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RE-EXAMINATION OF LEGRANDITE

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ABSTRACT

Legrandite is described from a second locality, the Ojuela mine, Mapimi, Durango, Mexico. Measurement of several crystals gave the axial ratio $a:b:c=1.606:1:1.287$, $\beta=104°21'$. Unit cell dimensions are $a=12.80$ Å, $b=7.94$ Å, $c=10.22$ Å, $\beta=104°12'$, yielding a calculated axial ratio of $a:b:c=1.612:1:1.287$. Symmetry is monoclinic prismatic $2/m$ with space group $P2_1/c$. Its physical and optical properties are as follows: {100} cleavage fair to poor, hardness $4\frac{1}{2}$, specific gravity 3.975 g/cm^3 (calculated 4.015), luster vitreous, biaxial (+), $\alpha=1.702$, $\beta=1.709$, $\gamma=1.740$, $2V=50°$. Chemical analysis gave ZnO 50.1, FeO 1.4, MnO 1.7, As_2O_5 37.7, H_2O 8.9, total 99.8%. A new formula, $Zn_2(OH)AsO_4 \cdot H_2O$, is given for the species with unit cell contents of $8[Zn_2(OH)AsO_4 \cdot H_2O]$.

INTRODUCTION

Legrandite was described as a new species from the Flor de Peña mine, Lampazos, Nuevo Leon, Mexico by Drugman and Hey (1932). Their data was sufficiently good to establish the species, but the poor quality and limited amount of material made an accurate chemical analysis impossible. The new occurrence at the Ojuela mine, near Mapimi, Durango, Mexico, produced a relatively large number of very pure and beautifully crystallized specimens. A few crystals were recovered measuring up to 60 mm in length.

The legrandite at the Ojuela mine occurs in cavities in a hard, compact limonite matrix and is usually associated with flat, lenticular, anhedral crystals of adamite. These adamite crystals occur mostly as single individuals but sometimes as globular aggregates. The association of these two zinc arsenates in the deposit suggests the possibility of other arsenates in the same environment. Recently a pale blue to colorless zinc arsenate has been found at the locality and is under investigation.

The geology and ore deposits of the general area near Mapimi have been described by Hayward and Triplett (1931) and Foshag (1934). Typical of many in northern Mexico, the Ojuela mine is a replacement deposit in a fracture system in limestone. Intensive oxidation of the primary sulfides, mainly arsenopyrite, argentiferous galena, pyrite and sphalerite, has taken place. Among the arsenates resulting from this oxidation, carminite, arseniosiderite, dussertite and scorodite have been described by Foshag (1937) and adamite by Mrose (1948). A member of the conichalcite-austinite series is also found there but has not been described. Others are almost certain to follow.

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Crystallography

Legrandite crystals from the Ojuela mine are long prismatic elongated parallel to [001]. They vary in length from 1 mm to 6 cm and attain a maximum diameter of 7.5 mm. Many, especially the smaller crystals, are doubly terminated and have faces producing excellent signals for goniometric measurement (Table I). Larger crystals tend to be multiple and unsuited for measurement. Aggregates of crystals in sprays or fans are

Table I. Measured Angles of Ojuela Mine Legrandite

Form	Number of Crystals	Number of Measurements	Measured Range		Weighted Mean	
			ϕ	ρ	ϕ	ρ
c 001	3	6	90°00′	14°11′–14°22′	90°00′	14°20′
a 100	11	22	90°00′	90°00′	90°00′	90°00′
m 110	11	44	32°39′–32°50′	90°00′	32°49′	90°00′
p $\bar{1}11$	11	22	−23°52′–−23°58′	54°38′–55°06′	−23°56′	55°02′
$\bar{h}kl$	3	6	−24°08′–−25°37′	86°14′–87°34′	−24°33′	86°52′

common. All the crystals are very simple in development having a maximum of four measurable forms. The form m{110} is dominant and most frequently is accompanied only by p{$\bar{1}11$}. Occasionally, the form a{100} occurs but is narrow and produces relatively poor signals. All of the first crystals of legrandite recovered from the Ojuela mine had only the unit pyramid plus two forms in the prism zone. In 1962 a new lot consisting of several hundred specimens produced a large number of crystals with c{001} assuming the same prominence as p{$\bar{1}11$}. With the acquisition of some of these crystals it became possible to determine a morphological axial ratio. This ratio had previously been calculated from the *x*-ray data because of the deficiency of measurable forms. The appearance of typical crystals is shown by the drawings in Fig. 1.

Elements derived from goniometric measurement of fourteen crystals are $a:b:c=1.606:1:1.287$, $\beta=104°21'$. These compare closely with $a:b:c=1.612:1:1.287$, $\beta=104°12'$ derived from *x*-ray precession data. They also compare closely with previously reported elements by Drugman and Hey (1932) of $a:b:c=1.6076:1:1.2886$, $\beta=104°14'$. An angle table for the forms observed on the Ojuela mine crystals is given in Table II.

The form {110} is often heavily striated parallel to [001] and frequently

TABLE II. LEGRANDITE ANGLE TABLE

(Calculated from x-ray data)
Monoclinic; prismatic $-2/m$

$a:b:c = 1.612:1:1.287$; $\beta = 104°12'$; $p_0:q_0:r_0 = .7983:1.248:1$
$r_2:p_2:q_2 = .8014:.6394:1$; $\mu = 75°48'$; $p_0' = .824$, $q_0' = 1.287$, $x_0' = .253$

Forms	ϕ	ρ	ϕ_2	ρ_2=B	C	A
c 001	90°00′	14°12′	75°48′	90°00′	—	75°48′
a 100	90°00′	90°00′	0°00′	90°00′	75°48′	—
m 110	32°38′	90°00′	0°00′	32°38′	82°24′	57°22′
p $\bar{1}11$	−23°56′	54°37′	119°44′	41°49′	61°18′	109°19′

Crystallographic Elements Derived from Morphology
$a:b:c = 1.606:1:1.287$; $\beta = 104°21'$; $p_0:q_0:r_0 = .8012:1.247:1$
$r_2:p_2:q_2 = .8025:.6426:1$; $\mu = 75°39'$; $p_0' = .827$, $q_0' = 1.287$, $x_0' = .256$

grossly distorted by vicinal faces. Some crystals exhibit strong diagonal striations on $(\bar{1}10)$ and $(\bar{1}\bar{1}0)$ due to oscillation between these prism faces and a form $\{\bar{h}kl\}$. The faces of this form are very small and have $\rho \cong 87°$ so that accurate determination of its indices is impossible. Measurement of faces of this form on three crystals indicates an index close to 10.15.1. The pyramid $p\{\bar{1}11\}$ is usually marked by vicinal planes.

PHYSICAL PROPERTIES

The cleavage of Ojuela mine legrandite is $\{100\}$ fair to poor and its

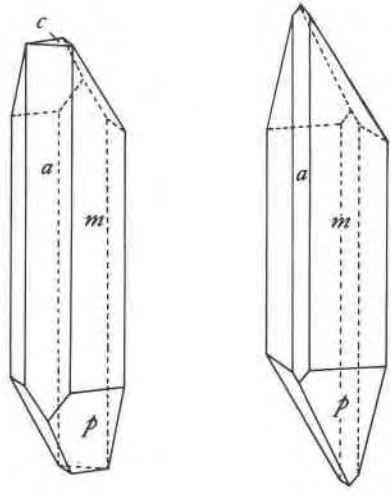

FIG. 1. Crystals of legrandite.

fracture uneven. The mineral is brittle with a hardness of $4\frac{1}{2}$. Density was determined by pycnometer, using toluene of known density. A 60–140 mesh sample weighing 433 mg gave a density of 3.98 g/cm^3. This compares closely with a calculated density from x-ray data of 4.015 g/cm^3 and with the density of 4.01 g/cm^3 reported by Drugman and Hey (1932). The crystals have irregular color distribution varying in blotches from almost colorless to wax yellow (Ridgeway #20). Variation in color intensity of the grains has no appreciable effect on refractive index but the strongly colored grains are obviously pleochroic. Smaller crystals are completely transparent becoming more translucent with increase in size. The luster is vitreous. Drugman and Hey (1932) suggest, for the Flor de Peña material, that the color, though spotty, is not due to inclusions of limonite. This is certainly true of Ojuela mine material.

Optical Properties

The optical properties of Ojuela mine legrandite are given in Table III. For comparison, data of Larsen and Berman (1934) and Drugman and Hey (1932) are also given.

Table III. Optical Properties

	Ojuela n(Desautels 1963)	Flor de Peña n(Larsen & Berman 1934)	Flor de Peña n(Drugman & Hey 1932)
Biaxial	1.702 ± .002 1.709 ± .002 1.740 ± .002	1.702 1.709 1.741	1.675 ± .005 1.690 ± .005 1.735 ± .005

Orientation
X = b
Z$\wedge$ c = 40°
Pleochroism
X colorless to yellow
Y colorless to yellow
Z yellow
2V = 50°
Dispersion r < v distinct
Sign +

X-ray Study

The unit cell dimensions were determined by single crystal precession camera photographs to be a = 12.80 Å ± .01, b = 7.94 Å ± .01, c = 10.22 Å ± .01, β = 104°12′. Systematic omissions of reflections conform to the space group $P2_1/c$. Crystallographic elements were also calculated from the x-ray data and compare closely, Table II, with those derived from

crystal morphology. The *x*-ray powder pattern of the Ojuela legrandite is identical with that of a specimen of the type legrandite obtained from the British Museum (Natural History). The *x*-ray powder data for CuK_α radiation, Ni filter, indexed as far as d = 1.9750 or $2\theta \cong 46°$ are given in Table IV. Intensities were determined by comparison with intensity film strips.

TABLE IV. *X*-RAY POWDER DATA FOR LEGRANDITE, $Zn_2(OH)AsO_4 \cdot H_2O$ FROM THE OJUELA MINE, MAPIMI, DURANGO, MEXICO

(Camera diameter 114.59 mm, Cu/Ni radiation, $CuK_\alpha = 1.5418$ Å)

Measured		Calculated		
I	d_{hkl}	d_{hkl}	hkl	
35	12.36	12.36	100	
71	6.68	6.68	110	
71	5.93	5.90	$\bar{1}11$	
18	5.04	5.04	$\bar{1}02$	
9	4.90	4.87	210	
50	4.19	4.19	012	
100	4.08	4.11	211	
13	3.76	3.74	112	
25	3.64	3.60	$\bar{3}02$	
18	3.44	3.44	121	
18	3.30	3.30	$\bar{2}21$	
4	3.21	3.21	311	
71	3.09	3.10	022	
35	3.03	3.01	$\bar{2}13$	
35	2.98	2.96	$\bar{4}02$	
4	2.89	2.88	$\bar{3}21$	410
9	2.86	2.84	320	
25	2.78	2.78	$\bar{3}13$	
25	2.68	2.67	312	
35	2.62	2.63	411	
3	2.58	2.58	$\bar{1}23$	
3	2.56	2.56	031	$\bar{1}04$
35	2.52	2.51	213	
13	2.48	2.47	$\bar{5}02$	
18	2.44	2.43	230	
25	2.36	2.36	014	
9	2.31	2.31	231	
18	2.22	2.23	313	
25	2.14	2.14	$\bar{3}32$	
4	2.09	2.09	$\bar{1}33$	
6	2.06	2.06	$\bar{2}33$	
6	2.01	2.01	430	
4	1.97	1.97	521	$\bar{2}15$

Chemistry

The legrandite taken for chemical analysis consisted of carefully selected fragments from U.S.N.M. specimen R9493. It was ground to pass 140 mesh in a boron carbide mortar. A semiquantitative spectrographic analysis by Helen Worthing, U. S. Geological Survey, indicated the presence of major amounts of zinc and arsenic, minor amounts of iron and manganese, and the absence of significant amounts of other detectable elements (Waring 1953).

ZnO and As_2O_5 were determined on a 227 mg sample. Arsenic was precipitated as As_2S_5 from cold 10 molal HCl, filtered, dried at 110° C., and weighed as As_2S_5. Zinc was separated as ZnS using a formic acid buffer, the sulfide ignited and weighed as ZnO. Total water was determined by the Penfield method on a 183 mg sample. The H_2O (−) determination and the acid insoluble were done on a 207 mg sample. Total iron was separated by cupferron from a 10% sulfuric acid solution of 124 mg of sample. The cupferrate was ignited to Fe_2O_3 dissolved in acid, and total

Table V. Chemical Analysis of Legrandite

Analysis[1]		Molecular Ratios		Theoretical Composition
ZnO	50.1	.616		53.4
FeO	1.4 } 53.2	.020 } .660	= 4 × .165	
MnO	1.7	.024		
As_2O_5	37.7	.164	= 1 × .164	37.7
H_2O (−)	0.1			
H_2O (+)	8.8	.494	= 3 × .165	8.86
Acid insoluble	0.2			
Total	100.0			

[1] Analyst: R. S. Clarke, Jr.

iron determined spectrophotometrically using o-phenanthrolene. This procedure gave a value of 1.38% calculated as FeO. The reducing capacity of the mineral was determined on a 101 mg sample. It was dissolved in 10% sulfuric acid and titrated potentiometrically with potassium permanganate. The total reducing capacity calculated as FeO gave a value of 1.45% FeO. The close agreement of this value with the value calculated from the total iron determination permitted the assignment of all the iron to the ferrous state. Manganese was determined spectrophotometrically on a 26 mg sample using potassium periodate to develop the permanganate color.

The formula calculated from this analysis, Table V, is $4ZnO \cdot As_2O_5 \cdot$

$3H_2O$. A thermogravimetric analysis was made by Charles A. Kinser of the U. S. Geological Survey, Figure 2. A 250 mg sample of legrandite was subjected to a temperature rise of 2° C. per minute over a range extending from 25° to 400° C. At 360° C. a 6% weight loss occurred representing the loss of water of hydration but retention of (OH). The theoretical water content based on the structural formula $Zn_2(OH)AsO_4 \cdot H_2O$ is 5.9%. An *x*-ray powder pattern of the residue from thermogravimetric analysis

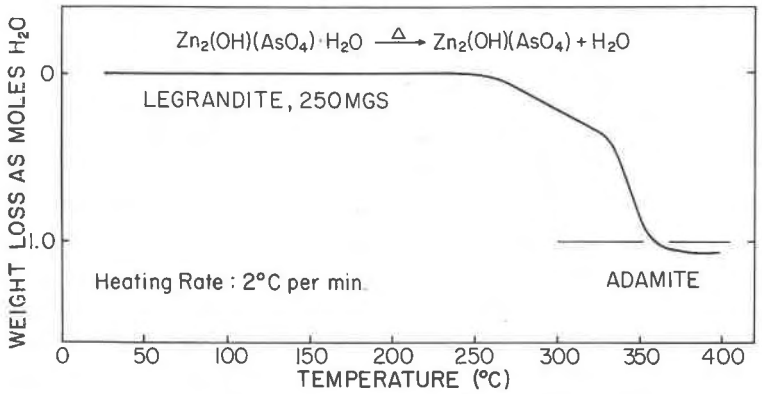

FIG. 2. Thermogravimetric analysis curve for legrandite.

was prepared and proved to be that of adamite $Zn_2(OH)AsO_4$. The structural formula for legrandite, then, is $Zn_2(OH)AsO_4 \cdot H_2O$. This is a new and simpler formula for the species, the original given by Drugman and Hey (1932) being $Zn_{14}(OH)(AsO_4)_9 \cdot 12H_2O$.

The unit cell contains $8[Zn_2(OH)AsO_4 \cdot H_2O]$.

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