

## THE SYMMETRY AND CRYSTAL STRUCTURE OF GORCEIXITE, $\text{BaAl}_3[\text{PO}_3(\text{O},\text{OH})]_2(\text{OH})_6$ , A MEMBER OF THE ALUNITE SUPERGROUP

TASHIA J. DZIKOWSKI, LEE A. GROAT<sup>§</sup> AND JOHN L. JAMBOR

Department of Earth and Ocean Sciences, University of British Columbia,  
Vancouver, British Columbia V6T 1Z4, Canada

### ABSTRACT

The crystal structure of the Ba–Al phosphate mineral gorceixite,  $a$  7.0538(3),  $c$  17.2746(6) Å,  $V$  744.4(2) Å<sup>3</sup>, space group  $R\bar{3}m$ ,  $Z = 3$ , has been refined to an  $R_1$  index of 2.3% on the basis of 253 unique reflections measured using MoK $\alpha$  radiation on an automated single-crystal diffractometer. The specimen, from the Rapid Creek area, Yukon Territory, has rhombohedral rather than monoclinic  $Cm$  symmetry previously reported for the species. The crystal-structure refinement shows that the atomic arrangement of gorceixite is similar to that of other members of the alunite supergroup. The Ba–O and Ba–OH distances are 2.825 and 2.859 Å (both  $\times 6$ ), respectively, and the volume of the  $\text{Ba}(\text{O},\text{OH})_{12}$  polyhedron is 55.64 Å<sup>3</sup>. Energy-dispersion spectra and electron-microprobe analyses indicate that the site is completely occupied by Ba, but the site occupancy refines to 88% occupancy; the reason for this is unclear. The average Al–O, OH and P–O distances are 1.906 and 1.544 Å, respectively, and the OH–H distance is 0.980 Å. Interatomic distances [H...O(2) = 1.904 Å and OH...O(2) = 2.884 Å] and a bond-valence analysis suggest that each O(2) atom is involved in hydrogen bonding (as an acceptor) with three different OH groups. However, the low bond-valence sum for O(2) suggests that it not only acts as an acceptor but functions as a donor as well. No hydrogen-atom sites could be identified from the difference-Fourier map, but the presence of OH groups at the O(2) site would help resolve the problem of charge balance. Assuming equal occupancy of the O(2) site by O and OH, the general formula of gorceixite is  $\text{BaAl}_3[\text{PO}_3(\text{O},\text{OH})]_2(\text{OH})_6$ . Although  $R\bar{3}m$  is the most appropriate space-group for the gorceixite sample studied here, we do not claim that all gorceixite samples crystallize in this space group. Different conditions of formation and compositions might be responsible for the lower symmetry observed previously, but the mechanism to achieve the symmetry lowering remains unclear.

**Keywords:** gorceixite, crystal structure, alunite supergroup, barium.

### SOMMAIRE

Nous avons résolu la structure cristalline de la gorceixite, minéral phosphaté de Ba–Al,  $a$  7.0538(3),  $c$  17.2746(6) Å,  $V$  744.4(2) Å<sup>3</sup>, groupe d'espace  $R\bar{3}m$ ,  $Z = 3$ , jusqu'à un résidu  $R_1$  de 2.3% en utilisant 253 réflexions uniques mesurées sur monocristal en rayonnement MoK $\alpha$  avec un diffractomètre automatisé. Le spécimen, prélevé dans la région de Rapid Creek, territoire du Yukon, possède une symétrie rhomboédrique plutôt que monoclinique  $Cm$ , comme l'indiquaient les résultats antérieurs. L'affinement montre que l'agencement des atomes dans la gorceixite ressemble à celui des autres membres du supergroupe de l'alunite. Les distances Ba–O et Ba–OH sont 2.825 et 2.859 Å (les deux  $\times 6$ ), respectivement, et le volume du polyèdre  $\text{Ba}(\text{O},\text{OH})_{12}$  est 55.64 Å<sup>3</sup>. Les spectres de dispersion d'énergie et les résultats d'analyses avec une microsonde électronique indiquent que le site  $D$  est complètement rempli par le Ba, quoique l'affinement de l'occupation du site ne montre que 88%; la raison de cet écart demeure méconnue. Les distances moyennes Al–O, OH et P–O sont 1.906 et 1.544 Å, respectivement, et la distance OH–H est 0.980 Å. Les distances interatomiques [H...O(2) = 1.904 Å et OH...O(2) = 2.884 Å] et une analyse des valences de liaisons font penser que chaque atome O(2) participe à des liaisons hydrogène (comme accepteur) avec trois groupes OH différents. Toutefois, d'après la faible somme des valences de liaisons pour O(2), il semble que cet atome agit aussi comme donateur. Aucun des sites des atomes d'hydrogène n'a pu être identifié à partir de la distribution des électrons par différence Fourier, mais la présence de groupes OH pourrait bien résoudre le problème du bilan des charges. En supposant l'occupation égale du site O(2) par O et OH, la formule générale de la gorceixite serait  $\text{BaAl}_3[\text{PO}_3(\text{O},\text{OH})]_2(\text{OH})_6$ . Quoique le groupe d'espace  $R\bar{3}m$  est le plus approprié pour l'échantillon de gorceixite que nous avons étudié, tous les échantillons ne répondent pas nécessairement aux exigences de ce groupe. Des conditions différentes de formation et d'autres compositions pourraient être responsables de la symétrie plus basse décrite antérieurement, mais le mécanisme impliqué pour atteindre cette symétrie inférieure demeure méconnu.

(Traduit par la Rédaction)

**Mots-clés:** gorceixite, structure cristalline, supergroupe de l'alunite, barium.

<sup>§</sup> E-mail address: lgroat@eos.ubc.ca

## INTRODUCTION

Interest in the minerals of the alunite supergroup has surged in recent years because of the prominence of some of these minerals both as oxidation products of sulfide-bearing mine wastes and as precipitates from the resulting acidic effluents (Bigham & Nordstrom 2000). Further environmental interest has focused on the possibility of using these minerals as storage materials for toxic metals (Baron & Palmer 1996, Kolitsch & Pring 2001). The alunite supergroup has the simplified general formula  $DG_3(TO_4)_2(OH, H_2O)_6$ . For gorceixite, the *D* is represented by Ba, *G* by Al, and *T* is dominated by P. As part of a more extensive study of the crystal chemistry of the alunite supergroup, we report here on the crystal structure of gorceixite, which has an ideal composition  $BaAl_3[PO_3(O, OH)]_2(OH)_6$ .

## BACKGROUND INFORMATION

Gorceixite has been observed at numerous localities and in diverse parageneses worldwide. It occurs as a primary mineral in igneous rocks, an authigenic mineral and a detrital mineral in sediments and sedimentary rocks, a metamorphic mineral in schists, and as a supergene product in weathered iron ore. Examples from the more recent literature include the description by van Hees *et al.* (2002) of gorceixite inclusions in secondary phosphate minerals in carbonate-derived eluvial sediments at the Agrium phosphate mine, Kapuskasing, Ontario. Baldwin *et al.* (2000) found gorceixite in brazilianite that replaced montebasite in rare-element pegmatites in Namibia. Gorceixite has also been described as a replacement product in fossil bones in Brazil (Coutinho *et al.* 1999), and Rasmussen *et al.* (2000) pointed out that early-diagenetic phosphatic minerals, including gorceixite, are widespread in Australian shallow-marine sandstones of all ages.

Schwab *et al.* (1990, 1991) synthesized end-member gorceixite [and arsenogorceixite,  $BaAl_3(AsO_4)(AsO_3)(OH)(OH)_6$ ]. In natural gorceixite, partial substitution of Ba by Sr or Ca is typical; among the rarely detected substitutions, Taylor *et al.* (1984) reported up to 4.7 wt.% F, and Johan *et al.* (1995) found up to 0.6  $V^{3+}$  *pfu* (per formula unit) and 0.18  $Cr^{3+}$  *pfu* (18% of the G site).

Of the more than 25 CNMMN-approved alunite-type minerals that have  $Al > Fe$  at *G*, only three have Ba dominant at *D*; these are gorceixite, arsenogorceixite, and walthierite  $Ba_{0.5}\square_{0.5}Al_3(SO_4)_2(OH)_6$ . Two other Ba-dominant minerals of the alunite type are dusserite,  $BaFe_3(AsO_4)_2(OH, H_2O)_6$ , and springcreekite,  $BaV_3^{3+}(PO_4)_2(OH, H_2O)_6$ . Previous single-crystal X-ray studies of alunite-type minerals have shown that all except a few crystallize in space group  $R\bar{3}m$  (Jambor 1999). Radoslovich & Slade (1980) determined that gorceixite is structurally similar to alunite, but that its true symmetry is *C*-centered monoclinic,

with  $a$  12.216(2),  $b$  7.033(2),  $c$  7.046(5) Å, and  $\beta$  125.4(1)°. The symmetry was observed to be strongly pseudotrigonal. To allow comparisons with chemically related minerals, the structure was refined in space group  $R3m$ , with  $a$  7.0363(2) and  $c$  17.2819(1) Å, to an unweighted agreement-factor of  $R_1 = 0.053$ . Subsequently, the structure of a sample of gorceixite from the same locality (Glen Alice, New South Wales) was refined by Radoslovich (1982) to  $R_1 = 0.031$  in space group  $Cm$ , with  $a$  12.195(8),  $b$  7.040(5),  $c$  7.055(5) Å,  $\beta$  125.19(5)°. The results showed two independent phosphate groups, both having point-group symmetry *m* but with quite different shapes. The authors stated that in contrast to crandallite, with reported structural formula  $CaAl_3(PO_3)(O_{1/2}(OH)_{1/2})_2(OH)_6$  (Blount 1974), the structure of gorceixite accommodates an extra proton at only one apical oxygen site, and the formula  $BaAl_3(PO_4)(PO_3)(OH)(OH)_6$  was therefore suggested. Blanchard (1989) collected powder X-ray-diffraction data from a sample of gorceixite from the Big Fish River – Rapid Creek area in the Yukon Territory, and indexed the reflections in space groups  $Cm$  and  $R\bar{3}m$ , obtaining figures of merit  $F_{28} = 7$  and 10, respectively. However, because eight out of the 28 reflections in the rhombohedral model had  $\Delta 2\theta$  values greater than 0.05°, it was suggested that this result “may be a clue that the [rhombohedral] space group assignment is in error.”

## EXPERIMENTAL

The sample used in this study is from Location 1, Area A, Crosscut Creek, in the Rapid Creek area, Yukon Territory, Canada (Canadian Museum of Nature, Mineral Collection no. 51269). The crystals occur as thin hexagonal plates up to  $0.10 \times 0.10 \times 0.01$  mm and are optically uniaxial. A Philips XL30 scanning electron microscope equipped with a Princeton Gamma-Tech energy-dispersion X-ray spectrometer was used to obtain qualitative chemical data. Compositional data were obtained from the same crystal used for the crystal-structure study (see below) with a CAMECA SX-50 electron microprobe operated in the wavelength-dispersion mode. Operating conditions were as follows: accelerating voltage 15 kV, beam current 10 nA, peak count-time 20 s, background count-time 10 s, spot diameter (standards and specimen) 30  $\mu$ m. Data reduction was done using the “PAP”  $\phi(\rho Z)$  method (Pouchou & Pichoir 1985). For the elements considered, the following standards, X-ray lines, and crystals were used: grossular,  $AlK\alpha$ , TAP; apatite,  $PK\alpha$ ,  $CaK\alpha$ , PET;  $SrTiO_3$ ,  $SrL\alpha$ , TAP; barite,  $BaL\alpha$ , PET. The formula was calculated on the basis of two P (as recommended by Scott 1987) and seven H atoms. The results are reported in Table 1.

For single-crystal X-ray-diffraction measurements, a gorceixite plate was glued to a glass fiber. We used a Bruker X8 APEX diffractometer with graphite-monochromated  $MoK\alpha$  radiation and a CCD detector. The

data were obtained at room temperature to a maximum  $2\theta$  value of  $55.7^\circ$ . Data were collected in a series of  $\phi$  and  $\omega$  scans in  $0.50^\circ$  oscillations with exposure times of 7.0 s. The crystal-to-detector distance was 40 mm. Of the 14,812 reflections that were collected, 253 are unique ( $R_{\text{int}} = 0.036$ ). Data were collected and integrated using the Bruker SAINT software package. The linear absorption coefficient,  $\mu$ , for MoK $\alpha$  radiation was  $4.21 \text{ mm}^{-1}$ . Data were corrected for absorption effects using the multiscan technique (SADABS), with minimum and maximum transmission-coefficients of 0.441 and 0.714, respectively. The data were corrected for Lorentz and polarization effects.

All refinements were performed using the SHELXTL crystallographic software package of Bruker AXS. Neutral-atom scattering factors were taken from Cromer & Waber (1974). Anomalous dispersion effects were included in  $F_{\text{calc}}$  (Ibers & Hamilton 1964); the values for  $\Delta f'$  and  $\Delta f''$  were those of Creagh & McAuley (1992). The values for the mass-attenuation coefficients were those of Creagh & Hubbell (1992).

The  $|E^2 - 1|$  value, 0.772, indicates a non-centrosymmetric space-group for our crystal; refinement was initiated in space group  $Cm$  using the atom positions from Radoslovich (1982). With all non-hydrogen atoms modeled anisotropically, the refinement converged to an unweighted agreement-factor  $R_1$  of 0.0230. However, some of the atoms were found to be non-positive definite, and the Flack  $x$  parameter is 0.48(3). The inverted structure was tested, and an attempt was made to refine  $x$  as a full-matrix parameter using the TWIN and BASF commands in SHELXTL. However, this was unsuccessful, and we conclude that  $Cm$  is not the correct space-group.

TABLE 1. ELECTRON-MICROPROBE-DERIVED COMPOSITION OF THE SINGLE CRYSTAL OF GORCEIXITE USED IN THIS STUDY

	Point 1	Point 2	Point 3
P <sub>2</sub> O <sub>5</sub> (wt.%)	27.02	27.03	28.79
Al <sub>2</sub> O <sub>3</sub>	28.74	28.94	29.09
CaO	0.05	0.02	0.12
FeO	0.12	0.12	0.12
SrO	0.25	0.28	0.26
BaO	29.50	29.43	29.51
Na <sub>2</sub> O	0.17	0.17	0.17
H <sub>2</sub> O*	11.97	11.98	12.78
F	0.07	0.05	0.01
O=F	-0.03	-0.02	0.00
Total	97.86	98.00	100.85
P <sup>5+</sup> (apfu)	2.000	2.000	2.000
Al <sup>3+</sup>	2.962	2.981	2.813
Ca <sup>2+</sup>	0.005	0.002	0.011
Fe <sup>2+</sup>	0.009	0.009	0.008
Sr <sup>2+</sup>	0.013	0.014	0.012
Ba <sup>2+</sup>	1.011	1.008	0.949
Na <sup>+</sup>	0.029	0.029	0.027
H <sup>+</sup>	6.981	6.986	6.997
F <sup>-</sup>	0.019	0.014	0.003
O <sup>2-</sup>	13.994	14.005	13.714

Note: Compositions were recalculated on the basis of 2 (P<sup>5+</sup>) apfu.

\* Determined by stoichiometry, assuming 7 (OH + F) pfu.

The structure was next refined in space group  $R3m$ , as had been done by Radoslovich & Slade (1980). However,  $R_{\text{int}}$  was found to be high at 0.17, there were 229 inconsistent equivalents,  $R_1 = 0.0443$ , and the Flack  $x$  parameter was 0.46(4). We concluded that  $R3m$  is not the correct space-group either.

The structure was next refined in space group  $R\bar{3}m$  using the atom positions for jarosite from Menchetti & Sabelli (1976). All non-hydrogen atoms were refined anisotropically. The A site was initially fixed to full occupancy with Ba, resulting in  $R_1 = 0.0318$ , but was subsequently allowed to refine. The extinction was refined, but returned a value of 0. The final cycle of full-matrix least-squares refinement [least-squares function minimized:  $\sum w(F_o^2 - F_c^2)^2$  on  $F^2$ ] was based on 253 reflections and 29 variable parameters and converged (largest parameter shift was 0.00 times its standard deviation) with  $R_1 = 0.0231$  and a weighted agreement-factor of  $wR_2 = 0.0629$ . The standard deviation of an observation of unit weight was 1.365. The weighting scheme was based on counting statistics. The maximum and minimum peaks on the final difference-Fourier map corresponded to 1.38 (0.81 Å from the Ba atom) and  $-0.60 e^-/\text{Å}^3$ , respectively.

Data collection and refinement parameters are summarized in Table 2, positional and displacement parameters in Table 3, and bond lengths and angles in Table 4. Tables listing the observed and calculated structure-factors may be obtained from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, K1A 0S2 Canada.

## RESULTS

The crystals were inspected with a petrographic microscope in plane- and cross-polarized light and with back-scattered-electron imaging in a scanning electron microscope and showed no optical or compositional zoning. The energy-dispersion spectra showed peaks corresponding only to those of the expected elements plus small amounts of Na and Fe. Wavelength-dispersion scans revealed no S or As. The electron-microprobe-established compositions (Table 1) show only

TABLE 2. GORCEIXITE: DATA COLLECTION AND STRUCTURE-REFINEMENT INFORMATION

$a$ (Å)	7.0538(3)	$F_o > 4\sigma(F_o)$	253
$c$ (Å)	17.2746(6)	$R_{\text{int}}$	0.036(3)
$V$ (Å <sup>3</sup> )	744.36(5)	Least-squares param.	29
Space Group	$R\bar{3}m$ (no. 166)	$R_1$ for $F_o > 4\sigma(F_o)$	0.0231
$Z$	3	$R_1$ for all unique $F_o$	0.0231
Crystal size (mm)	$0.10 \times 0.09 \times 0.007$	$wR_2$	0.0633
Radiation	MoK $\alpha$	$a$ (see Note)	0.0235
Monochromator	graphite	$b$ (see Note)	7.97
Total $F_o$	14812	Goof (= S)	1.355
Unique $F_o$	253		

Note:  $w = 1/[\sigma^2(F_o^2) + (a \times P)^2 + b \times P]$ , where  $P = [\text{Max}(F_o^2, 0) + 2 \times F_o^2]/3$

trace amounts of substituents and have reasonable totals.

The crystal-structure refinement indicates that the arrangement of atoms in gorceixite is similar to that of other members of the alunite–jarosite groups, *e.g.*, crandallite (Blount 1974), dussertite (Kolitsch *et al.* 1999b), florencite-(Ce) (Kato 1990), goyazite (Kato 1971, 1987), kintoreite (Kharisun *et al.* 1997), plumbogummite (Kolitsch *et al.* 1999c), and springcreekite (Kolitsch *et al.* 1999a). The coordination polyhedra of cations in the gorceixite structure are shown in Figure 1. The Ba atom at the A site, at special position  $3b$  ( $0,0,\frac{1}{2}$ ), is coordinated by six O atoms (from six separate  $\text{PO}_4$  groups) and six OH groups to form an icosahedron. The Ba–O and Ba–OH distances are 2.825 and 2.859 Å (both  $\times 6$ ), respectively (mean 2.842 Å), and the  $\phi$ –A– $\phi$  angles ( $\phi$ : unspecified anion) range from 55.9 to 124.44° (mean 90.0°). The bond-length and bond-angle distortion parameters ( $\Delta$  and  $\sigma^2$ ; Hawthorne *et al.* 1989) are 0.0004 and 729.53, respectively, and the polyhedron volume is 55.64 Å<sup>3</sup>. The EDS spectra and electron-microprobe results indicate that the A site is completely occupied by Ba, but the site occupancy refines to 88% Ba (and 12% vacancy). Presumably this could be due to an inaccurate absorption-correction or scattering curve for Ba; however, Radoslovich (1982) reported a site occupancy of 96% Ba (and 4% vacancy) in his *Cm* refinement. The bond-valence sum (Table 5), assuming complete occupancy by Ba, is 2.70 valence units (*vu*); this improves to 2.38 *vu* if we assume partial occupancy, but it is important to note that Ba compounds in general give poor bond-valence sums (Brown & Wu 1976).

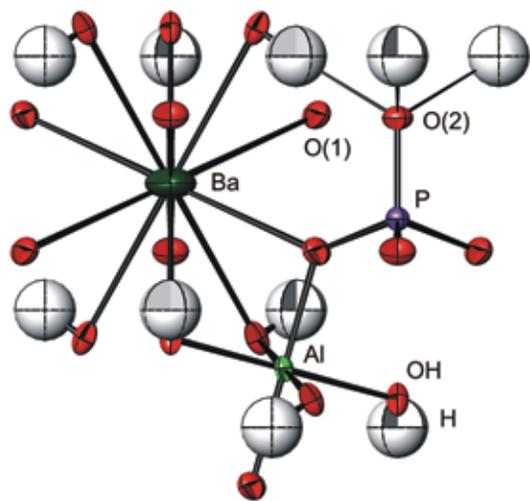


FIG. 1. Coordination polyhedra of cations in the gorceixite structure, projected onto (100). The atomic displacement ellipsoids represent 75% probability.

The atom at the *G* site, at special position  $9e$  ( $\frac{1}{2},0,0$ ), is coordinated by two O atoms (from two separate  $\text{PO}_4$  groups) and four OH molecules to form a distorted octahedron. The *G*–O and *G*–OH distances are 1.914 ( $\times 2$ ) and 1.902 Å ( $\times 4$ ), respectively (mean 1.906 Å), and the  $\phi$ –*G*– $\phi$  angles range from 87.9 to 92.1° (mean 90.0°). The O–OH and OH–OH edge lengths are 2.649 and 2.746, and 2.681 and 2.698 Å, respectively. The bond-length and bond-angle distortion parameters are 0.00005 and 2.993, respectively. The variance in the octahedron angle is 3.15, the mean octahedral quadratic elongation (Robinson *et al.* 1971) is 1.0009, and the polyhedron volume is 9.21 Å<sup>3</sup>. The EDS spectra, electron-microprobe-derived compositions, refined site-occupancy, and bond-valence analysis (3.01 *vu*, Table 5) indicate that the site is completely occupied by Al.

The atom at the *T* site, at special position  $6c$  ( $0,0,z$ ), is coordinated by three atoms at the O(1) site and one at the O(2) site that together form a tetrahedron. The *T*–O(1) and *T*–O(2) distances are 1.538 ( $\times 3$ ) and 1.563 Å, respectively. The O(1)–*T*–O(1) angles are 109.8°, and the O(1)–*T*–O(2) angles are 109.1° (each  $\times 3$ ; mean 109.5°). The bond-length and bond-angle distortion parameters are 0.0002 and 0.125, respectively. The variance in the tetrahedron angle is 0.1448, the mean quadratic elongation of the tetrahedra is 1.0001, and the polyhedron volume is 1.89 Å<sup>3</sup>. Although the bond-valence sum, 4.70 *vu*, is somewhat low, the EDS spectra, electron-microprobe-derived compositions, and refined site-occupancy indicate that the site is completely occupied by pentavalent phosphorus. The mean P–O(1),O(2) distance, 1.544 Å, is slightly longer than the  $\langle$ P– $\phi$  $\rangle$  distance ( $\phi$ : unspecified anion), 1.537 Å, reported by Baur (1974) and Huminicki & Hawthorne (2002) for inorganic phosphates.

The H atom site (at special position  $18h$ ,  $x, -x, z$ ) was identified from a difference-Fourier map. Without constraints, the OH–H distance refined to a distance of  $\sim 0.85$  Å; this was considered unrealistically short, and subsequently the distance was constrained to 0.98 Å. The high uncertainties associated with the positional and isotropic displacement parameters are most likely an artefact of the absorption correction. The interatomic distances and bond-valence analysis suggest that each O(2) atom is involved in hydrogen bonding (as an acceptor) with three different OH groups; the H–O(2) distance is 1.904 Å, the OH–O(2) distance is 2.884 Å, and the OH–H–O(2) angle is close to being linear (179°).

The low bond-valence sum, for O(2), 1.34 valence units, suggests that O(2) acts not only as an acceptor, but also as a donor. However, no hydrogen-atom sites could be identified from the difference-Fourier map. In terms of possible acceptors, there are three O(1) sites at distances of 2.527 Å from each O(2) position, and one O(2) site at the same distance from each O(1) position. An oxygen atom at O(1) could presumably act as an acceptor [this would also help improve the

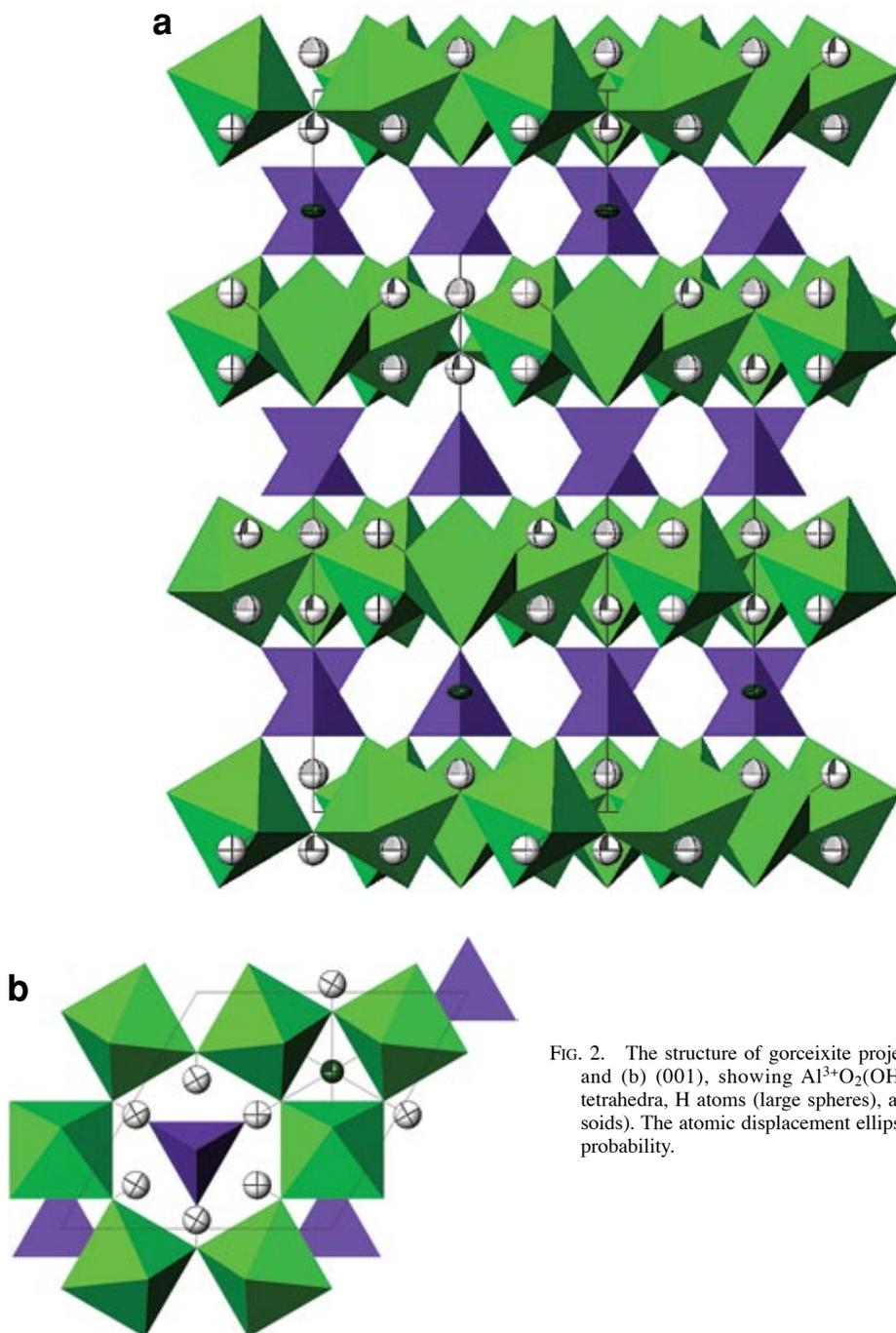


TABLE 3. ATOM PARAMETERS FOR GORCEIXITE

Site	Occ.	x	y	z	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$	$U_{eq}$
A (Ba)	0.882(6)	0	0	1/2	0.0119(3)	0.0119(3)	0.0165(4)	0.0059(1)	0	0	0.0134(2)
G (Al)	1.0	1/2	0	0	0.0101(7)	0.0104(9)	0.0238(9)	0.0052(4)	0.0005(3)	0.0010(7)	0.0147(5)
T (P <sup>5+</sup> )	1.0	0	0	0.1987(1)	0.0099(6)	0.0099(6)	0.027(1)	0.0049(3)	0	0	0.0155(5)
O(1)	1.0	0.5477(3)	0.4523(3)	0.1055(2)	0.013(1)	0.013(1)	0.026(1)	0.010(1)	-0.0007(6)	0.0007(6)	0.0159(7)
O(2)	0.5	0	0	0.1082(3)	0.018(2)	0.018(2)	0.023(3)	0.0090(9)	0	0	0.020(1)
OH(2)	0.5	0	0	0.1082(3)	0.018(2)	0.018(2)	0.023(3)	0.0090(9)	0	0	0.020(1)
OH(3)	1.0	0.4600(3)	0.5400(3)	0.3058(2)	0.011(1)	0.011(1)	0.026(2)	0.004(1)	0.0026(6)	-0.0026(6)	0.0172(7)
H(3)	1.0	0.530(4)	0.470(4)	0.278(5)							0.13(4)

TABLE 4. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN GORCEIXITE

A -O(1)a	× 6	2.825(3)	O(1)a -A-O(1)f	× 6	106.87(6)
A -OHb	× 6	2.859(3)	-A-O(1)g	× 6	73.13(6)
<A-O>		2.842	O(1)a -A-OHb	× 12	124.44(5)
G -O(1)c	× 2	1.914(3)	O(1)a -A-OHh	× 12	55.56(5)
G -OHd	× 4	1.902(1)	O(1)a -A-OHa	× 6	79.19(9)
<G-O>		1.906	O(1)a -A-OHi	× 6	100.81(8)
T -O(1)e	× 3	1.538(3)	OHb -A-OHf	× 2	55.9(1)
T -O(2)		1.563(6)	OHf -A-OHg	× 2	124.1(1)
<T-O>		1.544	<O-A-O>		90.0
OH-H		0.980(1)	O(1)c -G-OHd	× 4	92.1(1)
H...O(2)e		1.904(5)	O(1)c -G-OHi	× 4	87.9(1)
OH...O(2)e		2.884(4)	OHd -G-OHe	× 2	89.6(2)
			OHc -G-OHj	× 2	90.4(2)
			<O-G-O>		90.0
			O(1)e -T-O(1)k	× 3	109.8(1)
			O(1)c -T-O(2)	× 3	109.1(1)
			<O-T-O>		109.5
			OH-H...O(2)c		179(8)

Equivalent positions: a =  $x - y + \frac{1}{2}, x - \frac{1}{2}, -z + \frac{1}{2}$ ; b =  $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + \frac{1}{2}$ ; c =  $y, -x + y, -z$ ; d =  $x - y + \frac{1}{2}, x - \frac{1}{2}, -z + \frac{1}{2}$ ; e =  $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + \frac{1}{2}$ ; f =  $y - \frac{1}{2}, -x + y - \frac{1}{2}, -z + \frac{1}{2}$ ; g =  $-y + \frac{1}{2}, x - y + \frac{1}{2}, z + \frac{1}{2}$ ; h =  $x - \frac{1}{2}, y - \frac{1}{2}, z + \frac{1}{2}$ ; i =  $-x + y + \frac{1}{2}, -x + \frac{1}{2}, z - \frac{1}{2}$ ; j =  $x + \frac{1}{2}, y - \frac{1}{2}, z - \frac{1}{2}$ ; k =  $y - \frac{1}{2}, -x + y + \frac{1}{2}, -z + \frac{1}{2}$ .

somewhat low bond-valence sum to O(1) of 1.92 *vu*. Given the relatively short donor-acceptor distance and the T-O(2)-O(1) angle, 35.1°, the hypothetical O(2)-H...O(1) angle would be expected to be relatively sharp. Although it is beyond the scope of this study, it would be interesting to see if this hypothetical hydrogen-bonding scheme is detectable in spectroscopic studies of gorceixite. The infrared spectrum for gorceixite from the Kovdor massif in Russia shows a broad band at 1680 cm<sup>-1</sup> that might indicate the presence of H<sub>2</sub>O (Liferovich *et al.* 1999).

The presence of OH groups at the O(2) site would also help resolve the problem of charge balance. If the cation sites are fully occupied with Ba, Al, and P, the total charge is +21. Assuming O at all O(1) and O(2) sites, and OH at the OH site, the total negative charge is -22. This apparent imbalance may be resolved by assuming that the O(2) site is half-occupied by O and half-occupied by OH, which would lead to a general formula for gorceixite of BaAl<sub>3</sub>[PO<sub>3</sub>(O,OH)]<sub>2</sub>(OH)<sub>6</sub>.

TABLE 5. BOND-VALENCE\* ANALYSIS OF GORCEIXITE

Site	D (Ba <sup>2+</sup> )	G (Al <sup>3+</sup> )	T (P <sup>5+</sup> )	H	Total
O(1)	0.24 × 6 ↓	0.49 × 2 ↓	1.20 × 3 ↓		1.92
O(2)			1.12	0.08 × 3 -	1.34
OH	0.21 × 6 ↓	0.51 × 4 ↓ × 2 -		0.92	2.15
Total	2.70	3.01	4.70	1.00	

\* Calculated from the bond-valence parameters of Brese & O'Keeffe (1991).

The topology of the gorceixite structure is the same as that of other members of the plumbogummite group. The Al<sup>3+</sup>O<sub>2</sub>(OH)<sub>4</sub> octahedra share corner OH atoms to form sheets perpendicular to the *c* axis (Fig. 2a). The OH groups form a plane roughly parallel to (001). The O(1) atoms lie on opposite sides of the OH layers. The octahedra form six- and three-membered rings (Fig. 2b), and the three apical O(1) atoms from each triad of octahedra form the base of a PO<sub>4</sub> tetrahedron. Additional sheets of octahedra are located in such a way that two triads of OH ions enclose a site wherein the 12-coordinated Ba<sup>2+</sup> ion is located (Fig. 2). The apical O(2) atoms on each of the PO<sub>4</sub> tetrahedra point alternately up and down the *c* axis, and project into the six-membered rings of hydroxyl groups on the octahedra. Each O(2) atom forms weak hydrogen bonds with the three closest hydroxyl groups. The shortest O(2)-O(2) distance, 3.74 Å, precludes hydrogen bonding between atoms at these sites in members of the plumbogummite group (as grouped by Scott 1987).

## DISCUSSION

Although  $R\bar{3}m$  is the most appropriate space-group for the sample of gorceixite studied here, we do not claim that all samples of gorceixite or all minerals of the alunite supergroup crystallize in this space group. Several exceptions are known, and a recent example is that of Göttlicher & Gasharova (1999), who observed split reflections (except 00 $l$ ) in X-ray powder patterns

of synthetic jarosite crystals, indicating deviation from trigonal symmetry. Reflections and intensities indicate monoclinic  $C2/m$  if an orthohexagonal cell is chosen, and  $\beta$  deviates slightly from  $90^\circ$  in their sample. A dependence of  $\beta$  on composition was considered likely by Göttlicher & Gasharova (1999) because the K-free end-member of the solid-solution series  $(K,H_3O)Fe_3(SO_4)_2(OH)_6$  shows no splitting. For the K-rich members, the observed deviation is less than  $1^\circ$ . All synthesized samples of K-rich jarosite were found to be deficient in Fe, and in none did K fully occupy the A site. Increasing the temperature of synthesis was said to reduce the deviation of  $\beta$  from  $90^\circ$ . An explanation for the nonstoichiometry, which is common in synthetic jarosite-type compounds, and for the deviation from trigonal symmetry, was not given by Göttlicher & Gasharova (1999). Göttlicher *et al.* (2000) refined the crystal structure of synthetic jarosite in both  $R\bar{3}m$  (to  $R_1 = 0.025$ ) and  $C2/m$  (to  $R_1 = 0.028$ ) and concluded that there is a significantly better agreement of symmetrically equivalent reflections for the latter. They suggested that additional protons in the structure, perhaps to charge-balance the deficiency in Fe, might be responsible for the reduction in symmetry.

The gorceixite sample studied by Radoslovich & Slade (1980) and Radoslovich (1982) is from a different locality than the one studied here. The composition is also somewhat different, with 96% Ba at the A site (as opposed to 88% in our sample) and 2.3 wt.% F. Different conditions of formation and compositions might be responsible for the lowered symmetry, although the mechanism remains unclear. The question of the symmetry of minerals of the alunite supergroup has yet to be answered and will require more work.

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