

## Zoned phosphosiderite-metavariscite crystals from Eduardo Mine, Conselheiro Pena, Minas Gerais, Brazil

*Cristais zonados de fosfossiderita-metavariscita da Mina do Eduardo, Conselheiro Pena, Minas Gerais, Brazil*

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### ABSTRACT

Zoned phosphosiderite-metavariscite crystals are recorded for the first time, in a phosphate-rich granitic pegmatite, at the Eduardo mine, Conselheiro Pena, Minas Gerais, Brazil. Metavariscite is described for the first time in Brazil. Phosphosiderite and metavariscite occur as small friable, globular agglomerates, up to 2 mm, with purple to lilac color, in miarolitic cavities up to 1 cm in the pegmatite. Phosphosiderite, ideally  $\text{Fe}^{3+}(\text{PO}_4) \cdot 2\text{H}_2\text{O}$ , and metavariscite, ideally  $\text{Al}(\text{PO}_4) \cdot 2\text{H}_2\text{O}$ , are isostructural. Empirical formulae from EDS analysis ( $\text{H}_2\text{O}$  by difference) are, respectively,  $(\text{Fe}^{3+}_{0.65}\text{Al}_{0.24})_{\Sigma 0.89}[\text{PO}_{3.67}(\text{OH})_{0.33}] \cdot 0.96\text{H}_2\text{O}$  and  $(\text{Al}_{0.61}\text{Fe}^{3+}_{0.23})_{\Sigma 0.84}[\text{PO}_{3.52}(\text{OH})_{0.48}] \cdot 0.97\text{H}_2\text{O}$ . The differences between ideal and empirical formulae are attributed to the instability of the crystals under the electron beams. Only the peaks for phosphosiderite were observed in the X-ray powder diffraction pattern due to the small proportion of metavariscite in the mixture. Unit cell parameters calculated for phosphosiderite are:  $a$  5.368(7),  $b$  9.778(10),  $c$  8.710(9) Å,  $\beta$  90.9(1)°,  $V$  457.1(9) Å<sup>3</sup>.

**Keywords:** Phosphosiderite; Metavariscite; Conselheiro Pena; Minas Gerais; Zoned Crystals.

### Resumo

Cristais zonados de fosfossiderita-metavariscita são registrados pela primeira vez, em um pegmatito granítico rico em fosfato, na Mina do Eduardo, Conselheiro Pena, Minas Gerais, Brasil. Metavariscita é descrita pela primeira vez no Brasil. Fosfossiderita e metavariscita ocorrem como aglomerados globulares pequenos e friáveis, de até 2 mm, com cor púrpura a lilás, em cavidades miarolíticas de até 1 cm no pegmatito. Fosfossiderita, idealmente  $\text{Fe}^{3+}(\text{PO}_4) \cdot 2\text{H}_2\text{O}$ , e metavariscita, idealmente  $\text{Al}(\text{PO}_4) \cdot 2\text{H}_2\text{O}$ , são isoestruturais. Fórmulas empíricas a partir de análises por EDS ( $\text{H}_2\text{O}$  por diferença) são, respectivamente,  $(\text{Fe}^{3+}_{0.65}\text{Al}_{0.24})_{\Sigma 0.89}[\text{PO}_{3.67}(\text{OH})_{0.33}] \cdot 0,96\text{H}_2\text{O}$  e  $(\text{Al}_{0.61}\text{Fe}^{3+}_{0.23})_{\Sigma 0.84}[\text{PO}_{3.52}(\text{OH})_{0.48}] \cdot 0,97\text{H}_2\text{O}$ . As diferenças entre as fórmulas ideais e empíricas são atribuídas à instabilidade dos cristais sob os feixes eletrônicos. Apenas os picos da fosfossiderita foram observados nos difratogramas de raios X devido à pequena proporção de metavariscita na mistura. Parâmetros de cela unitária calculados para fosfossiderita são:  $a$  5,368(7),  $b$  9,778(10),  $c$  8,710(9) Å,  $\beta$  90,9(1)°,  $V$  457,1(9) Å<sup>3</sup>.

**Palavras-chave:** Fosfossiderita; Metavariscita; Conselheiro Pena; Minas Gerais; Cristais Zonados.

## INTRODUCTION

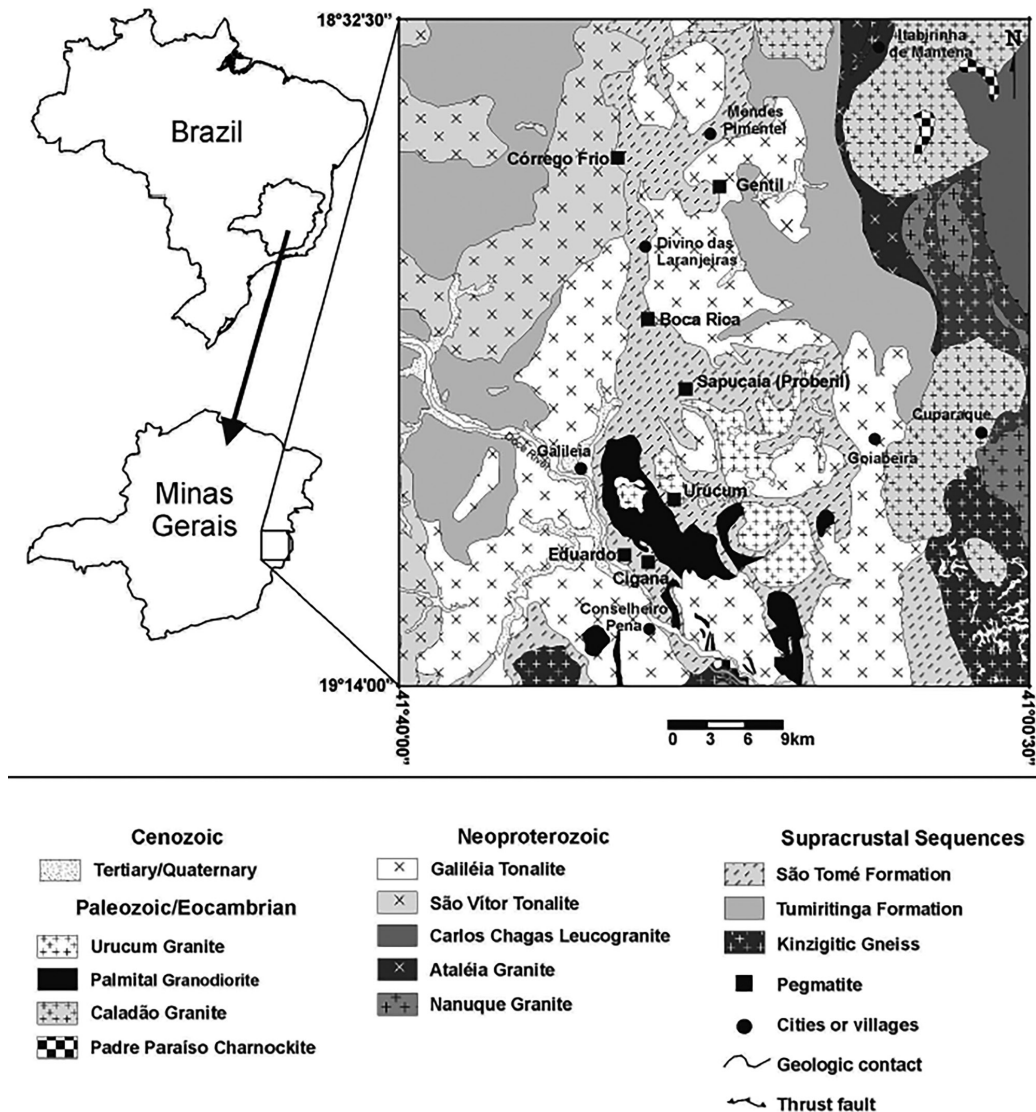
Phosphosiderite is ideally  $\text{Fe}^{3+}(\text{PO}_4) \cdot 2\text{H}_2\text{O}$ , and metavariscite, ideally  $\text{Al}(\text{PO}_4) \cdot 2\text{H}_2\text{O}$ . They are monoclinic, isostructural, and belong to the  $P2_1/n$  space group (Borensztajn, 1966). This is the first time that zoned crystals of these two minerals are recorded. In addition, this is the first time metavariscite is registered in Brazil.

## GEOLOGICAL SETTING

The basic geological information about Eduardo Mine was summarized by Scholz et al. (2014). This mine (“Lavra

do Eduardo”, in Portuguese), near Boa Vista creek, Conselheiro Pena municipality, Minas Gerais, Brazil ( $19^\circ 4' 53.09''\text{S } 41^\circ 30' 34.10''\text{W}$ ), was erroneously quoted as Boa Vista Mine, another famous mine, by Bermanec et al. (2011). It is located in Conselheiro Pena Pegmatite District (Figure 1), one of the subdivisions of the Eastern Brazilian Pegmatite province, that encompasses an area of about 150,000 km<sup>2</sup>, extending from Bahia to Rio de Janeiro states (Pedrosa-Soares et al., 2011). Around 90% of the province is situated in the eastern part of the state of Minas Gerais.

The Conselheiro Pena Pegmatite District, inserted in the central domain of Araçuaí Mobile Belt (Almeida, 1977), covers an area of about 5,000 km<sup>2</sup>, in the middle part of



**Figure 1.** Geological map of the Conselheiro Pena Pegmatite district and the location of the most important phosphate-rich pegmatites (after Netto et al., 1998 *apud* Scholz et al., 2014).

Doce River basin, approximately 360 km NE of the city of Belo Horizonte. It was formed during the Brasiliano orogeny (630-490 Ma) by accretion to the eastern margin of the São Francisco craton (Pedrosa-Soares et al., 2011). In this area, several suites of granitoid rocks are distinguished (e.g. Urucum and Palmital of Eocambrian to Paleozoic age, and Galileia of Neoproterozoic age), intruding schists of the Neoproterozoic São Tomé Formation (Nalini et al., 2008).

The pegmatite is heterogeneous, with well-developed mineralogical and textural zoning. It has symmetric lens shape, with the longer axis trending NW-SE and steeply dipping. Their minimum extension is around 20 m, and the thickness is 12 m. The pegmatite is hosted by quartz-mica schist with garnet, staurolite and sillimanite of the São Tomé Formation. Tourmalinization is observed in the contact between the pegmatite and the host rock. Hydrothermal and metasomatic fluids were responsible for the albitization and development of miarolitic cavities, and a complex secondary phosphate assemblage was described by Chaves et al. (2005). The pegmatite crops out on a steep hillside, and, at the uppermost end, pinches out to less than 1 m in width.

Eduardo Pegmatite was mined for industrial feldspar and with minor importance gemstones and samples for the collectors market, mainly phosphates (red variscite, phosphosiderite and cyrilovite) and arsenates (scorodite and pharmacosiderite). Other minerals found in the pegmatite, including secondary species, are albite, garnets of the almandine-spessartine solid-solution series, arsenopyrite, beryl, bismuth, bütschliite, cryptomelane, löllingite, fourmarierite, frondelite-rockbridgeite solid-solution series, heterosite, hureaulite, kaolinite, leucophosphite, manganese oxides, metatorbernite, microcline, muscovite, quartz, saléite, schorl, spodumene, strengite, triphylite, and ushkovite (Bermanec et al., 2011). Several other minerals were quoted: autunite, barbosalite, bermanite, goethite, gordonite, jahnsite-(CaMnMg), jarosite, laueite, lipscombite, meurigite-K, mitridatite, natrodufrénite, rockbridgeite, schoonerite, serrabrancaite, sulfur, symplectite, tavorite, whiteite-(CaFeMg), and whiteite-(MnFeMg) (<http://www.mindat.org/loc-211260.html>). Recently, the new mineral Césarferreiraite (Scholz et al., 2014) was described in Eduardo mine. At present, the Eduardo pegmatite is mined out.

## OCCURRENCE

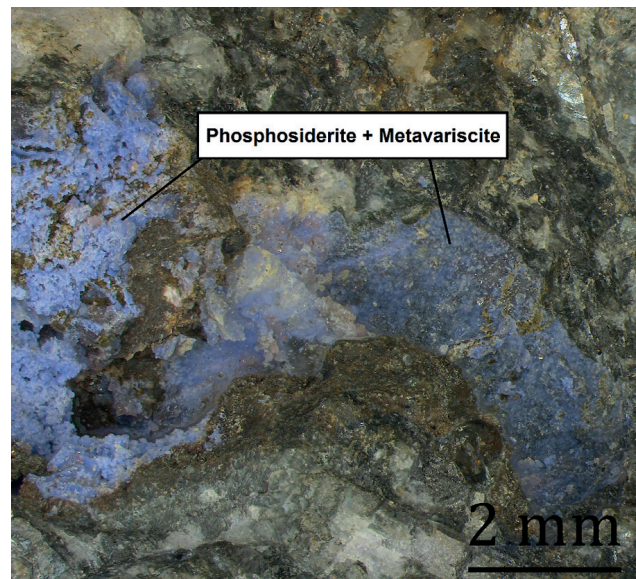
Phosphosiderite and metavariscite (Figure 2) occur as small friable, globular agglomerates, up to 2 mm, with purple to lilac color, in miarolitic cavities up to 1 cm in the pegmatite.

## METHODS

In this research there were used powder X-ray diffraction data for the phosphosiderite-metavariscite mixture, obtained with a D8 Advance DaVinci diffractometer using CuK $\alpha$  radiation. The chemical compositions were obtained using a LEO440 electron microscopy equipped with Si-Li detector (EDS mode, 15kV, 1.5 nA, 100s counting time) in the laboratories of Institute of Geosciences, University of São Paulo. The first one allows us to identify interplanar distances of crystalline reticulum whereas the Scanning Electron Microscopy (SEM) with EDS supplies chemical data and oxide proportions. Therefore, from these data, it is possible to calculate the chemical formulae of the analyzed mineral.

## CHEMICAL COMPOSITION

Chemical analyses were carried out on a zoned crystal (four analyses for phosphosiderite and five for metavariscite), and H<sub>2</sub>O was calculated by difference. Analytical data are given in Table 1. Empirical formulae (based on one P *apfu*) are, respectively, (Fe<sup>3+</sup><sub>0.65</sub>Al<sub>0.24</sub>)<sub>Σ0.89</sub> [PO<sub>3.67</sub>(OH)<sub>0.33</sub>].0.96H<sub>2</sub>O and (Al<sub>0.61</sub>Fe<sup>3+</sup><sub>0.23</sub>)<sub>Σ0.84</sub> [PO<sub>3.52</sub>(OH)<sub>0.48</sub>].0.97H<sub>2</sub>O. The differences between ideal and empirical formulae are attributed to the instability of the crystals under the electron beams. They were locally burst, as it is possible to observe in the secondary electrons image (Figure 3). Metavariscite is more unstable than phosphosiderite.



**Figure 2.** Minerals association of phosphosiderite and metavariscite in miarolitic cavity.

## CRYSTALLOGRAPHY

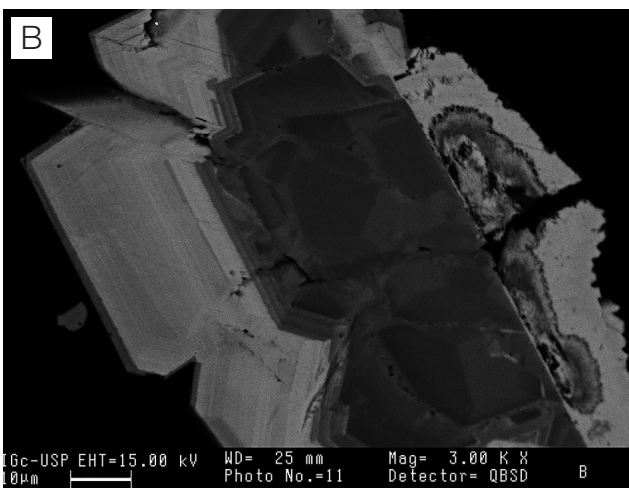
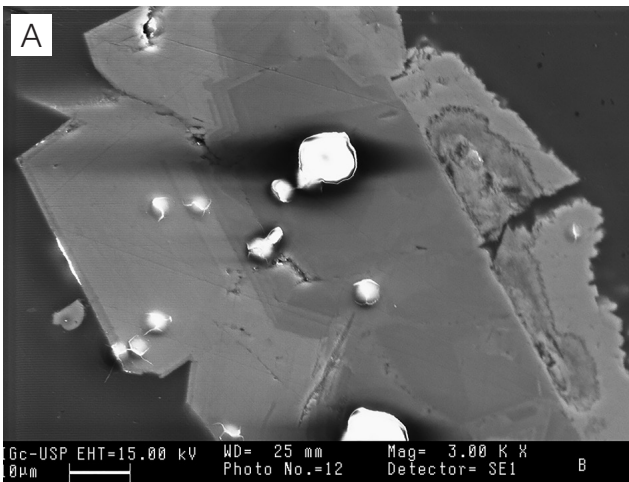
Only the peaks for phosphosiderite were observed due to the small proportion of metavariscite in the mixture

(Figure 4). The data are given in Table 2. Unit cell parameters calculated with the software CellCalc (Miura, 2003) are compared to those of phosphosiderite and metavariscite in Table 3.

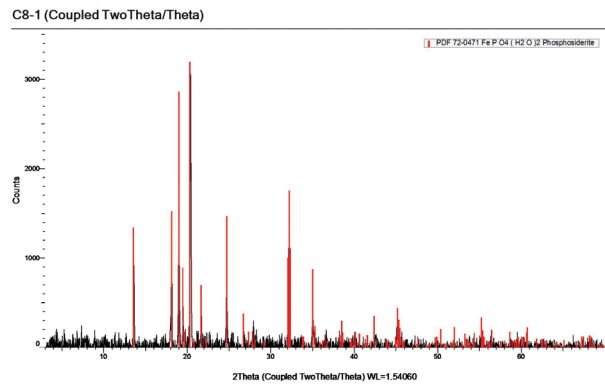
**Table 1.** Analytical data for phosphosiderite and metavariscite.

Constituent	Phosphosiderite		Metavariscite		Probe standard
	wt%	Range	wt%	Range	
Na <sub>2</sub> O			0.05	n.d. – 0.18	Albite
MnO			0.04	n.d. – 0.22	Mn
CoO	0.12	n.d. – 0.46	0.06	n.d. – 0.28	Co
Fe <sub>2</sub> O <sub>3</sub>	33.25	30.95 – 38.42	12.85	7.91 – 18.98	Fe
Al <sub>2</sub> O <sub>3</sub>	7.97	3.72 – 10.41	21.70	13.10 – 26.21	Al <sub>2</sub> O <sub>3</sub>
P <sub>2</sub> O <sub>5</sub>	45.65	44.52 – 46.93	50.01	49.42 – 50.90	GaP
H <sub>2</sub> O*	(13.01)		(15.09)		
Total	(100.00)		(100.00)	-	

\*By difference.



**Figure 3.** (A) Secondary and (B) backscattered electron images of a zoned crystal. The central part (darker) is aluminum-rich (metavariscite) and the outside part (clearer) is iron-rich (phosphosiderite).



**Figure 4.** X-ray diffractogram for phosphosiderite.

**Table 2.** X-ray powder diffraction data for phosphosiderite.

h	k	l	d <sub>calc.</sub> (Å)	d <sub>obs.</sub> (Å)	I <sub>obs.</sub>
0	1	1	6.503	6.479	16
0	2	0	4.889	4.880	100
1	1	0	4.705	4.662	83
-1	0	1	4.602	4.548	12
1	0	1	4.537	4.548	12
0	0	2	4.354	4.342	43
1	1	1	4.116	4.096	14
1	2	0	3.614	3.596	19
-1	2	1	3.351	3.328	7
-1	1	2	3.218	3.197	7
1	3	0	2.786	2.778	52
0	1	3	2.783	2.771	30
1	3	1	2.647	2.642	6
-1	0	3	2.570	2.565	6
3	2	0	1.680	1.681	4
-2	1	4	1.679	1.681	4
0	6	0	1.630	1.631	6
1	1	5	1.626	1.627	5

**Table 3.** Unit cell parameters for phosphosiderite from Eduardo mine compared to literature data for phosphosiderite and metavariscite.

	Phosphosiderite from Eduardo mine	Phosphosiderite <sup>1</sup>	Metavariscite <sup>2</sup>
<i>a</i> (Å)	5.368(7)	5.335(5)	5.178(2)
<i>b</i> (Å)	9.778(10)	9.808(12)	9.514(2)
<i>c</i> (Å)	8.710(9)	8.720(7)	8.454(2)
β(°)	90.9(1)	90.54(5)	90.35(2)
<i>V</i> (Å <sup>3</sup> )	457.1(9)	456.3	416.5

<sup>1</sup>Taxer and Bartl, 2004; <sup>2</sup>Kniep and Mootz, 1973.

## CONCLUSIONS

In brief, phosphosiderite and metavariscite, identified in analysis, had not been identified in Eduardo Mine (MG) yet. It is also the first time that zoned crystals of these two minerals are described, as well as it is the first register of occurrence of metavariscite in Brazil.

## ACKNOWLEDGEMENTS

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