

GUIMARÃESITE, A NEW Zn-DOMINANT MONOCLINIC ROSCHERITE-GROUP MINERAL FROM ITINGA, MINAS GERAIS, BRAZIL*

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Guimarãesite¹, Ca₂(Zn,Mg,Fe)₅Be₄(PO₄)₆(OH)₄·6H₂O, monoclinic, is a new member of the roscherite-group. It occurs as a late fracture-filling mineral in a phosphate-rich granite pegmatite near the Piauí river, Itinga county, Minas Gerais, Brazil. Associated minerals are: albite, microcline, quartz, elbaite, lepidolite, schorl, eosphorite, moraesite, saleeite, zanazziite, an iron-dominant roscherite-group mineral, opal. Guimarãesite forms peripheral zones (up to 0.1 mm thick) in crystals of roscherite-group minerals. The inner zones of the crystals are Mg-rich (and correspond to zanazziite) or Fe-rich (greifensteinite and/or ruifrancoite). Its colour is brown, the streak is white and the lustre is vitreous. Guimarãesite is transparent and non-fluorescent. Density (calc.) is 2.963 g/cm³. The mineral is biaxial (-), α 1.596(2), β 1.600(2), γ 1.602(2) (589 nm). 2V(obs.) 55-75°, 2V(calc.) 70°. The optical X axis coincides with the elongation direction, dispersion: none observed. It is colourless under the microscope. The chemical composition is (wt. %, ranges are indicated in brackets; EDS mode electron microprobe): CaO 9.72 (9.61-9.79); MgO 4.00 (3.61-4.74); MnO 2.18 (0.89-3.26); FeO 2.65 (1.40-4.45); ZnO 19.06 (16.33-20.50); Al₂O₃ 1.70 (1.53-1.92); BeO (calculated) 8.975; P₂O₅ 38.20 (37.61-37.78); H₂O (calculated by difference) 13.515, total 100.00. The empirical formula based on six (PO₄) groups per formula unit is Ca_{1.93}(Zn_{2.61}Mg_{1.11}Fe_{0.41}²⁺Al_{0.37}Mn_{0.34})_{Σ4.84}Be_{4.00}(PO₄)_{6.00}(OH)_{3.90}·6.41H₂O. The strongest reflections of the powder diffraction pattern [*d*, Å (*I*, %) (*hkl*)] are: 9.98 (90) (110), 5.98 (100) (020), 4.82 (80) (310), 3.152 (90) (-202), 3.052 (70) (-421), 2.961 (70) (040, 202), 2.841 (70) (-312), 2.708 (80) (041). Unit cell parameters refined from powder data are *a* = 15.98(1) Å, *b* = 11.84(2) Å, *c* = 6.63(1) Å, β = 95.15(15)°, *V* = 1249.4(34) Å³, *Z* = 2. The space group is *C2/c*. The name is for Djalma Guimarães (1895-1973), in recognition of his outstanding contributions to Brazilian mineralogy and geology. Holotype specimen of guimarãesite is deposited in the Museu de Geociências, Instituto de Geociências, Universidade de São Paulo, Brazil, registration number DR 591. 3 tables, 3 figures and 16 references

Introduction

As it was shown in the course of recent investigations (Atencio *et al.*, 2005; Chukanov *et al.*, 2006), hydrous berylophosphates of the roscherite group are characteristic minerals of late parageneses connected with phosphorus-rich rare metal granite pegmatites. These minerals are characterized by wide variations of chemical composition reflecting diversity of local conditions of mineral formation. Now Mn-, Mg-, Fe²⁺- and Fe³⁺-dominant monoclinic roscherite-group minerals are known (respectively, roscherite, zanazziite, greifensteinite and ruifrancoite), as well as two triclinic members of this group (atencioite and footemineite). New Zn-dominant monoclinic member of the roscherite group guimarãesite, Ca₂(Zn,Mg,Fe)₅Be₄(PO₄)₆(OH)₄·6H₂O described

in this publication was named in honour of the Brazilian mineralogist Djalma Guimarães (1895-1973). He published several papers and books on geology, petrology, mineralogy and geochemistry, and is the author of the mineral arrojadite and of problematic minerals as "eschwegeite", "giannettite" and "pennaite". Djalma Guimarães was honored with the name "djalmaite" (later renamed as uranmicrolite). The name "Guimarãesite" was improperly applied more than 50 years ago (Gagarin & Cuomo 1949) to an unnamed mineral, incompletely described by Guimarães (1926). The new mineral has been approved by the CNMNMN-IMA (vote 2006-028).

Holotype material is deposited under the number DR591 in the Museu de Geociências, Instituto de Geociências, Universidade de

* It was approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association on September, 1, 2006, No 2006-028



Fig. 1. Type locality of guimarã esite: sketch map

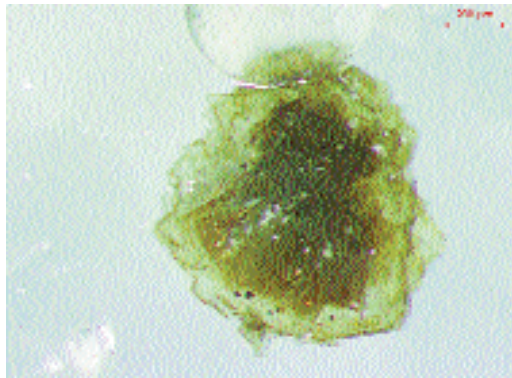


Fig. 2. Crystals of roscherite-group minerals with guimarã esite peripheral zones.

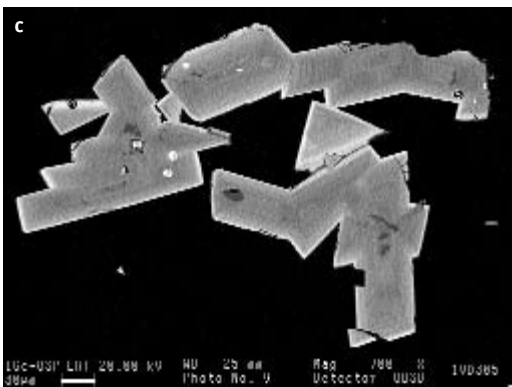
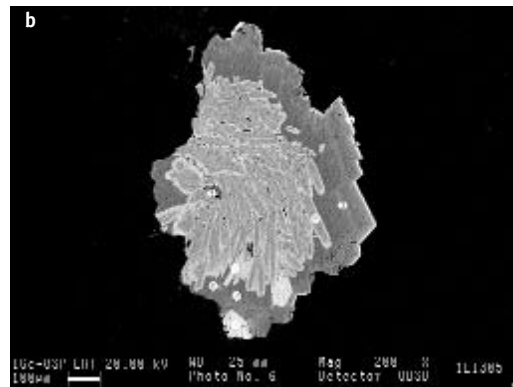
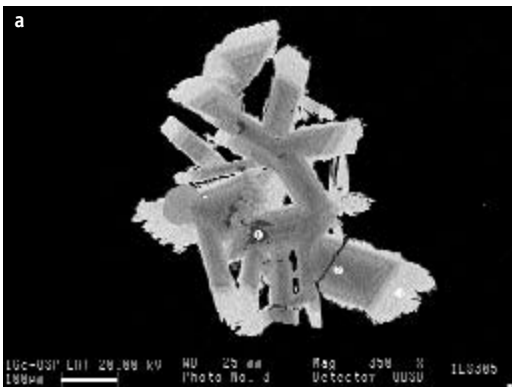
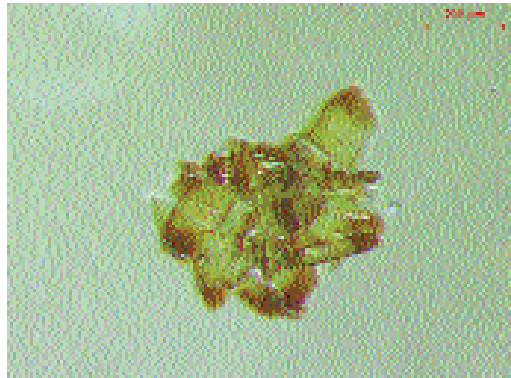


Fig. 3. Polished sections of aggregates of a roscherite-group mineral with guimarã esite peripheral zones. SEM-photos. The electron-microprobe analyses in the points 3 (on Fig. 3a), 6 (on Fig. 3b) and 4 (on Fig. 3c) correspond to guimarã esite.

Table 1. Chemical data for guimarã esite

Constituent	Wt.%,	Range	Probe Standard
CaO	9.72	9.61–9.79	Wollastonite
MgO	4.00	3.61–4.74	Diopside
MnO	2.18	0.89–3.26	MnTiO ₃
FeO	2.65	1.40–4.45	Fe
ZnO	19.06	16.33–20.50	Zn
Al ₂ O ₃	1.70	1.53–1.92	Al ₂ O ₃
P ₂ O ₅	38.20	37.61–38.78	LaPO ₄
BeO*	(8.975)		
H ₂ O*	(13.515)		
Total	(100.00)		

Notes: Calculated, see text

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Occurrence, appearance and physical properties

The mineral occurs as a late fracture-filling mineral in a phosphate-rich granite pegmatite near the Piauí river, Itinga county, Minas Gerais, Brazil (16°36'47"S and 41°45'55"W), Fig.1. Associated minerals are: albite, microcline, quartz, elbaite, lepidolite, schorl, eosphorite, moraesite, saleeite, zanazziite, an Fe-dominant roscherite-group mineral, opal.

Guimarã esite forms peripheral zones (up to 0.1 mm thick) in crystals of roscherite-group minerals. The inner zones of the crystals are Mg-rich (and correspond to zanazziite) or Fe-rich (greifensteinite and/or ruifrançoite?) (Figs. 2 and 3). Its colour is brown, the streak is white and the lustre is vitreous. Guimarã esite is transparent and non-fluorescent. Mohs hardness is probably about 4.5 by analogy with other roscherite-group minerals. The mineral is brittle. Density could not be measured because of zonal grains. Density calculated with empirical formula is 2.963 g/cm³. By analogy with other roscherite-group minerals, guimarã esite should have perfect cleavage on {100} and good cleavage on {010}. Fracture is uneven. The crystals are not adequate for morphological observations. Forms are probably {100}, {001} and {010} (from prismatic habit). The crystals are tabular parallel to (100). Twinning was not observed.

Optical properties

Guimarã esite is biaxial, negative, α 1.596(2), β 1.600(2), γ 1.602(2); $2V_{\text{obs.}} = 55 - 75^\circ$, $2V_{\text{calc.}} = 70^\circ$. Orientation: the optical X axis

Table 2. X-ray powder-diffraction data for guimarã esite

$I_{\text{obs.}}$	$d_{\text{obs.}}$	$d_{\text{calc.}}$	hkl
90	9.48	9.50	110
10	7.93	7.96	200
100	5.98	5.92	020
20	5.30	5.29	111
80	4.82	4.84	310
30	4.41	4.41	021
60	3.358	3.345	-131
90	3.152	3.151	-202
70	3.052	3.046	-421
70	2.961	2.960	040
		2.957	202
70	2.841	2.838	-312
60	2.798	2.797	331
80	2.708	2.701	041
20	2.528	2.530	241
		2.528	-132
40	2.423	2.427	-422
		2.421	620
50	2.360	2.354	-512
60	2.272	2.274	-441
		2.268	531
70	2.223	2.227	332
		2.217	-151
60	2.161	2.162	350
		2.158	512, -242
10	2.093	2.092	242
50	2.036	2.039	-223
		3.033	-622, 351
50	1.985	1.989	800
		1.983	602
30	1.925	1.928	-641
		1.927	-133
		1.922	-152
20	1.869	1.868	-513
20	1.826		
40	1.781		
40	1.751		
30	1.699		
70	1.642		
20	1.612		
30	1.587		

coincides with the elongation direction; $Z \approx a$. The mineral shows direct extinction with respect to elongation direction. Dispersion is none observed. The mineral is none-pleochroic, colourless under the microscope.

For dark (Fe-dominant) zones of crystals

Table 3. Comparative data for guimarã esite and isostructural minerals (all monoclinic, *C2/c*)

Name	Guimarã esite ¹	Ruifrancoite ²	Roscherite ³	Zanazziite ⁴	Greifensteinite ⁵
Chemical formula	Ca ₂ (Zn ,Mg,Fe) ₅ Be ₄ (PO ₄) ₆ (OH) ₄ ·6H ₂ O	Ca ₂ □ ₂ (Fe ³⁺ ,Mn,Mg) ₄ Be ₄ (PO ₄) ₆ (OH) ₄ ·6H ₂ O	Ca ₂ Mn ₃ Be ₄ (PO ₄) ₆ (OH) ₄ ·6H ₂ O	Ca ₂ Mg ₃ Be ₄ (PO ₄) ₆ (OH) ₄ ·6H ₂ O	Ca ₂ Fe ₅ ³⁺ Be ₄ (PO ₄) ₆ (OH) ₄ ·6H ₂ O
Unit-cell dimensions	<i>a</i> = 15.98 Å <i>b</i> = 11.84 Å <i>c</i> = 6.63 Å <i>β</i> = 95.15°	<i>a</i> = 15.92 Å <i>b</i> = 11.91 Å <i>c</i> = 6.61 Å <i>β</i> = 96.47°	<i>a</i> = 15.935 Å <i>b</i> = 11.963 Å <i>c</i> = 6.664 Å <i>β</i> = 94.77°	<i>a</i> = 15.874 Å <i>b</i> = 11.854 Å <i>c</i> = 6.605 Å <i>β</i> = 95.35(3)°	<i>a</i> = 15.903(7) Å <i>b</i> = 11.885(7) Å <i>c</i> = 6.677(3) Å <i>β</i> = 94.68°
Optical data	<i>n_p</i> = 1.596(2) <i>n_m</i> = 1.600(2) <i>n_y</i> = 1.602(2) 2 <i>V_{obs.}</i> = 55–75° 2 <i>V_{calc.}</i> = 70°	<i>n_p</i> = 1.665(3) <i>n_m</i> = 1.665(3) <i>n_y</i> = 1.682(3) 2 <i>V_{obs.}</i> = 0–10° 2 <i>V_{calc.}</i> = 0°	<i>n_p</i> = 1.624 <i>n_m</i> = 1.639 <i>n_y</i> = 1.643 2 <i>V_{calc.}</i> = 54°	<i>n_p</i> = 1.606(2) <i>n_m</i> = 1.610(2) <i>n_y</i> = 1.620(2) 2 <i>V_{obs.}</i> = 72° 2 <i>V_{calc.}</i> = 65.0°	<i>n_p</i> = 1.624(2) <i>n_m</i> = 1.634(2) <i>n_y</i> = 1.638(2) 2 <i>V_{obs.}</i> = 80(10) 2 <i>V_{calc.}</i> = 64(20)°

Note: Species-forming octahedral cations are given in bold.

¹This work; ²Atencio *et al.*, submitted; ³Rastsvetaeva *et al.*, 2005; Larsen, Berman, 1934; ⁴Leavens *et al.*, 1990; ⁵Chukanov *et al.*, 2002; Rastsvetaeva *et al.*, 2002.

mean refractive index is > 1.64 which can be connected with high content of Fe³⁺ (compare ruifrancoite, the Fe³⁺-member of the roscherite group).

Chemical data

Three point analyses were carried out by means of an electron microprobe (EDS mode, 15.7 kV, 0.5 nA, 8 μm beam diameter). The contents of K, Sr, Ba, Pb, Ni, Cr, Si, S, V, F are below their detection limits. BeO was calculated from the condition Be:P = 2:3 (the stable atomic proportion for roscherite-group minerals following from specific features of their crystal structures). H₂O was calculated by difference. Averaged analytical results are given in Table 1. The empirical formula, calculated based on six (PO₄) groups per formula unit is Ca_{1.93}(Zn_{2.61}Mg_{1.11}Fe_{0.41}²⁺Al_{0.37}Mn_{0.34})_{Σ4.84}Be_{4.00}(PO₄)_{6.00}(OH)_{3.90}·6.41H₂O. The simplified formula is Ca₂(Zn,Mg,Fe)₅Be₄(PO₄)₆(OH)₄·6H₂O. The end-member formula is: Ca₂Zn₅Be₄(PO₄)₆(OH)₄·6H₂O, which requires: CaO 9.43, ZnO 34.22, BeO 8.41, P₂O₅ 35.81, H₂O 12.12, total 99.99 wt.%.

Crystallography

Single-crystal electron-microdiffraction data revealed the mineral is monoclinic, space group *C2/c*, *a* 15.9(1)Å, *b* 11.85(15)Å, *c* 6.7(1) Å, *β* 95(1)°, *V* 1258(25)Å³, *Z* = 2. X-ray

powder-diffraction data (Table 2) have been obtained for most Zn-enriched particles with sizes 0.05–0.1 mm (selected using semi-quantitative electron microprobe analysis), with RKG 86 mm diameter Debye-Scherrer camera, using CuKα irradiation. Unit cell parameters refined from powder data are *a* = 15.98(1) Å, *b* = 11.84(2) Å, *c* = 6.63(1) Å, *β* = 95.15(15)°, *V* = 1249.4(34) Å³. The *a*:*b*:*c* ratio is: 1.3497:1:0.5600. Compatibility 1-(*K_p*/*K_c*) is 0.031, excellent.

Discussion: crystal chemistry of the roscherite group

The crystal structure of all representatives of the roscherite group studied previously (Fanfani *et al.*, 1975, 1977; Rastsvetaeva *et al.*, 2002, 2004a, 2004b, 2005; Barinova *et al.*, 2004; Chukanov *et al.*, 2006), is based on a three-dimensional framework composed of tetrahedra, octahedra, and calcium seven-vertex polyhedra. The Be and P tetrahedra form infinite chains combined into a mixed framework through *M* octahedra, which, in turn, form octahedral chains by sharing edges. Calcium occurs in the framework cavities. Monoclinic members of the roscherite group are characterized by the space group *C2/c*. Their simplified crystal-chemical formula is Ca₂D₂M₄Be₄(PO₄)₆(OH)₆·4H₂O where *D* and *M* are octahedral cations Mg, Mn²⁺, Fe²⁺, Fe³⁺, Al, Zn. The site *M* is fully occupied; the site *D* con-

tains 50% vacancies, hence the total number of octahedral cations is 5. *D*-polyhedron is characterized by enhanced cation-anion distances (as compared with *M*-polyhedron) and is populated mainly by divalent cations. Monoclinic mineral species from the roscherite group are distinguished by the prevailing octahedral cation. Earlier Mn-, Mg-, Fe²⁺- and Fe³⁺-dominant members have been described (see Table 3). In guimarã esite prevailing octahedral cation is Zn. In the structurally investigated Zn-rich greifensteinite from Brazil (Barinova *et al.*, 2004), all Zn is localized in the *M* site. By analogy, one can suppose that the same takes place in guimarã esite. Among monoclinic roscherite-group minerals, guimarã esite has the largest value of the a unit-cell dimension and the lowest value of refractive index γ (see Table 3).

Triclinic members of the roscherite group form another subgroup (Fanfani *et al.* 1977, Rastsvetaeva *et al.* 2004b, Chukanov, Möckel, 2005, Chukanov *et al.* 2006). Lowering of symmetry is connected with the splitting of the sites *D* and *M* into two pairs of non-equivalent (and differently occupied) sites.

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