

ELECTRON MICROSCOPIC IDENTIFICATION OF SINGLE CRYSTALS OF WAIRAKITE, A RARE COMPONENT IN CLAYS

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Abstract—Crystallites of the finest fraction of a clay mineral from Rosamund, California, which account for over 50 per cent of the total weight, are identified as wairakite single crystals of 0.1–1 μ size. High-magnification electron microscopy revealed flat, almost perfectly square-shaped lamellae, which consist of superimposed layers of approximately < 50 Å thickness. Electron diffraction patterns from a selected single crystal proved that the basal plane of the crystallite aligned perpendicular to the electron beam is the (111) plane. It is suggested on the basis of the present study and the report of previous investigators that the pseudocubic wairakite crystals cleave along their (111) and $\bar{1}\bar{1}\bar{1}$ planes. The indices of high order reflections, unpublished or previously reported as uncertain, are determined.

INTRODUCTION

A NEW, unusual zeolite mineral was discovered by A. Steiner in 1953 at Wairakei, New Zealand. This mineral, named wairakite, was characterized as the calcium analogue of analcime, with the chemical composition: $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 2\text{H}_2\text{O}$. Physical properties and the morphology of macroscopic crystals have been described. The crystal structure was determined by D. S. Coombs (1955) by means of X-ray diffraction, utilizing the Weissberg technique, on a macroscopic single crystal. The latter was an incomplete octahedron, 15 mm across. The structure was reported as pseudocubic with $a = 13.69 \text{ \AA}$, $b = 13.68 \text{ \AA}$, $c = 13.56 \text{ \AA}$, $\beta = 90.5^\circ$, with $8(\text{CaOAl}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 2\text{H}_2\text{O})$ per unit cell. Debye-Scherrer X-ray diffraction powder patterns were also obtained from wairakite powders.

Since the first report by Steiner (1955), wairakite has been detected at various other locations: at St. Croix and St. Thomas, Virgin Islands (*Whetten*, 1965; Donnelly, 1962) in Shimane Prefecture, Japan (Umegaki, 1965), in the Geysers of California (Steiner, 1958), and at Mt. Rainier Park, Washington (Wise, 1959) in the U.S.A. Synthetic wairakite was obtained by hydrothermal synthesis (Ames, 1958) and by exchange reaction at high pressure from leucite (Debron, 1965).

The clay investigated in the present study was a commercial product of Paramount Pacific Incorporated, deposited 10 miles east of Rosamond, California, a few miles from Edwards Air Force base and 90 miles from Los Angeles. This is a high desert area of about 2000 ft altitude with a semi-arid climate. The deposit is at the surface with

6"–2' overburden and covers two areas, each 10 miles square. The depth of the clay varies from 20 to 80 ft deep and is generally mined by open pit method.

The major constituent (over 50 per cent) of the sample proved to consist of extremely fine wairakite crystallites of 0.1–1 μ size. This phenomenon allowed a study on wairakite single crystals by electron microscopy and by electron diffraction from selected, individual crystallites. This complementary method to X-ray diffraction has the advantage that structure studies can be carried out on single crystals having dimensions smaller by orders of magnitude than the previously studied crystal and that the indices of high order reflections, not indexed previously or reported as uncertain, can be determined.

A further advantage of the electron diffraction study is that the presence of wairakite can be proved with certainty, even in the presence of large amounts of muscovite and feldspar. The spacings of the high intensity X-ray reflections of the latter minerals are very close to those of wairakite. Their simultaneous presence may prevent the recognition of wairakite, when only X-ray technique is applied.

EXPERIMENTAL

Fractionation of the clay. The separation of the silt and the clay fractions was achieved by sedimentation under gravity. The grains of the sample were ground lightly in a mortar and the sand was dispersed in cold water for 15 min utilizing a high speed Hamilton-Beach mixer. Sedimentation was

carried out in preweighed beakers and the liquid phase was removed by careful decantation. The fractions were dried at 90–100°C in an oven and exposed to the atmosphere for 24 hr prior to X-ray diffraction analysis to allow equilibration with atmospheric moisture.

Elemental analysis. Fraction 5 (See Table 1) was analyzed by emission spectrophotometry.

X-ray diffraction methods. A Phillips Norelco X-ray diffractometer with Ni filtered $\text{CuK}\alpha$ radiation was utilized at 40 kV and 35 mA. Random powders of untreated and dilute-glycerine treated fractions were investigated.

Electron optical methods. The samples for electron optical studies were taken from the highly dispersed, finest Fraction 5, prior to evaporation to dryness. A drop of the highly diluted suspension was deposited on a carbon coated electron microscope grid. After evaporation of the water, the samples were shadowed with a mixture of Pt–C in high vacuo, utilizing a 45° shadow angle. An RCA Model EMU-3 electron microscope was used for electron diffraction and high magnification bright field image studies. The spacings of the

experimental reflections were calculated using Pt reflections as internal standards. All distances were measured on the photographic plate. The theoretical spacings of the hkl reflections of wairakite were calculated by means of an IBM Model 7044 computer, assuming cubic symmetry and $a = 13.7 \text{ \AA}$ lattice constant.

RESULTS AND DISCUSSION

Table 1 summarizes the sedimentation times, composition and weight per cent of the fractions. Table 2 compares the experimental spacings of the X-ray diffraction powder pattern, obtained from Fraction 5, with those published for randomly distributed wairakite crystallites. The tables demonstrate that over 50 per cent of the clay is identified as wairakite by X-ray diffraction. Figure 1, a high magnification image of a representative wairakite crystal in Fraction 5 shows a nearly perfect square-shaped lamella of $0.25 \mu \times 0.25 \mu \times 0.01 \mu$ dimension ($\sim 100 \text{ \AA}$ thickness). The crystallite obviously consists of superimposed thinner lamellae of thickness estimated below 50 \AA .

Electron diffraction from this crystal produces

Table 1. Summary of sedimentation times, Weight per cent and composition of clay

Fraction no.	Sedimentation time	Wt. %	Composition					
			α -quartz	muscovite	feldspar	kaolinite	chlorite	wairakite
1	2'	9.87	major component	minor component	major component	traces	—	—
2	15'	5.2	major component	major component	major component	traces	large amount	traces
3	2 h-30'	15.6	large amount	large amount	minor component	traces	large amount	traces
4	24 h	18.87	—	large amount	—	considerable amount	—	large amount
5	Evap. to dryness	49.17	—	—	—	—	—	only mineral

Table 2. Comparison of X-ray reflections of Fraction 5 with values published for Wairakite

Experimental values			Published values	
(2 θ)	(d \AA)	(Rel. int.)	(d \AA)	(Rel. int.)
15.92	5.56	90	5.57	9
26.10	3.41	100	3.41	10
30.70	2.91	90	2.90	8

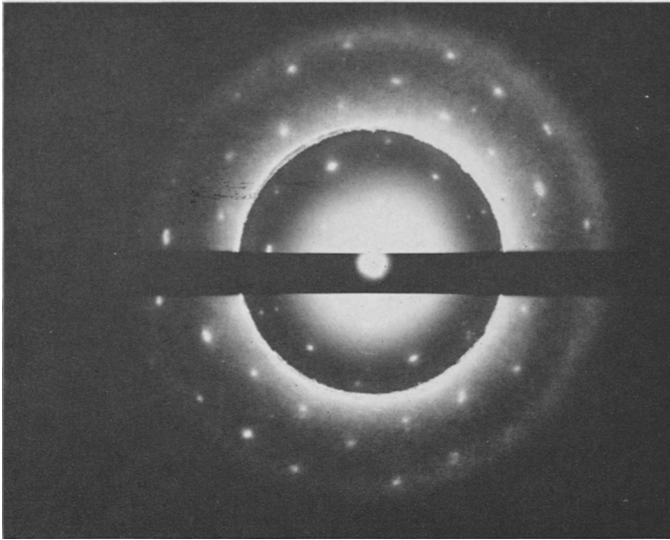


Fig. 2. Electron diffraction pattern from wairakite single crystal shown on Fig. 1. During printing of the positive, the central area was masked to decrease diffuse scattering from primary beam and obtain better image of the low order reflections.

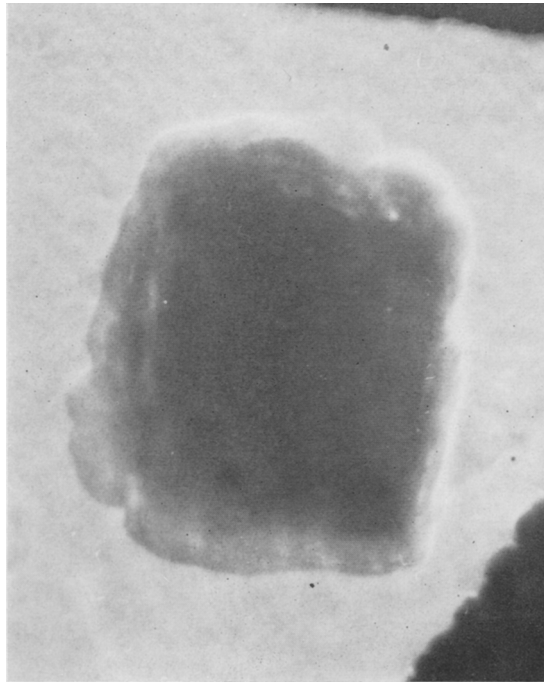


Fig. 1. High magnification bright field image of selected wairakite single crystal producing electron diffraction pattern exhibited on Fig. 2.

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the pattern shown on Fig. 2. The diagram of this well resolved single crystal pattern (Fig. 3) exhibits the indices of the reflections and demonstrates sixfold symmetry. The reflections obtained agree with those expected when a cubic crystal lies on its (111) plane, i.e. when this plane is aligned perpendicular to the electron beam. Several reflections included in the diagram, but unrecognizable on the print, were clearly visible on the photographic plate. The central dark stripe on the diffraction pattern is an artifact due to a frame used

as a substitute for the beamstop with which the electron microscope was not equipped, in order to decrease the intensity of the primary beam on the photographic plate.

Table 3 compares the spacings of the reflections with those calculated assuming cubic symmetry and a 13.7 Å lattice constant, and with data published by Coombs (1955) where available. The excellent agreement of experimental, calculated and published values is apparent.

The reflections of the single crystal pattern show

Table 3. Comparison of spacing of reflections on E.D. pattern with theoretical and published data

hkl	d Å Calc	d Å Lit	d Å Exp	Rel. int. †
0 2 2*	4.808	4.84	4.83	10
2 2 4*	2.776	2.770	2.752	30
4 4 0*	2.404	2.418	2.38	10
2 $\bar{4}$ 6	1.817	1.822	1.84	30
4 $\bar{2}$ 6	1.817		1.84	30
$\bar{2}$ $\bar{6}$ 4	1.817		1.84	50
6 2 4	1.817		1.84	80
$\bar{4}$ $\bar{6}$ 2	1.817		1.84	50
6 4 2	1.817		1.84	80
$\bar{6}$ $\bar{4}$ 2	1.817		1.84	50
4 6 2	1.817		1.84	80
$\bar{6}$ $\bar{2}$ 4	1.817		1.84	<80
2 $\bar{6}$ 4	1.817		1.84	80
$\bar{4}$ 2 $\bar{6}$	1.817		1.84	50
$\bar{2}$ 4 $\bar{6}$	1.817		1.84	<50
6 6 0	1.603	1.612	1.606	50
0 $\bar{6}$ 6				100
6 0 6				80
$\bar{6}$ 6 0				50
$\bar{6}$ 0 $\bar{6}$				50
0 $\bar{6}$ $\bar{6}$				100
4 $\bar{4}$ 8*	1.388	—	1.353	
2 $\bar{6}$ 8	1.334	—	1.353	<10
2 8 6	1.334		1.353	50
8 6 2	1.334		1.353	50
$\bar{2}$ $\bar{8}$ 6	1.334		1.353	50
$\bar{6}$ $\bar{8}$ 2	1.334		1.353	100
6 8 $\bar{2}$	1.334		1.353	100
6 2 $\bar{8}$	1.334		1.353	100
2 6 $\bar{8}$	1.334		1.353	10
6 $\bar{2}$ 8	1.334		1.353	<10
8 2 6	1.334		1.353	<10
$\bar{8}$ $\bar{6}$ $\bar{2}$	1.334		1.353	<10
$\bar{8}$ $\bar{2}$ 6	1.334		1.353	<10
8 8 0*	1.202	—	1.205	<10
10, 4, 6*	1.103	—	1.1086	<10
2, 10, $\bar{8}$ *	1.049	—	1.03	<10
8, 12, 4	0.909	—	0.94	<10
10, 0, 10*	0.960		0.94	<10

* — and all equivalent indices.

† Estimated by eye.

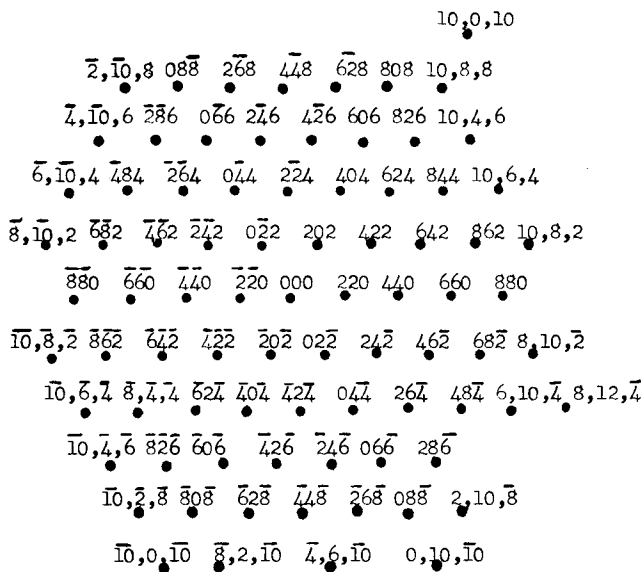


Fig. 3. Diagram of electron diffraction pattern exhibited on Fig. 2.

that the (111) plane and its higher order equivalents are perpendicular, and the [111] axis of the reciprocal lattice is parallel to the electron beam. The observation that the (111) planes of several single crystals were aligned perpendicular to the electron beam indicates, that the wairakite crystals cleave along their (111) and $(\bar{1}\bar{1}\bar{1})$ planes. The data collected in the present study are insufficient to allow a statement on a statistical basis and further work is necessary to substantiate this suggestion. A. Steiner (1955) described cleavage-like lines on powdered material obtained by crushing a megascopic crystal; he does not suggest, however, the index of the plane along which the cleavage has taken place.

The doubling of many reflections was observed on the electron diffraction pattern. Similar observations reported by D. S. Coombs (1955) were attributed to a measurable departure from cubic symmetry. It is suggested that the twinning of the crystals parallel to (110) planes, a characteristic property of wairakite (Steiner, 1955; Coombs, 1955) furthermore superposition of lamellae, which are rotated with respect to each other, may also contribute to the formation of double reflections.

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Résumé— Les cristaux de la fraction la plus fine d'un minéral d'argile provenant de Rosamund en Californie, qui représentent plus de 50% du poids total, sont identifiés comme des cristaux simples wairakite à dimensions de 0,1–1 μ . La microscopie électronique à grandissement élevé a montré des lamelles plates de forme presque parfaitement carrée, qui comportent des couches surimposées à épaisseur d'environ <50 Å. Les modèles de diffraction des électrons à partir d'un seul cristal sélectionné ont démontré que le plan de base du cristallite aligné de manière perpendiculaire au faisceau d'électrons est le plan (111). Sur la base de cette étude et selon le rapport antérieur d'autres chercheurs on suggère que les cristaux pseudo-cubiques de wairakite se fendent selon leurs plans (111) et ($\bar{1}\bar{1}\bar{1}$). On détermine les indices des réflexions d'ordre élevé qui n'ont pas été publiés antérieurement ou qu'on a indiqué comme étant incertains.

Kurzreferat— Kristallite aus den feinsten Fraktionen eines Tonminerals aus Rosamund, Kalifornien, die über 50% des Gesamtgewichtes ausmachen, werden als Wairakit Einzelkristalle von 0,1–1 μ Grösse identifiziert. Intensivvergrößerung durch Elektronenmikroskopie zeigt flache, beinahe perfekt quadratische Lamellen, die aus übereinander geschichteten Lagen von ca. <50 Å Dicke bestehen. Elektronenbeugungsbilder eines ausgewählten Einzelkristalles beweisen, dass die Basisebene des Kristallits, die normal zum Elektronenstrahl liegt, die (111) Ebene ist. Aufgrund der gegenwärtigen Untersuchung und der Arbeiten früherer Forscher wird angenommen, dass sich die pseudo-kubischen Wairakitkristalle entlang ihrer (111) und ($\bar{1}\bar{1}\bar{1}$) Ebenen spalten. Die bisher unveröffentlichten bzw. angezweifelte Reflexionsindexe höherer Ordnung werden bestimmt.

Резюме— Кристаллиты мельчайших фракций глинистого минерала из Розамунда (Калифорния), которые составляют почти 50% по весу, представляют монокристаллы вайракита размером 0,1—1 мк. Электронная микроскопия позволила обнаружить плоские, почти идеально квадратные пластинки, состоящие из наложенных слоев толщиной приблизительно <50 Å. Дифракционные картины показывают, что базальная плоскость кристаллита, перпендикулярная к электронному пучку, представляет плоскость (111). На основании настоящего исследования и данных предыдущих исследований есть основания полагать, что псевдокубические кристаллы вайракита раскалываются по плоскостям (111) и ($\bar{1}\bar{1}\bar{1}$). Определены индексы отражений высокого порядка.