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Revision 1

Correianevesite, $Fe^{2+}Mn^{2+}_2(PO_4)_2 \cdot 3H_2O$, a new reddingite-group mineral from the Cigana mine, Conselheiro Pena, Minas Gerais, Brazil

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ABSTRACT

Correianevesite, ideally $Fe^{2+}Mn^{2+}_2(PO_4)_2 \cdot 3H_2O$, is a new reddingite-group mineral approved by the CNMNC (IMA 2013-007). It occurs in a phosphate-rich granite pegmatite outcropped by the Cigana mine, Conselheiro Pena, Rio Doce valley, Minas Gerais, Brazil. Associated minerals are: triphylite, lithiophilite, frondelite, rockbridgeite, eosphorite, vivianite, fairfieldite, leucophosphite, cyrilovite, phosphosiderite, etc. Correianevesite occurs as grayish-brown to reddish-brown transparent bipyramidal crystals up to 4 mm in size. The streak is white, and the luster is vitreous. Mohs' hardness is 3½. Cleavage is poor on (010). Fracture is laminated, uneven across cleavage. The measured density is 3.25(2) g cm^{-3}; the calculated density is 3.275 g cm^{-3}. The mineral is biaxial (+), α = 1.661(5), β = 1.673(5), γ =1.703(5), $2V_{meas}$ = 70(10)º, $2V_{calc}$ = 65.6º. The IR spectrum confirms the presence of H_2O. The Mössbauer spectrum shows the presence of two sites for Fe^{2+} and one site for Fe^{3+} occupied in the ratio $Fe1^{2+}$:$Fe2^{2+}$:Fe^{3+} = 39:55:6. The chemical composition is (electron microprobe, H_2O determined by gas chromatography of ignition products, Fe apportioned between FeO and Fe_2O_3 based on Mössbauer data, wt.%): MnO 29.21, FeO 21.74 Fe_2O_3 1.54, P_2O_5 34.59, H_2O 12.6, total 99.68. The empirical formula, based on 11 O *apfu*, is $H_{5.78}Mn_{1.70}Fe^{2+}_{1.25}Fe^{3+}_{0.08}P_{2.015}O_{11}$. The strongest lines of the powder X-ray diffraction pattern [*d*, Å (*I*, %) (*hkl*)] are: 5.08 (43) (020), 4.314 (28) (002, 210), 3.220 (100) (221, 202), 3.125 (25) (122), 2.756 (35) (103, 230), 2.686 (25) (222, 113), 2.436 (22) (123) and 2.233 (23) (411, 331). The crystal structure is solved (R_1 = 0.0176). Correianevesite is orthorhombic, space group *Pbna*, *a* = 9.4887(2), *b* = 10.1149(2), *c* = 8.7062(2) Å, *V* = 835.60(3) $Å^3$, *Z* = 4. The refined crystal-chemical formula is: $(Fe^{2+}_{0.72}Mn^{2+}_{0.20}Fe^{3+}_{0.08})(Mn_{1.48}Fe^{2+}_{0.52})(PO_4)_2(H_2O,OH)_3$.

Keywords: correianevesite, new mineral, phosphate, reddingite group, Cigana mine, Conselheiro Pena, Rio Doce valley, Minas Gerais, Brazil, crystal structure, Mössbauer spectroscopy.

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INTRODUCTION

Correianevesite is a new mineral approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA no. 2013-007). It was discovered in a granite pegmatite outcropped by the Cigana mine (Lavra da Cigana; formerly known as Jocão mine), Rio Doce valley, Conselheiro Pena county, Minas Gerais, Brazil. The pegmatite belongs to the Conselheiro Pena pegmatite district, Eastern Brazilian pegmatite province known for a wide diversity of phosphate minerals (Pedrosa et al. 2011).

The Cigana pegmatite is mined out and in the past was mined for industrial feldspar and with minor importance gemstones and samples for the collectors market. The pegmatite is heterogeneous with well-developed mineralogical and textural zoning. It has symmetric lens shape with the longer axis trending to NW-SE and the body dipping subvertically. The extension is at least 50 m, and the thickness is up to 20 m. The pegmatite is hosted by quartz-mica schist with garnet, staurolite and sillimanite of the São Tomé Formation. Hydrothermal and metasomatic fluids were responsible for the albitization, the development of miarolitic cavities, and the formation of a complex secondary phosphate assemblage described by Chaves et al. (2005).

The primary mineral association is represented by quartz, muscovite, microcline, schorl, almandine-spessartine, spodumene and triphylite. The secondary association is mainly composed by albite, Ta and Nb oxides, hydrothermal beryl, cassiterite, pyrite and numerous phosphates formed as a result of alteration of triphylite (Chaves et al. 2005). The paragenetic assemblage of secondary phosphates is composed by lithiophillite, correianevesite, hureaulite, frondelite, fluorapatite, eosphorite, fairfieldite, gormanite, and vivianite.

The new mineral is named in memory of Professor José Marques Correia Neves (1929-2011), professor of the Instituto de Geociências, Universidade Federal de Minas Gerais, who was the most active geoscientist in the study of Brazilian pegmatites, especially in the region of Conselheiro Pena

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and Araçuai, as well as in Alto Ligonha in Mozambique, where he discovered hafnon, the Hf analogue of zircon.

The type specimen of correianevesite (a part of the holotype) is deposited in the mineralogical collections of the Museu de Ciência e Técnica, Escola de Minas, Universidade Federal de Ouro Preto, Praça Tiradentes, Centro, 35400-000 – Ouro Preto, MG, Brazil, with the registration number SAA-081B.

GENERAL APPEARANCE AND PHYSICAL PROPERTIES

Correianevesite occurs as light grayish-brown to reddish-brown transparent bipyramidal crystals up to 4 mm in size (Figure 1) in cavities of triphylite. The only form observed is {111}. The streak is white, and the luster is vitreous. The mineral is non-fluorescent under ultraviolet light. Mohs' hardness is 3½. Cleavage is poor on (010). Fracture is laminated, uneven across cleavage. The density measured by flotation in heavy liquids is 3.25(2) g cm^{-3}. The calculated density is 3.275 g cm^{-3} based on the empirical formula and unit-cell parameters obtained from the single-crystal X-ray diffraction data.

Thermal data for correianevesite were obtained using a Shimadzu analyzer in a nitrogen atmosphere, at a gas flow rate of 50 cm^3 min^{-1}. Differential thermal analysis (DTA) and thermogravimetric (TG) analyses were carried out simultaneously. Crushed samples with 14.88 mg weight were heated in an open platinum crucible at a rate of 10ºC min^{-1} up to a temperature of 800ºC. The TG curve of correianevesite in nitrogen atmosphere is given in Figure 2.

The lowered weight loss of 10.45 % obtained by TG, as compared with H_2O content of 12.6 wt.% obtained by gas chromatography of products of ignition (see below), is explained by self-oxidation (a phenomenon typical of Fe^{2+}- and Mn^{2+}-phosphates: see e.g. Frost et al. 2004; Chukanov et al. 2012), in accordance with the following simplified schemes (M = Fe, Mn):

$$2M^{2+} + H_2O \rightarrow 2M^{3+} + O^{2-} + H_2$$

$$2M^{2+} + 2H_2O \rightarrow 2M^{3+} + 2OH^- + H_2.$$

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These processes correspond to exothermic effects in the DTA curve (Figure 3) and may be explained by the partial oxidation of Fe^{2+} to Fe^{3+}.

In order to obtain infrared (IR) absorption spectrum, correianevesite powder was mixed with anhydrous KBr, pelletized, and analysed using an ALPHA FTIR spectrometer (Bruker Optics) at the resolution of 4 cm^{-1} and number of scans of 16. IR spectrum of analogous pellet of pure KBr was used as a reference.

Absorption bands in the IR spectrum of correianevesite (Figure 4) and their assignments are (cm^{-1}; s – strong band, w – weak band, sh – shoulder): 3457, 3200 (O–H stretching vibrations of H_2O molecules and OH^- anions, hydrogen bonds of medium strengths), 2530, 2033w, 1890 (vibrations of the fragments O–H···O– P, very strong hydrogen bonds of acidic OH groups), 2247w (overtone of asymmetric stretching vibrations of PO_4^{3-} anions), 1636w, 1575 (bending vibrations of H_2O molecules), 1054s, 1013s (asymmetric stretching vibrations of PO_4^{3-} anions), 758, 750sh, 661 (librational vibrations of H_2O molecules forming strong hydrogen bonds), 598, 570, 555sh (O–P–O bending vibrations of PO_4^{3-} anions), 476w, 417w, 384w (mixed lattice vibrations).

Bands of B-, C- and N-bearing groups are absent in the IR spectrum of correianevesite. The nature of anomalously strong hydrogen bonds is discussed below.

The IR spectrum of correianevesite is comparable to those of the isostructural minerals phosphoferrite and reddingite.

Mössbauer spectra were collected in constant acceleration transmission mode with a 10 mCi $^{57}Co/Rh$ source at 25 and 298 K. The data were stored in a 1024-channel MCS memory unit and were fitted using Lorentzian line shapes with a least-squares fitting procedure using the NORMOS program. Isomer shifts were calculated relatively to α-Fe.

According to Mössbauer spectroscopy data (Figure 5, Table 1), correianevesite contains three kinds of iron cations (two bivalent and one trivalent) having 6-fold coordination and present in the atomic proportions $Fe1^{2+}$:$Fe2^{2+}$:Fe^{3+} = 39:55:6.

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Correianevesite is optically biaxial (+), $\alpha = 1.661(5)$, $\beta = 1.673(5)$, $\gamma = 1.703(5)$, $2V_{meas} = 70(10)^{\circ}$, $2V_{calc} = 65.6^{\circ}$. Dispersion of optical axes is strong, $r > v$. The mineral is nonpleochroic, colourless under the microscope.

CHEMICAL COMPOSITION

Seven point analyses were carried out using using VEGA TS 5130MM SEM equipped with EDX analyser (INCA Si(Li) detector), at an operating voltage of an electron microprobe of 20 kV and a beam current of 0.5 nA. The beam was rasterized on an area 16 x 16 μm to minimise unstable sample damage. Attempts to use WDS mode, with higher beam current, were unsuccessful because of the instability of the mineral containing water. The contents of F, Na, Mg, Al, Si, S, K, Ca, Ti, Zn and As are below their detection limits. H_2O was analysed by gas chromatography of products of ignition at 1200°C. CO_2 was not analysed because of the absence of absorption bands corresponding to vibrations of C-O bonds in the IR spectrum. Analytical data are given in Table 2.

The empirical formula based on 11 O atoms is $H_{5.78}Mn_{1.70}Fe^{2+}_{1.25}Fe^{3+}_{0.08}P_{2.015}O_{11}$.The simplified formula is $Fe^{2+}Mn^{2+}_2(PO_4)_2 \cdot 3H_2O$, which requires MnO 34.63, FeO 17.54, P_2O_5 34.64, H_2O 13.19, total 100.00 wt%.

The Gladstone-Dale compatibility between chemical data, refractive indices and density is $(1-K_P/K_c) = 0.013$ (superior).

X-RAY DIFFRACTION DATA AND CRYSTAL STRUCTURE

The X-ray powder-diffraction data (Table 3) were collected with a STOE IPDS II single-crystal diffractometer equipped with an Image Plate detector using the Gandolfi method by employing the Mo*K*α radiation and a sample–detector distance of 200 mm. Orthorhombic unit-cell parameters refined from the powder data are as follows: $a = 9.491(7)$, $b = 10.121(7)$, $c = 8.721(9)$

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Å, V = 838(2) Å^3. Measured interplanar spacings and intensities of observed reflections are in a good agreement with corresponding values calculated from the crystal structure.

Single-crystal X-ray diffraction measurements were made with a single-crystal Xcalibur S diffractometer equipped with a CCD detector. Absorption correction was applied according to the shape of the crystal. The structure was solved by direct methods and refined anisotropically using SHELXS-97 and SHELXL-97 (Sheldrick, 2008), respectively, to R = 0.0176 for 1662 unique reflections with $I > 2\sigma(I)$ in space group *Pbna*. All hydrogen atoms of two water molecules were found and refined.

The structure model is in a good agreement with those of the other reddingite-group minerals. A small amount of Mn was added to the Fe-dominant $M(1)$ site, and a small amount of Fe was added to the Mn-dominant $M(2)$ site according to the results of the refinement of electronic composition of the site, chemical and Mössbauer data. The occupancy coefficients of the cations in $M(1)$ and $M(2)$ sites were fixed in the final stages of the refinement. The crystallographic characteristics of the mineral, the details of the X-ray diffraction study and the structure-refinement parameters are given in Table 4, atom coordinates and equivalent thermal displacement parameters – in Table 5, anisotropic displacement parameters – in Table 6 and selected interatomic distances – in Table 7.

Like other representatives of the phosphoferrite structure type, correianevesite contains (100) octahedral layers (Figure 6) formed by the parallel to the *c* axis chains of edge-sharing dimers of $M(2)O_4(H_2O)_2$ polyhedra connected *via* common edges with isolated from each other $M(1)O_4(H_2O)_2$ octahedra. Adjacent chains are connected with each other by the corners of $M(2)$ octahedra. The neighbouring octahedral layers are connected by PO_4 tetrahedra (Figure 7).

DISCUSSION AND IMPLICATIONS

The comparative crystal chemistry of different minerals with the phosphoferrite structure type has been discussed by Moore et al. (1980). All these minerals are orthorhombic phosphates with the

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general formula $M(1)M(2)_2(PO_4)_2(OH,H_2O)_3$ where octahedral sites $M(1)$ and $M(2)$ can contain Mn^{2+}, Fe^{2+}, Mg and Fe^{3+} (Table 8) with minor admixtures of Ca and Al and some other (trace) components. Mn^{2+} preferably occupies the larger octahedron $M(2)$, but in reddingite both $M(1)$ and $M(2)$ sites are dominantly occupied by Mn^{2+}.

Based on interatomic distances and observed trends in site populations, Moore et al. (1980) assumed the existence of a hypothetical reddingite-group mineral with the end-member formula $Fe^{2+}Mn^{2+}_2(PO_4)_2 \cdot 3H_2O$, in which Fe^{2+} occupies the $M(1)$ site and Mn^{2+} occupies the $M(2)$ site. The discovery of correianevesite confirmed this assumption.

Taking into account Mössbauer spectroscopy data (Table 1), the results of the crystal structure refinement (Tables 5, 6), compositional data (Table 2) and general trends in the cation distribution between the sites $M(1)$ and $M(2)$ (Moore et al. 1980), the crystal-chemical formula of correianevesite can be written as $(Fe^{2+}_{0.72}Mn^{2+}_{0.20}Fe^{3+}_{0.08})(Mn_{1.48}Fe^{2+}_{0.52})(PO_4)_2(H_2O,OH)_3$. This formula was derived assuming that the major part of Fe^{2+} (corresponding to $Fe1^{2+}$, by Mössbauer data) occupies the smaller octahedron $M(1)$. Note that, according to the assumption that $Fe1^{2+}$ corresponds to bivalent iron in the $M(2)$ site, the crystal chemical formula would be $(Fe^{2+}_{0.52}Mn^{2+}_{0.41}Fe^{3+}_{0.08})(Mn^{2+}_{1.29}Fe^{2+}_{0.73})(PO_4)_2(H_2O,OH)_3$ and also would correspond to a mineral with the end-member formula $Fe^{2+}Mn^{2+}_2(PO_4)_2 \cdot 3H_2O$. However, the latter variant of cation distribution is hardly probable taking into account cation-anion distances.

Comparative data for correianevesite and related minerals are given in Table 9. It is important to note that landesite and correianevesite cannot be distinguished by electron microprobe analysis, but landesite is characterized by much higher values of refractive indexes as a result of high Fe^{3+} content. Correianevesite and Fe-bearing reddingite can be distinguished only by means of Mössbauer spectroscopy.

The presence of acidic OH groups detected by IR spectroscopy data is due to the asymmetric polarization of H_2O molecules that form strong hydrogen bond Ow(2) – H(2)···O(1) (with the distance Ow(2)···O(1) of 2.539 Å) and act as proton donors. This phenomenon is very typical for nominally

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214 neutral sulphates, phosphates and arsenates and results in the dynamic acid-base equilibrium AO_4^{3-} +
215 $H_2O \leftrightarrow HAO_4^{2-} + OH^-$ (A = P, As or S) that is usually shifted towards left side (see *e. g*. Chukanov
216 et al. 2010, 2012; Nestola et al. 2012). Note that the presence of acid phosphate groups in
217 correianevesite (considered as reddingite before Mössbauer data have been obtained) was detected also
218 by means of Raman spectroscopy (Frost et al. 2012). In particular, a strong band at 1007 cm^{-1} was
219 assigned to symmetric stretching vibrations of $HOPO_3^{2-}$.
220

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222

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FIGURE CAPTIONS

Figure 1. Bipyramidal crystals of correianevesite on hureaulite. Field of view: 6 mm. Photo: Carlos Menezes.

Figure 2. TG curve of correianevesite obtained in nitrogen atmosphere at a heating rate of 10°C min^{-1}.

Figure 3. DTA curve of correianevesite obtained in nitrogen atmosphere at a heating rate of 10°C min^{-1}.

Figure 4. IR spectrum of powdered correianevesite in KBr pellet.

Figure 5. Mössbauer spectrum of correianevesite.

Figure 6. Octahedral layer in the structure of correianevesite. $M1O_6$ octahedra are dark, $M2O_6$ octahedra are light, H atoms are shown with small circles. Unit cell is outlined.

Figure 7. The crystal structure of correianevesite: *ab* projection. Unit cell is outlined.

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Table 1. Mössbauer data for correianevesite.

Cation	Isomer shift, mm s^{-1}	Quadrupole splitting, mm s^{-1}	Line width, mm s^{-1}	Area, %
$Fe1^{2+}$	1.23(4)	1.63(1)	0.27(2)	39(1)
$Fe2^{2+}$	1.23(4)	2.40(9)	0.29(1)	55(3)
Fe^{3+}	0.35(1)	1.20(3)	0.49(5)	6.0(3)

Table 2. Chemical composition of correianevesite.

Constituent	Content, wt%	Range	Standard deviation	Probe standard
MnO	29.21	27.87-30.14	0.78	$MnTiO_3$
FeO[a]	21.74	22.09-24.45[b]	0.77[b]	Fe_2O_3
Fe_2O_3[a]	1.54			
P_2O_5	34.59	34.19-35.02	0.27	$LaPO_4$
H_2O	12.6±0.1			
Total	99.68			

[a]Total iron content analysed using a microprobe and initially calculated as FeO was 23.13 wt%; it was apportioned between FeO and Fe_2O_3 (as well as between two sites) based on Mössbauer data (see Authors' Remarks).

[b]For total iron calculated as FeO.

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306 Table 3. X-ray powder diffraction data for correianevesite.
307

I_{obs}, %	d_{obs}, Å	I_{calc}, %*	d_{calc}, Å**	*h k l*
3	6.45	2	6.415	101
19	5.44	20	5.417	111
43	**5.08**	45	5.057	020
21	4.761	23	4.744	200
28	**4.314**	4, 27	4.353, 4.295	002, 210
8	3.985	8	3.972	121
4	3.886	2	3.852	211
13	3.471	17	3.460	220
100	**3.220**	100, 38	3.216, 3.208	221, 202
25	**3.125**	28	3.116	122
10	2.985	5, 8	2.985, 2.973	131, 301
35	**2.756**	15, 38	2.775, 2.748	103, 230
25	**2.686**	12, 29	2.709, 2.676	222, 113
5	2.567	5, 1	2.566, 2.563	132, 321
15	2.484	10, 20	2.517, 2.481	023, 312
22	**2.436**	29	2.433	123
8	2.355	13	2.353	141
23	**2.233**	16, 19	2.232, 2.230	411, 331
12	2.184	12, 4	2.187, 2.177	042, 004
13	2.136	3, 16	2.138, 2.131	303, 142
3	2.087	2, 1	2.092, 2.085	313, 421
6	2.040	1, 9	2.040, 2.038	412, 332
14	1.973	2, 18	1.978, 1.970	204, 323
17	1.933	1, 11	1.929, 1.926	151, 341
4	1.855	7	1.854	501
5	1.809	5	1.806	333
2	1.767	4	1.766	314
3	1.740	6	1.741	521
8	1.712	6, 4	1.714, 1.713	512, 105
9	1.649	7, 6, 5	1.650, 1.646, 1.645	044, 025, 522
15	1.630	14	1.630	161
9	1.588	2, 2, 13	1.589, 1.588, 1.587	260, 503, 352
13	1.561	3, 2, 15	1.563, 1.562, 1.558	261, 610, 244
10	1.520	3, 16	1.525, 1.516	305, 451
2	1.491	2	1.495	541
1	1.483	3	1.487	621
2	1.467	1, 4	1.471, 1.466	612, 361
4	1.452	3, 7	1.451, 1.448	006, 434
4	1.423	1, 6	1.426, 1.420	622, 116
4	1.419	1, 1	1.418, 1.416	145, 514
6	1.381	4, 4	1.382, 1.380	270, 126
5	1.340	1, 1, 7	1.342, 1.341, 1.339	354, 640, 701
2	1.320	1, 2	1.319, 1.317	552, 272
2	1.311	2	1.310	462
1	1.299	2	1.295	721
3	1.283	3, 2	1.283, 1.282	264, 173
2	1.273	2, 1	1.279, 1.271	604, 255

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1	1.262	1	1.264	080
2	1.242	3	1.240	624
2	1.232	1	1.228	364
3	1.210	1, 2	1.211, 1.210	562, 281
3	1.206	4	1.204	182
2	1.177	2	1.176	282
3	1.170	3	1.170	156
3	1.155	2, 2	1.153, 1.153	660, 455
4	1.147	2, 2	1.151, 1.145	183, 653
1	1.118	1	1.116	822
2	1.107	1, 4	1.108, 1.105	147, 743

*For the calculated X-ray powder pattern only reflections with $I_{calc} \geq 1\%$ are given.
**Calculated for unit cell parameters obtained from single-crystal data.

Table 4. Crystal parameters, data collection information and single-crystal structure refinement details for correianevesite

Formula	$(Fe^{2+}_{0.72}Mn^{2+}_{0.20}Fe^{3+}_{0.08})(Mn_{1.48}Fe^{2+}_{0.52})(PO_4)_2[(H_2O)_{2.92}(OH)_{0.08}]$
Formula weight	410.01
Crystal system, space group	Orthorhombic, *Pbna* (no. 60)
Z	4
a, b, c (Å)	9.48871(16), 10.11494(17), 8.70624(16)
V (Å^3)	835.61(3)
F(000)	801
Density ρ_{calc} (g·cm^{-3})	3.259(8)
Absorption coefficient μ (mm^{-1})	5.199
Crystal dimensions (mm)	$0.19 \times 0.32 \times 0.38$
Diffractometer	Xcalibur S CCD
λ (Mo-$K\alpha$) (Å), T (K)	0.71073, 293
Collection mode	(full) sphere
θ range for data collection(°)	3.18 - 34.94
h, k, l ranges	$-15 \leq h \leq 15$, $-16 \leq k \leq 16$, $-13 \leq l \leq 13$
Reflections collected	20430
Unique reflections	1781 (R_{int} = 0.0341)
Reflections with $I > 2\sigma(I)$	1662

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Structure solution	direct methods
Refinement method	full-matrix least-squares *on* F^2
Weighting parameters a, b	0.0174, 0.3503
Extinction coefficient	0.0047(4)
No. of refined parameters	90
Final *R* indices [$I>2\sigma(I)$]	$R1 = 0.0176$, w$R2 = 0.0417$
R indices (all data)	$R1 = 0.0204$, w$R2 = 0.0430$
GoF	1.134
$\Delta\rho_{min}$, $\Delta\rho_{max}$ (e/Å^3)	-0.31, 0.42

Table 5. Site coordinates and thermal displacement parameters (Å^2) of atoms for correianevesite.

Atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}
$M(1) = Fe_{0.80}Mn_{0.20}$[a]	0.0	0.0	0.0	0.00978(6)
$M(2) = Mn_{0.74}Fe_{0.26}$[a]	0.065331(19)	0.097199(18)	0.63633(2)	0.01010(5)
P	0.20457(3)	0.10607(3)	0.29198(3)	0.00713(6)
O(1)	0.21646(9)	0.25363(8)	0.33350(11)	0.01207(15)
O(2)	0.10430(9)	0.03779(9)	0.40585(10)	0.01146(15)
O(3)	0.35133(9)	0.04233(9)	0.30005(10)	0.01229(16)
O(4)	0.14828(10)	0.09733(9)	0.12677(10)	0.01383(17)
Ow(1)	-0.09290(17)	0.25	0.5	0.0198(3)
H	-0.139(3)	0.191(3)	0.454(3)	0.055(8)[b]
Ow(2)	-0.02810(10)	0.32654(9)	0.14686(10)	0.01156(15)
H(1)	0.018(3)	0.252(3)	0.134(3)	0.052(8)[b]
H(2)	-0.113(3)	0.287(3)	0.159(3)	0.054(7)[b]

[a] Fixed during the refinement
[b] U_{iso}

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Table 6. Anisotropic displacement parameters (in Å^2) for correianevesite

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
M(1)	0.01124(11)	0.00880(11)	0.00930(10)	-0.00005(8)	-0.00259(8)	-0.00117(8)
M(2)	0.01149(9)	0.00988(9)	0.00894(8)	-0.00086(5)	0.00013(6)	-0.00265(6)
P	0.00643(12)	0.00743(12)	0.00752(12)	-0.00028(9)	0.00035(9)	-0.00037(9)
O(1)	0.0116(4)	0.0077(3)	0.0169(4)	-0.0014(3)	0.0000(3)	0.0000(3)
O(2)	0.0109(3)	0.0133(4)	0.0103(3)	0.0003(3)	0.0024(3)	-0.0036(3)
O(3)	0.0088(3)	0.0125(4)	0.0155(4)	-0.0015(3)	0.0004(3)	0.0027(3)
O(4)	0.0150(4)	0.0183(4)	0.0082(3)	-0.0002(3)	-0.0019(3)	-0.0040(3)
Ow(1)	0.0208(7)	0.0171(6)	0.0216(7)	-0.0045(5)	0.000	0.000
Ow(2)	0.0114(4)	0.0093(4)	0.0140(4)	-0.0003(3)	-0.0001(3)	-0.0012(3)

Table 7. Selected interatomic distances (Å) in correianevesite.

M(1) – O(4) 2.0413(9) × 2 – Ow(2) 2.1873(9) × 2 – O(3) 2.2812(9) × 2 <*M*(1) – O> 2.170	*M*(2) – O(1) 2.0981(9) – O(2) 2.1270(9) – O(2) 2.1424(9) – O(3) 2.1562(9) – Ow(2) 2.2235(9) – Ow(1) 2.4600(10) <*M*(2) – O> 2.201
P – O(3) 1.5362(9) – O(4) 1.5369(9) – O(2) 1.5379(9) – O(1) 1.5399(9) <P – O> 1.5377	

Hydrogen bonds[a]			
Ow(1) – H	0.84(2)	Ow(1) – H···O(4)	3.104(4)
Ow(2) – H(1)	0.88(3)	Ow(2) – H(1)···O(4)	2.865(5)
Ow(2) – H(2)[b]	0.90(3)	Ow(2) – H(2)···O(1)	2.539(5)

[a] O-H distances were refined without restraints.
[b] Possibly bifurcated H-bond H(2)···O(3) with Ow(2)···O(3) distance of 3.128 Å.

Table 8. Dominant components in cationic sites of reddingite-group minerals.

Mineral	M(1)	M(2)
Reddingite	Mn^{2+}	Mn^{2+}
Phosphoferrite	Fe^{2+}	Fe^{2+}
Landesite	Fe^{3+}	Mn^{2+}
Kryzhanovskite	Fe^{3+}	Fe^{3+}
Garyanselite	Mg	Fe^{3+}
Correianevesite	Fe^{2+}	Mn^{2+}

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335 Table 9. Comparative data for correianevesite and related reddingite-group minerals.
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	Correianevesite	Reddingite	Phosphoferrite	Landesite
Formula	$Fe^{2+}Mn^{2+}_2(PO_4)_2 \cdot 3H_2O$	$Mn^{2+}Mn^{2+}_2(PO_4)_2 \cdot 3H_2O$	$Fe^{2+}Fe^{2+}_2(PO_4)_2 \cdot 3H_2O$	$Fe^{3+}Mn^{2+}_2(PO_4)_2(OH) \cdot 2H_2O$
Space group	*Pbna*	*Pbna*	*Pbna*	*Pbna*
a, Å	9.4887	9.489-9.49	9.460	9.458
b, Å	10.1149	10.08-10.126	10.024	10.185
c, Å	8.7062	8.70-8.710	8.670	8.543
Z	4	4	4	4
Strong lines of the X-ray powder-diffraction pattern: *d*, Å (*I*, %)	5.08 (43) 4.761 (21) 4.314 (28) 3.220 (100) 3.125 (25) 2.756 (35) 2.686 (25) 2.436 (22) 2.233 (23)	4.28 (70) 3.20 (100) 2.737 (80) 2.657 (70) 2.422 (70) 2.234 (70) 1.625 (70)	4.25 (70) 3.18 (100) 2.724 (80) 2.639 (70) 2.408 (70) 2.222 (70) 1.615 (70)	5.096 (54) 4.284 (27) 3.207 (100) 3.163 (35) 3.090 (23) 2.758 (29) 2.630 (24)
Optical data:				
α	1.661(5)	1.643 – 1.658	1.663 – 1.672	1.720
β	1.673(5)	1.648 – 1.664	1.674 – 1.680	1.728
γ	1.703(5)	1.674 – 1.685	1.699 – 1.700	1.735
Optical sign, 2V, °	(+) 70(10)	(+) 41 – 80	(+) 66 – 70	(-) large
Density, g cm^{-3}	3.25 (meas) 3.275 (calc)	3.10 – 3.24 (meas) 3.26 (calc)	3.10 – 3.29 (meas) 3.32 (calc)	3.026 – 3.03 (meas) 3.210 (calc)
Mohs hardness	3½	3-3½	3-4½	3-3½
References	This work	Tennyson (1954); Kleber and Donnay (1961); Feklichev (1989); Frost et al. (2012)	Tennyson (1954); Kleber and Donnay (1961); Moore and Araki (1976); Moore (1971); Moore et al. (1980); Feklichev (1989)	Moore (1964); Moore et al. (1980); Feklichev (1989)

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Figure 1. Bipyramidal crystals of correianevesite on hureaulite. Field of view: 6 mm. Photo: Carlos Menezes.

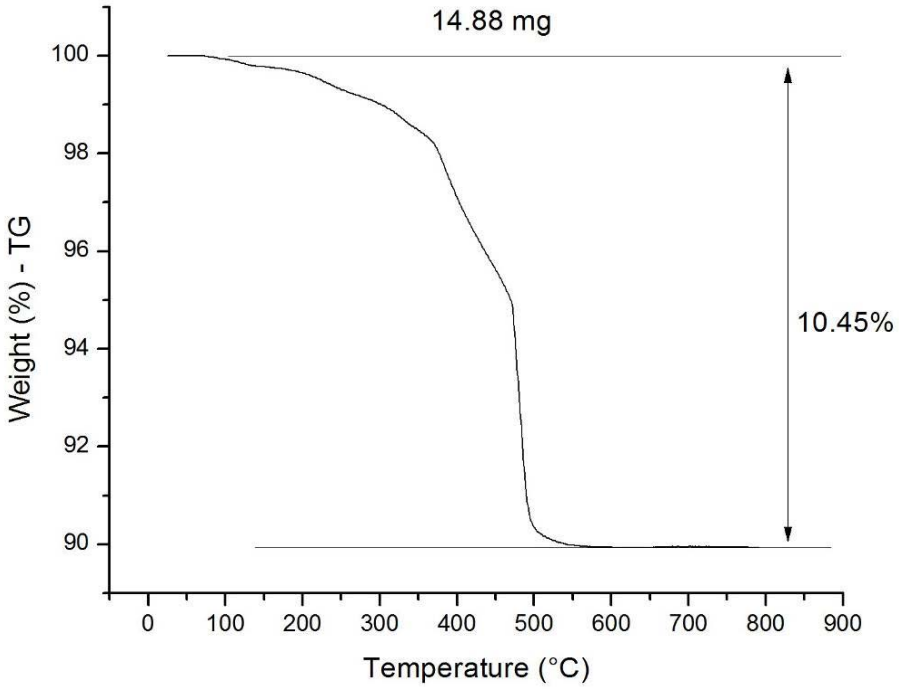

Figure 2. TG curve of correianevesite obtained in nitrogen atmosphere at a heating rate of 10°C min^{-1}.

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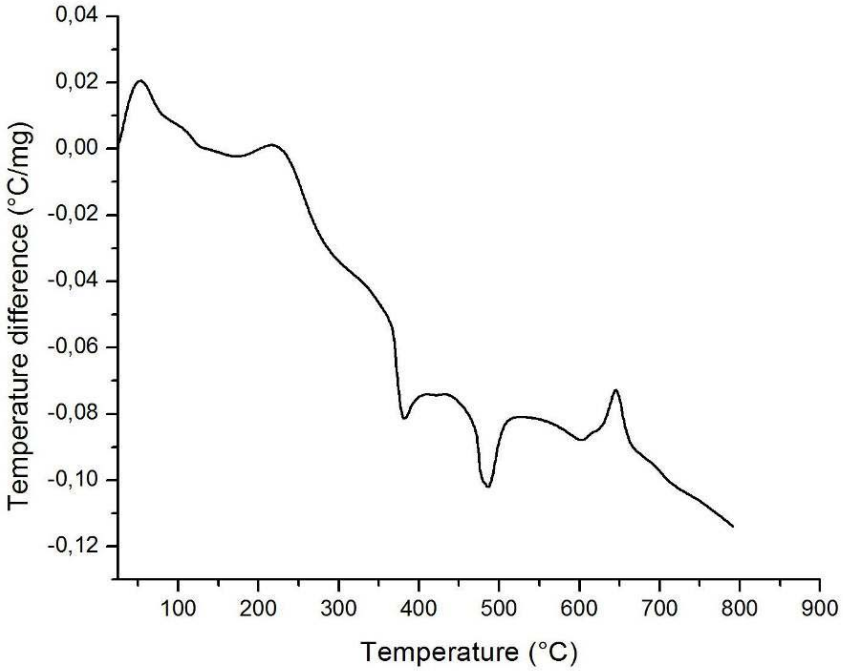

Figure 3. DTA curve of correianevesite obtained in nitrogen atmosphere at a heating rate of 10°C min^{-1}.

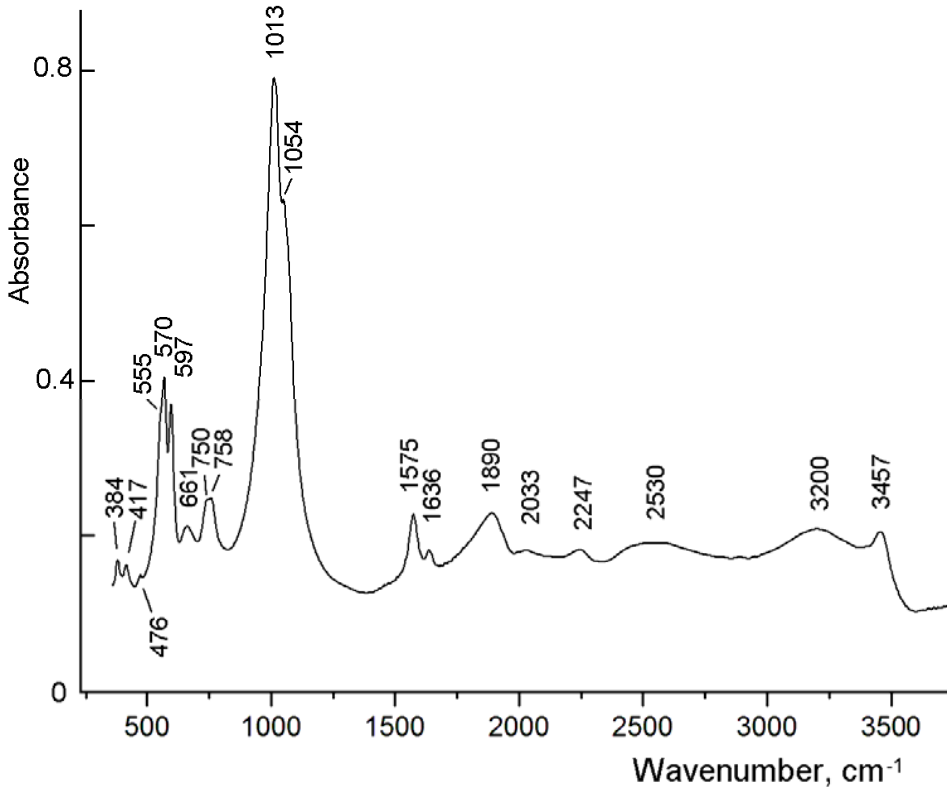

Figure 4. IR spectrum of powdered correianevesite in KBr pellet.

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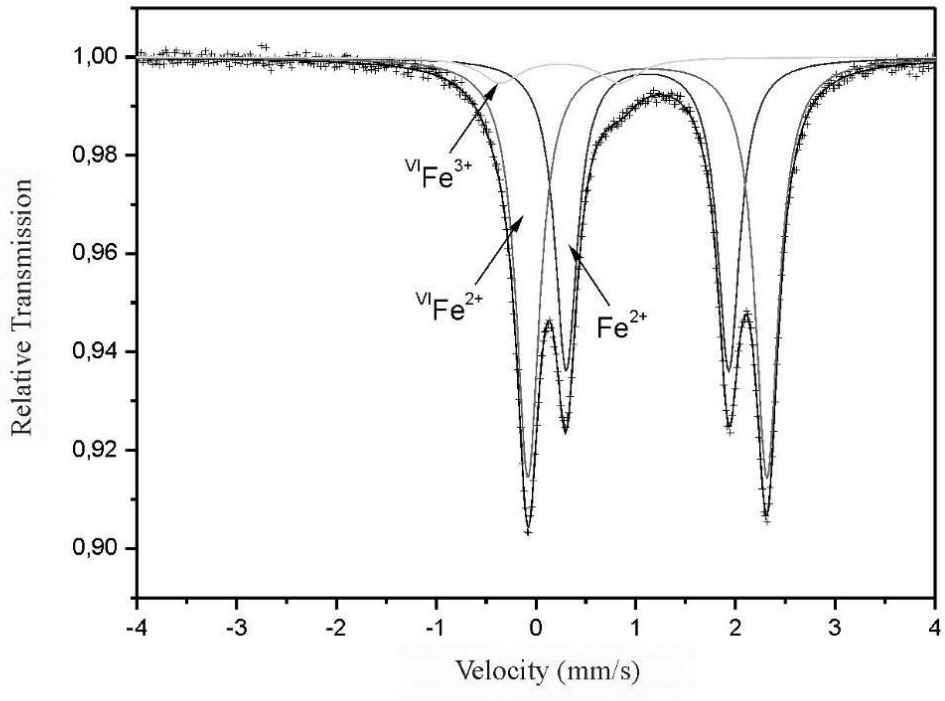
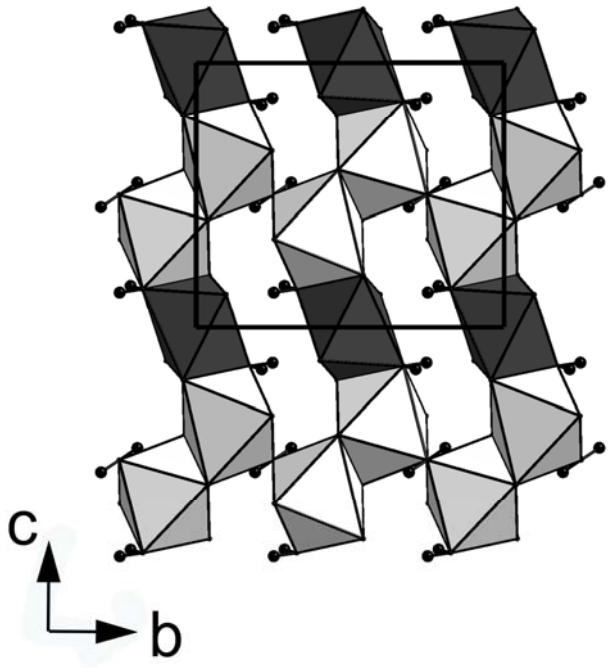


355
356 Figure 5. Mössbauer spectrum of correianevesite.



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358 Figure 6. Octahedral layer in the structure of correianevesite. $M1O_6$ octahedra are dark, $M2O_6$
359 octahedra are light, H atoms are shown with small circles. Unit cell is outlined.
360

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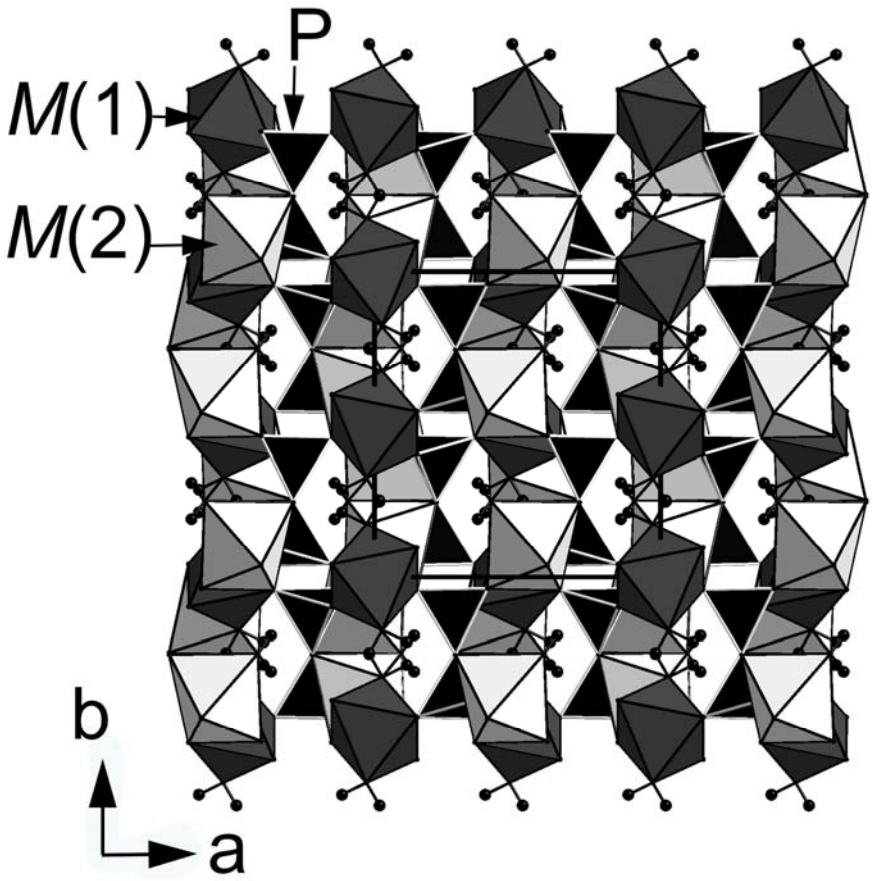

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362 Figure 7. The crystal structure of correianevesite: *ab* projection. Unit cell is outlined.

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