Article

Ferroberaunite, Fe$^{2+}$Fe$^{3+}$(PO$_4$)$_4$(OH)$_5$·6H$_2$O, a mixed-valence iron member of the beraunite series, from the Gravel Hill mine, Perranzabuloe, Cornwall, England

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Abstract

The new mineral ferroberaunite, Fe$^{2+}$Fe$^{3+}$(PO$_4$)$_4$(OH)$_5$·6H$_2$O (IMA2021-36; symbol: Fbru), occurs in cavities of ‘limonite’ iron ore from the Gravel Hill mine, Perranzabuloe, Cornwall, England. Its flattened prismatic crystals up to 400 µm long are dark green to olive green, transparent to translucent, with a vitreous lustre, pearly on cleavages. The Mohs hardness is ~3–4. The density measured by the flotation method is 2.94(2) g·cm$^{-3}$, the calculated density is 2.907 g·cm$^{-3}$. Ferroberaunite is biaxial (−), with $\alpha = 1.736(2)$, $\beta = 1.765(3)$, $\gamma = 1.786(5)$ at 589 nm, $2V$meas. = 68(3)$^\circ$, $2V$calc. = 79$^\circ$; dispersion of optical axes is strong, $r > v$; orientation is $Y = b$; $X \approx a$, $Z \approx c$. Pleochroism is strong: $X =$ bluish-green $> Z =$ green $> Y =$ yellow. Electron-microprobe analyses gave the empirical formula (Fe$_{2.75}$Ca$_{0.01}$Mn$_{0.02}$Fe$_{2.22(5)}$Al$_{0.03}$Fe$_{0.94}$)(PO$_4$_)$_{0.11}$(OH)$_{1.76}$·6H$_2$O. Ferroberaunite is monoclinic, $C2/c$, with $a = 20.8708(3)$, $b = 5.1590(8)$, $c = 19.2263(3)$ Å; $\beta = 93.3186(17)^\circ$; $V = 2066.7(3)$ Å$^3$ and $Z = 4$. The eight strongest lines in the powder X-ray diffraction pattern are $d_{\text{meas.}}$ Å ($I_{\text{rel.}}$, %) (hkl): 10.410 (100) (200), 9.606 (14) (002), 7.271 (11) (202), 5.203 (4) (400), 3.467 (12) (600), 3.325 (6) (620), 3.201 (6) (006), 2.600 (4) (800). The mineral is isostructural with beraunite, redefined recently as Fe$^{3+}$(PO$_4$)$_4$(OH)$_2$·6H$_2$O.

Keywords: ferroberaunite, new mineral, phosphate, crystal structure, Raman spectroscopy, XPS spectroscopy, Cornwall

Introduction

The mineral beraunite was discovered by Breithaupt (1840, 1841) on specimens that originated from the Hrbek iron ore mine at Svatá Dobrotivá (Sankt Benigna) in Central Bohemia, nowadays in the Czech Republic. In the decades following, similar hydrated basic iron phosphates were classified as either red beraunite or green dufrénite (basic iron phosphates were classified as either red beraunite or kraurite). These observations were followed up by Chukanov et al. (2017), who introduced the name ‘eleonorite’ for the Fe$^{3+}$ dominant phase and suggested using the name beraunite for the mixed-valence iron end-member.

A recent investigation of the original ‘beraunite’ material stored in collections of the Freeberg University of Mining and Technology, Germany, proved the identity of this mineral with ‘eleonorite’. The name ‘eleonorite’ has been credited and the formula of beraunite as Fe$_{3+}$(PO$_4$)$_4$(OH)$_2$·6H$_2$O was approved by proposal IMA 21-D (Miyawaki et al., 2021) of the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA–CNMNC). To avoid duplication of the mineral name ‘beraunite’, the end-member with mixed iron valence has been redefined and renamed. From several studied specimens of green-coloured ‘beraunites’ (e.g. Blaton, Belgium; Svappavaara, Sweden; Hagendorf-Süd, Germany; Krásno and Morávské, Czech Republic), a sample originating from the Gravel Hill mine,
Occurrence

The ferroberaunite specimen was collected around 2016 in the abandoned Gravel Hill mine, Perranzabuloe, Cornwall, England (50°22′27.0″N, 5°08′42.0″W). The mining at the Gravel Hill mine (formerly known as Penhale Iron mine, or Cliff Iron mine) culminated in the 18th Century. The mine was located on the western end of the Perran Iron Lode, represented here by two layers of oxide iron ore deposited in sedimentary rocks of the Middle Devonian age. The layers are 5 and 13 m thick and are separated by a 14 m thick barren horizon. The ores were formed irregularly on matrix or forming radial to spherical aggregates; parallel intergrowths are common (Figs 1, 2). The crystals are flattened on {100} and elongated along the b axis, with wedge-shaped terminations. The crystal forms assigned to the orientation given by Marzoni Fecia di Cossato et al. (1989) for manganese-rich beraunite from Mangualde, Portugal, comparing with our observation of morphology and powder X-ray diffraction data are [100], [201], [112] and [112] (Fig. 3); twinning is on [100] (from morphology).

The mineral is dark green to olive green, transparent to translucent, with a pale olive-green streak; it has a vitreous lustre, pearly on cleavages. The cleavage is very good parallel to {100}. The crystals are brittle with uneven fracture; the Mohs hardness is assumed to be 3–4. The density 2.94(2) g cm\(^{-3}\) was determined by the flotation method using the Mohr-Westphal scale and two different mixtures of liquids (diiodomethane and acetone; 1,1,2,2-tetrabromoethane and dioxane). The calculated density based on the empirical formula and unit-cell parameters from single-crystal diffraction is 2.907 g cm\(^{-3}\). Ferroberaunite dissolves easily in HCl (35%), slowly in H\(_2\)PO\(_4\) (85%); it does not dissolve in HNO\(_3\) (65%; room temperature; 24 hours observation).

The optical properties of ferroberaunite were measured at a wavelength of 589 nm using a microrefractometer spindle-stage (Department of Geological Sciences, Masaryk University in Brno). The extinction is parallel to the elongation. The mineral is biaxial (-), \(\alpha = 1.736(2)\), \(\beta = 1.765(3)\), \(\gamma = 1.786(5)\), \(2V_{\text{meas.}} = 68(3)°\) and \(2V_{\text{calc.}} = 79°\). Dispersion of optical axes is strong, \(r > v\). The orientation is \(Y = b\), \(X \approx a\), \(Z \approx c\). Pleochroism is strong, \(X = \text{bluish green} \gg Z = \text{green} > Y = \text{yellow}\). The Gladstone–Dale
compatibility using revised constants in table 7 of Mandarino (1981) is excellent; 0.038 for empirical formula and measured density, and 0.027 for empirical formula and density calculated from the single-crystal cell.

**Chemical composition**

The composition of ferroberaunite was determined on polished and carbon-coated fragments mounted in an epoxy cylinder using a Cameca SX 100 electron microprobe (Department of Mineralogy and Petrology, National Museum Prague). The instrument was operated in wavelength-dispersive mode at an accelerating voltage of 15 kV, beam current of 5 nA, with a beam diameter of 7 μm. The following X-ray lines and standards were selected; Kα lines: P, Ca (apatite), Al (Al₂O₃), Mn (rhodinite) and Fe (hematite). Contents of Na, Mg, Si, K, Cl, Ti, Co, V, Cu, F, Cr, N, As, Mo, Sn, Ba, Y, W, Bi, U, Pb and Th were below detection limits.

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Analytical data for ferroberaunite are given in Table 1. In addition to iron, the holotype specimen contains minor amounts of Al (0.04 atoms per formula unit), Mn (0.02 apfu) and Ca (0.01 apfu). The empirical formula of ferroberaunite calculated on the basis of P = 4 apfu is: (Fe³⁺₀.₆₇₋ₓCaₓMnₓ₀.₀₂₋ₓFe⁺ₓMn₀.₀₄₋ₓFe⁵⁺ₓAl₀.₀₄₋ₓ(MO₄)₀.₀₁₋ₓ(OH)₄₋ₓ)₁₋ₓ·6H₂O. The ideal formula is Fe²⁺Fe³⁺(PO₄)₄(OH)₄·6H₂O, which requires FeO 7.91, Fe₂O₃ 43.97, P₂O₅ 31.26, H₂O 16.86, total 100 wt. %.

**Raman spectroscopy**

The Raman spectrum of ferroberaunite (Fig. 4) was collected in the range 3600–50 cm⁻¹ using a DXR dispersive Raman Spectrometer (Thermo Scientific) mounted on a confocal Olympus microscope. The Raman signal was excited by an unpolished 633 nm He–Ne gas laser and detected by a CCD detector (size 1650 × 200 pixels, Peltier cooled to ~60°C, quantum efficiency 50% and dynamic range 360–1100 nm). The experimental parameters were: 100× objective, 10 s exposure time, 1800 exposures, 50 μm pinhole spectrograph aperture and 3 mW laser power level (estimated resolution 6.4–13.3 cm⁻¹, estimated spot size 0.8 μm). The spectra were acquired repeatedly from different grains in order to obtain a representative spectrum with the best signal-to-noise ratio. The possible thermal damage of the measured point was excluded by visual inspection of the exposed surface after measurement, observing possible decay of spectral features at the start of excitation, and checking for thermal downshift of Raman lines. The instrument was set up by a software-controlled calibration procedure using multiple neon emission lines (wavelength calibration), multiple polystyrene Raman bands (laser-frequency calibration) and standardised white-light sources (intensity calibration). Spectral manipulations were performed using the Omnic 9 software (Thermo Scientific).

The Raman spectrum shows bands induced by vibrations of OH units and water molecules, as well as (PO₄)³⁻ tetrahedral and Fe–O octahedral units, similar to other hydrated hydroxyphosphates (e.g. Frost et al., 2014, 2016). The high-energy region over 1300 cm⁻¹ is characterised by vibrations of OH ions and hydrogen-bonded water molecules. There occur two significant bands assigned to the v O–H stretching (3561 cm⁻¹) and to the H–O–H v₂ (δ) bending of water molecules (the broad peak at 1613 cm⁻¹). The next group of bands is connected with stretching vibrations of (PO₄)³⁻ units, namely to the v₃ antisymmetric (maxima at 1137 and 1051 cm⁻¹) and v₁ symmetric (1014 cm⁻¹) modes. The Raman bands at 681, 624 and 574 cm⁻¹ could be attributed to v₄ (δ) (PO₄)³⁻ out-of-plane bending vibrations. Bands of the v₂ (δ) in-plane bending vibrations of the same unit appear at lower wave-lengths (470 and 434 cm⁻¹). Further bands could be attributed to vibrations of Fe-centred octahedra in the crystal structure of ferroberaunite. Bands of Fe–O stretching (most likely at 399–294 cm⁻¹) and O–Fe–O symmetric bending (most likely at 232 and 201 cm⁻¹) overlap with the manifestations of external and lattice vibrations, which continue until the end of the spectrum with the maxima at 232, 201, 128 and 87 cm⁻¹.

**X-ray photoelectron spectroscopy**

Relative proportions of divalent and trivalent iron were estimated by the X-ray photoelectron spectroscopy (XPS) measurements.
carried out with the PHI 5000 VersaProbe II XPS system (Physical Electronics; Regional Centre of Advanced Technologies and Materials, Palacký University Olomouc) using a monochromatic AlKα source (15 kV and 50 W) and photon energy of 1486.7 eV. All the spectra were measured in a vacuum of $1.1 \times 10^{-7}$ Pa and at a temperature of 21°C. The analysed area on the sample was a spot 100 μm in diameter. The survey spectra were measured with a pass energy of 187.850 eV and electronvolt step of 0.8 eV, whereas the high-resolution spectra were measured with a pass energy of 23.500 eV and electronvolt step of 0.2 eV. Dual-beam charge compensation was used for all measurements. All binding energy values were referenced to the carbon peak C1s at 284.80 eV. Data were analysed with MultiPak (Ulvac-PHI, Inc.) software version 9.9.0.8 using Gaussian–Lorentzian function with iterated Shirley routine background subtraction (Shirley, 1972).

Generally, p orbitals exhibit spin-orbit splitting in XPS. The spin-orbit splitting is projected as a doublet in the XPS spectrum (Briggs, 2003). In the Fe 2p region, there is significant splitting of the Fe 2p 3/2 and Fe 2p 1/2 components (∼13 eV) with the ratio 2:1, respectively. Another spectral features in this region are shake-up lines caused by a finite probability that the ion will be left in an excited state a few electronvolts above the ground state. This leads to the formation of satellite peaks (Moulder et al., 1995). As the fitting procedure of the Fe 2p region is very complex, the simplifying practice used for the natural mineral phases by Kloprogge and Wood (2020) was chosen.

To estimate the valence states of iron, an empirical approach comparing Fe 2p3/2 spectra with standards was used, which avoids having to describe the peak shapes analytically (e.g. Rhodes, 2021). Holotype ferroberaunite was compared with the spectra of beraunite, vivianite and childrenite (Table 2). High-resolution spectra for the 707–717 eV binding energy section decomposed to three main peaks for Fe 2p3/2 are shown in Fig. 5. Although the determination of the iron oxidation state is complicated, the ratio Fe2+ : (Fe2++Fe3+) can be estimated from the relative area of the peak Fe 2p3/2(1) and the corresponding regression curve. The observed value of ∼12% Fe2+ corresponds to 0.72 apfu in the ferroberaunite formula.

Table 2. Estimation of a relative content of Fe2+ based on the area of the peak Fe 2p3/2(1).

| Mineral, locality, ideal formula | Peak | Binding energy (eV) | Area (%) | Fe2+ (%) |
|----------------------------------|------|--------------------|----------|---------|
| Ferroberaunite*                  | (1)  | 708.6              | 2.2      | 12      |
| Gravel Hill mine, Cornwall, UK   | (2)  | 710.8              | 76.1     |         |
| Fe2+Fe3+(PO4)4(OH)5·6H2O         | (3)  | shake-up            | 713.0    | 21.8    |
| Beraunite**                     | (1)  | 709.4              | 1.2      | 0       |
| Hrbek mine, Bohemia, Czech Republic | (2) | 711.7              | 62.9     |         |
| Fe3+(PO4)4O(OH)4·4H2O           | (3)  | shake-up            | 713.5    | 35.9    |
| Vivianite***                    | (1)  | 709.3              | 8.8      | 92      |
| Roșia Poieni, Alba, Romania     | (2)  | 711.0              | 59.3     |         |
| Fe2+(PO4)2·8H2O                 | (3)  | shake-up            | 713.8    | 31.9    |
| Childrenite                     | (1)  | 709.0              | 9.5      | 100     |
| George & Charlotte mine, Devon, UK | (2) | 710.9              | 64.9     |         |
| Fe2+Al[PO4]2(OH)2·H2O           | (3)  | shake-up            | 714.0    | 25.6    |

* Holotype specimen; ** neotype specimen (sample NM; Vrtiška et al., 2022); *** probably partly oxidised.

X-ray diffraction data and crystal structure

Powder X-ray diffraction data for ferroberaunite were recorded at room temperature using a Bruker D8 Advance diffractometer equipped with solid-state LynxEye detector and secondary monochromator producing CuKα radiation (Department of Mineralogy...
Childrenite

Vivianite

Beraunite (eleonorite)

Ferroberaunite

Fig. 5. Comparison of high resolution Fe 2p3/2 XPS spectrum of ferroberaunite with patterns of ferric (beraunite/eleonorite) and ferrous phosphates (vivianite and childrenite). The spectra are vertically shifted. The numbering of peaks corresponds to Table 2; the peaks Fe2p3/2(1) used to estimate a relative content of Fe2+ are highlighted.

Table 3. Powder diffraction data (d in Å) for ferroberaunite*.

| hkl   | d_meas | d_calc | h  | k  | l  |
|-------|--------|--------|----|----|----|
| 100.0 | 10.4096| 10.3993| 2  | 0  | 0  |
| 14.2  | 9.6065 | 9.6001 | 0  | 0  | 2  |
| 11.3  | 7.2709 | 7.2656 | 2  | 0  | 2  |
| 4.2   | 5.2035 | 5.1962 | 4  | 0  | 0  |
| 3.3   | 4.8252 | 4.8265 | 1  | 1  | 1  |
| 1.1   | 4.4517 | 4.4570 | 2  | 0  | 4  |
| 1.3   | 4.4155 | 4.4128 | 1  | 1  | 2  |
| 2.0   | 3.7531 | 3.7529 | 3  | 1  | 2  |
| 0.7   | 3.4881 | 3.4885 | 1  | 1  | 4  |
| 12.0  | 3.4675 | 3.4664 | 6  | 0  | 0  |
| 6.2   | 3.3253 | 3.3221 | 6  | 0  | 2  |
| 5.8   | 3.2015 | 3.2000 | 3  | 1  | 0  |
| 0.3   | 3.1749 | 3.1692 | 5  | 1  | 0  |
| 1.1   | 3.1117 | 3.1093 | 2  | 0  | 6  |
| 2.5   | 3.0821 | 3.0819 | 3  | 1  | 4  |
| 0.7   | 2.8917 | 2.8904 | 6  | 0  | 4  |
| 1.1   | 2.7992 | 2.7982 | 4  | 0  | 6  |
| 1.5   | 2.7405 | 2.7416 | 5  | 1  | 4  |
| 2.6   | 2.7135 | 2.7131 | 1  | 1  | 6  |
| 3.8   | 2.5997 | 2.5998 | 8  | 0  | 0  |
| 0.7   | 2.5738 | 2.5781 | 0  | 2  | 0  |
| 0.7   | 2.5738 | 2.5744 | 7  | 1  | 0  |
| 1.1   | 2.4294 | 2.4308 | 7  | 1  | 3  |
| 0.7   | 2.4141 | 2.4133 | 2  | 2  | 2  |
| 1.6   | 2.3115 | 2.3098 | 4  | 2  | 0  |
| 1.3   | 2.2278 | 2.2285 | 4  | 0  | 8  |
| 1.2   | 2.1086 | 2.1077 | 3  | 1  | 8  |
| 1.4   | 2.0793 | 2.0799 | 10 | 0  | 0  |
| 1.1   | 2.0085 | 2.0081 | 6  | 2  | 2  |
| 0.8   | 1.9239 | 1.9240 | 7  | 1  | 3  |
| 0.7   | 1.7212 | 1.7222 | 6  | 0  | 10 |
| 2.5   | 1.6888 | 1.6887 | 12 | 0  | 2  |
| 0.8   | 1.6618 | 1.6612 | 12 | 0  | 4  |
| 1.0   | 1.6185 | 1.6188 | 10 | 2  | 0  |
| 0.4   | 1.5672 | 1.5671 | 1  | 3  | 5  |
| 0.5   | 1.4847 | 1.4856 | 14 | 0  | 0  |

*The strongest peaks are reported in bold.

α = 20.833(4) Å, β = 5.1562(13) Å, γ = 19.232(7) Å, β = 93.30(4)° and V = 2062.5(9) Å³.

Table 4. Details for the data collection and refinement of the structure of ferroberaunite.

| Crystal data |
|--------------|
| Chemical formula | Fe₆H₁₇O₂₇P₄ |
| Mr | 908.1 |
| Crystal system, space group | Monoclinic, C2/c |
| Temperature (K) | 298 |
| a, b, c (Å) | 20.8708(3), 5.1590(8), 19.2263(3) |
| β (°) | 93.3186(17) |
| V (Å³) | 2066.7(3) |
| Z | 4 |
| Radiation type | Mo Kα |
| μ (mm⁻¹) | 4.54 |

| Data collection |
|-----------------|
| Crystal size (mm) | 0.089 × 0.014 × 0.013 |
| Diffractometer | Rigaku SuperNova CCD |
| Absorption correction | Empirical (multi-scan), CrysAlis |
| T_min, T_max | 0.738, 1.000 |
| No. of measured, independent and observed [I > 3σ(I)] reflections | 18965, 2506, 2301 |
| R_int | 0.0296 |
| R | 0.0202, 0.0652, 1.54 |
| wR | 0.0202, 0.0652, 1.54 |
| No. of reflections | 2506 |
| No. of parameters | 195 |
| No. of restraints | 10 |
| H-atom treatment | H atoms treated by a mixture of independent and constrained refinement |
| Δρ_max, Δρ_min (e Å⁻³) | 0.30, −0.56 |

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Table 5. Atom coordinates and displacement parameters (as isotropic or equivalent; in Å²) for the structure of ferroberaunite.

| Atom   | Wyckoff | x/a   | y/b   | z/c | $U_{eq}$/$U_{eq}$ |
|--------|---------|-------|-------|-----|-------------------|
| Fe1(M1) | 4a      | ½     | ½     | ½   | 0.00962(12)       |
| Fe2(M4) | 8f      | 0.391901(14) | 0.53696(6) | 0.585364(15) | 0.00917(9) |
| Fe3(M3) | 8f      | 0.544145(13) | 0.78095(6) | 0.672652(15) | 0.00882(9) |
| Fe4(M4) | 4d      | ½     | ½     | ½   | 0.01053(12)       |
| P1     | 8f      | 0.605152(10) | 0.97529(10) | 0.52421(3)  | 0.00709(14) |
| P2     | 8f      | 0.407725(3)  | 1.0445610(6) | 0.68178(3)  | 0.00819(15) |
| O1     | 8f      | 0.57679(7)  | 1.2342(3) | 0.49702(8) | 0.0122(4) |
| O2     | 8f      | 0.67768(7)  | 0.9840(3) | 0.51606(8) | 0.0114(4) |
| O3     | 4e      | ½     | ½     | ½   | 0.0142(6)         |
| O4     | 8f      | 0.57518(7)  | 0.7503(3) | 0.48031(8) | 0.0115(4) |
| O5     | 8f      | 0.49277(7)  | 0.5406(3) | 0.60748(8) | 0.0121(4) |
| O6     | 8f      | 0.47887(7)  | 1.0511(3) | 0.66704(8) | 0.0126(4) |
| O7     | 8f      | 0.39947(7)  | 0.9880(3) | 0.75910(8) | 0.0148(4) |
| O8     | 8f      | 0.37049(7)  | 0.8419(3) | 0.63714(8) | 0.0129(4) |
| O9     | 8f      | 0.59099(8)  | 0.9420(3) | 0.60010(8) | 0.0155(4) |
| O10    | 8f      | 0.37842(7)  | 1.3116(3) | 0.66419(8) | 0.0123(4) |
| O11    | 8f      | 0.37060(7)  | 0.5228(3) | 0.53742(8) | 0.0130(4) |
| O12    | 8f      | 0.25248(8)  | 0.4133(3) | 0.40139(8) | 0.0181(5) |
| O13    | 8f      | 0.61512(9)  | 0.4862(3) | 0.68038(11) | 0.0247(5) |
| O14    | 8f      | 0.26908(10) | 0.1399(5) | 0.28417(11) | 0.0385(7) |
| H1o14  | 8f      | 0.2475(4)  | −0.018(4) | 0.2797(18) | 0.046(2)  |
| H1o5   | 8f      | 0.497(11)   | 0.370(3) | 0.6226(12) | 0.0145(2) |
| H1o12  | 8f      | 0.213(1)   | 0.496(4) | 0.3918(12) | 0.0217(2) |
| H1o13  | 8f      | 0.3079(12)  | 0.681(3) | 0.5160(12) | 0.0156(2) |
| H1o13  | 8f      | 0.6376(12)  | 0.465(4) | 0.6407(10) | 0.0296(2) |
| H2o12  | 8f      | 0.2550(10)  | 0.290(4) | 0.3666(10) | 0.0217(2) |
| H2o13  | 8f      | 0.6181(13)  | 0.328(3) | 0.7028(11) | 0.0296(2) |
| Ho14   | 8f      | 0.3099(9)   | 0.078(6) | 0.2741(17) | 0.0462(2) |

M1–M4 denotes metal cation site labelling, according to Moore and Kampf (1992).

and Petrology, National Museum, Prague). The instrument was operating at 40 kV and 40 mA. In order to minimise the background, the powder samples were placed (without any liquid) on the surface of a flat silicon wafer. The powder pattern was collected in the Bragg–Brentano geometry in the range 3–70°2θ, step 0.01° and counting time of 20 s per step (total duration of the experiment ≈ 30 hours). The positions and intensities of diffractions were found and refined using the Pearson VII profile-shape function of the ZDS program package (Ondruš, 1993). Powder diffraction data are given in Table 3; the unit-cell parameters were refined by the least-squares algorithm implemented by

Fig. 6. Octahedral trimer in ferroberaunite. M1 is occupied by Fe2+ and M4 by Fe3+. P tetrahedrons are purple and H atoms grey.

Table 6. Selected interatomic distances (in Å) and polyhedral measures for ferroberaunite.

| Distance | Formula | Value |
|----------|---------|-------|
| Fe1–O1  | 2.1125(15) | Fe2–O1  | 2.1093(16) |
| Fe1–O1  | 2.1125(15) | Fe2–O4  | 2.0888(16) |
| Fe1–O4  | 2.0836(15) | Fe2–O5  | 2.1236(15) |
| Fe1–O4  | 2.0836(15) | Fe2–O8  | 1.9280(16) |
| Fe1–O5  | 2.0912(15) | Fe2–O10a| 1.9435(16) |
| Fe1–O5  | 2.0912(15) | Fe2–O11 | 1.9398(15) |
| <Fe1–Fe > | 2.056 | <Fe2–Fe > | 2.022 |
| V<sub>1</sub> | 11.64 Å³ | V<sub>1</sub> | 10.75 Å³ |
| ECoN<sub>1</sub> | 5.993 | ECoN<sub>1</sub> | 5.564 |
| Distortion<sub>1</sub> | 0.340 | Distortion<sub>2</sub> | 17.979 |

Fe4–O2  | 1.9710(15) | P1–O1  | 1.5400(16) |
| Fe4–O2  | 1.9710(15) | P1–O2  | 1.5315(15) |
| Fe4–O11 | 1.9604(15) | P1–O4  | 1.5499(16) |
| Fe4–O11 | 1.9604(15) | P1–O9  | 1.5153(17) |
| Fe4–O12 | 2.0816(15) | <P1–Fe > | 1.533 |
| <Fe4–Fe > | 2.004 | <P1–Fe > | 2.007 |
| V<sub>1</sub> | 10.71 Å³ | ECoN<sub>2</sub> | 5.840 |
| Distortion<sub>2</sub> | 7.432 | Distortion<sub>2</sub> | 9.336 |

Symmetry codes: (i) x+1, y+1, z+1; (ii) x, y, 1, z; (iii) x−1, y, z; (iv) x, y+1, z; (v) x+1, y, z; (vi) x−1, y−1, z; (vii) x−1, y+1, z; (viii) x−1, y−1, z. ECoN – effective coordination number (Hoppe, 1979); distortion – octahedral distortion (Brown and Shannon, 1973).
Burnham (1962) as: \( a = 20.833(4) \, \text{Å}, b = 5.1562(13) \, \text{Å}, c = 19.232(7) \, \text{Å}, \beta = 93.30(4)° \) and \( V = 2062.5(9) \, \text{Å}^3 \).

For the single-crystal diffraction experiment, a long-prismatic crystal was separated under a polarising microscope and mounted on a glass fibre. The diffraction experiment (see Table 4 for details) was performed at room temperature with a Rigaku SuperNova single-crystal diffractometer equipped with the Atlas S2 CCD detector and a microfocus MoK\( \alpha \) source (Institute of Physics, CAS, Prague). Data reduction was performed using CrysAlisPro Version 1.171.39.46 (Rigaku, 2019). The data were corrected for the Lorentz factor and polarisation effects. An absorption correction (empirical scaling using spherical harmonics) was applied in Jana2020 (Petříček et al., 2020).

The single-crystal X-ray experiment revealed a monoclinic unit cell: \( a = 20.8708(3), b = 5.1590(8), c = 19.2263(3) \, \text{Å}, \beta = 93.3186(17)°, V = 2066.7(3) \, \text{Å}^3 \) and \( Z = 4 \).

The structure of ferroberaunite was solved from the X-ray data using the intrinsic phasing algorithm of the SHELXT program (Sheldrick, 2015) in the monoclinic space-group \( \text{C}2/c \). A centrosymmetric space-group was indicated from the reflection statistics (observed, \( |E| - 1 | = 1.006; \) expected centrosymmetric = 0.968 vs. non-centrosymmetric 0.736). The refinement was performed using the full-matrix least-squares algorithm of the Jana2020 program (Petříček et al., 2020). It revealed the same general model as provided for the beraunite-related structures (Fanfani and Zanazzi, 1967; Moore and Kampf, 1992; Chukanov et al., 2017; Aksenov et al., 2018; Tvrdý et al., 2020). The refinement converged smoothly, including H-atom sites located by Fourier syntheses (H atoms refined using soft constrains on the O–H distances and \( U_{	ext{iso}} \) of the H atoms were set at 1.2 times that of the corresponding donor O atom), to the final \( R = 0.0203 \) for 2301 unique reflections of \( I > 3 \sigma(I) \) with a goodness of fit = 1.35; the highest peak that resides in the electron density was 0.37 e\( ^{-} \)Å\(^{-3}\), only. The details for the refinement are given in Table 4. Atom coordinates, atomic displacement parameters and site occupancies are given in Table 5, selected interatomic distances in Table 6 and bond-valence analysis in Table 7. The crystallographic information files have been deposited with the Principal Editor of Mineralogical Magazine and are available as Supplementary material (see below).

**Table 7. Bond-valence analysis for the structure of ferroberaunite (values in valence units, \( \text{vu} \)).**

| \( \text{Fe1} \) | \( \text{Fe2} \) | \( \text{Fe3} \) | \( \text{Fe4} \) | \( \text{P1} \) | \( \text{P2} \) | \( \Sigma \text{BV-H} \) | \( \Sigma \text{BV+H} \) |
|-----------------|--------------|--------------|--------------|--------|--------|-------------|-------------|
| \( O1 \)        | 0.36 \( ^{a} \) | 0.39         |              | 1.23   |        | 1.98        | 1.98        |
| \( O2 \)        |              | 0.57 \( ^{a} \) |              | 1.26   |        | 1.83        | 1.93        |
| \( O3(\text{OH}) \) | 0.53         |              |              |        |        | 1.07        | 2.06        |
| \( O4 \)        | 0.39 \( ^{a} \) | 0.41         |              | 1.22   | 2.01   | 2.01        | 2.01        |
| \( O5(\text{OH}) \) | 0.38 \( ^{a} \) | 0.37         | 0.49         |        |        | 1.26        | 2.18        |
| \( O6 \)        |              | 0.60         |              | 1.24   | 1.84   | 1.97        |             |
| \( O7 \)        |              | 0.49         |              | 1.26   | 1.75   | 1.96        |             |
| \( O8 \)        |              | 0.64         |              | 1.26   | 1.90   | 1.90        |             |
| \( O9 \)        |              | 0.62         |              | 1.31   | 1.94   | 1.93        |             |
| \( O10 \)       |              | 0.61         |              | 1.26   | 1.88   | 1.88        |             |
| \( O11(\text{OH}) \) | 0.62         |              | 0.58 \( ^{a} \) | 1.20   | 2.17   |             |             |
| \( O12(\text{H,O}) \) |              |              | 0.42 \( ^{a} \) | 0.42   | 2.34   |             |             |
| \( O13(\text{H,O}) \) |              |              | 0.37         |        | 0.37   | 2.31        |             |
| \( O14(\text{H,O}) \) |              |              |              |        |        | 0.00        | 2.09        |
| \( \Sigma \text{BV} \) | 2.25        | 3.03         | 3.11         | 3.13   | 5.02   | 5.02        |             |

*Bond-valence parameters were taken from Gagné and Hawthorne (2015). \( \Sigma \text{BV-H} \) = summation of bond valences without considering H bonds; \( \Sigma \text{BV+H} \) = summation of bond valences with H bonds considered.
Ferroberaunite possesses some structural elements common to basic phosphates of ferrous and ferric iron (Moore, 1969, 1970). Distinct fundamental building blocks are trimers of face-shared $M_1$- and $M_4$-octahedra, where the inner $[\text{MnO}_4(\text{OH})_2]_3$-octahedron occupies the 4$a$-site and the outer $[\text{MnO}_4(\text{OH})(\text{OH}_2)]$-octahedra occupy 8$f$-sites, for the $C2/c$ structures (Fig. 6). The trimers are further linked via two isolated $[\text{PO}_4]$-tetrahedra along the $b$ direction. Along the $c$ direction they are connected by corner-sharing with $[\text{MnO}_4(\text{OH})(\text{OH}_2)]$-octahedra and $[\text{PO}_4]$-tetrahedra, which results in heteropolyhedral layers (Fig. 7). These layers are then linked via $M_2$-octahedra forming a framework containing wide channels running parallel to $b$ and hosting $\text{H}_2\text{O}$. The seven structural blocks of these octahedra (triplets with corner shared octahedra) are referred to as the $h$-clusters by Moore (1969, 1970).

The distinction between beraunite (formerly 'eleonorite'; IMA 21-D, Miyawaki et al., 2021) and ferroberaunite is the occupancy of the $M_1$ site. Whereas for beraunite, $M_1$ is populated by trivalent iron, ferroberaunite contains divalent iron at $M_1$. This has been proved unambiguously by the results of the bond-valence analysis (Table 7), consistent with a site occupancy of $75\% \text{Fe}^{2+}$ and $25\% \text{Fe}^{3+}$. The formula of ferroberaunite, reflecting the occupancy of the $M_1$ site as suggested by the bond-valence analysis and which is in line with the results from electron microprobe spectroscopy, is $(\text{Fe}^{2+}_{0.75}\text{Fe}^{3+}_{0.25})\text{Fe}^{2+}_{3.38}(\text{PO}_4)_3\text{Al}_0(\text{OH})_3(\text{H}_2\text{O})_6$; this formula is not electroneutral, having $+0.25$ charge. The exact mechanism of the charge-balance is probably via $\text{OH}$$\leftrightarrow$O substitution. In the case of ferroberaunite, its resolution is far beyond the capabilities of the current X-ray data. The ideal, electroneutral formula for ferroberaunite is $\text{Fe}^{2+}_{0.75}\text{Fe}^{3+}_{3.38}(\text{PO}_4)_3\text{Al}_0(\text{OH})_3(\text{H}_2\text{O})_6$, $Z = 4$ and $D_{\text{calc}} = 2.919$ g cm$^{-3}$.

**Discussion**

The crystal structure of minerals of the ferroberaunite–ferroberaunite series has been investigated by several authors. Fanfani and Zanazzi (1967) studied, using the Weissenberg method, a crystal of 'red' beraunite from the Eleonore iron mine near Giessen, Germany. For this sample, the authors determined by microchemical analysis (colorimetric test), somewhat surprisingly, a ratio of divalent to trivalent iron of $1:5.9$ and a formula corresponding to the present-day ferroberaunite. Nevertheless, the refined bond lengths within the Fe-octahedra unambiguously show iron as trivalent (Fe1 $= 2.96$ valence units (vu), Fe2 $= 3.43$ vu, Fe3 $= 3.15$ vu, Fe4 $= 2.99$ vu; using bond-valence parameters given for Fe$^{3+}$ by Gagné and Hawthorne, 2015). Subsequently, Moore (1970) published refined unit-cell data derived from a powder image of 'green beraunite' (i.e. ferroberaunite) from the Palermo No. 1 Pegmatite, New Hampshire, USA. In the Mn-rich 'red' beraunite from Manguade, Portugal, Marzoni Fecia di Cossato et al. (1989) hypothesised the presence of exclusively trivalent iron and the dominance of divalent manganese at the $M_2$ site; these conclusions were discussed subsequently by Moore and Kampf (1992) and Aksenov et al. (2018). In this site, divalent manganese cannot be present, based on refined bond lengths (Mn2 $= 2.97$ vu; using bond-valence parameters given for Mn$^{2+}$ by Gagné and Hawthorne, 2015), and the rest of the sites assigned to Fe are dominated by trivalent iron (Fe1 $= 2.77$ vu, $\sim 24\%$ Fe$^{2+}$ and $77\%$ Fe$^{3+}$; Fe3 $= 3.10$ vu; and Fe4 $= 3.01$ vu; using bond-valence parameters given by Gagné and Hawthorne, 2015). Moore and Kampf (1992) analysed the published structural data and compared it with new measurements on 'green beraunite' from Mullica Hill, New Jersey, USA. There is little doubt that they analysed what is approved now as ferroberaunite (Fe1 $= 2.30$ vu, $\sim 70\%$ Fe$^{2+}$ and $30\%$ Fe$^{3+}$; Fe3 $= 3.40$ vu; Fe3 $= 3.15$ vu; Fe4 $= 2.99$ vu; using bond-valence parameters given by Gagné and Hawthorne, 2015).

Further structural data are later reported by Chukanov et al. (2017) for beraunite ('eleonorite') and by Aksenov et al. (2018) for Mn-rich beraunite ('eleonorite'). In the case of the sample studied by Aksenov et al. (2018), the authors concluded that all octahedral sites are occupied dominantly by trivalent iron, Mn$^{3+}$ is present in an amount of only 0.28 apfu in $M_1$ and its excess ($\sim 0.3$ apfu) is disordered between $M_2$–$M_4$ sites with different Fe$^{3+}$: Mn$^{3+}$ ratios. 'Eleonorite', re-established by Chukanov et al. (2017), is a mineral with the Fe$^{3+}$ dominating over all the octahedral metal sites in the structure. The structure model of Chukanov et al. (2017) corresponds to an average structure of the centrosymmetric
monoclinic space group \( \text{C2/m} \). This model comprises a partially occupied OH1 site (50% O and 50% OH). This means there must also be an H site with 50% occupancy. The OH1 site is related to the M1-octahedron, which hosts Fe\(^{3+} \) in the case of beraunite (‘eleonorite’ of Chukanov et al., 2017). The structure model for beraunite proposed by Vršička et al. (2022) adopts a non-centrosymmetric monoclinic space group \( \text{Cc} \), with the fully occupied H site linked to the O5_2 site of the M1-octahedron, equivalent to the O5\(^{1-\text{c}} \), 1-\text{y} - 2\) site in ferroberaunite (Fig. 6). Such a model provides a non-averaged structure with one of the vertices of the M1-octahedron deprotonated, resulting in the formula Fe\(^{2+} \)(PO\(_4\))\(_2\)(OH)\(_4\)\(_{1}\)\_\_6H\(_2\)O. In contrast to the centrosymmetric structure of ferroberaunite, Fe\(^{2+} \text{Fe}^{3+} \)(PO\(_4\))\(_2\)(OH)\(_3\)\_6H\(_2\)O, two of the M1-octahedral vertices (represented by the symmetrically related O\(_5\) atoms) are linked to H atoms of the OH groups.

Conclusions

The redetermination of beraunite and the approval of the new mineral name ferroberaunite should correctly clarify the status of these structurally and chemically close, but distinct, mineral phases. Ferroberaunite is a Fe\(^{2+} \) analogue of zincoberaunite (Zn dominant name ferroberaunite should correctly clarify the status of these minerals). The identification of these minerals is possible only by both chemical and structural analyses. For Fe\(^{2+} /\text{Fe}^{3+} \) valence bands of iron, the rule ‘dark green ferroberaunite’ and ‘red-brown beraunite’ generally applies.

Supplementary material. To view supplementary material for this article, please visit https://doi.org/10.1180/mgm.2022.15

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