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The Crystal Structure of Grandidierite, (Mg, Fe)Al₃SiBO₉

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Grandidierite, (Mg_{0.9}Fe_{0.1})Al₃SiBO₉, $a = 10.335 \pm 0.002$, $b = 10.978 \pm 0.002$, $c = 5.760 \pm 0.002$ Å, *Pbnm*, $Z = 4$, has Al-O octahedra, Al-O and Mg-O trigonal bipyramids, Si-O tetrahedra, and B-O triangles. Two independent sets of edge-linked Al-O octahedral chains run parallel to *c* [001] and are connected along *a* [100] by the B-centered triangles and Al-centered trigonal bipyramids and along *b* [010] by the Mg-centered trigonal bipyramids and silicate tetrahedra. The crystal structure of grandidierite is related to andalusite. Average M-O distances are Al^{VI}-O 1.897 and 1.910, Al^V-O 1.838, Mg^V-O 2.042, Si^{IV}-O 1.619, and B^{III}-O 1.358 Å.

1. Introduction and description of the material

Grandidierite was described and named as a new mineral by Lacroix (1902). Its type locality is Andrahomana, near Fort Dauphin, in the southern extremity of Madagascar, where the mineral occurs as elongated anhedral individuals up to 8 cm in length associated with quartz, orthoclase, almandine, spinel, biotite, and andalusite, often poikilistically enclosing grains of these minerals. Our specimen label simply gave the location as Fort Dauphin, the bluish-green grandidierite occurring as small rounded grains and aggregates associated with pale blue spinel and distributed through platy masses of phlogopite.

The precise chemistry of grandidierite was not revealed until recently. The original analysis of Pisani in Lacroix appears in Table 1 along with a recent analysis by Scoon in McKie (1965). Our sample was qualitatively examined for Mg, Fe, Al, and Si by X-ray emission microanalysis and it gave good agreement with the element ratios cited in McKie's paper. Thus, we elected the composition (Mg_{0.90}Fe_{0.10})Al₃SiBO₉ for our structure analysis.

Prior to the appearance of McKie's article, we obtained crystal data for grandidierite which proved to be in very good agreement with his data. These data are given in Table 2. It was then considered that grandidierite may be structurally related to sillimanite,

Table 1. *Grandidierite. Chemical analyses*

	Pisani in Lacroix (1902)	Scoon in McKie (1965)
SiO ₂	20.46	20.39
TiO ₂	—	0.13
Al ₂ O ₃	51.75	52.12
B ₂ O ₃	2.81	11.57
Fe ₂ O ₃	7.29	0.80
FeO	4.11	2.87
MnO	—	0.04
MgO	7.91	12.04
CaO	0.86	nil
Na ₂ O	2.94	0.04
K ₂ O	0.38	0.09
H ₂ O ⁺	1.64	—
H ₂ O ⁻	—	nil
	100.15	100.09

Table 2. *Grandidierite. Crystal data*

	This paper*	McKie†
<i>a</i>	10.34 Å	10.335 Å
<i>b</i>	10.99	10.978
<i>c</i>	5.75	5.760
Space group	<i>Pbnm</i>	
<i>Z</i>	4	
Formula	(Mg _{0.9} Fe _{0.1})Al ₃ SiBO ₉	
<i>q</i> _{obs}	2.99	2.97 ₆
<i>q</i> _{calc}		2.96
α		1.590
β		1.618
γ		1.623
$2V$		30°

* Estimated standard errors ± 0.01 Å.

† Estimated standard errors ± 0.002 Å. These data were used in the final refinement.

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Al_2SiO_5 , a speculation also made by McKie – principally on the basis of the nearly identical *c*-axis translations which define the axis of AlO_6 edge-linked octahedral chains.

2. Collection of intensities

Three-dimensional data, consisting of 674 independent reflections of the 0-, 1-, 2-, 3-, and 4-levels with *c*-rotation axis using a manual equi-angle Weissenberg counter-diffractometer and Zr-filtered Mo radiation, were obtained in this study. The crystal was a nearly spherical grain of 0.15 mm mean radius. These data were then corrected for absorption, Lorentz and polarization effects, using the GNABS program of Burnham (author's copy) modified by Knowles and Stephenson (personal communication).

3. Deduction of the structure

A three-dimensional Patterson map was prepared. The projection $P(xy)$ gave clues to the structure. We assumed initially a centrosymmetric structure and a relationship with sillimanite. Hence, one set of Al–O was placed at the cell origin. Since the unit cell contains $(\text{Mg}, \text{Fe})_4\text{Al}_{12}\text{Si}_4\text{B}_4\text{O}_{36}$, the (Mg, Fe), Si and B and some or all of the Al atoms must be confined to fourfold special positions with point symmetries $\bar{1}$ or *m*.

The Patterson section $P(xy0)$ suggested a second Al–O chain at $\frac{1}{2}, 0, 0$ and consequently the remaining Al atoms must also be confined to a fourfold special position. In fact, since the $\bar{1}$ positions are filled, the remaining cations must appear on the special positions $x, y, \frac{1}{4}$. The Al atoms at $0, 0, 0$ and $\frac{1}{2}, 0, 0$ then permitted location of these other cations (except B) since the Patterson section $P(xy\frac{1}{4})$ shows two well-defined molecular images. The oxygen atoms were then located by geometrical considerations and at the $R=0.16$ stage, the remaining B atom was located by a difference synthesis.

4. Refinement

Scattering factor tables were prepared for $(0.90\text{Mg}^+ + 0.10\text{Fe}^+)$, Al^{2+} , Si^{2+} , B^{2+} , and O^- from the data given in *International Tables for X-ray Crystallography* (1962). The data were refined by the program *ORFLS*

of Busing, Martin & Levy (1962). At the final stage of full-matrix refinement, 24 strong reflections showing extinction were excluded from the refinement and all other reflections were given unit weight. The final reliability index is 0.078, including isotropic temperature factor refinement. When refined for anisotropic thermal motion, all r.m.s. displacements were spherical within the limits of error. The final coordinates and isotropic temperature factors are given in Table 3 and the F_o and F_c values are presented in Table 5. Pertinent interatomic distances, to be discussed later, are labelled in Fig. 1.

5. Discussion of the structure

The grandierite structure consists of four kinds of oxygen polyhedra: boron centered triangular groups; silicon centered tetrahedra; magnesium (iron) centered and aluminum centered distorted trigonal bipyramids; and aluminum centered octahedra (Fig. 1). Of considerable interest is the occurrence of magnesium in fivefold coordination, previously encountered in only one other silicate mineral structure, yoderite (Fleet & Megaw, 1962), though in that mineral much of the magnesium in the *A*(2) site is mixed with aluminum. Our average $(\text{Mg}_{0.90}\text{Fe}_{0.10})\text{—O}$ bond distance is 2.042 Å, significantly larger than the value of 1.935 Å for the *A*(2) site of Fleet & Megaw. Their *A*(3) site is also the midpoint of a trigonal bipyramid containing aluminum, of mean distance 1.870 Å corresponding to our Al(3)–O distance of 1.838 Å. Regarding fivefold coordination for magnesium in silicate structures, these recent findings are not particularly unusual; magnesium has a range of coordination numbers, from eight in pyrope garnet to four in the melilites.

The five-coordinated Al and Mg have polyhedra that are substantially distorted and geometrically lie somewhere between the trigonal bipyramid and the tetragonal pyramid. For the ideal trigonal bipyramid, one O–X–O angle is 180°, three are 120°, and the remaining six are 90°. The tetragonal pyramid is not as simple as the central cation is not fixed in the plane of the base. However, two angles should be expected to lie somewhere below 180°, four angles somewhat greater than 90°, and four less than 90°. Table 4 is a summary of angles observed for five-apex polyhedra in the grandierite

Table 3. *Grandierite. Final coordinates and standard errors (in parentheses)*

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
Mg	0.0933 (2)	0.2188 (2)	$\frac{1}{4}$	0.53 (5)
Al(1)	0	0	0	0.39 (5)
Al(2)	$\frac{1}{2}$	0	0	0.39 (5)
Al(3)	0.2262 (2)	0.4478 (2)	$\frac{1}{4}$	0.33 (5)
Si	0.4339 (2)	0.2633 (2)	$\frac{1}{4}$	0.27 (5)
B	0.2508 (7)	0.0003 (7)	$\frac{3}{4}$	0.30 (13)
O(1)	0.2760 (4)	0.2881 (4)	$\frac{1}{4}$	0.35 (9)
O(2)	0.1187 (4)	0.0218 (4)	$\frac{1}{4}$	0.62 (10)
O(3)	0.1217 (5)	–0.0036 (4)	$\frac{3}{4}$	0.57 (10)
O(4)	0.4737 (4)	0.1211 (4)	$\frac{1}{4}$	0.33 (10)
O(5)	0.5460 (4)	0.0992 (4)	$\frac{3}{4}$	0.47 (10)
O(6)	–0.0077 (3)	0.1703 (3)	–0.0239 (7)	0.53 (7)
O(7)	0.1804 (3)	0.5019 (3)	–0.0462 (7)	0.62 (8)

dierite, andalusite, and yoderite structures. Although the angles vary substantially from structure to structure, they may be regarded as examples of distorted trigonal bipyramids.

The remaining aluminum atoms, Al(1) and Al(2) occur in the centers of edge-linked octahedra having average Al-O distances of 1.897 and 1.910 Å respectively. The chains of octahedra run parallel to the *c*

axis and are responsible for the *c*-translation of 5.76 Å, the repeat distance for two octahedral units. Bridging the two non-equivalent aluminum-oxygen octahedral chains along the *a* axis are boron-centered triangles as well as aluminum-centered trigonal bipyramids. Along the *b* axis, the non-equivalent octahedral chains are bridged by magnesium-centered trigonal bipyramids and silicate tetrahedra.

Table 4. Interatomic angles for Mg-O and Al-O five-coordinated polyhedra in mineral silicates

Tetragonal pyramid*	Trigonal bipyramid	Grandierite		Andalusite†	Yoderite‡	
		Mg-O	Al-O		A ₂ -O	A ₃ -O
141.1°	180.0°	174.6°	168.9°	160.9°	180.0°	176.5°
141.1	120.0	126.2	132.1	126.2	124.6	120.4
109.5	120.0	126.2	112.1	126.2	124.6	120.4
109.5	120.0	112.9	112.1	105.9	110.5	113.5
109.5	90.0	112.9	100.5	98.9	98.4	100.2
109.5	90.0	106.7	99.2	98.9	98.4	100.2
83.6	90.0	105.1	99.2	92.5	97.3	93.8
83.6	90.0	81.6	94.7	92.5	82.6	84.4
83.6	90.0	78.2	94.7	86.9	82.6	84.4
83.6	90.0	78.2	88.1	74.1	81.3	82.4

* For a model with X-O distances = 1.80 Å. X is 0.60 Å from the base.

† Coordinates from Burnham & Buerger (1961).

‡ Coordinates from Fleet & Megaw (1962). A₂ and A₃ are their sites with mixed species.

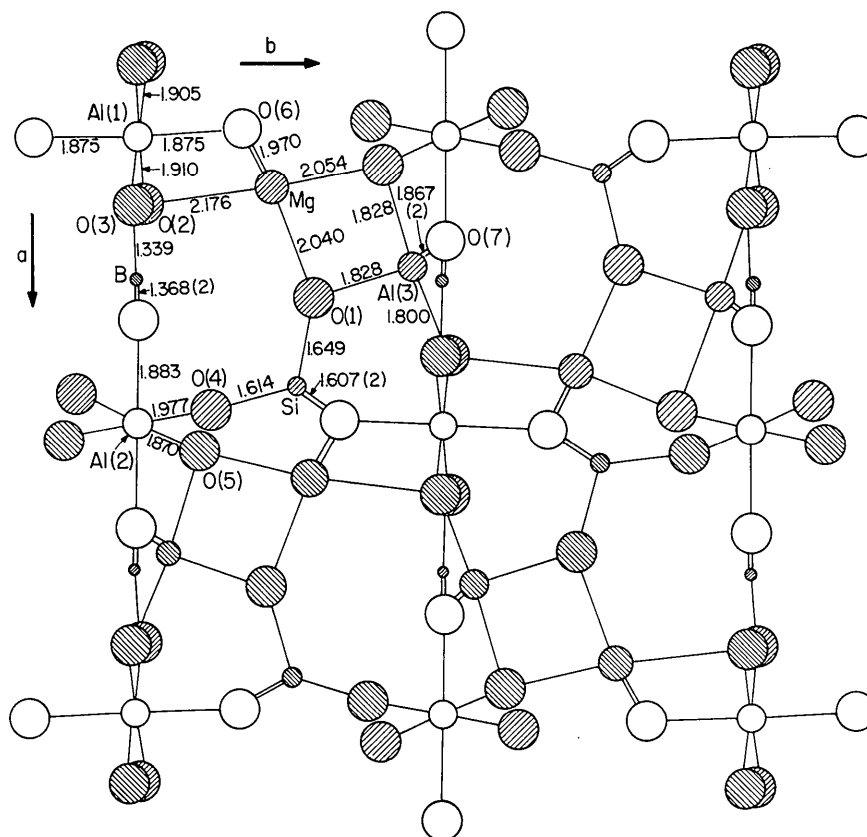


Fig. 1. The *z*-axis projection of one unit cell of grandierite. Open circles are at $z \sim 0$ and $\frac{1}{2}$, ruled circles running NE-SW are at $z = \frac{1}{4}$ and running NW-SE at $z = \frac{3}{4}$. Atoms in one asymmetric unit are identified and metal-oxygen distances are given. E.s.d.s are ± 0.004 (Al^{IV}-O), ± 0.006 (Al^V-O, Mg-O, and Si-O), and ± 0.010 Å (B-O). E.s.d.s in bond angles are 0.2° , except for O-B-O which is 0.5° .

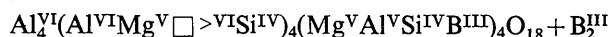
this is true for Al(3)-O(7) and B-O(7), but Al(2)-O(7) does not conform to this expectation.

Relationship with andalusite

Grandierite appears to be more closely related to andalusite than sillimanite. Andalusite has $a=7.794$, $b=7.898$, $c=5.559$ Å, space group $Pnmm$ (Burnham & Buerger, 1961) and if a new cell with $\mathbf{A} = -(\mathbf{a} + \mathbf{b})$, $\mathbf{B} = \mathbf{a} - \mathbf{b}$, and $\mathbf{C} = \mathbf{c}$ with twice the volume of the standard andalusite cell is chosen, an orientation of the octahedral chains similar to grandierite is evident. This cell has dimensions $A=B=11.10$ Å and $\beta=90^\circ 05'$.

The andalusite crystal structure as refined by Burnham & Buerger (1961) is drawn in Fig. 2 to show the relationship with grandierite. In this diagram, the metals are identified as those which appear in the grandierite structure and it is seen that the following formulae relate grandierite to andalusite:

Grandierite



Andalusite



Grandierite cannot be considered a derivative structure of andalusite strictly on the basis of ordering of cations over the positions in andalusite since the 'substitutions' do not involve the same coordination numbers. Even though the two structures are topologically distinct, we suggest that their structural relationship is sufficient to warrant classification of grandierite with andalusite.

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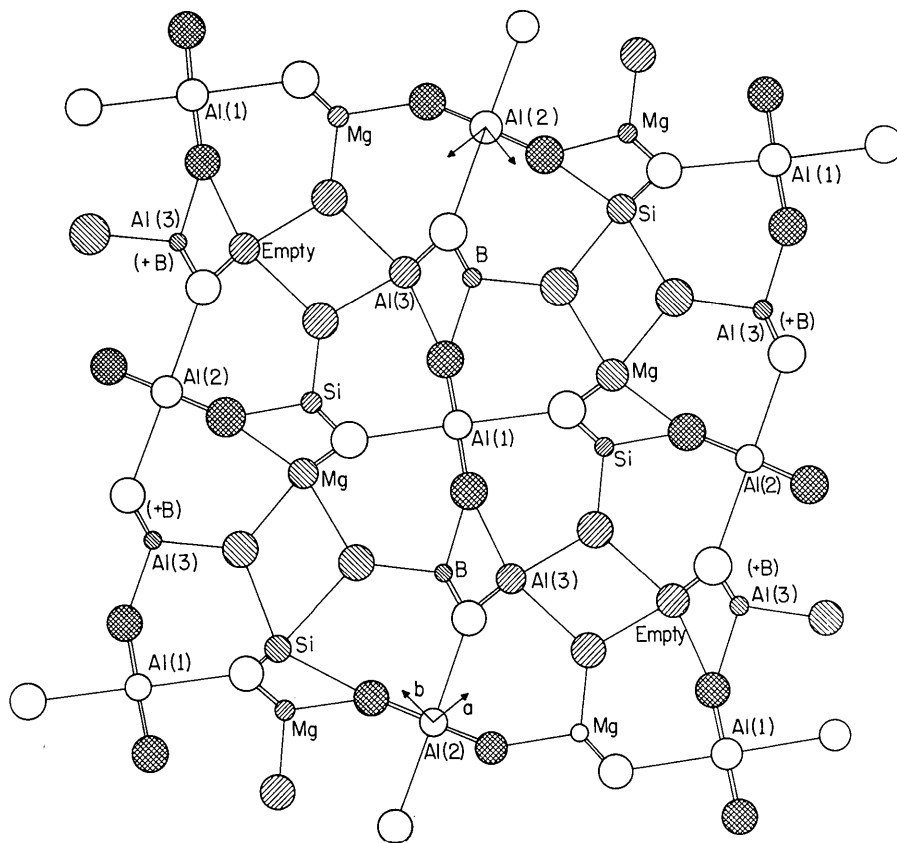


Fig. 2. The z-axis projection of the crystal structure of andalusite [coordinates from Burnham & Buerger (1961)] reoriented to show its relationship with grandierite. Open circles are at $z \sim \frac{1}{4}$ and $\frac{3}{4}$, ruled circles running NE-SW are at $z = \frac{1}{2}$ and running NW-SE at $z = 0$. Cross-hatched circles represent atoms at both $z = \frac{1}{4}$ and $z = \frac{3}{4}$. The identified metals refer to the species which approximate these positions in the grandierite structure.