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Surface Microtopography of Pyrophyllite Crystals from Gussi Deposit, Korea

전남 구시광산에서 산출하는 엽납석 결정의 표면 미세형태

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ABSTRACT : The surface microtopography of pyrophyllite collected from the Gussi deposit, Korea was observed by mean of transmission electron microscopy (TEM) with the gold decoration technique. As results, closed step patterns with malformed circular islands were characteristically observed on the (001) surface of pyrophyllite, contrasting with spiral step patterns common in illite and kaolinite. Gussi pyrophyllite was likely crystallized from hydrothermal solution of higher temperature and/or higher supersaturation than those of other clay minerals. Comparing with microtopographies of pyrophyllite from the Shokozan and the Uku deposits, southwest Japan, growth mechanism of Gussi pyrophyllite is almost equivalent to those from the Shokozan and the Uku deposits.

Key words : pyrophyllite, surface microtopography, transmission electron microscopy (TEM), crystal growth, clay mineral

요약 : 한국 전남지역 구시광상에서 채취한 엽납석 시료에 대해 금 부착방법으로 투과전자현미경 (TEM)을 사용하여 결정표면의 미세 형태를 관찰하였다. 그 결과, 일라이트 및 고령석과 같은 점토광물에 일반적인 나선형 계단형태와 달리, 구시광상 엽납석의 (001)표면에는 다소 기형적인 원형의 섬 모양을 가진 폐쇄된 계단형태가 특징적으로 잘 관찰되었다. 이러한 관찰결과로 보아, 구시광상 엽납석은 다른 점토광물에 비하여 상대적으로 높은 온도와 혹은 더 과포화된 열수용액에서 성장한 것으로 사료된다. 구시광상 엽납석의 미세형태는 서남 일본에 위치하는 쇼코잔광산과 우쿠광산의 엽납석과 매우 유사하므로, 엽납석의 결정성장 매카니즘도 이들과 거의 동일할 것으로 보인다.

주요어 : 엽납석, 표면 미세형태, 투과전자현미경, 결정성장, 점토광물

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Introduction

The row materials composed mainly of pyrophyllite, which were formed by the hydrothermal alteration of volcanic rocks, are generally called "Roseki" as special name in Japan. Although numerous pyrophyllite deposits occur in all over the world, they are highly concentrated in the East Asia and Urals (Zaykov *et al.*, 1988). For Example, in East Asia a lot of pyrophyllite deposits occurr in eastern part of China, southern part of Korea and southwest Japan. They are ordered from south to north direction. Many researchers report the occurrences and genesis of pyrophyllite deposits distributed in southwest Japan (Fiji *et al.*, 1979; Hida *et al.*, 1996; Ishihara and Imaoka, 1999; Matsumoto, 1979). The formation ages of pyrophyllite deposits in China, Korea, and Japan based on K-Ar radiometric dating of the paragenetic illite range from late Cretaceous (100 Ma) to Tertiary (25 Ma) (Shibata and Fujii, 1971; Kitagawa *et al.*, 1999; Kim and Nagao, 1992).

The environmental condition of crystal growth of pyrophyllite is not enough up to the present. To discuss this problem, the growth patterns (surface microtopography) on pyrophyllite crystal surface from the pyrophyllite deposits in southwest Japan were analysed under TEM by the Au decoration method (Kitagawa, 1992; Jige *et al.*, 2002). According to their observations, two dimensional nucleation growth and spiral growth patterns were found on the surfaces of pyrophyllite crystal. Therefore, it is considered that pyrophyllite crystals were crystallized by the different environmental condition of growth. In this study, the surface microtopography of pyrophyllite crystals collected from the Gussi pyro-

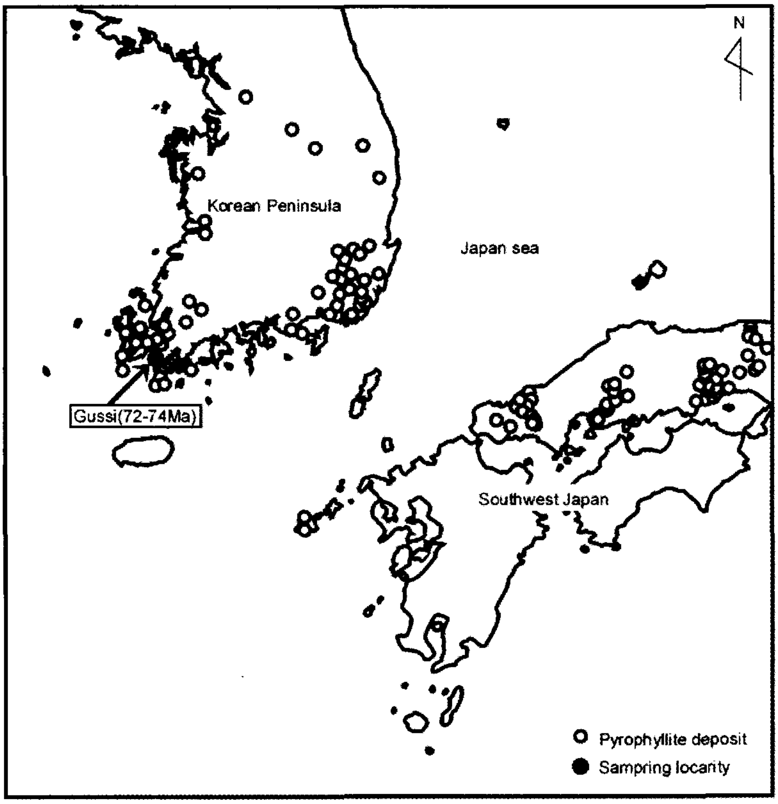

Fig. 1. Map showing distribution of pyrophyllite deposits in the Korean Peninsula and southwest Japan.

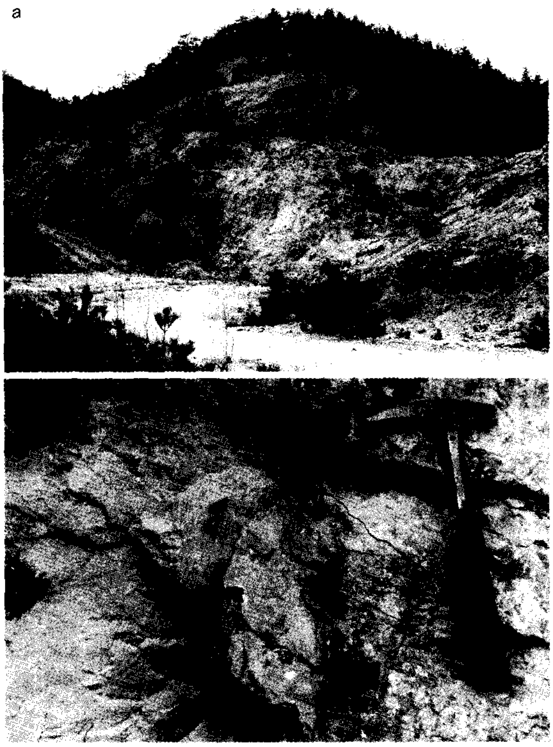

Fig. 2. Gussi deposit, Korean Peninsula. a : hydrothermal alteration zone; b: ore body which consists mainly of pyrophyllite ore.

phyllite deposit, southeast of Korean Peninsula was observed to compare with growth pattern on the crystal surface of pyrophyllite from some massive pyrophyllite deposits in Japan.

Specimens

Pyrophyllite deposits in Korean Peninsula are mainly distributed in Chonnam and Kyongsang regions. According to Koh *et al.* (2000), the geology of Chonnam region is mainly composed of volcanic and granitic rocks of late Cretaceous age. On the other hand, the Kyongsang region is mainly located within Kyongsang Basin comprising volcanic, sedimentary and granitic rocks of Cretaceous and Tertiary age. The geology and geochemistry of the clay deposits in both regions have been characterized by Koh *et al.* (2000).

Pyrophyllite specimens examined in this study were collected from the Gussi pyrophyllite deposit in Chonnam area (Figs. 1 and 2). The K-Ar ages of sericite (illite) in the Gussi pyrophyllite deposit are $72.3\sim74.6$ Ma (Kim and Nagao, 1992). The pyrophyllite massive ores collected in the Gussi pyrophyllite deposit are characteristically green in color.

The samples in this study were analyzed by the powder X-ray diffraction (XRD) to obtain a pure pyrophyllite specimen for observation of surface microtopography (Fig. 3). According to XRD, the specimen is composed mainly of pyrophyllite accompanied with alunite and quartz, as shown in Fig. 3. Morphologies of pyrophyllite crystals were observed by means of both scanning and transmission electron microscopes (SEM and TEM). Irregular plates of pyrophyllite crystals were observed under SEM and TEM (Figs. 4 and 5). Particle sizes of pyrophyllite crystals are generally several micrometers (Fig. 5).

Methods

Gold-decoration technique was applied to observe the microtopographies on crystal surfaces of pyrophyllite (less than a few nanometer in size). This technique has been developed and applied extensively to study the growth mechanisms and conditions of clay minerals (Sunagawa and Koshino, 1975; Sunagawa *et al.*, 1975; Sunagawa, 1977; Tomura *et al.*, 1979). It was also successfully applied to observe surface microtopographies of clay minerals of different origins. The gold-decoration technique applied in this study follows that described by Kitagawa (1997, 1998), as outlined below (Fig. 6).

The specimens were dispersed in distilled water and collected on a thin cover glass. After drying, these mounts was heated at $400\sim500$℃ in a vacuum of 10^{-4} torr for $2\sim3$ hours. Heating the specimens gives clear surfaces lacking impurities and promotes greater gold mobility, enabling selective nucleation of gold along the growth steps (Tomura *et al.*, 1979). Gold was flash-evaporated from a tungsten coil heater, followed by carbon evaporation. Minute grains

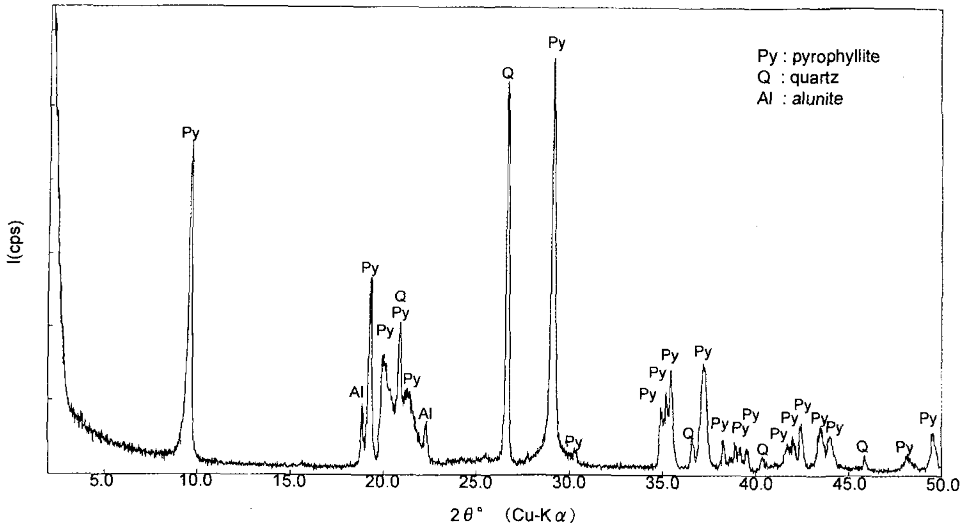

Fig. 3. X-ray powder diffraction pattern of investigated specimen.

Fig. 4. Characteristic scanning electron microphotograph of pyrophyllite particles.

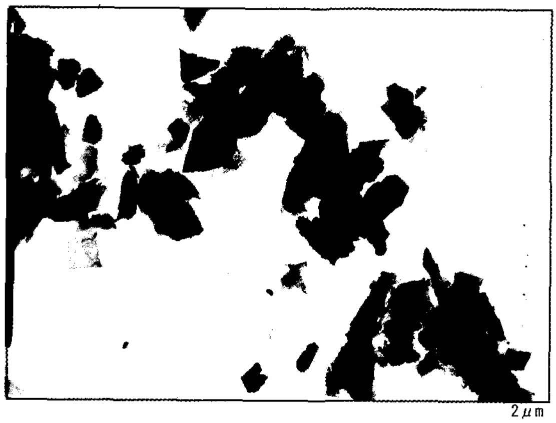

Fig. 5. Representative transmission electron microphotograph of pyrophyllite crystals.

of gold preferentially nucleate along the steps on the surfaces, thus revealing the surface microtopography of the crystal faces. The amount of evaporated gold is very critical, and can be judged by observing the appearance of the cover glass. Very light pink is the proper color, while light blue indicated the gold layer is too thick. Gold crystallites appear preferentially along steps, and not on the cleavage surface. Following this, the specimens were immersed in a solution of 10~12% HF for 10~12 days (occasionally one week) to completely dissolve the specimens and glasses. After soaking the remains in distilled water, the thin carbon films and their gold grains were collected on copper mesh grids for observation with TEM.

Results and Discussion

Clay minerals, particularly in pyrophyllite, are easily separated from cleavage planes. Therefore, it is possible that observed surfaces are corresponded to cleavage planes. Sato (1970) and Sunagawa *et al.* (1975) indicated that cleavage surfaces of clay minerals exhibit characteristic gold decoration patterns in which steps may terminate at points on the surface or may intersect each other. On the other hand, gold grains pre-

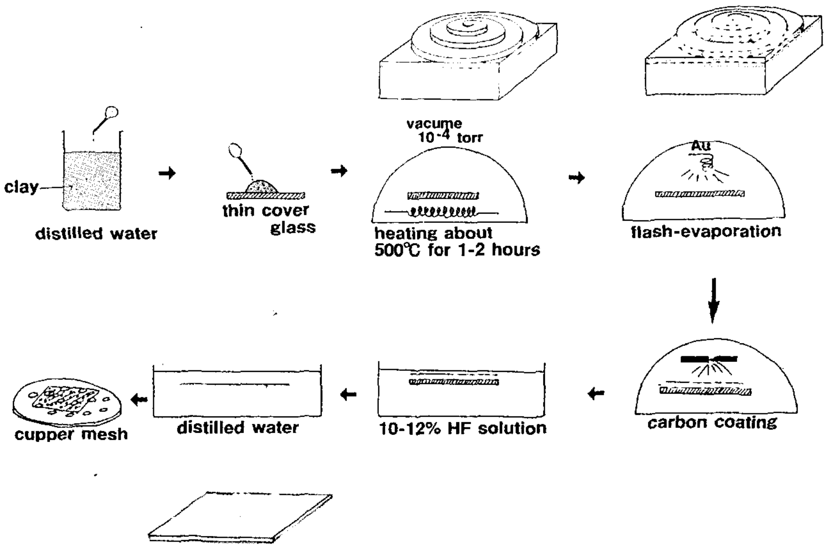

Fig. 6. Arrangement of Au-decoration technique (After Kitagawa, 1997).

Fig. 7. Surface microtopographies of pyrophyllite crystals collected from the Gussi deposit. Malformed circular step patterns with comparatively regular separations between the neighboring steps.

cipitate not only along steps, but also on whole surfaces. Thus, we used these criteria to distinguish growth surfaces from cleavage surfaces. According to the discussion as above, the observed step patterns shown in Figs. 7 and 8 are likely to represent growth surfaces.

In Figs. 7 and 8, layer by layer step growth patterns of the malformed circular single step patterns are found on crystal surfaces of pyrophyllite from the Gussi deposit. The step separation observed on the central part of crystal is wider than the other part, as shown in Fig. 8. The average of step separations is about 5~50 nm.

According to Sunagawa *et al.* (1975) and Tomoura *et al.* (1979), circular or malformed circular spirals have, in general, a narrower step separation than polygonal spirals. It is assumed that crystal with circular growth patterns were formed under the conditions of higher polygonal ones. Furthermore, Sunagawa (1981) indicated phyllosilicate minerals grown from vapor phase exhibited step separation versus step high ratios ranging $10^4 \sim 10^5$, as compared with much narrower ratios $10^2 \sim 10^3$ for those grown from hydrothermal solutions.

Pyrophyllite crystals from the Gussi deposit exhibit malformed circular steps with narrow

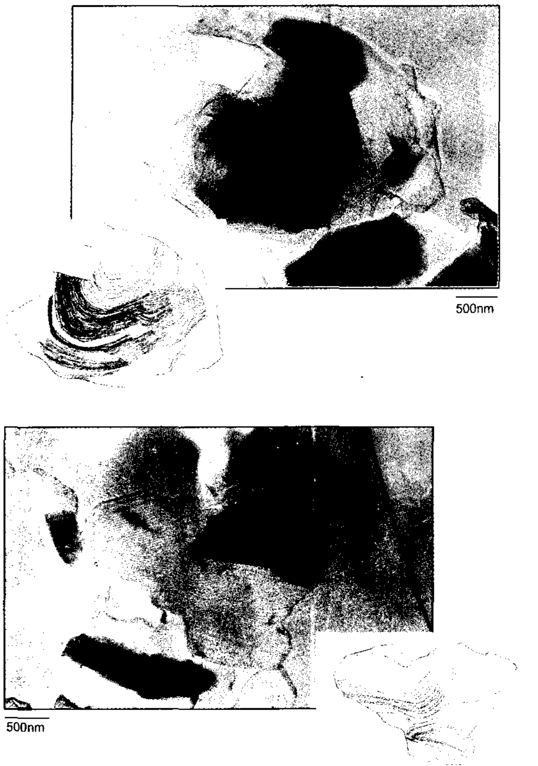

Fig. 8. Surface microtopographies of pyrophyllite crystals collected from the Gussi deposit. Malformed circular step patterns with irregular separations between the neighboring steps.

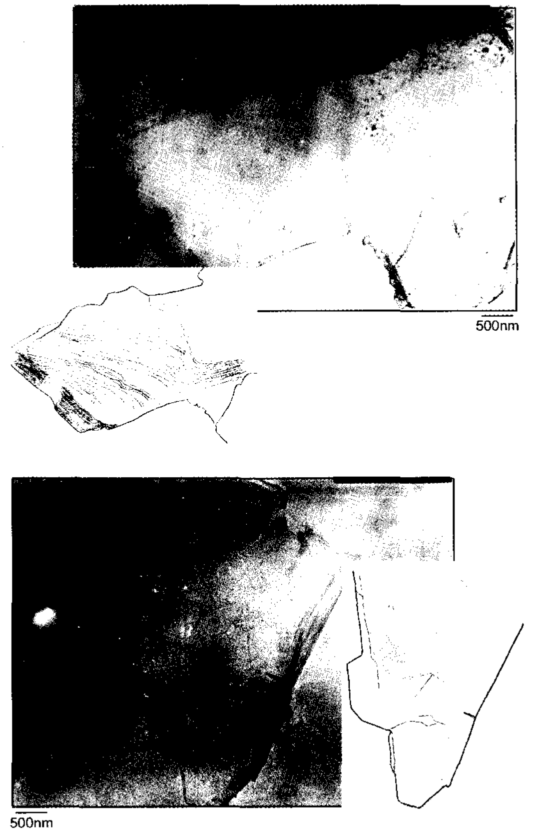

Fig. 9. Surface microtopographies of pyrophyllite crystals collected from the Uku deposit, Japan.

step separations as shown in Figs. 7 and 8. The ratio of step separation is 10^1 or less. These observations support that pyrophyllite crystals grew from hydrothermal solution phase rather than from high temperature vapor phase.

When a structure contains zigzag stacking, growth patterns can be expected paired steps or interlaced patterns to appear by a spiral growth process (Sunagawa *et al.*, 1975; Tomura *et al.*, 1979). Paired steps and interlaced patterns will appear, depending upon the symmetries of the elemental sheet, their mode of stacking, and the number of stacked sheets, owing to the difference in rate of advance in the same direction among the successive elemental sheets. Pyrophyllite crystals have two different polytypes i.e. triclinic pyrophyllite (1T) and two layers monoclinic pyrophyllite (2M) (Brindley and Wardle, 1970). Judging from these observations, pyrophyllite crystals showing paired steps and interlaced patterns may be 2M polytype, while single step crystals may be 1T polytype. Based on the hydrothermal experiment of pyrophyllite performed by Eberl (1979), 2M polytype is crystallized at the lower temperature than 1T polytype. Pyrophyllite crystals in samples used for surface microtopographic observation consist of 1T and 2M polytypes based on XRD analysis. However, growth patterns of pyrophyllite from the Gussi deposit show single step pattern, implying that pyrophyllite crystals from Gussi deposit were formed at the comparatively higher temperature.

Kitagawa (1992) has reported the different surface microtopographies of pyrophyllite crystals from Shokozan mine, Hiroshima Prefecture, Japan. Jige *et al.* (2002) indicated that surface microtopography of pyrophyllite from Uku deposit, Yamaguchi Prefecture, Japan, shows malformed circular pattern with layer by layer step growth patterns (Fig. 9). Growth pattern of pyrophyllite from Gussi deposit is almost similar to that of pyrophyllite from the Shokozan and Uku deposits. Therefore, these results indicated that pyrophyllite crystals in the Gussi deposit were formed under the growth condition similar to that in the Shokozan and Uku deposits.

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