

THE CRYSTAL STRUCTURE OF LEGRANDITE

W. JOHN MCLEAN AND JOHN W. ANTHONY, *Department of Geosciences,
University of Arizona, Tucson, Arizona 85721;*

JOSEPH J. FINNEY, *Department of Geology, Colorado School of Mines,
Golden, Colorado 80401 AND*

ROBERT B. LAUGHON, *NASA, Manned Spacecraft Center,
Houston, Texas 77058.*

ABSTRACT

The crystal structure of the mineral legrandite, $Zn_4(AsO_4)_2(OH)_2 \cdot 2H_2O$, has been determined using the Patterson function and refined to an R factor of 5%. The arsenate groups are tetrahedrally coordinated and zinc atoms are four to six coordinated by oxygen. The structure contains an infinite, undulating, edge-sharing chain of zinc polyhedra parallel to the a axis which is weakened once per repeat unit by the presence of a 2.99 Å Zn-O bond. The arsenate tetrahedra share apices with the zinc polyhedra and serve to link chains together.

INTRODUCTION

The mineral legrandite was originally described by Drugman and Hey (1932) and was re-examined more recently by Finney (1963) and also by Desautels and Clarke (1963) on material from Mapimi, Durango, Mexico. These latter two publications established the chemical composition of legrandite as $4[Zn_4(AsO_4)_2(OH)_2 \cdot 2H_2O]$ in the space group $P2_1/c$.

EXPERIMENTAL

Cleavage fragments of Mapimi legrandite (University of Arizona Mineralogical Museum No. 4191) were ground into spheres and a sphere of radius .069 mm was chosen for data collection. In the process of setting the crystal for data collection on an automated four circle diffractometer, the unit cell was refined by least squares methods with the following results: a 12.805(2) Å, b 7.933(1), c 10.215(2), and β 104° 23.3(3)'. Standard deviations, in parentheses, refer to the last digit. Monochromatized MoK α radiation was used to collect 1712 reflections of intensity data. Of these, 1375 were sufficiently strong to be considered as observed. The intensities were corrected for absorption by linear interpolation of the spherical corrections taken from the *International Tables for X-Ray Crystallography*, Vol. II, pp. 304 and 305 with μR equal to 1.155.

STRUCTURE DETERMINATION

The intensities were reduced to structure factors and the structure was solved routinely for the Zn and As atoms from a three-dimensional Patterson function. The four Zn and two As atoms were found in general positions. Crude positional parameters were refined one cycle by full matrix least squares and the R factor ($R = \sum ||F_o| - |F_c|| / |F_o|$) after refinement was 26 percent. The twelve symmetry independent oxygen atoms were located in general positions in a difference synthesis. Insertion

TABLE 1. ATOMIC PARAMETERS FOR LEGRANDITE^a

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> ₁₁	<i>B</i> ₂₂	<i>B</i> ₃₃	<i>B</i> ₁₂	<i>B</i> ₁₃	<i>B</i> ₂₃
As(1)	.1499 (1)	.0548 (2)	.2202 (2)	.51	.37	.32	-.03	-.01	.06
As(2)	.3853 (1)	.4221 (2)	.2140 (2)	.51	.38	.30	.04	.05	-.11
Zn(1)	.4031 (2)	.0500 (3)	.3896 (2)	.88	.86	.71	-.03	-.06	.02
Zn(2)	.2529 (2)	.3314 (3)	.4625 (2)	.63	.85	.80	-.07	.04	-.06
Zn(3)	.3620 (2)	.8063 (2)	.1282 (2)	1.05	.50	.78	.04	-.05	.18
Zn(4)	.0100 (2)	.2417 (3)	.4408 (2)	.91	1.22	.98	-.01	.21	-.07
O(1)	.269 (1)	.955 (2)	.260 (1)	1.26	.81	.66	.53	-.09	-.29
O(2)	.140 (1)	.159 (2)	.073 (1)	.83	.83	.28	.38	-.38	-.20
O(3)	.133 (1)	.188 (1)	.340 (1)	.13	2.36	.70	-.39	.00	-.29
O(4)	.050 (1)	.913 (2)	.206 (1)	1.55	.90	.90	-.86	.48	-.63
O(5)	.479 (1)	.950 (1)	.241 (1)	1.00	.84	.86	-.34	.40	-.82
O(6)	.352 (1)	.344 (2)	.057 (1)	2.18	1.06	-.22	-.23	.47	-.78
O(7)	.344 (1)	.290 (1)	.320 (1)	.99	.43	.62	-.17	.78	1.28
O(8)	.320 (1)	.608 (2)	.218 (1)	1.34	.92	.79	.41	.27	.22
O(9)	.081 (1)	.534 (2)	.143 (1)	1.89	1.65	2.37	-.16	.47	.95
O(10)	.448 (1)	.663 (1)	.014 (1)	.85	.95	.64	.47	.13	-.05
O(11)	.275 (1)	.578 (2)	.468 (1)	1.94	1.75	.48	.06	.71	-.23
O(12)	.089 (1)	.731 (2)	.435 (1)	1.66	2.54	2.13	.15	.20	.02

^a Standard deviations in parentheses refer to the last digit. Atomic numbering is shown in Figure 3.

of these reduced *R* to 19 percent and three cycles of least squares refinement with isotropic temperature factors reduced *R* to 8 percent. One additional cycle with anisotropic temperature factors reduced *R* to 5 percent for observed reflections only and 7 percent for all reflections. A final difference map showed background errors to be about as high as was expected for one electron of scattering matter and the hydrogen atoms were not located. The final atomic parameters are given in Table 1 and the final structure factors are listed in Table 2¹. The atomic scattering factors used were for Zn²⁺, As²⁺, and O¹⁻ ions as given in the *International Tables for X-Ray Crystallography*, Vol. III, pp. 202-207.

DESCRIPTION OF THE STRUCTURE

The crystal structure of legrandite is more complex than the relatively simple composition would indicate. We know of no structure with which it is easily compared.

¹ To obtain a copy of Table 2, order NAPS Document #01481 from National Auxiliary Publications Service, of the A.S.I.S., c/o CCM Information Corporation, 909 Third Avenue, New York, N. Y. 10022; remitting \$2.00 for microfiche or \$5.00 for photocopies, in advance, payable to CCMIC—NAPS.

The unit cell of legrandite contains $4[\text{Zn}_4(\text{AsO}_4)_2(\text{OH})_2 \cdot 2\text{H}_2\text{O}]$ in the space group $P2_1/c$. The two arsenate groups in the asymmetric unit are approximately tetrahedral with As-O distances ranging from 1.67 to 1.70 Å and O-As-O angles varying from 106.1 to 113.5°. Interatomic distances and angles are detailed in Table 3. The four asymmetric Zn atoms are four to six coordinated by oxygen. Zn(1) has six neighbors with Zn-O distances ranging from 2.03 to 2.15 and O-Zn-O angles between 82 and 106° and these form a slightly distorted octahedron. Zn(4) is five-coordinated with oxygen atoms at distances of 1.99 to 2.12 Å. These form a polyhedron that is probably best described as a somewhat distorted tetragonal pyramid with the Zn located near the center of the base, but slightly within the polyhedron. A sixth oxygen is 2.99 Å from the Zn and, if included in the coordination polyhedron, forms a considerably

TABLE 3. INTERATOMIC DISTANCES AND ANGLES^a

<i>i</i>	<i>j</i>	<i>d_{ij}</i>	<i>i</i>	<i>j</i>	<i>k</i>	Angle (<i>ijk</i>)
As(1)-O(1)		1.68 Å	O(1)-As(1)-O(2)			107.9
As(1)-O(2)		1.69	O(1)-As(1)-O(3)			113.5
As(1)-O(3)		1.67	O(1)-As(1)-O(4)			109.5
As(1)-O(4)		1.67	O(2)-As(1)-O(3)			110.3
	aver.	1.678	O(2)-As(1)-O(4)			109.5
			O(3)-As(1)-O(4)			106.1
As(2)-O(5)		1.70	O(5)-As(2)-O(6)			107.6
As(2)-O(6)		1.67	O(5)-As(2)-O(7)			111.8
As(2)-O(7)		1.68	O(5)-As(2)-O(8)			111.1
As(2)-O(8)		1.70	O(6)-As(2)-O(7)			110.1
	aver.	1.688	O(6)-As(2)-O(8)			109.6
			O(7)-As(2)-O(8)			106.7
Zn(1)-O(1)		2.03	O(1)-Zn(1)-O(5)			81.9
Zn(1)-O(5)		2.14	O(1)-Zn(1)-O(6)			106.9
Zn(1)-O(6)		2.14	O(1)-Zn(1)-O(7)			86.7
Zn(1)-O(7)		2.11	O(1)-Zn(1)-O(10)			98.9
Zn(1)-O(10)		2.11	O(1)-Zn(1)-O(10)			167.6
Zn(1)-O(10)		2.11	O(5)-Zn(1)-O(6)			171.0
	aver.	2.107	O(5)-Zn(1)-O(7)			106.4
			O(5)-Zn(1)-O(10)			91.5
Zn(2)-O(2)		2.04	O(5)-Zn(1)-O(10)			88.3
Zn(2)-O(3)		2.07	O(6)-Zn(1)-O(7)			76.3
Zn(2)-O(6)		1.97	O(6)-Zn(1)-O(10)			85.5
Zn(2)-O(7)		2.11	O(6)-Zn(1)-O(10)			83.2
Zn(2)-O(9)		3.81 ^b	O(7)-Zn(1)-O(10)			161.8
Zn(2)-O(11)		1.98	O(7)-Zn(1)-O(10)			88.8
	aver.	2.034	O(10)-Zn(1)-O(10)			88.9
			O(2)-Zn(2)-O(3)			80.3
			O(2)-Zn(2)-O(6)			102.4
			O(2)-Zn(2)-O(7)			167.7
			O(2)-Zn(2)-O(9)			96.9

^a Standard deviations of distances are about 0.014 Å and of angles about 0.5°. Atomic numbering is shown in Figure 3.

^b Omitted from average.

TABLE 3.—(Continued)

i	j	d_{ij}	i	j	k	Angle (ijk)
Zn(3)	O(1)	2.32	O(2)	Zn(2)	O(11)	93.5
Zn(3)	O(5)	2.00	O(3)	Zn(2)	O(6)	101.5
Zn(3)	O(8)	1.97	O(3)	Zn(2)	O(7)	87.4
Zn(3)	O(10)	2.12	O(3)	Zn(2)	O(9)	61.9
Zn(3)	O(11)	1.96	O(3)	Zn(2)	O(11)	129.9
			O(6)	Zn(2)	O(7)	80.0
			O(6)	Zn(2)	O(9)	152.0
	aver.	2.074	O(6)	Zn(2)	O(11)	128.1
			O(7)	Zn(2)	O(9)	94.4
Zn(4)	O(2)	2.03	O(7)	Zn(2)	O(11)	77.0
Zn(4)	O(3)	2.12	O(9)	Zn(2)	O(11)	69.8
Zn(4)	O(4)	1.99	O(1)	Zn(3)	O(5)	78.1
Zn(4)	O(9)	2.07	O(1)	Zn(3)	O(8)	83.9
Zn(4)	O(9)	2.99 ^b	O(1)	Zn(3)	O(10)	177.6
Zn(4)	O(12)	2.01	O(1)	Zn(3)	O(11)	88.7
			O(5)	Zn(3)	O(8)	116.0
	aver.	2.044	O(5)	Zn(3)	O(10)	101.8
			O(5)	Zn(3)	O(11)	113.9
O(9)	O(4)	2.76	O(8)	Zn(3)	O(10)	94.0
O(9)	O(8)	3.02	O(8)	Zn(3)	O(11)	126.7
O(11)	O(8)	2.76	O(10)	Zn(3)	O(11)	93.5
O(12)	O(4)	2.73	O(2)	Zn(4)	O(3)	79.5
O(12)	O(11)	2.62	O(2)	Zn(4)	O(4)	108.8
			O(2)	Zn(4)	O(8)	76.4
			O(2)	Zn(4)	O(9)	150.2
			O(2)	Zn(4)	O(12)	94.4
			O(3)	Zn(4)	O(4)	89.3
			O(3)	Zn(4)	O(9)	93.1
			O(3)	Zn(4)	O(9)	92.6
			O(3)	Zn(4)	O(12)	169.2
			O(4)	Zn(4)	O(9)	174.6
			O(4)	Zn(4)	O(9)	99.7
			O(4)	Zn(4)	O(12)	101.2
			O(9)	Zn(4)	O(9)	75.3
			O(9)	Zn(4)	O(12)	76.7
			O(9)	Zn(4)	O(12)	88.3

distorted octahedron. Zn(2) is also five-coordinated with distances of 1.97 to 2.11 Å and the resulting polyhedron may be described as either a tetragonal pyramid or a trigonal dipyramid. The sixth oxygen, which tends to form a very distorted octahedron, is situated at 3.81 Å from Zn(2). Zn(3) is three coordinated at 1.96–2.01 Å forming a fairly regular trigonal planar arrangement. The fourth oxygen, which produces a slightly distorted trigonal pyramid, is at 2.12 Å and the fifth oxygen, which gives a somewhat distorted trigonal dipyramid, is at 2.32 Å.

All four apices of both arsenate groups are shared with Zn polyhedra: three apices are shared by two Zn polyhedra which themselves share an edge, and one apex is shared by only a single Zn polyhedron. If Zn(4) is considered to possess octahedral coordination the Zn(1), Zn(2), and Zn(4) polyhedra form a continuous edge-sharing chain through the

structure with each polyhedron sharing two edges with other polyhedra of this chain. The Zn(3) trigonal dipyramid shares one edge with the Zn(1) octahedron and thus becomes a side member to the chain. The polyhedra of Zn(1), Zn(2), Zn(4) and Zn(3) share 3, 2, 2, and 1 edges respectively.

The edge-sharing chain undulates through the structure with its general trend parallel to the a axis. Most of the lateral undulation is parallel to b and the chain viewed from the c direction forms a symmetrical "S" across the a periodicity, as shown in Figure 1.

The structure is two chains deep in the c direction with adjacent chains related by the c glide as is shown in Figure 2. Glide-related chains and those related by the b periodicity are linked by corner sharing through both arsenate tetrahedra and the trigonal dipyramid of Zn(3). All three of these polyhedra have two apices in common with one chain and one apex each linked to a glide-related chain and to a chain periodically above or below in the b direction.

The cleavage of legrandite was determined by Desautels and Clarke (1963) as fair to poor parallel to $\{100\}$. Examination of the structure reveals an undulating slot-shaped cavity parallel to $\{100\}$ and that cleavage of the structure through this cavity would require a minimum of bond breakage.

As stated in a previous paragraph, the Zn(4) polyhedron was assumed to be an octahedron to produce the continuous undulating chain-like feature. In reality the Zn(4)-O(9) distance is 2.99 Å and if it is disregarded as a bond, the polyhedron becomes a tetragonal pyramid and the chain is broken in the center of the slot-shaped cavity. This leaves only one arsenate tetrahedron to bridge the slot, and the breaking of only four Zn-O bonds per cell is required to produce cleavage.

The structure of legrandite is shown in perspective and in stereo in Figures 3 and 4.

Despite the fact that the hydrogen atoms were not located, it is possible to speculate that O(10) and O(11) are hydroxyl oxygens and O(9) and O(12) are water oxygens. The hydroxyl groups, because they are charged, should have a greater tendency to form bonds than uncharged, but dipolar, water molecules. O(10) forms three ionic bonds to zinc atoms and apparently no hydrogen bonds; O(11) forms two ionic bonds to zinc, and appears to donate its hydrogen to O(8). O(9) and O(12) form only one strong ionic bond each. In addition, O(9) may form the weak (2.99 Å) bond previously mentioned, and donate its hydrogens to O(4) and O(6); O(12) apparently donates its hydrogens to O(4) and O(11).

Temperature factors of the heavy atoms appear to be reasonable, with isotropic temperature factors for zincs ranging from 0.81 to 1.10

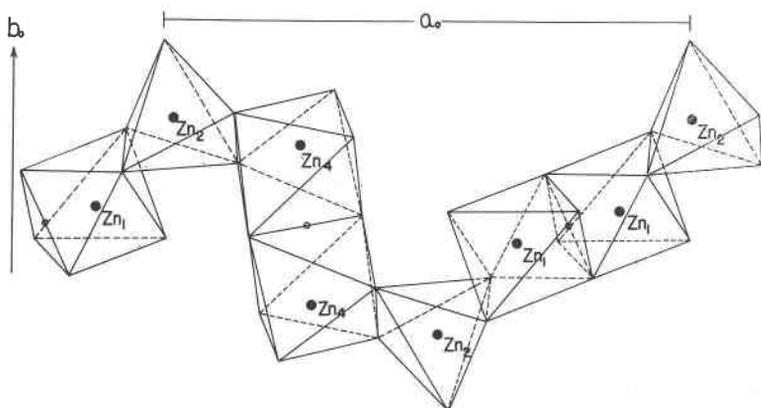


FIG. 1. An undulating chain in the structure of legrandite. The chain is viewed from the $-c$ direction; a is horizontal.

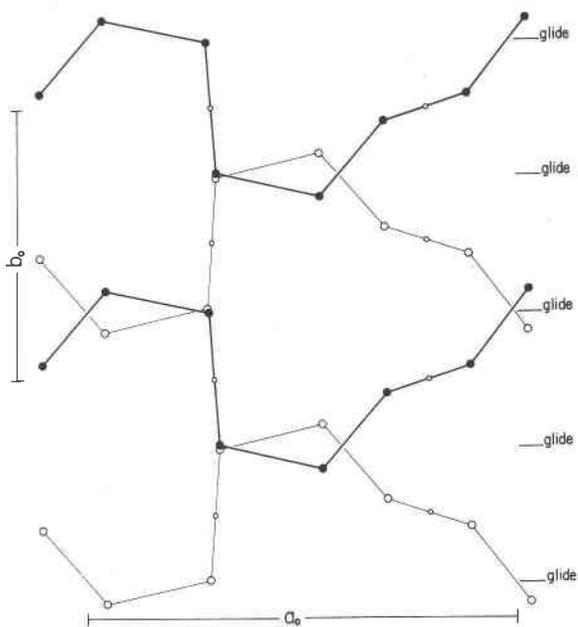


FIG. 2. Schematic diagram of four undulating chains in the structure of legrandite, viewed from the $-c$ direction with a horizontal. The two chains in front (heavy) are related to one another by the b periodicity. The pair of light chains is related to the heavy pair by the c glide and is displaced half the c periodicity (5.11 \AA) into the plane of the paper.

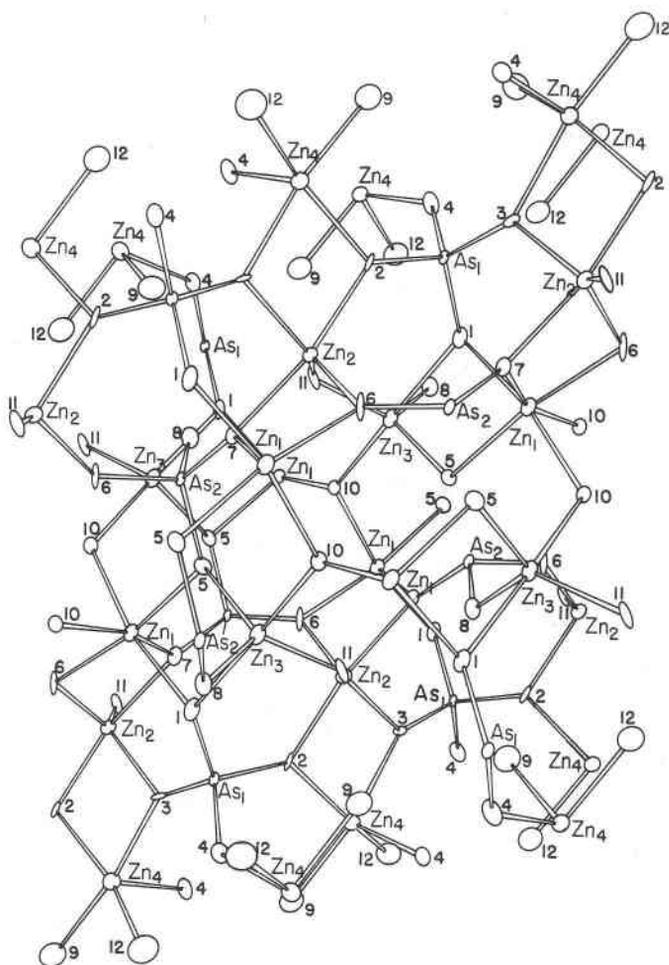


FIG. 3. Perspective view of the structure of legrandite seen from the $-b$ direction with $+a$ down and $+c$ to the right.

and for arsenics 0.44 and 0.45. Several oxygens are very anisotropic, but magnitudes seem to be generally reasonable and to reflect the strength with which the atom is bonded. O(9) and O(12) which are single bonded have temperature factors of about 2.0 and 2.1. The temperature factor of O(11), which is double bonded, is 1.4, that of O(10), which is triple bonded, is 0.8, and arsenate oxygens with the strong As-O bond and either one or two bonds to zinc have temperature factors from about 0.6 to 1.1.

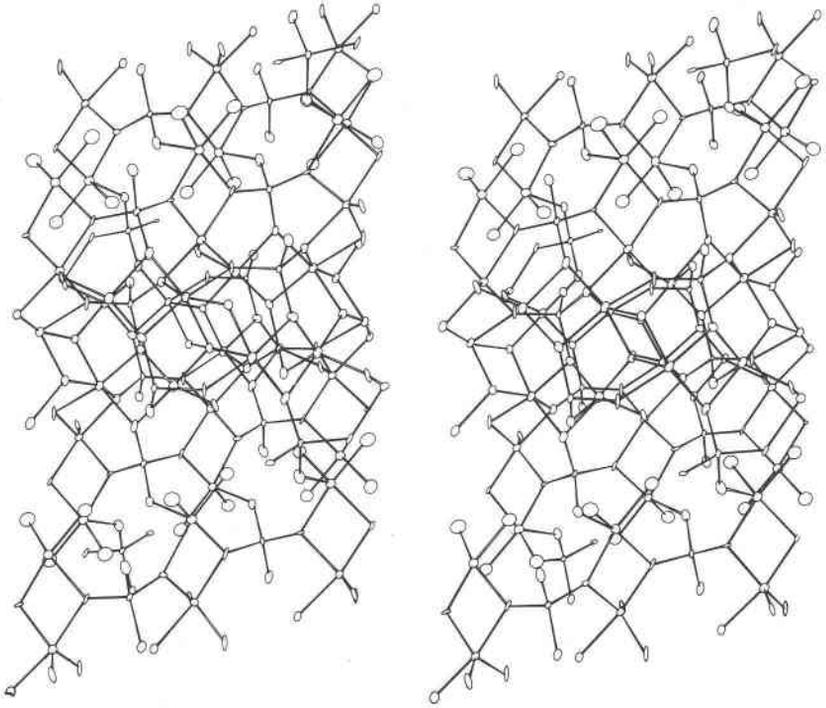


FIG. 4. Stereo view of the legrandite structure. Orientation is the same as Fig. 3.

ACKNOWLEDGMENTS

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