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THE OCCURRENCE OF NATROALUNITE AT ANAK KRAKATAU, INDONESIA

By

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Abstract

Natroalunite occurs as masses of platy crystals on the surface of an andesite in Anak Krakatau, Indonesia. The composition of the natroalunite was determined by x-ray diffraction method. The natroalunite is very close to the sodium end member of alunite-natroalunite series.

Introduction

Alunites are characteristic minerals produced by the acid-sulfate alteration of silicate rocks. Alunite often occurs in areas where volcanic rocks of rhyolitic to andesitic composition have undergone surficial solfataric or acid hot spring alteration. The mud post and acid hot springs in Yellowstone (FENNER, 1936) and Lassen (ANDERSON, 1935) National Parks, and some areas of Wairakei, New Zealand (STEINER, 1963) are good examples of alunite formation in present-day hydrothermally active areas. Numerous occurrences of alunite in the Tertiary period and more recent geologic periods have been described, but occurrence of natroalunite remains very rare. An alunite from Anak Krakatau gave a distinctive x-ray diffraction pattern which was similar to that of natroalunite. Because thin-bedded deposits of the mineral on the andesite surface were obtained by scratching the surface with a knife, only small amounts of the sample were obtained. X-ray diffraction was used to estimate the composition of the alunite in the alunite-natroalunite series for fear that the collected sample contained amorphous silica, volcanic glass and some impurities. Because naturally occurring alunite of the alunite-natroalunite series often contain some impurities, synthetic alunites of pure K and Na end members were prepared by the present writers, so a comparison can be made with the natroalunite gathered from Anak Krakatau.

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Locality and Occurrence

Anak Krakatau is a volcano found among the Krakatau Group consisting three other islands, namely Sertung, Rakata and Small Rakata, and is located in the Sunda Strait between Jawa and Sumatra (Fig. 1). Anak Krakatau is composed of andesitic lavas and pyroclastic materials. The natroalaunite occurs as masses of platy crystals on the surface of the slope of the central cone, which is composed of an andesite. The white natroalaunite occurs at places where solfataric alteration has occurred.

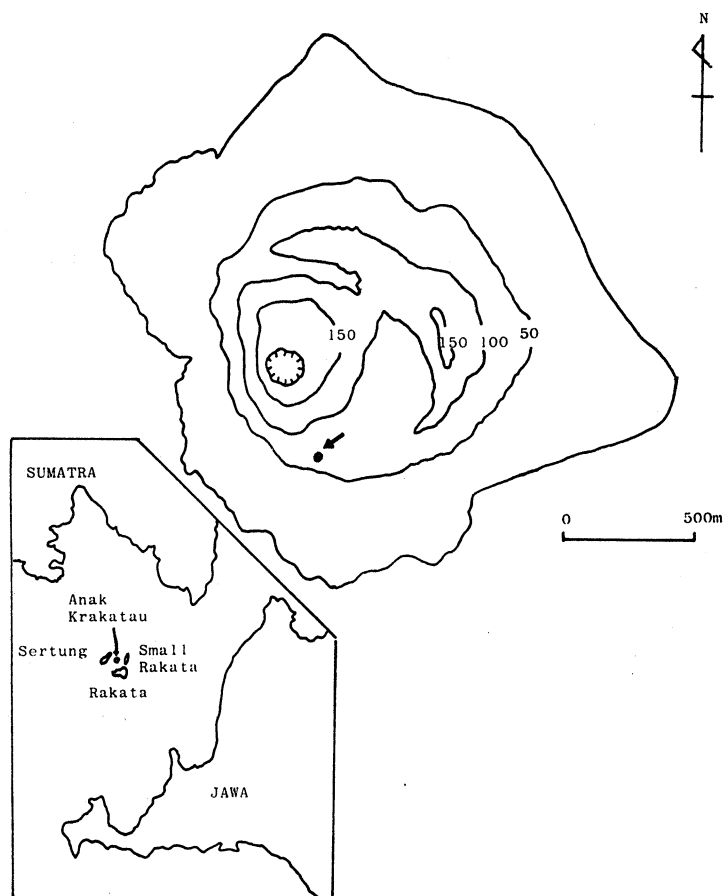


Fig. 1. Map showing the sample locality.

X-ray Study

Because the natroalaunite obtained by scratching the andesite surface contains small amounts of mixtures of andesite fragments and amorphous silica, the sodium component of the alunite-natroalaunite series could be determined by x-ray diffraction method. The plot of *a* and *c* of alunites against their relative atomic percentages of potassium and sodium indicates the nature of the isomorphous series. The *a* dimension is nearly constant for natural alunites. The *c* dimensions shows a marked linear shrinkage of the unit cell with increasing sodium content. Such relationships satisfy Vegard's

law, which requires that unit cell dimensions vary linearly with change in composition, expressed in atomic percent (PARKER, 1962). The variation diagram of the *a* and *c* dimensions with changes in the relative atomic percentages of potassium and sodium in natural alunites made by PARKER (1962) is available to estimate the sodium percent of the natroalunite, but plots of *a* and *c* dimensions vs. composition of natural alunite samples show reverse S-shaped curve for the alunite-natraolaunite isomorphous series which deviates slightly from a straight-line curve. It is mainly due to the fact that Parker used some natural alunites containing impurities. PARKER (1962) found that synthetic alunites heated to 300°C for 1 hour have *a* and *c* dimensions nearly the same as natural alunites. The present authors synthesized sodium and potassium end members of alunites by using chemical reagents (K_2SO_4 and $Al_2(SO_4)_3 \cdot 18H_2O$ for alunite, and Na_2SO_4 and $Al_2(SO_4)_3 \cdot 18H_2O$ for natroalunite), and heated the synthetic samples to 300°C for 1 hour, and used them for the estimation of sodium percentage of the alunite-natroalunite series. The natural and synthetic samples were examined with a x-ray diffractometer set to traverse at the rate of one-fourth degree (2θ) per minute, using a chart speed of 1 cm per minute. The instrument was standardized using silicon powder. Copper radiation was used exclusively. Computations are

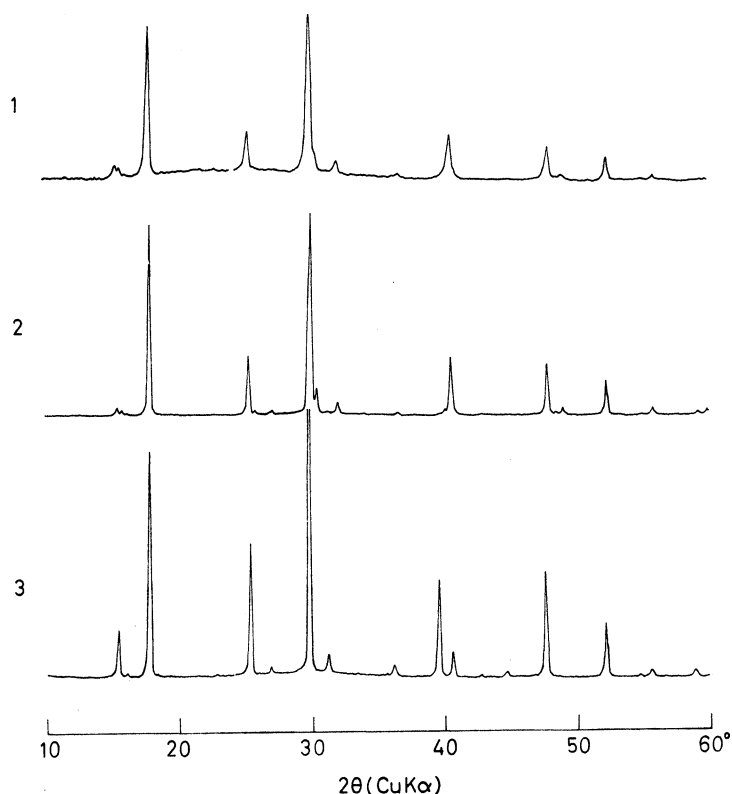


Fig. 2. X-ray powder diffraction patterns for the natroalunite from Anak Krakatau, and the synthetic natroalunite and alunite.

1: the natroalunite from Anak Krakatau; 2: synthetic natroalunite; 3: synthetic alunite.

based on $\text{CuK}\alpha$ radiation for reflections with 2θ less than 36° and $\text{CuK}\alpha_1$ radiation for reflections with 2θ greater than 36° .

X-ray powder patterns of the natroalunite from Anak Krakatau, synthetic alunite and synthetic natroalunite are shown in Fig. 2. The x-ray powder pattern of the natroalunite from Anak Krakatau is very similar to that of the synthetic natroalunite. From the powder data $a=6.97 \text{ \AA}$ and $c=16.73 \text{ \AA}$ were obtained for the natroalunite from Anak Krakatau. X-ray powder data for the natroalunite from Anak Krakatau, the synthetic alunites and some natural alunites are listed in Table 1. The plots of a and c of the heated synthetic alunites are shown in Fig. 3. The a and c dimensions of the natroalunite from Anak Krakatau are plotted as A and B respectively in the Fig. 3. The relative atomic percentage of sodium in the natroalunite from Anak Krakatau is very close to 100%. The natroalunite from Anak Krakatau and the synthetic alunite and natroalunite were heated to 1000°C for 1 hour. X-ray powder diffraction

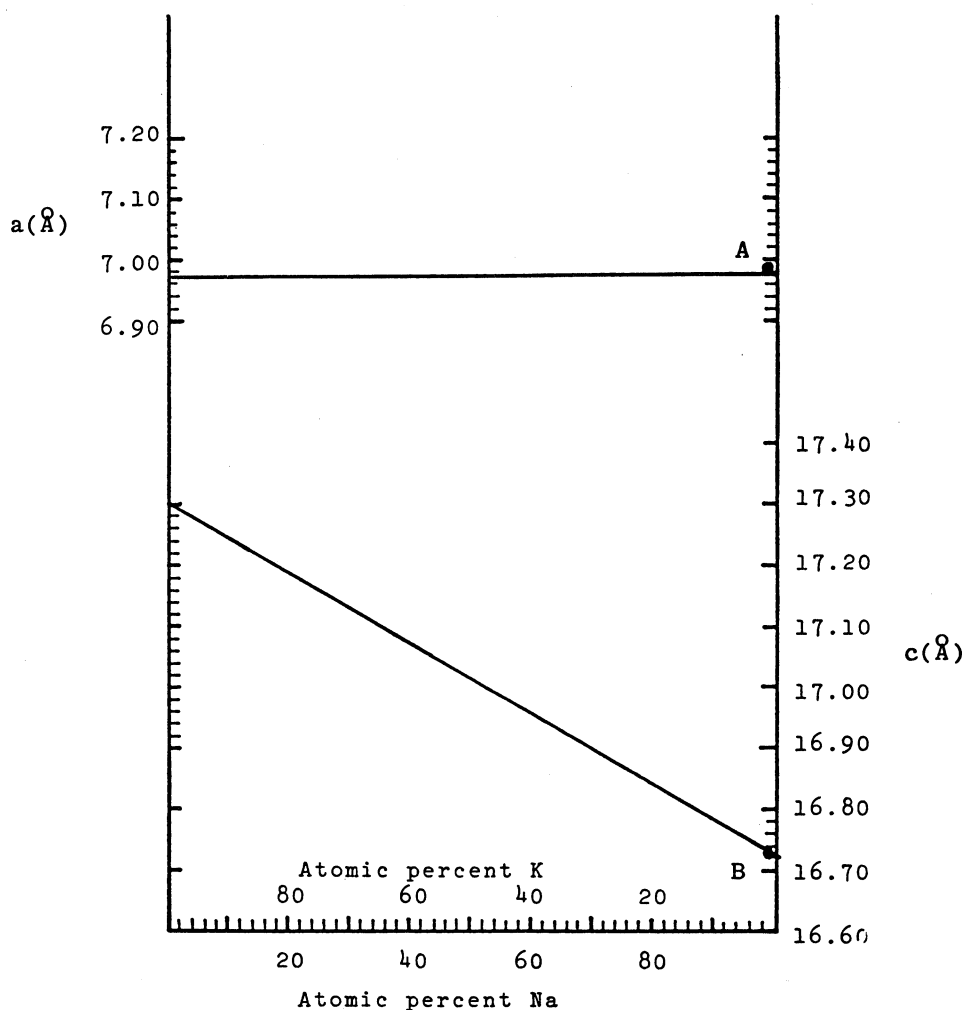


Fig. 3. Variation of the unit cell dimensions, a and c , with changes in the relative atomic percentages of potassium and sodium in synthetic alunites, and plot of the natroalunite from Anak Krakatau.

patterns of the three heated samples are shown in Fig. 4. Na_2SO_4 was formed from the natroalunite from Anak Krakatau and from the synthetic natroalunite, whereas K_2SO_4 was formed from the synthetic alunite. The x-ray powder diffraction pattern of the natroalunite from Anak Krakatau is very similar to that of the synthetic natroalunite heated to 1000°C , and different from that of the heated synthetic alunite. This fact indicates that the chemical composition of the natroalunite from Anak Krakatau is similar to that of the synthetic natroalunite.

Table 1. X-ray diffraction data for natural and synthetic alunite and natroalunite.

hkl	1 d(Å)	2 d(Å) I	3 d(Å) I	4 d(Å) I	5 d(Å) I	6 d(Å) I
101	5.68	5.68 8	5.68 3	5.69 12	5.72 10	5.72 15
003	5.58	5.58 6	5.58 4	5.58 12	5.77 3	5.77 28
012	4.90	4.90 92	4.90 95	4.90 76	4.97 47	4.96 53
110	3.485	3.49 26	3.49 30	3.49 24	3.50 28	3.49 21
104	3.438					
021	2.97	2.98 86	2.97 70	2.97 70		
113	2.955	2.96 100	2.96 100	2.96 100	2.99 100	2.99 100
015	2.926	2.93 14	2.93 13	2.93 17		
006	2.788	2.788 10	2.79 6	2.79 17	2.87 4	2.89 106
024	2.447				2.48 2	2.477 6
205						
107	2.222	2.221 28	2.220 30	2.221 48	2.28 20	2.293 81
122	2.201	2.204 9		2.202 12	2.217 5	2.211 6
300	2.012					2.038 2
214	2.003				2.026 2	2.022 2
018	1.976					
033	1.893	1.896 26	1.898 26	1.894 29	1.904 11	1.903 29
027	1.874	1.876 2	1.874 2	1.874 2		
009	1.858	1.859 5	1.856 4	1.857 10	1.908 22	1.926 70
220	1.743	1.746 15	1.747 17	1.744 21	1.752 12	1.746 16
208	1.719					1.762 2
131	1.666					1.667 2
223	1.663					
119	1.640	1.647 3	1.646 4	1.643 5	1.677 1	1.684 2
306	1.632					
134	1.554	1.554 2				
123	1.542	1.542			1.569 2	1.572 2
312	1.509				1.652 2	1.648 2
315	1.497		1.501 2	1.501 5	1.510 2	1.509 4
226	1.478	1.479 3				1.494 9
0210	1.463	1.462 8	1.463 10	1.463 12	1.497 9	1.503 36

1. Calculated d values using $a=6.97 \text{ \AA}$ and $c=16.73 \text{ \AA}$.
2. Natroalunite from Anak Krakatau.
3. Synthetic natroalunite.
4. Natroalunite from Big Star deposit, Marysvale, Utah (relative atomic percentages of K and Na are 18 and 82 respectively) (after Parker, 1962).
5. Synthetic alunite.
6. Alunite from Mineral Products mine, Marysvale, Utah (relative atomic percentages of K and Na are 96 and 4) (after Parker, 1962).

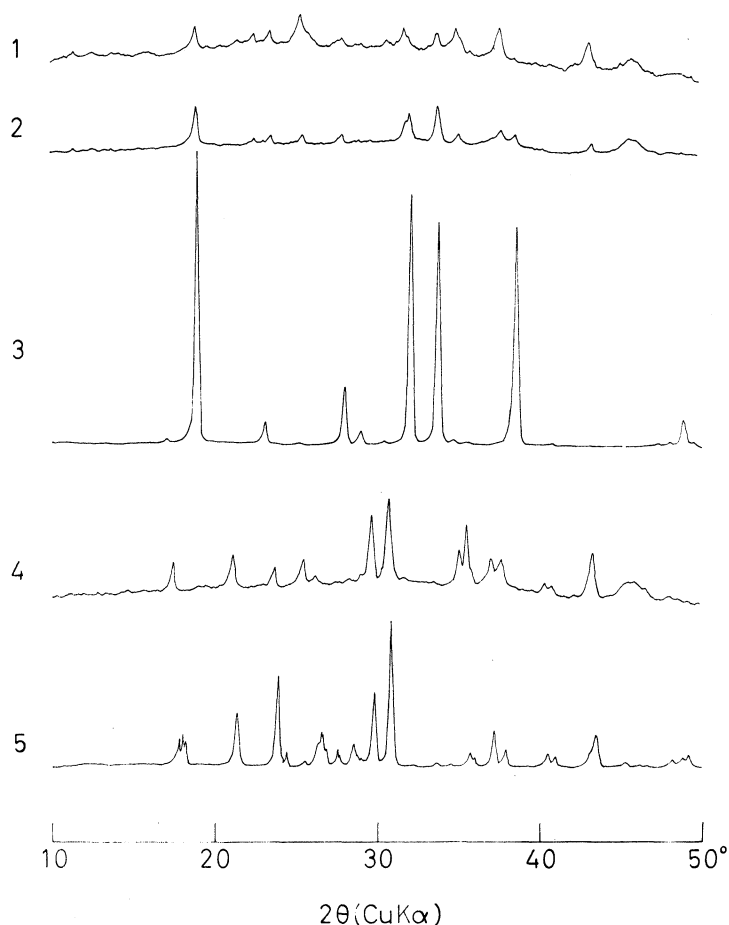
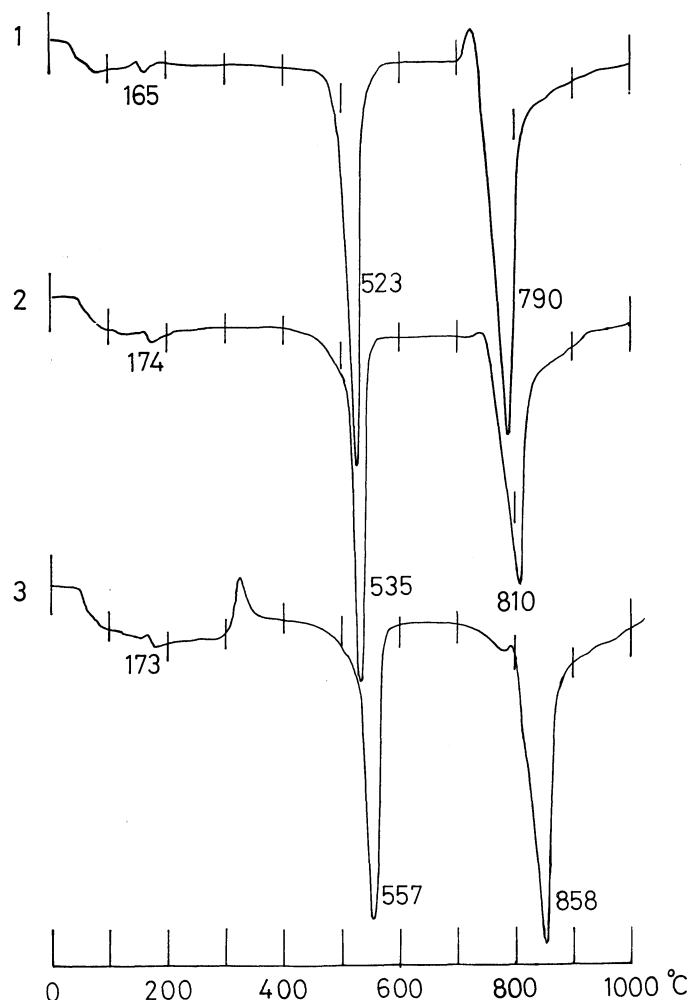


Fig. 4. X-ray powder diffraction patterns for the natroalunite from Anak Krakatau, synthetic natroalunite, synthetic alunite, Na_2SO_4 and K_2SO_4 after heating to 1000°C for 1 hour. 1: natroalunite from Anak Krakatau; 2: synthetic natroalunite; 3: Na_2SO_4 ; 4: synthetic alunite; 5: K_2SO_4 .

Differential Thermal Analysis

A differential thermal analysis curve was taken with a automatic thermal analyser at a heating rate of 10°C per one minute. The differential thermal analysis curve of the natroalunite from Anak Krakatau is shown in Fig. 5 together with those of the synthetic alunite and the synthetic natroalunite. These three samples give rather similar thermal curves. An endothermic peak for the natroalunite from Anak Krakatau at 165°C is attributable to dehydration of adsorbed water. An endothermic peak at 523°C is due to dehydroxylation of (OH). The natroalunite decomposes at 790°C . The temperatures of three endothermic peaks of the synthetic natroalunite are lower than those of the synthetic alunite. The three endothermic peaks of the natroalunite from Anak Krakatau show lower temperatures than the three endothermic peaks of the synthetic natroalunite. It is concluded that the particle size of the natroalunite from Anak Krakatau is smaller than that of the synthetic natroalunite.

Fig. 5. Differential thermal analysis curves.
 1: natroalunite from Anak Krakatau; 2: synthetic natroalunite; 3: synthetic alunite.



Scanning Electron Microscopy

Using a JEOL JSM-25SII scanning electron microscope, the morphological observation of the natroalunite was made. The sample was cemented with dotite paste to a half-inch diameter brass disc. The sample was then coated with a composite film of gold to insure electrical conductivity, thus preventing charging effects in the microscope. Scanning electron micrographs of the natroalunite from Anak Krakatau, the synthetic natroalunite and alunite are shown in Fig. 6. According to a recent investigation of the alunite rocks of the Tolfa district of Italy (LOMBARDI, 1967), electron-optical examination showed the alunite to occur as bulky crystals of rhombohedral shape varying from 10 to 20 μm in size. On the contrast the crystals of the natroalunite from Anak Krakatau are much smaller and show platy form (Fig. 6A). Crystals of the synthetic alunite and natroalunite show also plates, but they are much larger than those of the natroalunite from Anak Krakatau. It is because of the smaller particle size that the natroalunite from Anak Krakatau showed lower temperatures of the endothermic peaks in its DTA curve.

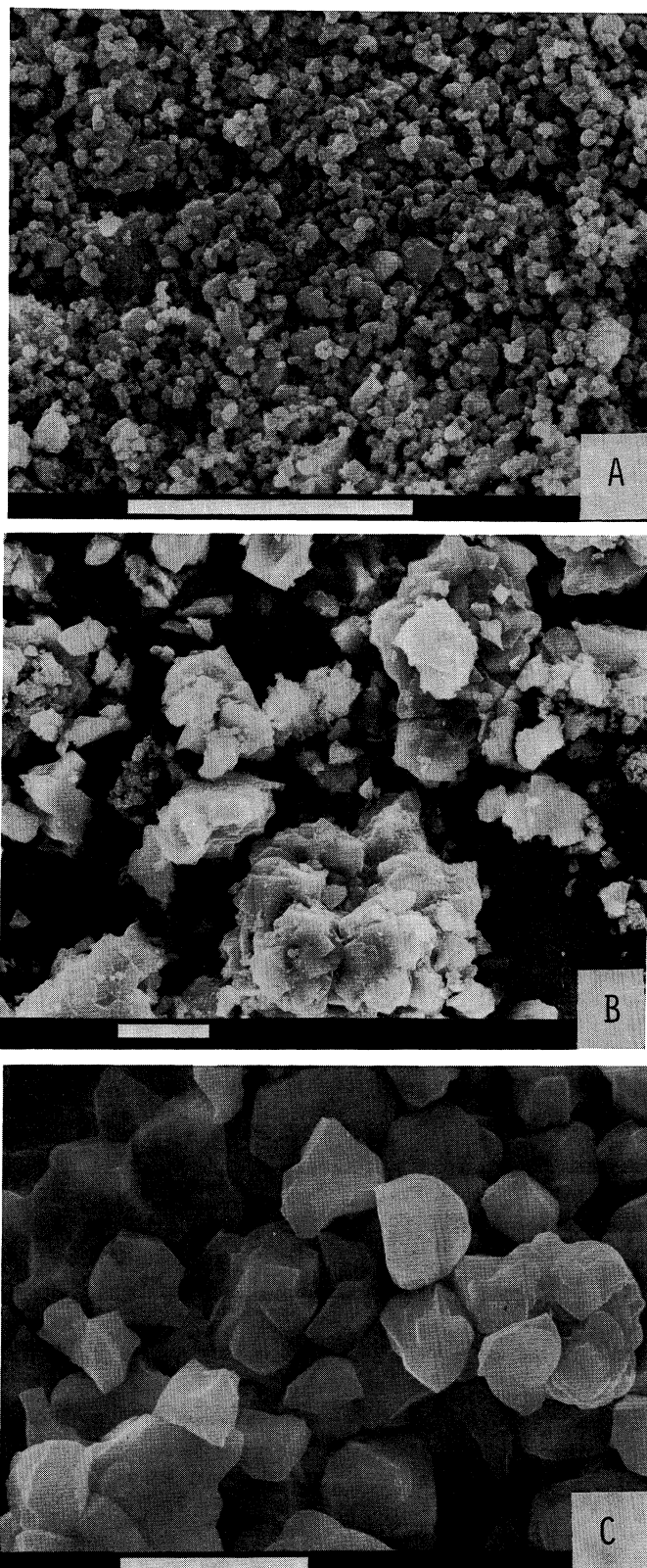


Fig. 6. Scanning electron micrographs.
A: natroalunite from Anak Krakatau; B: synthetic natroalunite; C: synthetic alunite. The scale bars are 10 μm .

Infrared Absorption Spectra

Infrared absorption spectra of the natroalunite were obtained by the Nujol paste method. Figure 7 shows the infrared absorption spectra of the natroalunite from Anak Krakatau (Fig. 7-1) together with those of the synthetic alunite and natroalunite. The IR spectra of three specimens are similar, but those of the synthetic alunite and natroalunite show a very broad absorption band between 3400–3000 cm^{-1} and a band at 1640 cm^{-1} . They are attributable to adsorbed water. H_2O stretching modes are found between 3450–3000 cm^{-1} , and the bending mode is at 1640 cm^{-1} . SO_4^{2-} has four modes of vibration when it retains its full symmetry; these are ν_1 , ν_2 , ν_3 and ν_4 . The fundamental frequencies of SO_4^{2-} are ν_1 : 983, ν_2 : 450, ν_3 : 1105 and ν_4 : 611 (NAKAMOTO,

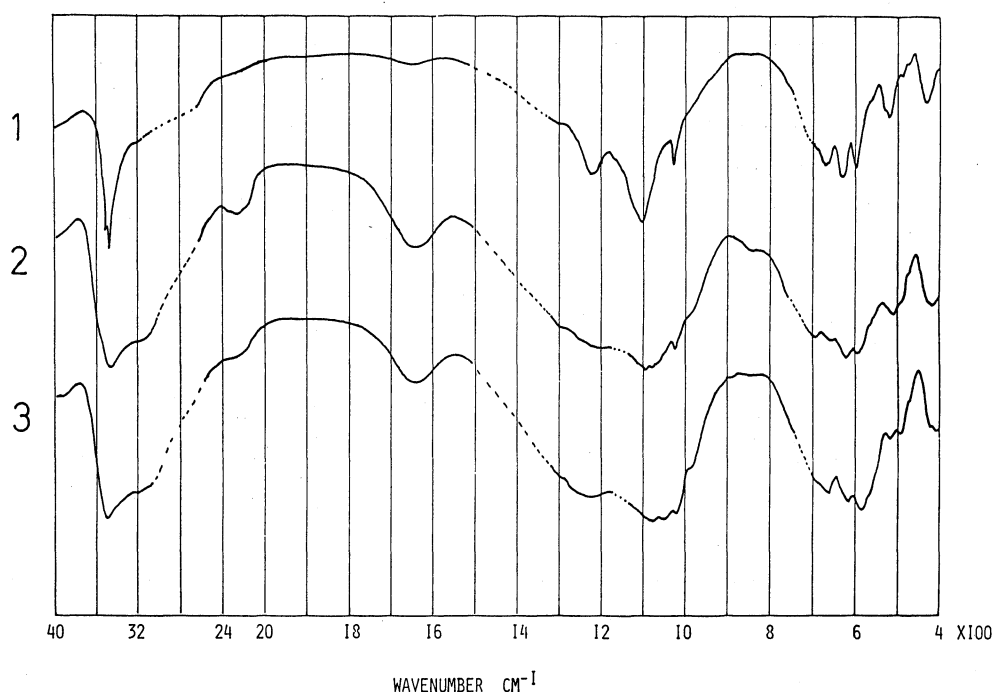


Fig. 7. IR spectra for the natroalunite, synthetic natroalunite and alunite.
1: natroalunite from Anak Krakatau; 2: synthetic natroalunite; 3: synthetic alunite.

Table 2. IR spectra of natural and synthetic alunite and natroalunite

	ν_1	ν_2	ν_3	ν_4	OH	
					Stretching	Bending
1	1030	475	1170, 1086	632, 605	3485	802, 780, 505
2	1025	486	1100	628, 599	3500, 3470	520
3	1022	487	1090	620, 590	3480	505
4	1020	490	1080	620, 581	3490	520

1. Alunite studied by Moenke (1962, 1966).
2. Natrolaunite from Anak Krakatau.
3. Synthetic natroalunite.
4. Synthetic alunite.

1970). For the alunite-natroalunite series the space group is C_{3v}^5 with the sulphate ions on C_{3v} sites; thus, six sulphate fundamentals should appear (Ross, 1974). IR spectra of the natroalunite and the synthetic natroalunite and alunite are listed in Table 2.

Discussion

Alunites are characteristic minerals produced under conditions of acid-sulphate alteration of silicate rocks. The most common occurrence of alunite is in areas where volcanic rocks of rhyolitic to andesitic composition have undergone surficial solfataric or acid hot spring alteration. In these occurrences, sulfuric acid appears to be produced by surface or near surface oxidation of H_2S , and alunite ordinarily occurs from the surface down to immediately below. Oxidation of H_2S and SO_2 to H_2SO_4 gives rise to strong argillic alteration to alunite. Alunite is typically present in volcanic sulfur deposits (KATO *et al.*, 1934). Sulfate concentrations on the order of pH values of 2–3 are required to produce alunite at temperature of approximately $300^\circ C$ (MEYER *et al.*, 1968). By contrast, low temperature formation of alunite (30 – $35^\circ C$), apparently occurring at the present time in an acid lake environment, has been described by Zotov (1967). Most alunite in acid hot spring areas occurs in moist rock above the water table where temperature range from 20 to $100^\circ C$. It is certain that the natroalunite at Anak Krakatau was formed above temperature described by Zotov (1967). Relative atomic percent of $Na/(Na+K)$ in the natroalunite is very high. The high content of Na in the natroalunite is a question. Some hypotheses can be considered for the formation of the natroalunite at Anak Krakatau. The present authors consider that sodium was probably supplied by the sodium rich plagioclase in the host andesitic rocks, and the natroalunite was formed. The ratios of Na_2O/K_2O in the andesites at Anak Krakatau are high (ŌBA *et al.*, 1982).

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