

Césarferreiraite, $\text{Fe}^{2+}\text{Fe}_2^{3+}(\text{AsO}_4)_2(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, from Eduardo mine, Conselheiro Pena, Minas Gerais, Brazil: Second arsenate in the laueite mineral group

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ABSTRACT

Césarferreiraite, $\text{Fe}^{2+}\text{Fe}_2^{3+}(\text{AsO}_4)_2(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, is a new laueite-group mineral (IMA 2012-099) of triclinic symmetry, from Eduardo pegmatite mine, Conselheiro Pena municipality, Minas Gerais, Brazil. Intimately associated minerals are pharmacosiderite, scorodite, and earlier arsenopyrite, and probably césarferreiraite replaces the latter. It occurs as fibrous-to-tabular aggregates up to 2 mm. Single crystals, up to 10 μm long with a thickness of about 1–2 μm , are elongated along [001] and flattened on (100). The fibers have almost rectangular cross-section apparently bound by the {100} and {010} pinacoid forms. Color and streak are pale to greenish yellow. Luster is vitreous; individual crystals are transparent and masses are translucent. Cleavage is distinct, presumably on {010} and {100}. Calculated density is 2.934 g/cm^3 . The mineral is biaxial (+), $n(\text{min}) = 1.747(3)$, $n(\text{max}) = 1.754(3)$ (589 nm). IR spectrum of césarferreiraite is unique and can be used for the identification of the mineral. Chemical composition ($n = 4$, WDS, calculated for the condition $\text{Fe}^{2+}:\text{Fe}^{3+} = 1:2$, H_2O for the ideal structural formula, wt%) is: FeO 11.50, Fe_2O_3 25.56, CaO 15.41, As_2O_5 33.51, H_2O 26.01, total 100.12. The empirical formula (based on 18 O apfu) is $\text{Fe}_{0.98}^{2+}\text{Fe}_{1.96}^{3+}[(\text{AsO}_4)_{1.79}(\text{PO}_4)_{0.31}](\text{OH})_{1.52} \cdot 8.08\text{H}_2\text{O}$. The strongest eight X-ray powder-diffraction lines [d in Å (hkl)] are: 9.85(95)(010), 6.35(100)(001), 3.671(29)($\bar{1}21$), 3.158(32)($\bar{1}30$), 2.960(39)(022), 2.884(35)($\bar{1}31$), 2.680(29)($\bar{2}11$), and 2.540(23)($\bar{2}10$). Unit-cell parameters refined from powder data indexed by analogy with related laueite-group minerals (space group: $P\bar{1}$) are: $a = 5.383(2)$, $b = 10.363(3)$, $c = 6.878(2)$ Å, $\alpha = 96.42(4)$, $\beta = 109.19(3)$, $\gamma = 102.30(2)^\circ$, $V = 347.1(2)$ Å³, and $Z = 1$. Gladstone-Dale compatibility is -0.020 (excellent). Césarferreiraite is the arsenate analog of ferrolaueite.

Keywords: Césarferreiraite, new mineral, granitic pegmatite, Conselheiro Pena, Minas Gerais, Brazil, laueite group, iron arsenate

INTRODUCTION

In May 2009, during the preparation of the Eastern Brazilian Pegmatite field trip for the 4th International Symposium on Granitic Pegmatites (PEG 2009), two of the authors (R.S. and A.W.R.) found a centimetric cavity covered by pharmacosiderite and an unusual yellowish fibrous aggregate. The latter turned out a new mineral species belonging to the laueite group, with the formula $\text{Fe}^{2+}\text{Fe}_2^{3+}(\text{AsO}_4)_2(\text{OH})_2 \cdot 8\text{H}_2\text{O}$. It was approved by the IMA CNMNC on March 1, 2013, with the name césarferreiraite (IMA 2012-099).

The name is in honor of César Mendonça Ferreira (b. 1942). Graduating as a Geology Engineer in the School of Mines of Ouro Preto in 1970, Ferreira developed a long career as Professor in

Mineralogy and Gemology. He engaged in many studies of the mineralogy of ores and in the field of metallurgy. During the last 15 years, he was responsible for establishing the Gemological Laboratory of the Federal University of Ouro Preto. Professor Ferreira has agreed to the naming of the mineral. The holotype has been deposited in the mineralogical collection of the Museu de Ciência e Técnica, Escola de Minas, Universidade Federal de Ouro Preto, Praça Tiradentes, Centro, 35400-000—Ouro Preto, Minas Gerais, Brazil, registration number SAA-011.

GEOLOGICAL SETTING AND OCCURRENCE

Césarferreiraite occurs in a 1 cm^3 miarolitic cavity in albite in the Eduardo pegmatite mine (“Lavra do Eduardo,” in Portuguese), near Boa Vista creek, Conselheiro Pena municipality, Minas Gerais, Brazil (19°4′53.09″S 41°30′34.10″W), in associa-

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tion with pharmacosiderite, scorodite, and earlier arsenopyrite and probably replaces the latter. Césarferreiraite is known in only one block of pegmatite rock, and total amount of available substance did not exceed 2 mg.

The Eduardo mine (erroneously quoted as Boa Vista mine, another famous mine, by Bermanec et al. 2011) is located in the Conselheiro Pena pegmatite district (Fig. 1), one of the subdivisions of the Eastern Brazilian Pegmatite province that encompasses an area of about 150 000 km², 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 covers an area of about 5000 km², in the middle part of the Doce River basin, approximately 360 km at NE of the city of Belo Horizonte

The Conselheiro Pena pegmatite district is inserted in the central domain of the Araçuaí mobile belt (Almeida 1977), 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 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). At present, the Eduardo pegmatite is mined out. The pegmatite is heterogeneous with well-developed mineralogical and textural zoning. It has symmetric lens shape with the longer axis trending northwest to southeast and steeply dipping. The 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

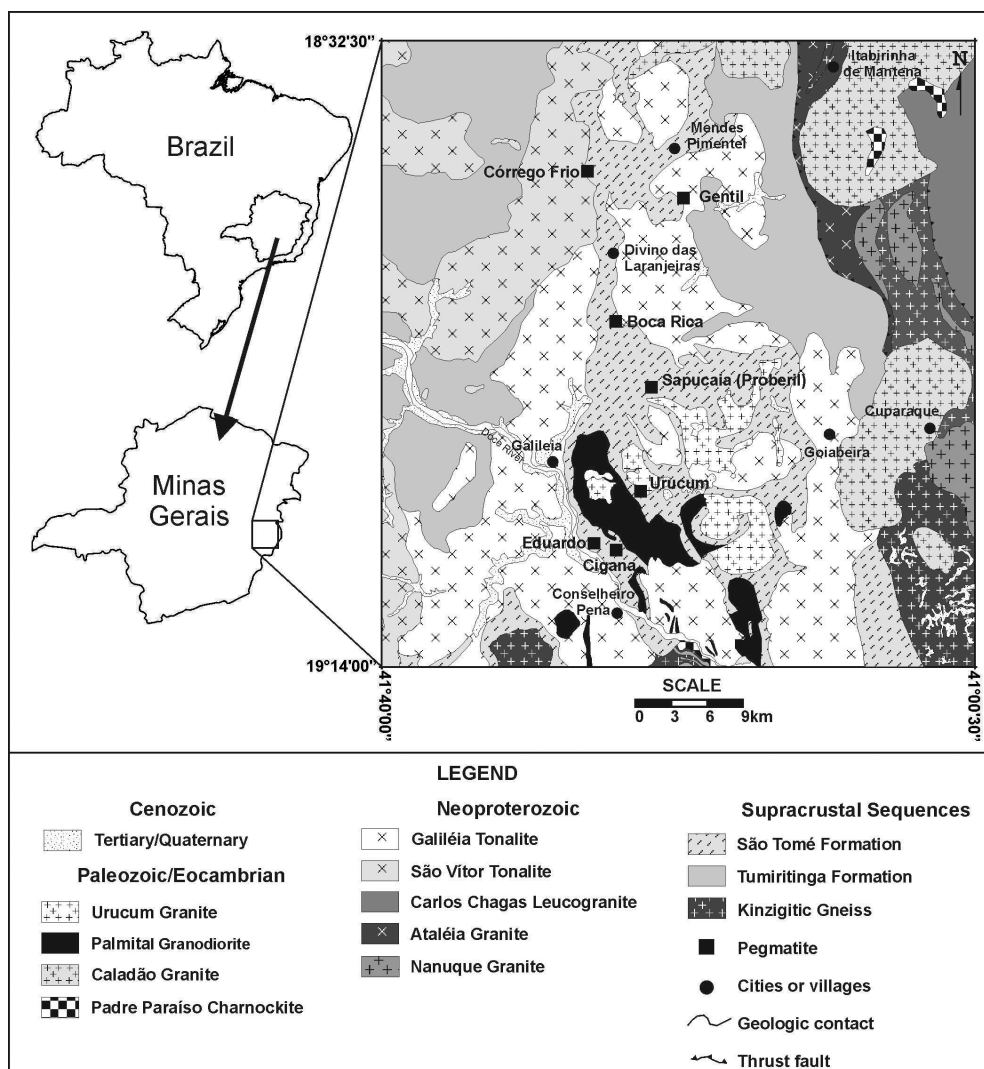


FIGURE 1. Geological map of Conselheiro Pena Pegmatite Province and the location of the most important phosphate rich pegmatites (after Netto et al. 1998).

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. Other minerals found in the pegmatite, including secondary species, are albite, garnets of the almandine-spessartine solid-solution series, arenopyrite, beryl, bismuth, bütschliite, cryptomelane, cyrilovite, löllingite, fourmarierite, frondelite-rockbridgeite solid-solution series, heterosite, hureaulite, kaolinite, leucophosphite, manganese oxides, metatorbenite, microcline, muscovite, pharmacosiderite, phosphosiderite, quartz, saleeite, schorl, scorodite, spodumene, strengite, triphylite, ushkovite, and variscite (Bermanec et al. 2011).

APPEARANCE AND PHYSICAL PROPERTIES

Césarferreiraite occurs as fibrous (random and subparallel) to tabular aggregates up to 2 mm. Single crystals are imperfect, flattened, and lath-shaped. Crystals, up to 10 μm long with a thickness of about 1–2 μm , are elongated along [001] and flattened on (100). The fibers have a near-rectangular cross section apparently bound by the {100} and {010} pinacoid forms (Figs. 2 and 3). Twinning was not observed. The color and also the streak of césarferreiraite vary from pale yellow to greenish yellow. The luster is vitreous; the individual crystals are transparent and masses are translucent. The mineral is non-fluorescent under short- and long-wave ultraviolet light. Due to the small sizes of crystals and too little pure material, the Mohs hardness was not measured, but the mineral is easily crushed between two glass slides. The tenacity is brittle and the cleavage is distinct, presumably on {010} and {100}. Parting was not observed and fracture is uneven. Density could not be measured because of small crystal sizes. Calculated density based on the empirical formula is 2.934 g/cm³.

Acicular crystals of césarferreiraite consist of very thin fibrous differently oriented blocks. Therefore only minimum and maximum refractive indices were measured. The mineral is biaxial (+), $n(\text{min}) = 1.747(3)$, $n(\text{max}) = 1.754(3)$ (589 nm). The mean n value is about 1.751.

CHEMICAL COMPOSITION

Chemical analyses ($n = 4$) were carried out using a JEOL JXA8900R electron microprobe housed in the Physics Department of the Federal University of Minas Gerais, Belo Horizonte (WDS mode, 15 kV, 20 nA, ca. 5 μm beam diameter). CO₂ was not analyzed because bands for CO₃²⁻ anions are absent in the IR spectrum. Contents of Mg, Al, and Mn are below detection limits. Too little material was available for a direct determination of H₂O, but its presence was confirmed by IR spectroscopy. Analytical data are given in Table 1.

The empirical formula (based on 18 O apfu) is, with rounding errors, Fe_{0.98}Fe_{1.96}[(AsO₄)_{1.79}(PO₄)_{0.31}](H_{17.68}O_{9.60}), or Fe_{0.98}Fe_{1.96}[(AsO₄)_{1.79}(PO₄)_{0.31}](OH)_{1.52}·8.08H₂O. The simplified formula is Fe²⁺Fe₂³⁺(AsO₄)₂(OH)₂·8H₂O, which requires FeO 11.52, Fe₂O₃ 25.61, As₂O₅ 36.86, H₂O 26.01, total 100.00 wt%.

The IR spectrum of césarferreiraite (Fig. 4) is unique and can be used for the identification of the mineral. Absorption bands and their assignments (cm⁻¹; s = strong band, w = weak band,

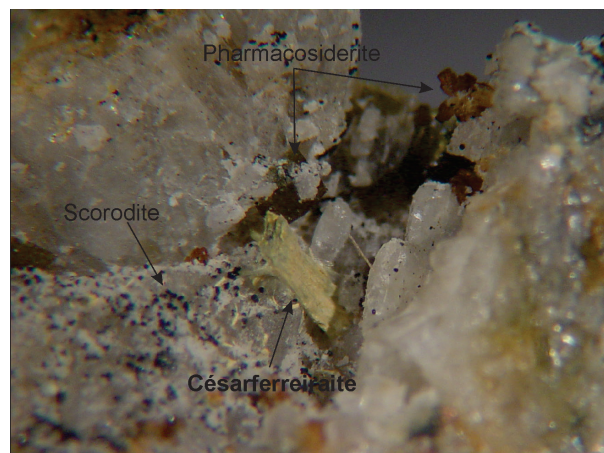


FIGURE 2. Césarferreiraite crystal aggregate (2 mm) in association with pharmacosiderite and scorodite. Field of view: 1.0 cm.

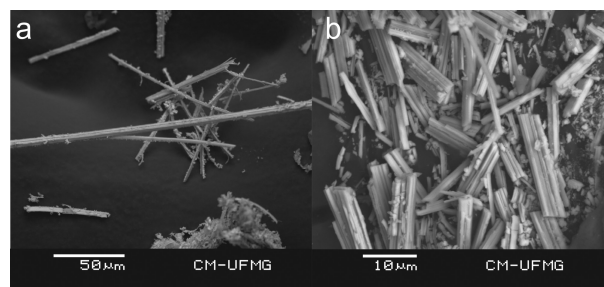


FIGURE 3. BSE-SEM images of césarferreiraite.

TABLE 1. Analytical data for césarferreiraite

Constituent	wt%	Range	Standard deviation	Probe standard
FeO ^a	11.50	11.29–11.70	0.10	Magnetite
Fe ₂ O ₃ ^a	25.56	22.58–23.39	0.37	Magnetite
As ₂ O ₅	33.51	30.80–36.96	2.57	FeAs ₂
P ₂ O ₅	3.54	2.36–4.98	0.88	Astimes apatite
H ₂ O ^b	26.01			
Total	100.12			

^a Calculated from the condition Fe²⁺:Fe³⁺ = 1:2, taking into account that for laueite-group minerals M²⁺:M³⁺ = 1:2.

^b Calculated by stoichiometry for the ideal structural formula.

sh = shoulder) are 3456s, 3352s, 3200sh (O–H stretching vibrations of H₂O molecules and OH groups), 1647, 1550w (bending vibrations of H₂O molecules), 1096sh, 1050, 1026 (asymmetric stretching vibrations of PO₄³⁻ anions), 860sh, 830s, 759s (asymmetric stretching vibrations of AsO₄³⁻ anions), 592w (bending vibrations of PO₄³⁻ anions), 470s (lattice mode involving Fe³⁺–O and Fe²⁺–O stretching and possibly low-frequency vibrations of anions and water molecules). The presence of two bands in the range 1500–1700 cm⁻¹ indicates the presence of non-equivalent H₂O molecules in the mineral. Bands characteristic of CO₃²⁻ anions and B–O bonds are absent in the IR spectrum.

CRYSTALLOGRAPHY

Powder X-ray diffraction data were obtained with a D8 Advance DaVinci diffractometer using CuK radiation (Table 2).

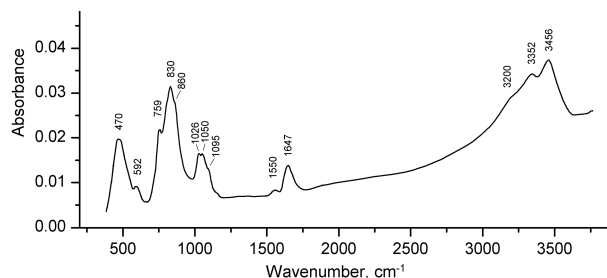


FIGURE 4. The IR spectrum of Césarferreiraite.

TABLE 2. X-ray powder diffraction data for Césarferreiraite

I_{rel}	d_{obs} , Å	d_{calc} , Å	h	k	l
95	9.85	9.927	0	1	0
100	6.35	6.369	0	0	1
21	4.963	4.963	0	2	0
17	4.534	4.542	$\bar{1}$	1	1
13	3.997	3.993	1	1	0
29	3.671	3.671	$\bar{1}$	2	1
32	3.158	3.160	1	$\bar{3}$	0
39	2.960	2.958	0	2	$\bar{2}$
35	2.884	2.884	$\bar{1}$	3	1
29	2.680	2.680	$\bar{2}$	1	1
23	2.540	2.541	$\bar{2}$	1	0
8	2.475	2.474	2	$\bar{2}$	0
8	1.9968	1.9970	0	1	3
8	1.9968	1.9964	$\bar{2}$	2	0
5	1.9129	1.9132	$\bar{1}$	5	1
7	1.8798	1.8800	$\bar{2}$	3	$\bar{1}$
7	1.6252	1.6249	$\bar{2}$	5	2
7	1.6153	1.6153	3	1	3

Unit-cell parameters refined (CellCalc program, Miura 2003) from powder data indexed by analogy with related laueite-group minerals (triclinic, space group: $P\bar{1}$) are as follows: $a = 5.383(2)$, $b = 10.363(3)$, $c = 6.878(2)$ Å, $\alpha = 96.42(4)$, $\beta = 109.19(3)$, $\gamma = 102.30(2)^\circ$, $V = 347.1(2)$ Å³, and $Z = 1$. The $a:b:c$ ratio calculated from the unit-cell parameters is 0.783:1:1.507. Gladstone-Dale compatibility $1 - (K_p/K_c) = -0.020$ (excellent) using the empirical formula and the average refractive index. Due to the tiny size of single crystals forming friable aggregates, single-crystal diffraction data were not obtained. However, the analogy with laueite-group minerals in stoichiometry and X-ray powder diffraction data, as well as the excellent compatibility confirms the correctness of the data obtained.

The laueite group (Krivovichev 2004) includes seven phosphates (ferrolaueite, gordonite, laueite, mangangordonite, paravauxite, sigloite, ushkovite) and only two arsenates: maghrebite, recently described by Meisser et al. (2012), and Césarferreiraite, here described. Stewartite and pseudolaueite are polymorphs of laueite. Kastningite is isostructural with stewartite and dimorph with mangangordonite. Maghrebite is the arsenate analog of gordonite, and Césarferreiraite is the arsenate analog of ferrolaueite, recently published (Segeler et al. 2012; Ferraiolo 2012). Arsenate members of the laueite group substantially differ from its phosphate members in the values of unit-cell parameters α and γ . The properties of Césarferreiraite are compared with those of maghrebite and ferrolaueite in Table 3.

TABLE 3. Comparative data for Césarferreiraite and related minerals

Mineral	Césarferreiraite	Maghrebite	Ferrolaueite
Simplified formula	$\text{Fe}^{2+}\text{Fe}^{3+}_2(\text{AsO}_4)_2$	$\text{MgAl}_2(\text{AsO}_4)_2$	$\text{Fe}^{2+}\text{Fe}^{3+}_2(\text{PO}_4)_2$
	$(\text{OH})_2 \cdot 8\text{H}_2\text{O}$	$(\text{OH})_2 \cdot 8\text{H}_2\text{O}$	$(\text{OH})_2 \cdot 8\text{H}_2\text{O}$
Symmetry	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$
a , Å	5.383(2)	5.436(2)	5.34(8)
b , Å	10.363(3)	10.500(3)	10.63(8)
c , Å	6.878(2)	7.075(2)	7.21(8)
α , °	96.42(4)	97.701(7)	107.35(8)
β , °	109.19(3)	110.295(5)	111.26(8)
γ , °	102.30(2)	102.021(6)	71.27(8)
Z	1	1	1
Strong lines of the X-ray powder-diffraction pattern:			
d , (Å) (I_{rel})	9.851 (95)	9.9 (100)	9.87 (90)
	6.346 (100)	6.4 (90)	6.56 (100)
	3.671 (29)	4.90 (80)	4.90 (80)
	3.158 (32)	3.198 (60)	3.97 (60)
	2.960 (39)	2.885 (60)	3.92 (50)
	2.884 (35)	2.622 (60)	3.28 (100)
	2.680 (29)	4.08 (50)	3.10 (50)
Optical data:			
n_{min}	1.747(3)	$\alpha = 1.562(2)$	$\alpha = 1.610(3)$
n_{max}	1.754(3)	$\beta = 1.574(2)$	$\beta = 1.665(3)$
		$\gamma = 1.586(2)$	$\gamma = 1.692(3)$
Optical sign, $2V$, °	+	-87	-68(2)
Density, g/cm ³	2.934 (calc)	2.60 (meas)	2.23 (meas)
		2.46 (calc)	2.22 (calc)
References	This work	Meisser et al. (2012)	Segeler et al. (2012)

TABLE 4. Members of the laueite group

M1	M2	Phosphates	Arsenates
Mg	Fe ³⁺	ushkovite	
Mn	Fe ³⁺	laueite	
Fe ²⁺	Fe ³⁺	ferrolaueite	Césarferreiraite
Fe ³⁺	Fe ³⁺		
Mg	Al	gordonite	maghrebite
Mn	Al	mangangordonite	
Fe ²⁺	Al	paravauxite	
Fe ³⁺	Al	sigloite	

IMPLICATIONS

The general formula of laueite-group minerals is $M1M2_2(\text{TO}_4)_2(\text{OH})_{2-3} \cdot 8-7\text{H}_2\text{O}$ where $M1$ is typically a bivalent cation, $M2 = \text{Fe}^{3+}$ or Al, $T = \text{P}$ or As. Minerals with $M1 = \text{Fe}^{2+}$ can oxidize and transform to their Fe^{3+} -analogs. This phenomenon is typical for ferrous phosphates; in particular, sigloite forms pseudomorphs after paravauxite (compare with the transformations vivianite $\rightarrow$ metavivianite, ferrostrunzite $\rightarrow$ ferristrunzite). The bivalent state of iron in $M1$ of Césarferreiraite is confirmed by excellent Gladstone-Dale compatibility. Césarferreiraite is the second arsenate belonging to the laueite group. The discovery of this additional arsenate suggests that there are several other (at least six) new arsenates to be discovered, taking into account only the cations that have been found in the phosphates described till now (see Table 4).

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