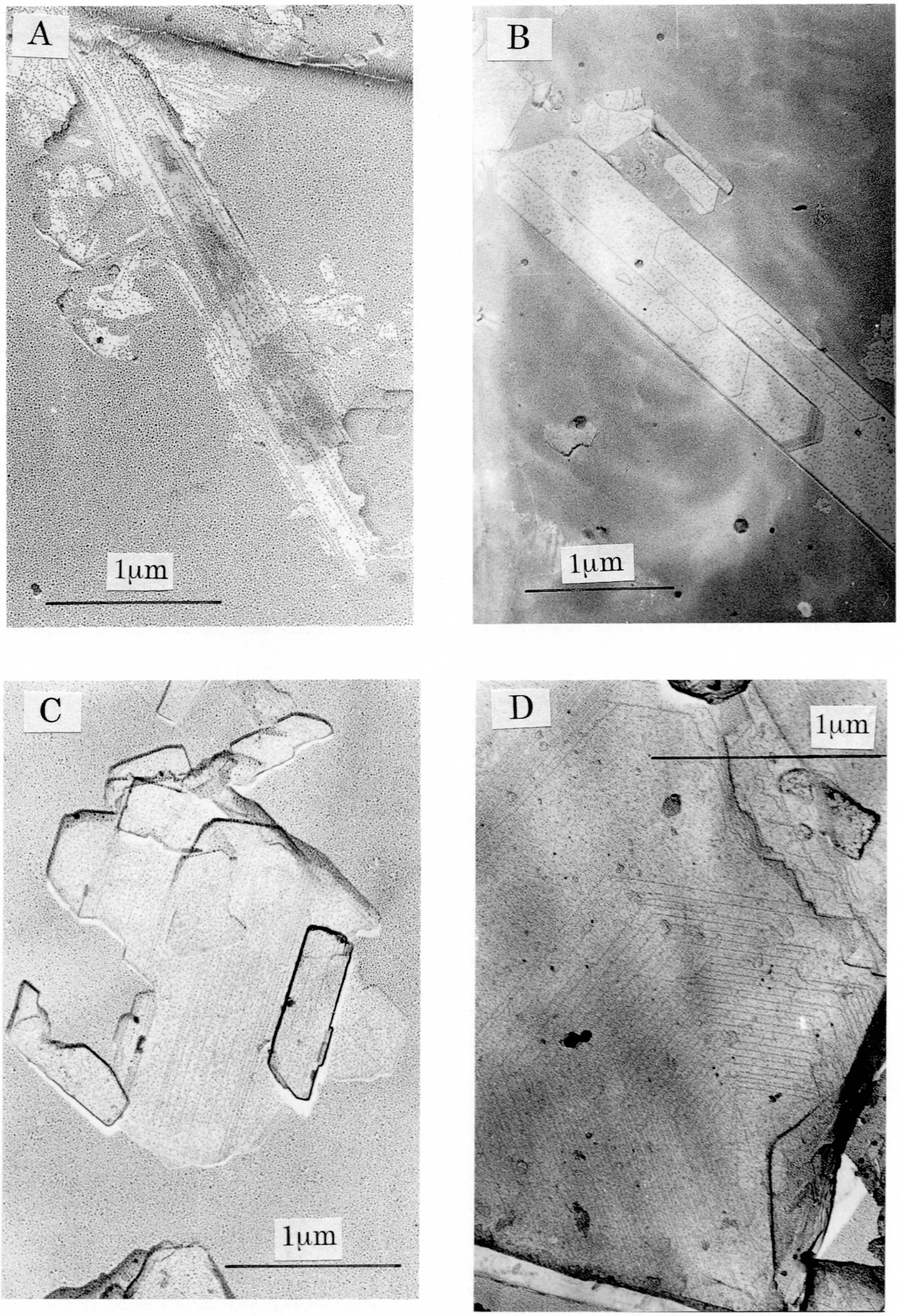

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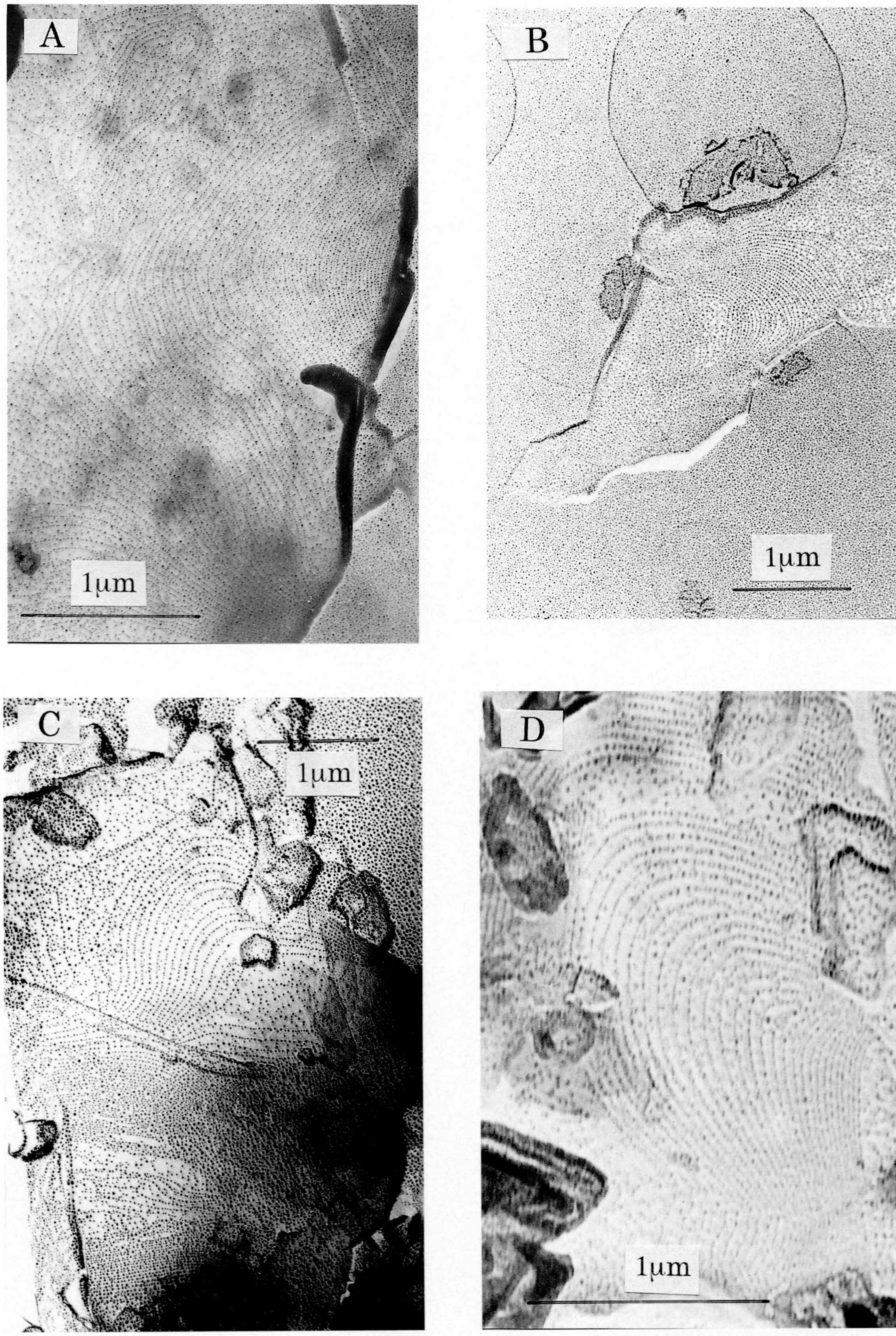

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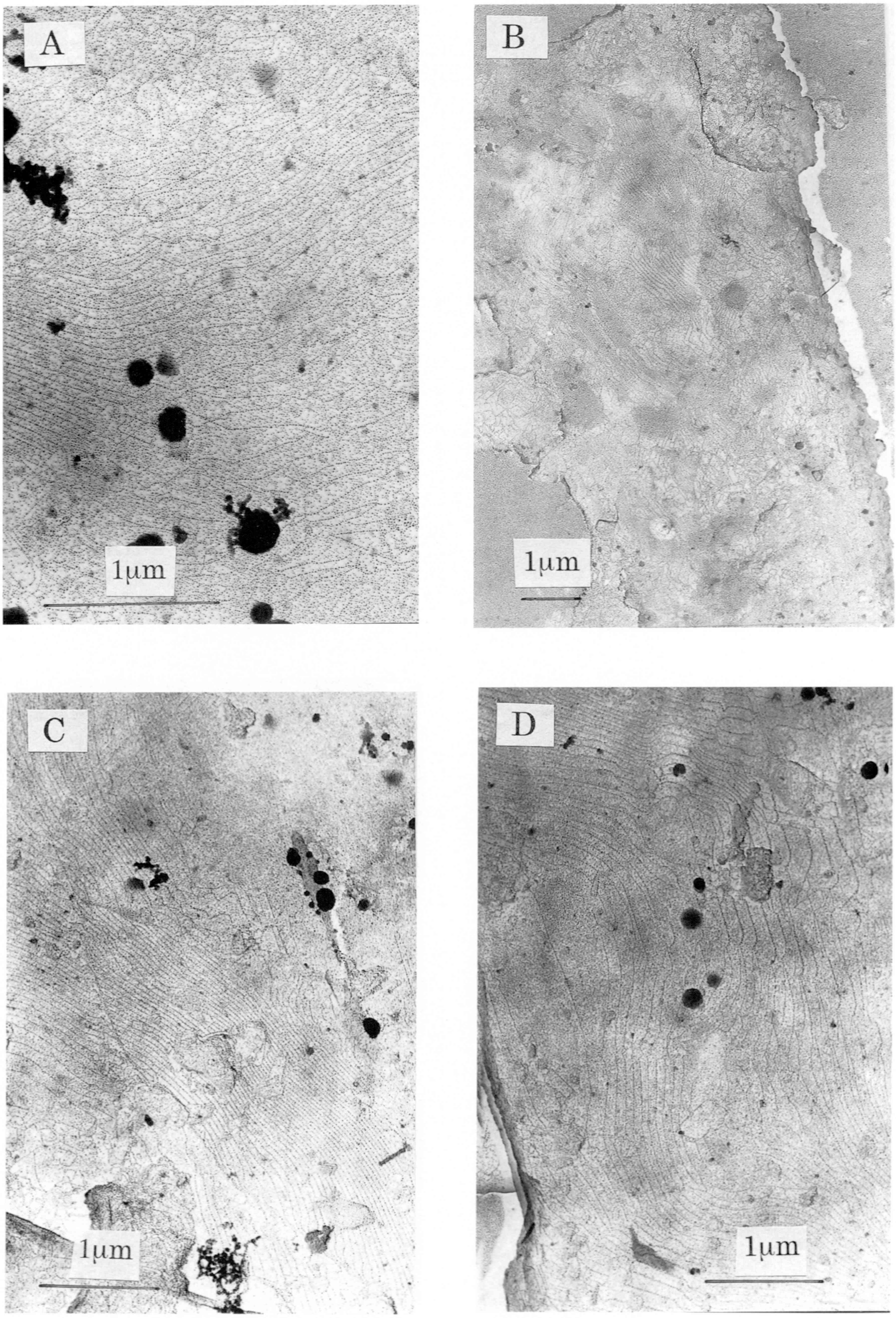

Plate VII

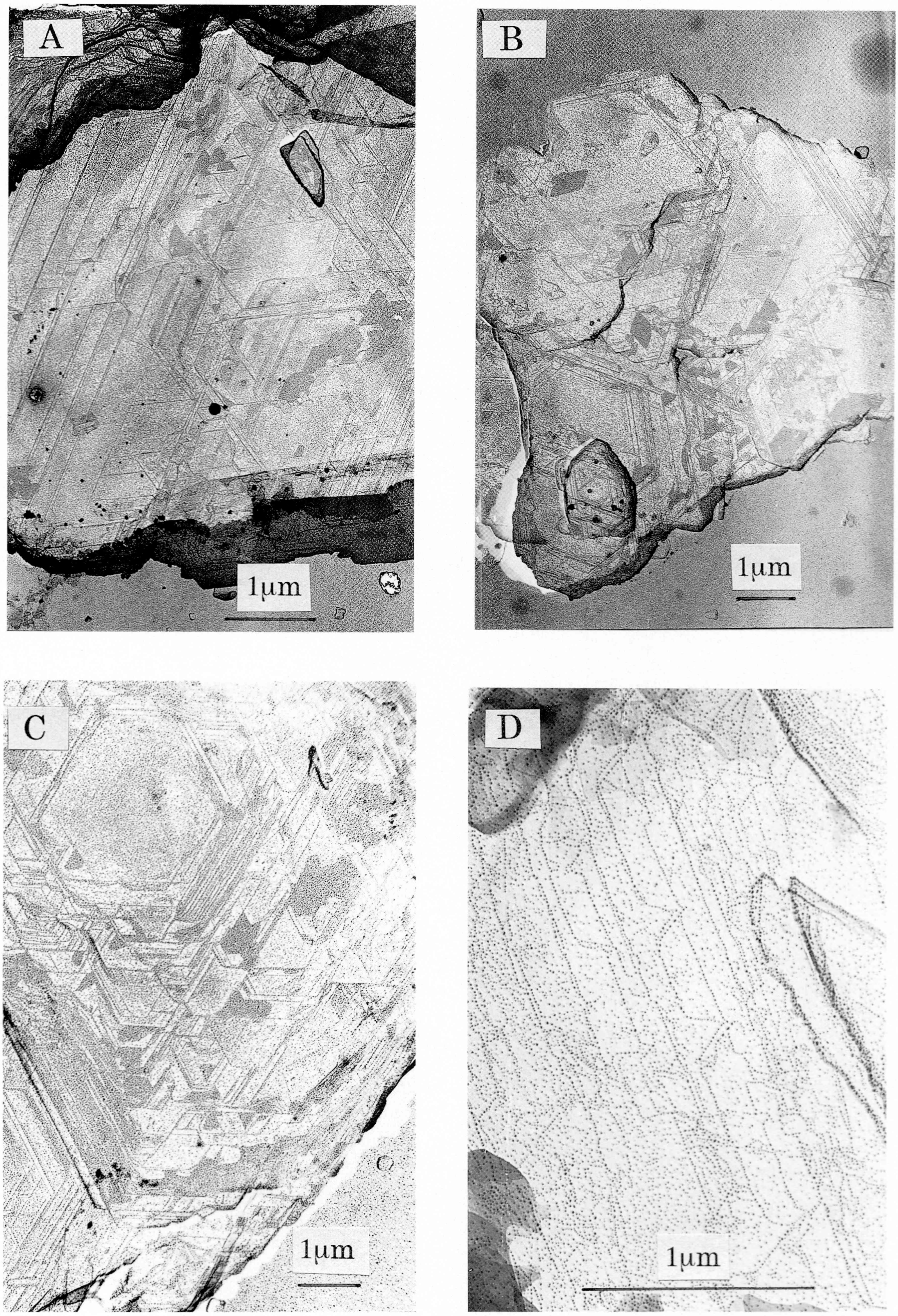

Plate VIII