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The identity of almeriïte with natroalunite.

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Summary. Two specimens of almeriïte from the type locality have been examined by chemical analysis, d.t.a., and X-ray powder photography and shown to be identical with natroalunite. A little illite and kaolinite are present as impurities. X-ray powder data for natroalunite are presented.

O^N reviewing the collection of minerals at one of the geological laboratories in the University of Granada, two specimens labelled almeriïte and calafatite were found. Both resembled alunite or some member of the alunite group.

There has been some confusion as to the chemical composition of minerals related to the alunite-jarosite group and new names were given to some of them; further studies have shown them to be alunite or jarosite. Moss (1957) came to the conclusion that carphosiderite, borgströmite, utahite, cyprusite, and raimondite were identical with jarosite or natrojarosite, and Van Tassel (1958) showed carphosiderite from Greenland to be natrojarosite.

Calderon (1910) gave the name almeriite to a mineral discovered by Calafat in Adra (Almería), Spain; he described it as a whitish, compact substance, which turns earthy through alteration, with the following chemical composition: $34.77 \% SO_3$, $37.98 Al_2O_3$, $9.64 Na_2O$, and $17.61 H_2O$, and the formula $(SO_4)_3Al_2.SO_4Na_2.5Al(OH)_3.H_2O$; D = 2.5. According to Novo and Chicarro (1957) almeriite is similar to mendozite, NaAl $(SO_4)_2.12H_2O$.

We have studied almeriïte by chemical analysis, X-ray powder photographs, and d.t.a. Two samples from Adra (Almería) were used: no. 1, Laboratory of Geology, University of Granada; no. 2, sample number 17.328 in the Natural Sciences Museum, Madrid.

X-ray diffraction study. Table I records the measured spacings and estimated intensities of samples 1 and 2, compared with those of alunite

				2-0	703	1-0879			
1.		2.		A.S.2	Г.М.	A.S.T.M.			
9.9-10	vvw	9.9-10	vw	probably I	llite				
7.30	vw	7.37	vvw	probably I	Kaolinite				
5.67	w	5.62	$\mathbf{m}\mathbf{w}$	5.70	20	5.71	25		
4.90	\mathbf{ms}	4.89	\mathbf{ms}	4.92	40	4.94	50		
4.44	vvw								
3.48	m	3.48	\mathbf{m}	3.50	20	3.49	41		
2.96	vvs	2.96	vvs	2.96	100	2.98	100		
2.78	vw	2.76	mw	2.85	5	2.88	6		
		2.44	w	2.47	50	2.47	9		
2.21	\mathbf{ms}	2.21	\mathbf{ms}	2.24	50	2.29	50		
						$2 \cdot 20$	19		
1.89	\mathbf{ms}	1.89	\mathbf{ms}	1.89	50	1.89	59		
1.85	vw	1.85	w						
1.74	\mathbf{ms}	1.74	\mathbf{ms}	1.74	50	1.74	50		
1.64	vw	1.64	w	1.65	5	1.64	6		
1.55	vw	1.56	vw	1.56	3	1.56	6		
		1.54	w			1.54	3		
1.50		1.50		1 40	60	1.40	50		
1.48	шw	1.48	шw	1.49	60	1.49	90		
,		1.46	w	1.44	3				
1.42	vw	1.42	w			1.42	6		
1.37	w	1.37	w	1.37	20	1.38	6		
		1.32	vw	1.32	3	1.32	3		
1.28	$\mathbf{m}\mathbf{w}$	1.28	mw	1.29	20	1.28	25		
1.20	$\mathbf{m}\mathbf{w}$	1.20	mw	1.20	20	1.20	25		
1.18	w	1.18	w						
1.16	w	1.16	w	1.16	5	1.16	6		
1.14	w	1.14	w	1.13	20	1.13	6		

TABLE I. X-ray spacings and estimated intensities of X-ray powder diagrams.

2–0703 and 1–0879 from the ASTM index. There is a close correspondence of the spacings and intensities for both natroalunite (almeriïte) samples with those of alunite, the main difference being the lower intensity of the line 1.48 Å. The absence of lines at 2.47, 1.54, and 1.44 Å in the photograph of sample 1 may be due to a smaller natroalunite content, as those reflections are, in general, very weak.

The spacings at 9.9-10 Å, 4.44 Å, and some others correspond to illite. It was suspected that the line at 9.9-10 Å could be due to $4H_2O$ -halloysite, but the same line remains in the photograph obtained from a sample heated to 110° C.

The presence of a member of the kaolinite group may explain the line

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at $7\cdot30-7\cdot37$ Å and the broadening of line at $1\cdot48-1\cdot50$ Å. Few lines of this mineral appear in the photograph and they are very weak.

Differential thermal analysis. The d.t.a. curves, fig. 1, show two strong endothermic effects (490–510° C and 800–810° C), corresponding to the loss of water and evolution of SO₃ respectively, from the alunite, and an exothermic effect at 710–720° C due to γ -Al₂O₃ crystallization, which is in good agreement with the data given by Tzvetkov and Valyashikhina (1953) and Bayliss and Koch (1955).



FIG. 1. Differential thermal analysis curves for almeriïte (natroalunite).

No indication of illite or a member of the kaolinite group was obtained by d.t.a.; their amount may be too small to be detectable.

Chemical analysis. The results of chemical analysis carried out according to the methods described by Kolthoff and Sandell¹ and especially the molar ratios given in table II clearly show the identity of almeriïte with natroalunite. The presence of illite and a member of the kaolinite group accounts for the $SO_3: R_2O_3, SO_3: (Na, K)_2O$, and $SO_3: H_2O^+$ molar ratios values being lower than for pure natroalunite.

Table II contains also the atom number calculated from the results of chemical analysis and referred to 2 sulphur atoms, as well as the probable atom distribution to form natroalunite, illite, and kaolinite; the H and O atoms from H_2O — are not included. For calculation of the minerals found from X-ray diffraction data and d.t.a. curves, all S has been supposed to form natroalunite with the required (Al, Fe'''), (Na,K), H, and O atom numbers; the proportion in which (Al, Fe'''), on the one

¹ I. M. Kolthoff and E. B. Sandell, Tratado de Quimica Analítica Cuantitativa, edn Niger, Buenos Aires, 1943, p. 881.

 TABLE II. Chemical analyses, atom distribution, and mineral composition of two samples of almeriïte (1 and 2) from Adra (Almería),

 Spain, to show the identity with natroalunite (3).

			1.	2.	3.											
			Wt. %	Wt. %	Wt. %		1*.	<i>1</i> †.	1‡.	1§.	1]].	2*.	2†.	<i>2</i> ‡.	$2\ .$	A
SiO ₂			7.11	3.03	••	\mathbf{Si}	0.564		0.045	0.505	+0.014	0.214		0.214	••	H
SO3		•••	33.46	37.29	40.20	\mathbf{S}	2.000	2.000	••	••	••	2.000	2.000	••	••	ΥO
Al_2O_3			37.51	38.27	38.44	\mathbf{Al}	3.517	3.000	0.036	0.505		3.219	3.000	0.171	-10.086	$^{\rm so}$
Fe_2O_3		•••	0.41	0.47	••	\mathbf{Fe}	0∙024∫	0 000	0 000	0 000	••	0∙038∫	0 000	0171	+0.000	U
K ₂ O	•••		0.55	0.71	••	К	0∙057 (1.000	0.009			0.060)	1.000	0.043		E
Na ₂ O	•••	•••	6.18	7.10	7.79	Na	0·952 J	* 000	0 000	••		0·983 (. 000	0.010	••	A
$H_2O +$	•••	•••	14.32	12.77	13.57	н	7.612	6.000	0.027	1.010	+0.575	6.090	6.000	0.128	-0.038	ST
H2O	•••	•••	0.68	0.41	••	0	16.749	14.000	0.161	2.272	+0.312	14.880	14.000	0.770	+0.110	RO
			$\overline{100.22}$	$\overline{100.05}$	100.00											AN
Molar ratios:																μ
SO,: R,O,			1.13	1.23	1.33			*	Atom n	umber t	o 2 S.					: د
SO3: (Na,	, K),0		3.96	3.82	4.00	† Atom number to form natroalunite.										
SO3:H2O	+		0.52	0.65	0.66			‡	Atom n	umber te	o form illi	te.				Ē.
Mineral composition:					§ Atom number to form kaolinite.											
			Wt. %	Wt. %		,						•	,-			ž
Natroalur	nite		82.5	91·9												
Illite			1.7	5.8												
Kaolinite			13.4	••												

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hand and (Na, K), on the other, enter into the natroalunite crystal lattice is taken to be the same as that obtained from chemical analysis, though it is possible that all Na may be as natroalunite and K as illite.

The small alkali excess remaining once all S has been combined to form natroalunite may be accounted for by the presence of a certain amount of illite, greater in sample no. 2; the required atom numbers to form illite have been taken on the basis of the theoretical formula $Si_{3.33}Al_{0.67}O_{10}(OH)_2Al_2K_{0.67}$ for that mineral.

Kaolinite may be formed in sample no. 1 by combining the excess of silicon with the required amount of the corresponding atoms.

Once these three minerals are formed, there is an excess of 0.014 Si atoms (equivalent to $0.17 \% SiO_2$) in sample no. 1, and of 0.086 Al atoms (equivalent to $1.02 \% Al_2O_3$) in sample no. 2. The excess of H and 0 in sample no. 1 may be due to a higher degree of hydration than that assigned to the mineral of the kaolinite group, which would be in a good agreement with the X-ray data, as the basal spacing for that mineral seems to be somewhat higher than 7.15 Å.

From the above calculations the following formulae can be obtained for the natroalunites from Adra:

 $\begin{array}{l} \text{Sample no. 1: } (\text{SO}_4)_2(\text{OH})_6\text{Al}_{3-2\cdot98}\text{Fe'''}_{0-0\cdot02}\text{Na}_{1-0\cdot95}\text{K}_{0-0\cdot05} \\ \text{Sample no. 2: } (\text{SO}_4)_2(\text{OH})_6\text{Al}_{3-2\cdot96}\text{Fe'''}_{0-0\cdot04}\text{Na}_{1-0\cdot94}\text{K}_{0-0\cdot05}, \end{array}$

instead of $(SO_4)_3Al_2.SO_4Na_2.5Al(OH)_3.H_2O$ ascribed by Calderon (1910) to the mineral almeriïte, a name which should disappear in mineral nomenclature.

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