

## Gorceixite from Catalão, Goiás, Brazil: Rietveld Crystal Structure Refinement

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### ABSTRACT

Gorceixite is an abundant aluminum phosphate in Brazilian laterite phosphate ores and is one of the most important gangue minerals. Catalão I mine, Goiás, Brazil, one of the biggest phosphate mines in Brazil, contains great amounts of gorceixite, whose structural formula, as suggested by microprobe analysis, is  $(\text{Ba}_{0.76}\text{Ca}_{0.19}\text{Sr}_{0.10}\text{Ce}_{0.01})_{\Sigma 1.06}(\text{Al}_{2.74}\text{Fe}^{3+}_{0.25})_{\Sigma 2.99}(\text{P}_{0.96}\text{Si}_{0.03})_{\Sigma 0.99}\text{O}_4(\text{PO}_3\text{OH})(\text{OH})_{6.02}$ . Its crystal structure, rich in Ca, Sr, and Fe, was refined by the Rietveld method applied to X-ray powder diffraction data for trigonal and monoclinic structural models. The statistical parameters for the two models are so similar that they do not allow clear distinction of which is the better structural model for gorceixite. The cell parameters obtained for the trigonal model, space group  $R3m$ , are  $a = 7.0791(3)$  Å,  $c = 17.089(1)$  Å,  $V = 741.68(7)$  Å<sup>3</sup>,  $Z = 3$ , and for the monoclinic model, space group  $Cm$ ,  $a = 12.195(8)$  Å,  $b = 7.040(5)$  Å,  $c = 7.055(5)$  Å,  $\beta = 125.19(5)^\circ$ ,  $V = 495$  Å<sup>3</sup>,  $Z = 2$ . A particular feature of the Catalão gorceixite is the replacement of some Al in the X-site by Fe<sup>3+</sup>, with minor distortions in crystallochemical sites. These features may alter physical-chemical mineral characteristics, such as density and heavy metal retention capacity.

**Palavras-chave:** gorceixita, estrutura cristalina, refinamento Rietveld, difração de raios X.

### RESUMO

Gorceixita é o mais abundante dos fosfatos aluminosos encontrados nos minérios fosfáticos lateríticos brasileiros, sendo um dos principais minerais de ganga destes minérios oxidados. A jazida de Catalão I (GO), uma das maiores do Brasil, contém grande quantidade de gorceixita, cuja fórmula estrutural sugerida pelos resultados de análises por microssonda eletrônica é  $(\text{Ba}_{0.76}\text{Ca}_{0.19}\text{Sr}_{0.10}\text{Ce}_{0.01})_{\Sigma 1.06}(\text{Al}_{2.74}\text{Fe}^{3+}_{0.25})_{\Sigma 2.99}(\text{P}_{0.96}\text{Si}_{0.03})_{\Sigma 0.99}\text{O}_4(\text{PO}_3\text{OH})(\text{OH})_{6.02}$ . Sua estrutura cristalina, rica em Ca, Sr, e Fe, foi refinada pelo método de Rietveld aplicado aos dados de difração de raios X, considerando tanto a estrutura monoclinica, quanto a trigonal. Os parâmetros estatísticos para ambos os modelos são muito similares e não permitem discriminar qual o melhor modelo de estrutura. Os resultados dos parâmetros de cela para o modelo trigonal, grupo espacial  $R3m$ , são:  $a = 7.0791(3)$  Å,  $c = 17.089(1)$  Å,  $V = 741.68(7)$  Å<sup>3</sup> e  $Z = 3$ , e para o modelo monoclinico, grupo espacial  $Cm$ , são:  $a = 12.195(8)$  Å,  $b = 7.040(5)$  Å,  $c = 7.055(5)$  Å,  $\beta = 125.19(5)^\circ$ ,  $V = 495$  Å<sup>3</sup>,  $Z = 2$ . A gorceixita de Catalão apresenta Fe substituindo Al na posição do sítio X e pequenas distorções nos diferentes sítios cristalinos. Estas características podem alterar as propriedades físico-químicas dos minerais que as contêm, como densidade e capacidade de fixação de metais pesados.

## INTRODUCTION

Gorceixite is a crandallite-group mineral first recorded from Brazil but also known elsewhere (Coutinho et al., 1999; Toledo, 2000; Dill, 2001; Toledo et al., 2002). Its potential economic value continues to grow as high-quality phosphate deposits become scarce.

Crystal structure investigation of crandallite-group minerals may be useful for the development of processing techniques for low-grade  $P_2O_5$  ores. Hence, these minerals are being tested as substitutes for apatite in fertilizer production (Hill et al., 1950; Doak et al., 1965; Lehr, 1967; Gilkes and Palmer, 1979; Hoare, 1980; Francisco et al., 2006a, 2006b). Furthermore, gorceixite presents an open structure, similar to that in zeolites, that may accommodate metallic ions, so that gorceixite-rich materials from the Catalão laterite mantle offer promise for environmental applications. Monteagudo et al. (2003), for example, have studied the use of crandallite-group minerals to eliminate mercury from contaminated environments.

Radoslovich and Slade (1980) and Radoslovich (1982) refined the crystal structure of gorceixite and concluded that the space group is monoclinic *Cm*, although strongly pseudorhombohedral *R3m*. Blanchard (1989) obtained new X-ray powder data for gorceixite and observed a better fit of the d values in *Cm* than in *R3m* for the ICDD patterns. Gorceixite is the only monoclinic mineral in both the crandallite group and alunite supergroup. It has not yet been proved that gorceixite with a conventional rhombohedral cell exists, but such a mineral would simply be designated as gorceixite-1cR (Jambor, 1999). The gorceixite crystal studied by Radoslovich and Slade (1980) and Radoslovich (1982) is an almost pure Ba, Al, and  $PO_4$  end-member. Ca, Sr, and Ce, however, often substitute for Ba; Al for Fe; and  $SO_4$  for  $PO_4$ . But are these intermediate members also monoclinic? This paper presents the results of Rietveld refinement of the crystal structure of a Ca-, Sr-, and Fe-rich gorceixite from Catalão that bear upon this question.

## BACKGROUND INFORMATION

Crandallite comprises a group of hydrous aluminous phosphates that generally form under surface conditions by the weathering of P-rich materials present in sedimentary rocks, such as marine deposits, and in alkaline igneous rocks (Toledo, 1999; Dill, 2001). Its general formula is  $XAl_3(PO_4)(PO_3OH)(OH)_6$ , where X may be represented by cations such as Ca, Sr, Ba, Pb, or rare earth elements in different proportions (Bottinelly, 1976).

Aluminum plays an important role in phosphate genesis in superficial environments (Vieillard et al., 1979; Toledo et al., 2002). In laterite weathering profiles derived from both P- and

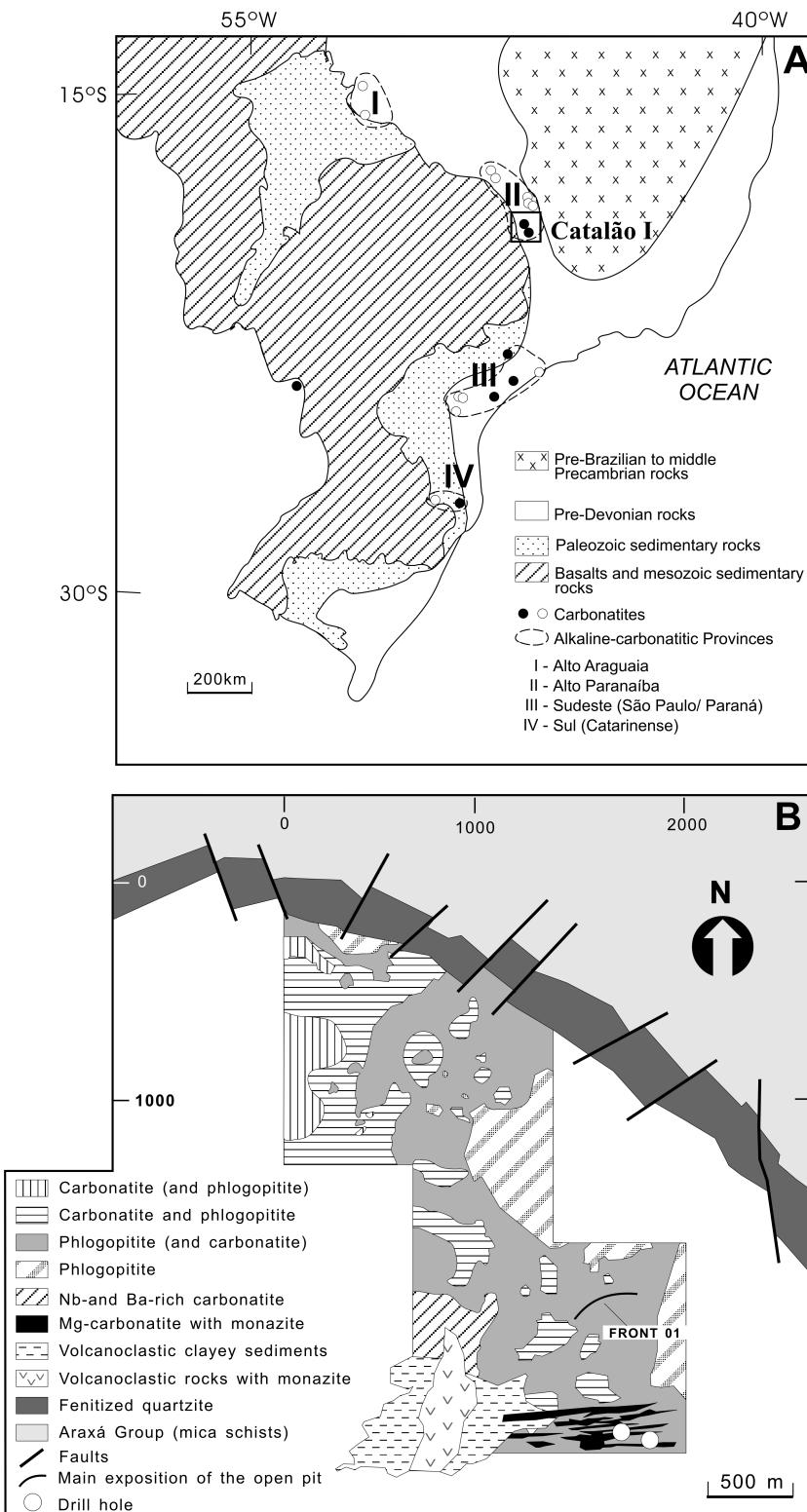
Al-rich rocks, as in Catalão I, geochemical evolution leads to extensive aluminum-phosphate (crandallite group) formation. This kind of formation is observed in several Brazilian carbonatite complexes including Juquiá (Alcover Neto and Toledo, 1993), Tapira (Ferrari et al., 2001), and Catalão I (Toledo, 2000), all sites of important Brazilian phosphate mines.

Despite its low solubility, crandallite was first studied as a P fertilizer for direct application to soils (Hoare 1980). After heating, however, its solubility is higher (Doak et al., 1965; Gilkes and Palmer, 1979; Bolland and Gilkes, 1987). Crandallite has been described from several regions in Brazil, like the phosphate deposits in the State of Maranhão (Oliveira and Costa, 1984; Lima and Reymão, 1983) and elsewhere (Toledo, 2000; Toledo et al., 2002). The agronomic use of aluminum-iron phosphates from Maranhão was evaluated by Braun (1983) and Câmara et al. (1984). More recently, Francisco et al. (2006a, 2006b), in a study of Brazilian crandallite-group samples from Catalão, Juquiá and Tapira, showed that samples heated for 2 h at 500°C increased dry matter yield and P uptake in upland and flooded rice. Moreover, because of the capacity of its open crystal structure to retain some metallic ions, this mineral also offers promise for environmental remediation.

## GEOLOGICAL SETTING

The Catalão I Complex belongs to the Alto Paranaíba alkaline-carbonatitic province along with several other complexes, emplaced along deep NW-trending faults related to the Alto Paranaíba cratonic arc between the Paraná Basin and the São Francisco craton. A Late Cretaceous age ( $85.0 \pm 0.9$  Ma) was obtained for syenites by Amaral et al. (1967; recalculated by Sonoki and Garda, 1988). Eby and Mariano (1992) determined an age of 114 Ma using fission track analysis in apatite. Rocks present there include intrusive dunite, pyroxenite, phoscorite, phlogopite, and carbonatite, as well as volcanoclastic rocks. The Catalão I complex exhibits high relief and is surrounded by a ring of quartzite; outside this ring occur mica-schists of the Mesoproterozoic Araxá Group (Figure 1). A weathering mantle more than 100 m thick has developed upon the intrusive body and contains abundant residual apatite, pyrochlore, monazite, Ti-minerals (perovskite, ilmenite, and anatase), and vermiculite.

The geological, geochemical, petrological and mineralogical features of this complex have been studied by Carvalho (1974), Araújo and Gaspar (1992), Lenharo (1994), Lapido-Loureiro (1995), Pereira (1995), Oliveira and Imbernon (1998), Toledo (1999), and Toledo et al. (2002, 2004). Of the main concentrations of apatite, pyrochlore, monazite, anatase and vermiculite already characterized in the complex, only the first two are presently being exploited; apatitic phosphate is mined by Fosfertil and Copebrás, and niobium is exploited by Mineração Catalão.



**Figure 1.** Geological map of southeastern Brazil displaying the alkaline-carbonatitic complexes (Rodrigues and Lima, 1984) **(A)**, and geological map of the Catalão I complex (Ribeiro, 1998) **(B)**, with the location of the open pit (front 1) and the sampled drill holes.

## OCCURRENCE

Gorceixite is by far the most abundant crandallite-group mineral in laterites developed upon Brazilian phosphate deposits. In Catalão, Goiás, it is associated with supergene goethite, kaolinite and magnetite, and the residual primary minerals fluorapatite, quartz and anatase. Generally gorceixite forms micrometric crystals filling fissures and alterite voids or is the secondary weathering plasma. Microprobe chemical data for the Catalão gorceixite (Table 1) may be found in Toledo (2000).

## EXPERIMENTAL PROCEDURE

Rietveld refinement is a technique devised by Rietveld (1969) for use in the characterization of crystalline materials. Neutron and X-ray diffraction of powder samples results in a pattern characterized by peaks in intensity at certain positions. The height, width and position of these peaks can be used to determine many aspects of the material's structure. The Rietveld method uses a least squares approach to refine a theoretical line profile until it matches the measured profile. The introduction of this technique was a significant step forward in the diffraction analysis of powder samples as, unlike other techniques at that time, it was able to deal reliably with strongly overlapping reflections.

Polycrystalline sample CAF42 from Catalão, studied by Toledo (2000), was used for the present crystal structure refinement. The sample was milled to 150 mesh and deferrified by the De Endredy (1963) method. X-ray powder diffraction data were obtained at the Instituto de Geociências of the Universidade de São Paulo on a Siemens D5000 instrument using Bragg-Brentano parafocusing geometry and CuK $\alpha$  radiation. Receiving and divergence slits with 0.2° were used but no soller slit was applied. Data were collected from 6° to 120° 2θ with steps of 0.02° 2θ and 10 s count time for each step. Refinement was obtained using the GSAS program (Larson and von Dreele, 1986). Peak profiles were modeled using a pseudo-Voight function with GU, GW, LX, LY. The profile coefficients LX, GU and GW are parameters of the Lorentzian [ $\sigma = (LX)\tan(\theta)+(LY)/(\cos\theta)+Z$ ] and Gaussian [ $\sigma^2 = (GU)\tan^2(\theta)+(GV)\tan(\theta)+(GW)+P\cos^2(\theta)$ ] broadening in the pseudo-Voigt function. L is the diffractometer radius; H and S are the sample and detector heights.

The GSAS program includes Le Bail and Rietveld refinement methods. The Le Bail full-profile refinement method (structureless whole profile fitting) (Le Bail et al., 1988) allows whole profile unit cell refinement involving overlapping reflections, extraction of |F|hkls for structure solution and space group determination. Le Bail fitting is considered as a standard function in any modern Rietveld software; it is recommended that Le Bail fitting be applied to

the powder pattern prior to structure solution or even prior to structure refinement. In the first stage of refinement the cell and profile parameters were determined using the Le Bail technique. These parameters were kept constant later, when the Rietveld refinement began. During application of the Rietveld method the parameters were liberated in the following sequence: background coefficients of the polynomial function; scale factors; and, simultaneously, cell parameters and sample displacement. Only after convergence were the profile parameters liberated in the order LX and GU, GW, H/L and S/L, reducing the steps in profile parameter interaction and increasing the Marquart factor. In this stage refinement for both monoclinic (Radoslovich, 1982) and trigonal (Radoslovich and Slade, 1980) structure models were made, and the statistical convergence parameters compared.

In order to simplify the refinement process, atomic positions were liberated in a second stage, and the "soft constraints" artifice was used to calculate interatomic distances within the PO<sub>4</sub> and (Al,Fe)O<sub>6</sub> polyhedra. In both stages, thermal coefficients and atomic occupation were kept constant.

The atomic coordinates for gorceixite were taken from Radoslovich and Slade (1980) and Radoslovich (1982) (Table 2). The atomic coordinates for the minerals associated with gorceixite were taken from Levien et al. (1980) for quartz, from Sudarsanan et al. (1972) for fluorapatite, and from Burns et al. (1997) for magnetite.

The refined structure models were tested by bond valence calculations (Brown and Altermatt, 1985) in order to verify their proximity to real physical models.

## DISCUSSION

Because the statistical parameters (Rp, Rwp,  $\chi^2$ , R) for the two models are very similar (Table 3, Figure 2), they do not indicate which is the better model for gorceixite from Catalão. Consequently, the cell parameters and the interatomic distances for the two models will be discussed.

Compared to cell parameters in Radoslovich's (1982) monoclinic model, *a* and *b* found in the present study are, respectively, 0.060 Å and 0.038 Å greater; *c* is 0.061 Å smaller; and  $\beta$  is 0.29° greater, with proportional variation in cell parameter dimensions. For the trigonal model, *a* is 0.043 Å greater, and *c* is 0.192 Å smaller than the cell parameters recorded by Radoslovich and Slade (1980). These results reveal a larger variability in the *c* parameter due to chemical substitutions.

In both models there is a shortening of the unit cell in the *c* direction and a small increase in the *a* axis. The increase of the *a* dimension with the incorporation of iron has already been observed in minerals of the alunite-jarosite series by Botinelli (1976) and Manchetti and Sabeli (1976), who

**Table 1.** Chemical composition (wt.%) and atoms per formula unit (p.f.u.) of gorceixite. **1.** Gorceixite, ideal composition  $\text{BaAl}_3(\text{PO}_4)(\text{PO}_3\text{OH})(\text{OH})_6$ . **2.** Gorceixite from Catalão, Goiás, Brazil, microprobe data (sample CAF42, #6, Toledo et al., 2002).  $\text{H}_2\text{O}$  calculated by difference. Structural formulae calculated on the basis of 10.5 oxygen ions assuming anhydrous stoichiometry (cf. Taylor et al., 1984).

|                         | <b>1</b> | <b>2</b> |
|-------------------------|----------|----------|
| CaO                     |          | 2.03     |
| SrO                     |          | 1.97     |
| BaO                     | 30.00    | 22.77    |
| $\text{La}_2\text{O}_3$ |          | 0.03     |
| $\text{Ce}_2\text{O}_3$ |          | 0.17     |
| $\text{Al}_2\text{O}_3$ | 29.91    | 27.18    |
| $\text{Fe}_2\text{O}_3$ |          | 3.90     |
| $\text{SiO}_2$          |          | 0.37     |
| $\text{P}_2\text{O}_5$  | 27.76    | 26.97    |
| $\text{H}_2\text{O}$    | 12.33    | 12.61    |
| Total                   | 100.00   | 100.00   |
| Ca                      |          | 0.19     |
| Sr                      |          | 0.10     |
| Ba                      | 1.00     | 0.76     |
| Ce                      |          | 0.01     |
| A site                  | 1.00     | 1.06     |
| Al                      | 3.00     | 2.74     |
| $\text{Fe}^{3+}$        |          | 0.25     |
| B site                  | 3.00     | 2.99     |
| Si                      |          | 0.03     |
| P                       | 2.00     | 1.96     |
| X site                  | 2.00     | 1.99     |

observed that the *c* dimension does not change with this substitution. The decrease of the *c*-axis dimension for gorceixite from Catalão may be related to such substitutions as Ba for Ca and Sr.

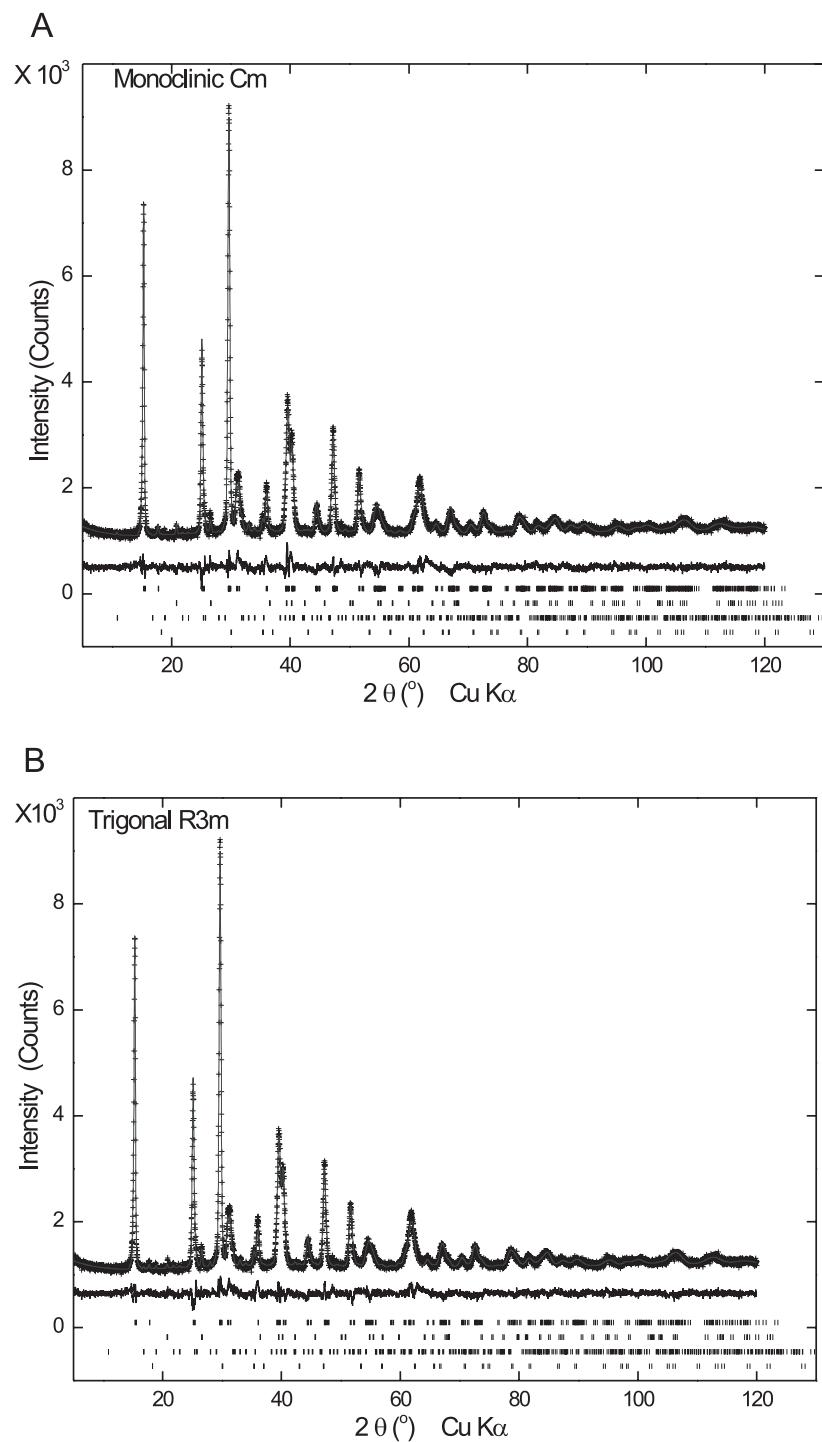
The atomic coordinates for the two models are presented in Tables 4 and 6. The observed bond valence values for cations and anions in the monoclinic structure (Table 5) deviate from the expected values and from the values calculated by Radoslovich (1982). The largest deviations are observed for the Ba and P sites. The trigonal structure also showed larger deviations for Ba sites and smaller ones for P sites (Table 7).

It can be noted that the P1-O3 and P2-O4 distances obtained here for the monoclinic model are greater and the P1-O1 distance for the trigonal model is lower than those observed in the initial model (Tables 5 and 7). A slight expansion in the  $\text{PO}_4$  tetrahedra was already noted by Kato (1971) for the alunite-woudhouseite-goyazite series. Distortion was also seen in the Al octahedra with significant increase of the Al1-O22 and Al2-OH12 distances for the monoclinic model. Only the Al1-OH2 distance suffered a larger increase in the trigonal model. For the Ba-site there was a decrease in the Ba1-O2 and Ba1-O33 distances and an increase in the Ba1-O3 and Ba1-O22 distance for the monoclinic model. There was a decrease in the Ba1-OH1 and an increase in the Ba1-OH2 distance for the trigonal model.

Rietveld refinement of the crystal structure of the Catalão gorceixite revealed a tendency for distortion in the A, B and X sites in both models (monoclinic and trigonal). Structural problems persist, however, due to the nature of the models initially adopted and because of the difficulty to define the more appropriate space group and the positions of hydrogen atoms. Future research using transmission electron microscopy could help resolve the question of the space group, whereas neutron diffraction could define the positions of the hydrogen atoms.

**Table 2.** Gorceixite data from literature.

| Crystal system       | Monoclinic   | Trigonal  |
|----------------------|--|---|
| Formula              | $\text{BaAl}_3(\text{PO}_4)[\text{PO}_3(\text{OH})](\text{OH})_6$                      | $\text{Ba}_{0.95}\text{Al}_3(\text{PO}_4)_2(\text{OH})_5(\text{H}_2\text{O})$ |
| Reference            | Radoslovich, 1982  | Radoslovich and Slade, 1980   |
| Space group          | Cm ( $n^o$ 8)  | R3m ( $n^o$ 160)  |
| Unit cell parameters | $a = 12.195(8)$ Å<br>$b = 7.040(5)$ Å<br>$c = 7.055(5)$ Å<br>$\beta = 125.19(5)^\circ$ | $a = 7.0363(2)$ Å<br>$c = 17.2819(1)$ Å                                       |
| Unit cell volume     | $495 \text{ \AA}^3$  | $740.99 \text{ \AA}^3$  |
| <i>Z</i>             | 2  | 3   |



**Figure 2.** Observed (crosses), calculated (continuous line), and difference curve from the Rietveld refinement of gorceixite (**A**: monoclinic; **B**: trigonal). Gorceixite, quartz, fluorapatite, and magnetite (from top to bottom) are the phases corresponding to the diffraction reflections represented in the lower part of the graphs.

**Table 3.** Structure refinement summary for gorceixite from Catalão (sample CAF42).

| Crystal data                                     |   |  |
|--|---|--|
| Formula  | (Ba <sub>0.76</sub> Ca <sub>0.19</sub> Sr <sub>0.10</sub> Ce <sub>0.01</sub> ) <sub>1.06</sub> (Al <sub>2.74</sub> Fe <sub>0.25</sub> ) <sub>2.99</sub> (P <sub>0.96</sub> Si <sub>0.03</sub> ) <sub>0.99</sub> O <sub>4</sub> (PO <sub>3</sub> OH)(OH) <sub>6.02</sub> |  |
| Crystal system, space group                      | monoclinic, Cm (nº 8)   | trigonal, R3m (nº 160)                 |
| Unit cell dimensions                             | a = 12.254(1) Å<br>b = 7.0776(6) Å<br>c = 6.9940(8) Å<br>β = 125.48(1) °  | a = 7.0791(3) Å<br><br>c = 17.089(1) Å |
| Unit cell volume                                 | 493.97(7) Å <sup>3</sup>  | 741.68(7) Å <sup>3</sup>               |
| Z, calculated density                            | 2, 3.346 g/cm <sup>3</sup>  | 3, 3.329 g/cm <sup>3</sup>             |
| Formula weight                                   | 497.66  |  |
| Data collection                                  |   |  |
| Diffractometer                                   | Siemens D500  |  |
| Radiation  | CuKα (λ = 1.5405 Å)   |  |
| Temperature                                      | 25° C   |  |
| Scan range, step size                            | 6 to 120°, 0.02° (2θ)   |  |
| Refinement data                                  |   |  |
| Observed reflections                             | 797   | 317                                    |
| Refined parameters number                        | 63  | 43                                     |
| Refinement software                              | GSAS  |  |
| Refinement method                                | LeBail, Rietveld  |  |
| R <sub>p</sub> , R <sub>w</sub> , χ <sup>2</sup> | 0.0302, 0.0393, 2.193   | 0.0287, 0.0367, 1.913                  |
| R <sub>F</sub>                                   | 0.0491  | 0.0477                                 |

**Table 4.** Atomic coordinates for Catalão gorceixite indexed as monoclinic. (\*) The equivalent isotropic displacement coefficients have been calculated from the published (Radoslovish, 1982) refined isotropic thermal parameters and kept constant during Rietveld refinement.

| Atom | Wyckoff | Symmetry | Occupation | x          | y          | z          | Uiso*100 (Å <sup>2</sup> ) (*) |
|------|---------|----------|------------|------------|------------|------------|--------------------------------|
| Ba1  | 2a      | m        | 0.76       | 0          | 0          | 0          | 0.671                          |
| Ca1  | 2a      | m        | 0.19       | 0          | 0          | 0          |                                |
| Sr1  | 2a      | m        | 0.10       | 0          | 0          | 0          |                                |
| P1   | 2a      | m        |            | 0.2990(15) | 0          | 0.9202(20) | 0.861                          |
| P12  | 2a      | m        |            | 0.6555(13) | 0          | 0.0767(21) | 0.431                          |
| Al1  | 2a      | m        | 0.91       | 0.9833(14) | 0          | 0.4785(26) | 0.469                          |
| Fe1  | 2a      | m        | 0.09       | 0.9833(14) | 0          | 0.4785(26) |                                |
| Al2  | 4b      | 1        | 0.91       | 0.7491(13) | 0.2400(18) | 0.5088(22) | 0.443                          |
| Fe2  | 4b      | 1        | 0.09       | 0.7491(13) | 0.2400(18) | 0.5088(22) |                                |
| O1   | 2a      | m        |            | 0.4372(26) | 0          | 0.1933(30) | 0.507                          |
| O12  | 2a      | m        |            | 0.598(4)   | 0          | 0.8247(27) | 1.102                          |
| O2   | 2a      | m        |            | 0.1514(15) | 0          | 0.825(4)   | 0.823                          |
| O22  | 2a      | m        |            | 0.8230(14) | 0          | 0.173(4)   | 0.697                          |
| O3   | 4b      | 1        |            | 0.3614(15) | 0.1478(25) | 0.8400(25) | 1.051                          |
| O33  | 4b      | 1        |            | 0.6722(25) | 0.1920(19) | 0.1989(25) | 0.823                          |
| OH1  | 2a      | m        |            | 0.2733(28) | 0          | 0.425(5)   | 0.899                          |
| OH12 | 2a      | m        |            | 0.7260(29) | 0          | 0.594(5)   | 1.254                          |
| OH2  | 4b      | 1        |            | 0.9147(14) | 0.1980(24) | 0.5738(29) | 0.443                          |
| OH22 | 4b      | 1        |            | 0.0734(14) | 0.1855(24) | 0.4314(30) | 0.621                          |

**Table 5.** Interatomic distance (Å) and estimated bond valence (v.u.) for gorceixite indexed as monoclinic.  $\Sigma a^v$  = valences of bonds emanating from cation summed over the bonded anions. **1.** Gorceixite from New South Wales, Australia (Radoslovich, 1982). **2.** Gorceixite from Catalão, Goiás, Brazil (this study).

|                    |             | 1            |              | 2         |              |
|--------------------|-------------|--------------|--------------|-----------|--------------|
|                    |             | distance     | bond valence | distance  | bond valence |
| <b>Ba</b>          |             |              |              |           |              |
| Ba1                | - O2        | 2.847(49)    | 0.17         | 2.752(29) | 0.26         |
|                    | - O22       | 2.804(50)    | 0.18         | 3.036(28) | 0.13         |
|                    | - O3 (x2)   | 2.791(39)    | 0.18         | 2.854(17) | 0.20         |
|                    | - O23 (x2)  | 2.881(44)    | 0.16         | 2.781(19) | 0.24         |
|                    | - OH1       | 2.876(138)   | 0.16         | 2.915(28) | 0.18         |
|                    | - OH12      | 2.857(138)   | 0.16         | 2.876(29) | 0.19         |
|                    | - OH2 (x2)  | 2.799(41)    | 0.18         | 2.885(20) | 0.19         |
|                    | - OH22 (x2) | 2.925(40)    | 0.15         | 2.913(21) | 0.18         |
|                    |             | $\Sigma a^v$ | 2.01         |           | 2.38         |
| <b>Tetrahedron</b> |             |              |              |           |              |
| P1                 | - O1        | 1.631(62)    | 0.98         | 1.662(21) | 0.91         |
|                    | - O2        | 1.475(38)    | 1.45         | 1.522(26) | 1.25         |
|                    | - O3 (x2)   | 1.522(16)    | 1.29         | 1.578(26) | 1.10         |
|                    |             | $\Sigma a^v$ | 5.01         |           | 4.36         |
| P12                | - O12       | 1.452(56)    | 1.53         | 1.470(25) | 1.41         |
|                    | - O22       | 1.591(44)    | 1.06         | 1.750(24) | 0.74         |
|                    | - O23 (x2)  | 1.535(16)    | 1.23         | 1.554(17) | 1.16         |
|                    |             | $\Sigma a^v$ | 5.05         |           | 4.47         |
| <b>Octahedron</b>  |             |              |              |           |              |
| Al1                | - O2        | 2.024(97)    | 0.34         | 2.079(24) | 0.32         |
|                    | - O22       | 1.802(85)    | 0.67         | 1.885(23) | 0.51         |
|                    | - OH2 (x2)  | 1.933(21)    | 0.45         | 1.940(26) | 0.45         |
|                    | - OH22 (x2) | 1.859(18)    | 0.56         | 1.864(25) | 0.54         |
|                    |             | $\Sigma a^v$ | 3.03         |           | 2.81         |
| Al2                | - O3        | 1.990(50)    | 0.42         | 2.047(21) | 0.35         |
|                    | - O23       | 1.818(46)    | 0.63         | 1.825(22) | 0.59         |
|                    | - OH1       | 1.985(15)    | 0.38         | 2.005(22) | 0.38         |
|                    | - OH12      | 1.805(16)    | 0.65         | 1.875(23) | 0.52         |
|                    | - OH2       | 1.833(34)    | 0.59         | 1.828(25) | 0.58         |
|                    | - OH22      | 1.975(26)    | 0.39         | 1.963(25) | 0.42         |
|                    |             | $\Sigma a^v$ | 3.06         |           | 2.84         |

**Table 6.** Atomic coordinates for gorceixite indexed as trigonal. (\*) The equivalent isotropic displacement coefficients have been calculated from the published (Radoslovish and Slade, 1980) refined isotropic thermal parameters and kept constant during Rietveld refinement.

| Atom | Wyckoff | Symmetry | Occupation | x          | y          | z           | Uiso*100 (Å <sup>2</sup> ) (*) |
|------|---------|----------|------------|------------|------------|-------------|--------------------------------|
| Ba1  | 3a      | 3m       | 0.76       | 0          | 0          | 0           | 0.633                          |
| Ca1  | 3a      | 3m       | 0.19       | 0          | 0          | 0           |                                |
| Sr1  | 3a      | 3m       | 0.10       | 0          | 0          | 0           |                                |
| P1   | 3a      | 3m       |            | 0          | 0          | 0.3146(6)   | 0.76                           |
| P2   | 3a      | 3m       |            | 0          | 0          | -0.3013(6)  | 0.633                          |
| Al1  | 9b      | m        | 0.91       | 0.5012(8)  | -0.5012(8) | 0.5029(7)   | 0.633                          |
| Fe1  | 9b      | m        | 0.09       | 0.5012(8)  | -0.5012(8) | 0.5029(7)   |                                |
| O1   | 3a      | 3m       |            | 0          | 0          | 0.4032(8)   | 0.887                          |
| O2   | 3a      | 3m       |            | 0          | 0          | -0.3849(9)  | 0.633                          |
| O3   | 9b      | m        |            | 0.2174(7)  | -0.2174(7) | -0.0522(7)  | 1.14                           |
| O4   | 9b      | m        |            | -0.2119(7) | 0.2119(7)  | 0.0679(7)   | 0.76                           |
| OH1  | 9b      | m        |            | 0.1202(7)  | -0.1202(7) | 0.1408(12)  | 0.507                          |
| OH2  | 9b      | m        |            | -0.1390(7) | 0.1390(7)  | -0.1415(11) | 0.76                           |

**Table 7.** Interatomic distance (Å) and estimated bond valence (v.u.) for gorceixite indexed as trigonal.  $\Sigma a^v$  = valences of bonds emanating from cation summed over the bonded anions.  
**1.** Gorceixite from New South Wales, Australia (Radoslovich, 1982). **2.** Gorceixite from Catalão, Goiás, Brazil (this study).

|                    |       |      | 1            |              | 2         |              |
|--------------------|-------|------|--------------|--------------|-----------|--------------|
|                    |       |      | distance     | bond valence | distance  | bond valence |
| <b>Ba</b>          |       |      |              |              |           |              |
| Ba1                | - O3  | (x3) | 2.835(3)     | 0.21         | 2.811(7)  | 0.23         |
|                    | - O4  | (x3) | 2.836(1)     | 0.21         | 2.845(7)  | 0.21         |
|                    | - OH1 | (x3) | 2.910(3)     | 0.18         | 2.822(18) | 0.22         |
|                    | - OH2 | (x3) | 2.815(3)     | 0.22         | 2.958(15) | 0.16         |
|                    |       |      | $\Sigma a^v$ | 2.46         |           | 2.46         |
| <b>Tetrahedron</b> |       |      |              |              |           |              |
| P1                 | - O1  |      | 1.607(9)     | 1.03         | 1.514(17) | 1.28         |
|                    | - O3  | (x3) | 1.507(2)     | 1.3          | 1.532(8)  | 1.22         |
|                    |       |      | $\Sigma a^v$ | 4.93         |           | 4.94         |
| P2                 | - O2  |      | 1.493(8)     | 1.34         | 1.429(18) | 1.55         |
|                    | - O4  | (x3) | 1.541(2)     | 1.2          | 1.610(6)  | 1.02         |
|                    |       |      | $\Sigma a^v$ | 4.94         |           | 4.61         |
| <b>Octahedron</b>  |       |      |              |              |           |              |
| Al1                | - O3  |      | 1.962(11)    | 0.42         | 2.001(16) | 0.39         |
|                    | - O4  |      | 1.846(11)    | 0.56         | 1.828(16) | 0.58         |
|                    | - OH1 | (x2) | 1.930(7)     | 0.46         | 1.881(9)  | 0.51         |
|                    | - OH2 | (x2) | 1.861(7)     | 0.54         | 1.944(8)  | 0.44         |
|                    |       |      | $\Sigma a^v$ | 2.98         |           | 2.88         |

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