

Oscillatory Zoning in Alunite from the Sungsan Mine, Korea

해남 성산광산의 명반석 내 진동누대구조에 관한 연구

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ABSTRACT: The oscillatory zoning pattern in alunite from the Sungsan mine, Korea was studied by the back-scattered electron(BSE) imaging and electron microprobe analysis. This zoning is not visible under the polarizing microscope, but is spectacularly illustrated in BSE image. Electron microprobe analysis reveals that the zoning is substantially due to the variation in the content of Na substituting for K in the A site of the alunite structure. With increasing brightness in BSE image, content of K increases but that of Na decreases. Delicate fine-scale zoning and sharp boundaries between adjacent zones suggest that the zoning would be ascribed to the variation in the composition of hydrothermal fluid around the growing alunite crystals. The effective factors for such a variation would be 1) the fluctuation in the composition of entering fluid, and/or 2) the rapid change in composition of fluid due to the rapid precipitation of more stable, Na-poor alunite.

요약 : 해남 성산광산에서 산출되는 명반석에서 나타나는 진동누대구조를 back-scattered electron (BSE) 상과 전자현미분석기를 이용하여 연구하였다. 이런 누대구조는 편광현미경 하에서는 관찰되지 않지만, BSE상에서는 아주 명확히 관찰된다. 전자현미분석에 의하면 이런 누대구조는 명반석 구조 내 A 자리에서 칼륨을 치환하는 나트륨의 양적인 차이에 의하여 생긴다는 것을 지시한다. BSE상에서 밝기가 증가함에 따라 칼륨의 양은 증가하지만, 나트륨의 양은 감소한다. 섬세한 작은 규모의 누대구조와 인접한 zone 사이의 명확한 경계는 이런 진동누대구조가 성장하는 명반석 결정 주변의 열수용액의 성분의 변화에 기인하여 형성된 것임을 가리킨다. 이러한 변화를 초래한 요인은 1) 유입되는 유체 성분의 변화 및 2) 보다 안정한, 나트륨이 적은 명반석의 빠른 침전에 의한 용액 성분의 변화일 것으로 생각된다.

INTRODUCTION

Oscillatory zoning of minerals has been studied by many mineralogists and geologists because it contains significant information concerning the chemical and physical environments of formation. It is commonly found in garnet, plagioclase, pyrite, and arsenopyrite from the hydrothermal ore veins, igneous plutons, and metamorphic rocks (Bottinga et al., 1966; Lessing and Standish, 1973; Sibley et al., 1976; Cathelineau et al., 1988; Fleet et al., 1988; Jamtveit, 1991). These minerals usually show a wide cation substitution in its crystal structure.

Alunite group minerals have the general formula $AR_3(SO_4)_2(OH)_6$, in which A refers to

large cations, especially K^+ , Na, or H_3O^+ , and R is either Fe^{3+} or Al^{3+} . S ions are surrounded by four oxygens which form tetrahedra, R ions are octahedrally coordinated with 4 OH^- and 2 oxygens, and A ions hold the 12-fold coordination between the sheets of R octahedra (Menchetti and Sabelli, 1976; Scott, 1987, 1990). Alunite, $KAl_3(SO_4)_2(OH)_6$, and natroalunite, $NaAl_3(SO_4)_2(OH)_6$, form a complete solid solution series due to the extensive substitution between potassium and sodium in A site (Hendricks, 1937, 1965; Brophy et al., 1962; Menchetti and Sabelli, 1976; Parker, 1962). If aluminum is replaced by iron in the alunite-natroalunite series, the series converts to jarosite-natrojarosite series (Brophy et al., 1962; Brophy and Sheridan, 1965).

Although many authors have worked on various aspects of the solid solution of natural and synthetic alunite group minerals, the study on the compositional zoning of these minerals has not been made yet. In alunite from the Sungsan mine, sodium replaces potassium extensively, but iron substitutes for aluminum limitedly (below than 0.3 atomic percentage Fe, Cho, 1990).

In this paper, the oscillatory zoning of alunite has been investigated using the BSE imaging and electron microprobe analysis. In addition, the favorable factors for the formation of oscillatory zoning in alunite are briefly discussed.

OCCURRENCE

The alunite samples were collected from the Sungsan mine which is located 27 km south of Mokpo City, Jeonra-namdo, Korea. This mine produces monthly about 5,000 tons

of agamatolite and porcelain clay. The alunite is associated with dickite, quartz, and rarely barite, all of which were formed by precipitation from the hydrothermal solution or by hydrothermal alteration of the Cretaceous volcanoclastic rocks of the Hwangsan Formation (Moon, 1975; Cho, 1990; Shin, 1990).

Alunites are found in three different types of ore, that is, 1) massive, 2) cavity-filling, and 3) veinlets. In the first two types, alunite occurs as very fine prismatic grains smaller than 50 μm in length, whereas the last one as euhedral to subhedral crystals up to 2 mm in diameter. The alunite samples studied were collected from the veinlets which are precipitated from the hydrothermal solution, because they are better crystallized and display distinct zoning. Alunite grains in veinlets usually occur along the vein walls, whereas dickites fill the interstices between alunite grains and sometimes replace alunite (Fig. 1A).

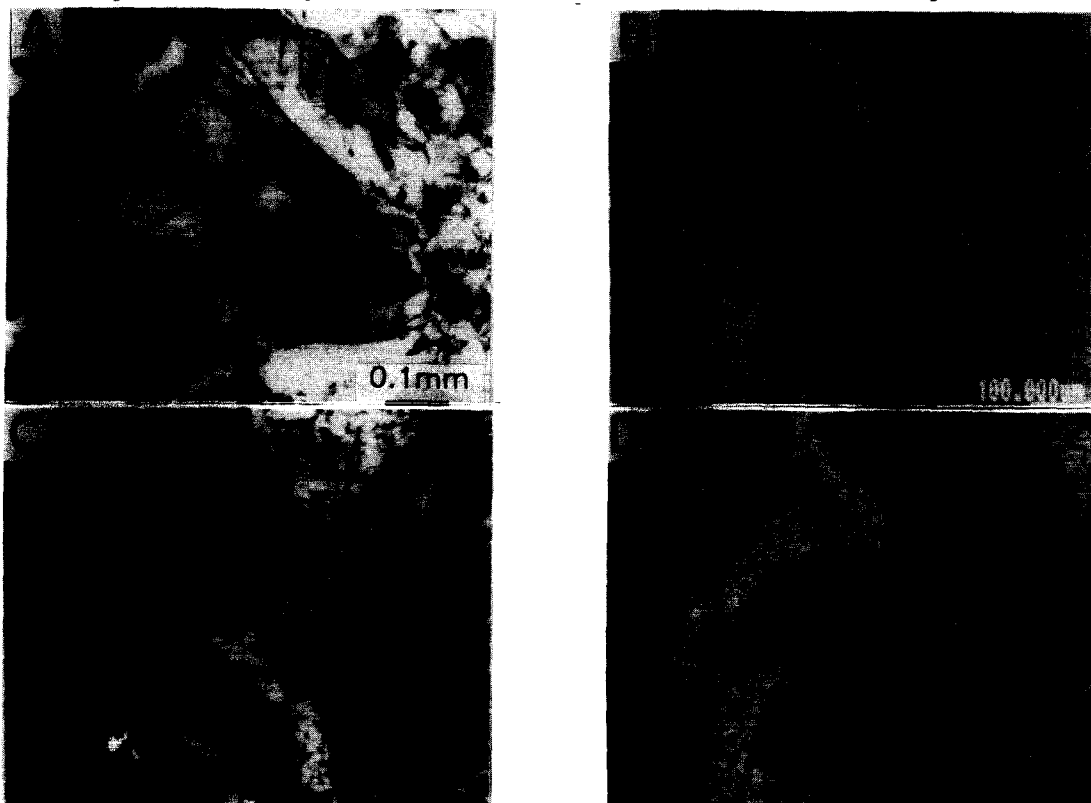


Fig. 1. A. Photomicrograph of alunite showing growth zoning (Crossed nicols). Dickite(dc) fills the interstices of alunite grains, and sometimes replaces alunite. B. BSE image showing oscillatory zoning in the same area as in A. All alunite grains show similar zoning pattern. The horizontal black line marks the position of the microprobe traverse. C. X-ray image of Na. D. X-ray image of K.

EXPERIMENTAL DETAILS

Alunites were studied using the polarizing microscope and electron microprobe. BSE image as well as X-ray images for Na and K (Fig. 1B–1D) was taken at 15 kV, 2 nA beam current using the LINK energy-dispersive X-ray spectroscopy attached to a JEOL-733 superprobe in the Department of Geological Sciences, Seoul National University. The brightness in BSE image is related to the differences in average atomic number within grains, thus it provide information about the distribution of elements in alunite crystals. Three zones differing in brightness were empirically defined by visual inspection. They are 1) light gray, 2) gray, and 3) dark gray zones.

Chemical compositions of alunites were analyzed by wavelength-dispersive and energy-dispersive X-ray spectroscopy. Instrumental conditions were: accelerating potential 15 kV, specimen current 5 nA, and spot size approximately 5 μm . The chemical variation of alunite across the zoning was studied at 5–35 μm intervals along a 655 μm traverse (Fig. 1B). Several points per each zone were analyzed, averaged, and reported in Table. 1.

RESULTS

Alunite crystals frequently show growth zonings under the polarizing microscope that are manifested by the crystal faces of different stage (Fig. 1A). However, any color zoning is not detected along the growth zones as shown by the homogeneous interference color in each grain. In BSE image, however, the alunite crystals display very complicated oscillatory zoning that is composed of a number of alternating light gray and dark gray zones with several dark gray bands in the middle part.

In the oscillatory zoning, individual fine-scale zones range down to less than 10 μm in width. Generally the brighter zone is broad whereas the darker zone is narrow. The polygonal boundaries between zones are generally

sharp and nearly parallel to the outer shape of alunite crystals, implying growth zoning.

Table 1. Electron microprobe analyses of alunite from the Sungsan mine, Korea.

No. anal.	light gray	gray zone	dark gray
	zone		zone
	20	15	3
K ₂ O	10.11	8.23	6.90
Na ₂ O	0.56	1.70	2.61
CaO	0.33	0.31	0.34
Al ₂ O ₃	36.27	36.49	36.39
Fe ₂ O ₃ *	0.05	0.15	0.05
CuO	0.10	0.10	0.02
ZnO	0.07	0.14	0.00
SO ₃	38.95	39.23	39.31
P ₂ O ₅	0.01	0.02	0.03
total	86.46	86.38	85.66
Numbers of ions on the basis of 11 oxygens			
K	0.980	0.720	0.604
Na	0.076	0.226	0.348
Ca	0.025	0.023	0.025
Σ A site	0.990	0.968	0.977
Al	2.950	2.949	2.994
Fe	0.003	0.008	0.002
Cu	0.005	0.005	0.001
Zn	0.004	0.007	0.000
Σ R site	2.962	2.969	2.947
S	2.018	2.018	2.025
P	0.000	0.001	0.002
Na atom. %	11.66	23.34	35.60

* total Fe as Fe₂O₃

Chemical compositions of alunites are given in Table 1. And the variation of CaO, Na₂O, and K₂O along the traverse in Fig. 1B is shown in Fig. 2. Fig. 2 shows that each different brightness zone has different chemical composition. Cation substitutions in the R site are negligible, but significant in the A site showing considerable variation from zone to zone. Correlation of brightness and chemical composition of zones reveals that the brightness is closely related to the kind and extent of cations occupying the A site. The content of Ca ion appears to have no definite relationship with brightness of the zone. However, the content of K or Na is closely related to the bright-

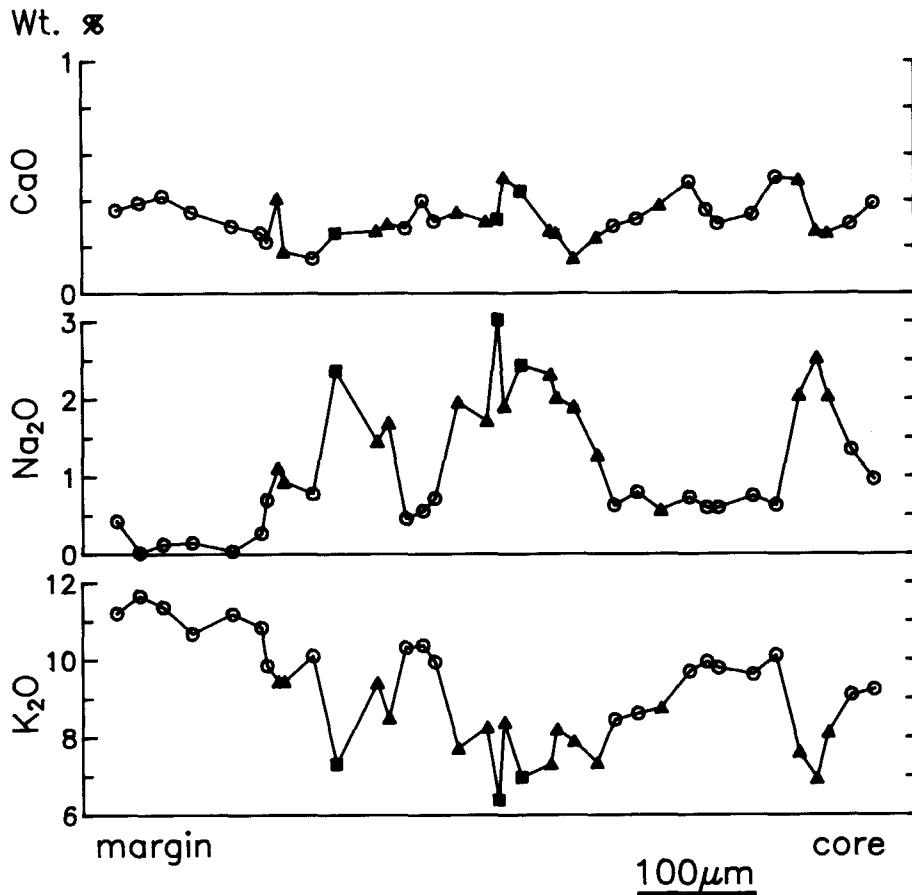


Fig. 2. Variation in CaO, Na₂O, and K₂O along the traverse shown in Fig. 1B. Open circles, light gray zone; closed triangles, gray zone; and closed squares, dark gray zone in BSE image.

ness. The dark gray zone has high Na and low K contents, whereas the light gray zone has low Na and bright K contents, and the gray zone has intermediate contents of Na and K between two zones (Fig. 2). The X-ray images for Na and K reveal that the brighter the zone, the higher the K content and the lower the Na content. It can be concluded that the oscillatory zoning in alunite is primarily attributed to the different content of Na replacing K in the A site of the alunite structure.

DISCUSSION

Although the oscillatory zoning is a well-known phenomenon for many minerals form-

ing solid-solution series, it have been rarely reported for alunite group minerals. The oscillatory zoning pattern in alunite from the Sungsan mine is similar to that of sphalerite from Mississippi Valley type and epithermal deposits (Barton et al., 1977; Barton and Bethke, 1987). In sphalerite, this zoning is due to Fe content, and is ascribed to variations in fluid composition during crystallization. By analogy, other study of As zoning in pyrite from strata-bound and stratiform gold deposits (Fleet et al., 1988) suggested that the zoning is interpreted as due to the rapid variations in As content of mineralization fluids.

It turned out that the oscillatory zoning in alunite is due to the variation in Na and K contents from this study. The alunite shows

delicate fine-scale zoning and sharp contacts between zone lamellae. Such an oscillatory zoning suggests its origin by growth banding rather than diffusion after crystal growth (Lessing and Standish, 1973; Fleet et al., 1988).

Compositional growth banding in crystals is commonly regarded as a result of either rapid crystallization or periodic changes of composition in the nutrient solution. As pointed out by Fleet et al. (1988), the rate of crystallization might not be a significant factor. Therefore, it appears that the oscillatory zoning might be formed by the rapid variation in the composition of fluid around the growing alunite crystals. Such a rapid variation in the composition of fluid might be possible in two ways.

Firstly, the composition of the hydrothermal solution supplied might fluctuate in some periodic manner. An examination of Figs. 1. and 2 show that K or Na content is considerably variable even in the same brightness zone, and that the dark gray zone is found in the middle part of the oscillatory zoned alunite. Moreover, Na-rich zone is not found in the margin. All these facts suggest that the composition of the hydrothermal fluid was not uniform but significantly fluctuated with time.

Secondarily, the chemical composition of hydrothermal fluid might be changed by the precipitation of more stable phase. Hemley et al. (1969) suggested that Na-rich alunite has considerably lower stability relative to Na-poor phase on the basis of the greater difficulty of synthesis and the greater rarity of Na-rich phase in nature. Zotov (1967) also reported an aqueous molar Na : K = 14:1 and a pH of 2.5 for alunite of Na : K = 1:1.5 forming at low temperatures. It, therefore, is expected that the formation of Na-rich phase requires high aqueous Na:K ratios. If a new fluid is supplied, the more stable, Na-poor alunite (brighter zone) will first crystallize, resulting in the concentration of Na ions in the residual solution from which the Na-rich phase (darker zone) precipitates. Every new pulse of hydrothermal fluid might lead to the crystallization of Na-poor alunite first followed by

more Na-rich alunite. The repetition of such a process might result in the formation of fine-scale oscillatory zoning consisting of alternating brighter and darker zones.

In conclusion, the oscillatory zoning of alunite is attributed to the rapid change in the fluid composition by either the fluctuation in the composition of entering fluid or the change of fluid composition by the rapid precipitation of more stable, Na-poor alunite, or both.

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