

Ferrirockbridgeite, $(\text{Fe}_{0.67}^{3+}\square_{0.33})_2(\text{Fe}^{3+})_3(\text{PO}_4)_3(\text{OH})_4(\text{H}_2\text{O})$, and the oxidation mechanism for rockbridgeite-group minerals

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Abstract: Ferrirockbridgeite, ideally $(\text{Fe}_{0.67}^{3+}\square_{0.33})_2(\text{Fe}^{3+})_3(\text{PO}_4)_3(\text{OH})_4(\text{H}_2\text{O})$, is a new member of the rockbridgeite group. The type specimen is from the Palermo No. 1 pegmatite in North Groton, Grafton County, New Hampshire, USA. Electron microprobe analysis, coupled with Mössbauer spectroscopy for FeO and thermogravimetric analysis (TGA) for H₂O gives the empirical formula $\text{Mn}_{0.31}^{2+}\text{Fe}_{0.08}^{2+}\text{Mg}_{0.01}\text{Zn}_{0.03}\text{Ca}_{0.05}\text{Fe}_{4.18}^{3+}\text{P}_{2.87}\text{O}_{17}\text{H}_{6.11}$. Ferrirockbridgeite is orthorhombic, space group *Bbmm* with $a = 13.853(1)$, $b = 16.928(1)$, $c = 5.1917(5)$ Å and $Z = 4$. Optically, ferrirockbridgeite is biaxial (–), with $\alpha = 1.875(5)$, $\beta = 1.890(\text{calc})$, $\gamma = 1.900(5)$ (measured in white light) and $2V(\text{meas})$ is $78(1)^\circ$ from extinction data. The dispersion is strong, with $r > v$. The optical orientation is $X = c$, $Y = a$, $Z = b$. The pleochroism is $X = \text{yellow brown}$, $Y = \text{olive brown}$, $Z = \text{dark olive green}$; $Z > Y > X$. Crystal structure refinements on ferrirockbridgeite and other oxidized rockbridgeite-group species, including type rockbridgeite and type frondelite, show that oxidation is accompanied by loss of Fe²⁺ from the *M2* site according to the reaction $[\text{3Fe}^{2+}] \rightarrow [\text{2Fe}^{3+} + \square] + \text{Fe}^{2+}(\text{removed}) + 2\text{e}^-$. A variable portion of the Fe removed from the *M2* site becomes trapped at *M3* site vacancies. A general formula for oxidized rockbridgeite-group minerals is presented.

Key-words: ferrirockbridgeite; new mineral; rockbridgeite group; oxidation mechanism; crystal structure; Mössbauer.

1. Introduction

The International Mineralogical Association Commission on New Minerals, Nomenclature and Classification (IMA CNMNC) recently approved the establishment of the rockbridgeite group with a revised general formula based on the crystal structure (IMA CNMNC Newsletter 41, January 2018; Grey *et al.*, 2019). Previously, rockbridgeite and related minerals frondelite and plimerite were described by the formula $A\text{B}_4(\text{PO}_4)_3(\text{OH})_5$, where $A = \text{Fe}^{2+}$ for rockbridgeite, Mn^{2+} for frondelite and Zn for plimerite and $B = \text{Fe}^{3+}$. This formula was established before the crystal structure was known (Lindberg, 1949). Moore (1970) subsequently established the structural formula for minerals with the rockbridgeite structure as $M1(M2)_2(M3)_2(\text{PO}_4)_3(\text{OH}, \text{H}_2\text{O})_5$. This is simplified to $A_2B_3(\text{PO}_4)_3(\text{OH}, \text{H}_2\text{O})_5$, where A corresponds to the *M2* site and contains all divalent cations, while $B = M1 + M3$ and contains predominantly Fe³⁺. The different rockbridgeite-group minerals are distinguished by the occupancy of the *M2* site. Rockbridgeite is ideally $(\text{Fe}_{0.5}^{2+}\text{Fe}_{0.5}^{3+})_2\text{Fe}_3^{3+}(\text{PO}_4)_3(\text{OH})_5$, and frondelite is

$(\text{Mn}_{0.5}^{2+}\text{Fe}_{0.5}^{3+})_2\text{Fe}_3^{3+}(\text{PO}_4)_3(\text{OH})_5$. Plimerite (Elliott *et al.*, 2009) with ideally two Zn atoms per formula unit (*apfu*), requires replacement of one hydroxyl ion by H₂O for charge balance, giving $\text{Zn}_2\text{Fe}_3^{3+}(\text{PO}_4)_3(\text{OH})_4(\text{H}_2\text{O})$. The substitution of H₂O for OH in a rockbridgeite-group mineral containing predominantly divalent cations in the *M2* site has recently been confirmed by Röska *et al.* (2018) using neutron diffraction.

We have recently reported the characterization of ferrirockbridgeite, $\text{Fe}_2^{2+}\text{Fe}_3^{3+}(\text{PO}_4)_3(\text{OH})_4(\text{H}_2\text{O})$ as the member with dominant Fe²⁺ in the *M2* site. The mineral and its name have been approved by the IMA CNMNC, IMA2018-004 (Grey *et al.*, 2019). We describe here the characterization of the Fe³⁺ end-member species, ferrirockbridgeite, which has been approved by the IMA CNMNC (IMA2018-065). Moore (1970) originally proposed the formula $\text{Fe}_5^{3+}(\text{PO}_4)_3\text{O}(\text{OH})_4$ for fully oxidized rockbridgeite. This formula, however, does not take account of non-stoichiometry that accompanies oxidation. As we have previously reported for a frondelite specimen with 98% of the iron in the ferric form, the iron oxidation is accompanied by

selective removal of iron from the *M2* site, resulting in up to 17% vacancies in *A* (Grey *et al.*, 2018). In this study, we have extended crystal-structure refinements to a number of oxidized rockbridgeite-group minerals, including type rockbridgeite and type frondelite, and find a consistent relationship between the extent of oxidation of the iron and the concentration of vacancies in the *M2* site, which leads to a modification of the general formula for rockbridgeite-group minerals to take account of non-stoichiometry.

2. Description of ferrirockbridgeite

Ferrirockbridgeite is from the Palermo No. 1 pegmatite in North Groton, Grafton County, New Hampshire, USA. (43° 45.038'N 71° 53.378'W). The specimen now designated as the holotype is one that was used by Frondel as part of his 1949 study, in which he defined rockbridgeite as a species distinct from dufrenite (Frondel, 1949). He described it as being in the form of radial fibrous crusts and masses, derived from the alteration of triphylite. It is important to note that most material previously designated as “rockbridgeite” from the Palermo No. 1 pegmatite is rockbridgeite, and only the more oxidized material qualifies as ferrirockbridgeite. Frondel (1949) reported an analysis of the Palermo specimen made by N.H. Gonyer giving (wt%) FeO 0.99, MnO 2.24, Fe₂O₃ 55.84, P₂O₅ 32.86, H₂O 7.96, Σ99.89. Frondel’s reported measured density is 3.33 g cm⁻³.

For this study, a portion of the specimen studied by Frondel (1949) was obtained from the Harvard University Mineralogical and Geological Museum (specimen #95086). It comprised millimetre-sized chips, composed of compact intergrowths of reddish-brown blade-like crystals, flattened on {010} and elongated on [001] (Fig. 1). The density, measured using a Berman balance with toluene is 3.33 g cm⁻³ whereas the calculated density, based on the empirical formula and X-ray powder diffraction, is 3.42 g cm⁻³. The lower measured density is most likely due to micropores that are not accessible by the density liquid (Grey *et al.*, 2019).

Optically, ferrirockbridgeite is biaxial (–), with the indices of refraction $\alpha = 1.875(5)$, $\beta = 1.890(\text{calc})$, $\gamma = 1.900(5)$ (measured in white light). The measured 2V is 78(1)° from extinction data using EXCALIBUR (Gunter *et al.*, 2004). The β index could not be measured because of the unfavorable orientation of cleavage fragments. Consequently, β was calculated from α , γ and 2V. The dispersion is strong, with $r > v$. The optical orientation is $X = c$, $Y = a$, $Z = b$. The pleochroism is $X = \text{yellow brown}$, $Y = \text{olive brown}$, $Z = \text{dark olive green}$; $Z > Y > X$. The Gladstone-Dale compatibility (Mandarino, 1981) $1 - (K_P/K_C) = 0.03$ (excellent), based on the empirical formula with the calculated density and the indices of refraction. Chemical analyses, spectroscopic studies and crystal-structure refinement for ferrirockbridgeite will be described below, together with the results for other specimens of oxidized rockbridgeite-group minerals

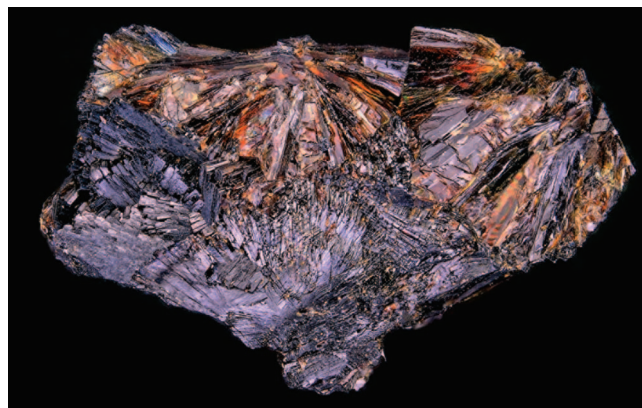


Fig. 1. Ferrirockbridgeite from Palermo #1 pegmatite, New Hampshire, USA. Field of view (FOV) 3.5 mm.

3. Experimental procedure

3.1. Samples

In addition to the ferrirockbridgeite from the Palermo No. 1 Pegmatite, described in Section 2, the following specimens were studied.

3.1.1. Type rockbridgeite

Approximately 1.2 g of millimetre-sized black chips from the type specimen (Fig. 2) were supplied by the Harvard University Mineralogical and Geological Museum (HMM#80600). The type specimen is from the outcroppings of a limonite deposit on South Mountain, one mile east of Midvale in Rockbridge County, Virginia. It was described by Frondel (1949) as forming dark greenish-black, compact fibrous masses with yellow limonite. The limonite associated with the rockbridgeite (Fig. 2) was shown by PXRD to be predominantly goethite. Frondel reported two chemical analyses, made by J.I. Campbell and F.A. Massie, which are in close agreement for the major elements, giving average results (wt%) of FeO 6.1, MnO 0.32, Fe₂O₃ 50.85, Al₂O₃ 0.25, P₂O₅ 31.7, H₂O 8.4. Inconsistent reported analyses for MgO (0.76 and 2.16 wt%) and CaO (1.12 and 0.0 wt%) suggest that these are from contaminant phases. Frondel’s reported measured density for the Rockbridge material is 3.37 g cm⁻³.

3.1.2. Type frondelite

A small sample (16 mg) of coarse powder from the type specimen was provided by the Department of Mineral Sciences at the Smithsonian Institution (NMNH#1059460). The type frondelite locality is the Sapucaia pegmatite, Minas Gerais, Brazil. Type frondelite was described by Lindberg (1949) as a dark-brown, radially fibrous mineral occurring as crusts, botryoidal and drusy masses, associated with triphylite, vivianite and a member of the heterosite–purpurite series. Analysis of type frondelite by Lindberg (1949) gave (wt%) FeO none, MnO 7.74, MgO 0.20, CaO 0.02, Na₂O 0.98, K₂O 0.12, Fe₂O₃ 48.85, Mn₂O₃ 1.75, Al₂O₃ 1.31,



Fig. 2. Type rockbridgeite, Rockbridge County, Virginia, USA, Harvard specimen 80600. Black rockbridgeite associated with yellow limonite (predominantly goethite). FOV ~10 cm; Harvard University Mineralogical and Geological Museum image.

P_2O_5 31.28, H_2O 7.52, $\Sigma 99.77$. Lindberg's measured density is 3.476 g cm^{-3} .

3.1.3. Hagendorf Süd frondelite IGC89

Frondelite specimen IGC89 was collected by one of the authors (EK) from the 93 m level of the Hagendorf Süd pegmatite mine. It is a dark brown mineral similar in appearance to type frondelite. Individual thin blades of the mineral are a yellow brown colour. Wet-chemical analyses by EK (unpublished) gave (wt%) FeO 0.17, MnO 6.29, MgO 0.11, CaO 0.75, Fe_2O_3 51.49, P_2O_5 32.04, H_2O 8.98, $\Sigma 99.83$.

3.2. Mössbauer spectroscopy

The Mössbauer spectra were taken using a conventional constant-acceleration drive with a symmetrical sawtooth waveform (Wissel). The source of ^{57}Co in rhodium was maintained at room temperature. The spectra were fitted with four Lorentzian doublets (three for Fe^{3+} and one for Fe^{2+}). The spectra-fitting parameters are reported in Table 1 and the fit to the spectrum for ferrorockbridgeite is shown in Fig. 3. The amounts of Fe^{2+} and Fe^{3+} in Table 1 were used in the calculation of empirical formulae from electron microprobe analyses, and in the assignment of Fe^{2+} and Fe^{3+} in the structural formulae.

3.3. Infrared spectroscopy

Attenuated total-reflection (ATR) infrared spectroscopy on ground crystals of ferrorockbridgeite was conducted using a Bruker Equinox IFS55 spectrometer fitted with Judson MCT detector and Specac diamond ATR. One hundred co-added scans were employed at a spectral resolution of 4 cm^{-1} . The infrared spectrum is shown in Fig. 4. In the OH stretching region, weak sharp peaks at 3520 and 3565 cm^{-1} are assigned to hydroxyl ion vibrations while a broad peak at 3230 cm^{-1} is attributed to H_2O groups.

Table 1. Mössbauer parameters for rockbridgeite-group minerals. Isomer shift δ , quadrupole splitting Δ , half-width-half-maximum (HWHM) and area of doublet A .

δ (mm/s)	Δ (mm/s)	HWHM (mm/s)	A (%)
<i>Ferrorockbridgeite</i> , $\chi^2 = 0.79$			
0.37(1)	0.35(3)	0.14(2)	27
0.37(1)	0.61(4)	0.15(5)	38
0.36(1)	0.94(7)	0.22(2)	33
1.05(3)	2.85(6)	0.18(5)	2
<i>Type rockbridgeite</i> , $\chi^2 = 0.73$			
0.36(1)	0.35(8)	0.15(5)	22
0.37(1)	0.61(6)	0.17(9)	38
0.36(1)	0.92(9)	0.24(2)	31
1.09(1)	3.05(1)	0.21(2)	9
<i>Type frondelite</i> , $\chi^2 = 0.62$			
0.37(1)	0.36(3)	0.14(2)	30
0.38(1)	0.64(4)	0.17(5)	41
0.36(1)	0.97(9)	0.23(2)	27
1.07(4)	3.05(9)	0.20(7)	2
<i>Hag. Süd frondelite (IGC89)</i> , $\chi^2 = 0.87$			
0.39(1)	0.36(3)	0.14(2)	40
0.39(1)	0.67(3)	0.15(4)	33
0.39(1)	1.01(6)	0.20(1)	26
1.21(3)	3.05(9)	0.20(7)	1

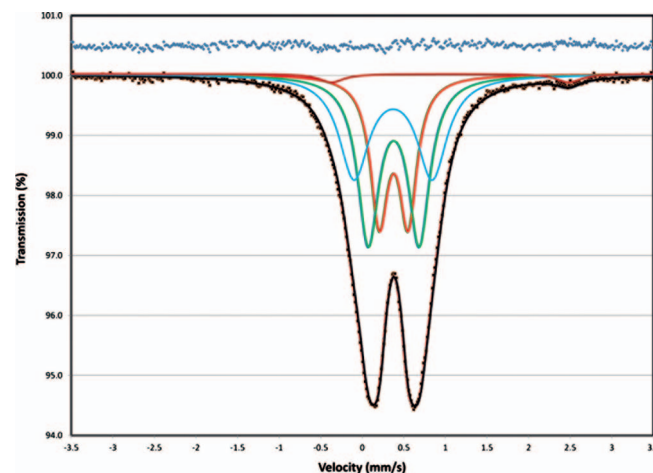


Fig. 3. Fitted Mössbauer spectrum for ferrorockbridgeite.

There is a corresponding H–O–H bending vibration for water molecules at $\sim 1600 \text{ cm}^{-1}$. A weak shoulder at $\sim 1400 \text{ cm}^{-1}$ may be due to carbonate because the mass spectrometer showed CO_2 evolution during the TGA run. Three $(PO_4)^{3-}$ stretching vibrations, at 1165 , 1030 and 930 cm^{-1} are in similar positions to those reported for the isostructural mineral plimerite (Sejkora *et al.*, 2011).

3.4. Thermogravimetric analysis (TGA)

TGA and differential thermal analysis (DTA) were performed on ground samples of ferrorockbridgeite (26 mg) and type rockbridgeite (30 mg) using a Netzsch STA 449 F1 Jupiter Simultaneous TGA/DSC thermal analyser. The samples were contained in alumina crucibles and were

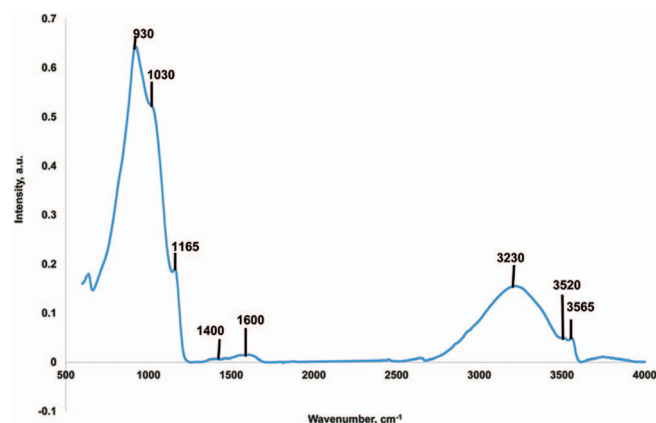


Fig. 4. Infrared spectrum for ferrirockbridgeite.

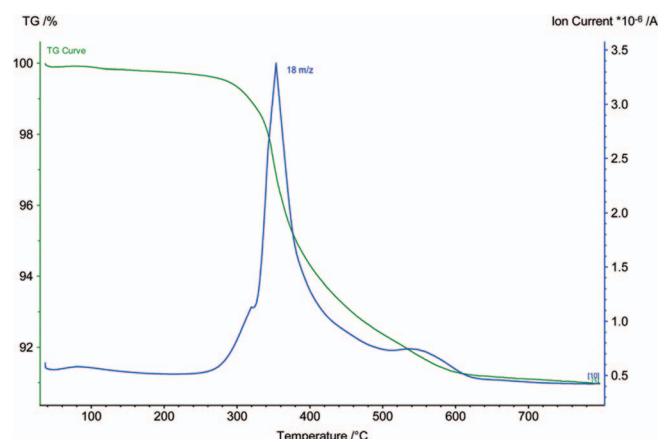


Fig. 5. Thermogravimetric curve and mass spectroscopy spectrum for evolved H₂O (18 *m/z*) for ferrirockbridgeite.

heated in nitrogen, with a ramp rate of 10 °C/min, between 30 and 800 °C. Evolved-gas analysis was made using a coupled ThermoStar Pfeiffer mass spectrometer (MS). The TGA and MS curves for ferrirockbridgeite (Fig. 5) show that H₂O evolution occurred up to 600 °C. The H₂O contents from the TGA are given in Table 2.

3.5. Electron microprobe analyses

Crystals of the rockbridgeite-group minerals were analysed using wavelength dispersive spectrometry on a JEOL JXA 8500F Hyperprobe electron microprobe (EMP) operated at an accelerating voltage of 15 kV and a beam current of 4 nA. The beam was defocused to 5 µm. The standards used were rhodonite (Mn), spinel (Mg), phosphophyllite (Zn), berlinite (Al, P), wollastonite (Ca) and hematite (Fe). Matrix correction was performed using the exponential Pouchou and Pichoir model XPP (Pouchou & Pichoir, 1991). Analytical results are given in Table 2. Included in Table 2 are the previously published results for a Hagendorf Süd frondelite, specimen IGC14 (Grey *et al.*, 2018). The FeO/Fe₂O₃ contents were determined by Mössbauer spectroscopy and the

water contents are from TGA or from the original analysis of type frondelite by Lindberg (1949) and of IGC89 by EK. The empirical formulae from the EMP analyses, normalized to 17 anions, are given in Table 2.

3.6. Powder X-ray diffraction (PXRD)

PXRD data on ground samples were collected at room temperature in the 2θ range 10 to 140° using a Philips diffractometer employing CoKα radiation. The unit-cell parameters were refined using the Rietveld program FULLPROF (Rodríguez-Carvajal, 1990), giving the unit-cell parameters reported in Table 3. The indexed powder pattern for ferrirockbridgeite (space group *Bbmm*) is given in Table S1 in Supplementary Material linked to this article and freely available at <https://pubs.geoscienceworld.com/eurjmin>.

For the type frondelite specimen, suitable crystals for a single-crystal structure refinement were not available, and so Rietveld refinement of the PXRD data was used to refine the structure and establish the site-occupancies of the metal atom sites *M2* and *M3*. This approach was first tested with several rockbridgeite-group minerals for which we had single-crystal refinement results. We confirmed that the site occupancies from the Rietveld refinements of PXRD data agreed with the results from the single-crystal refinements within the associated standard deviations. Rietveld refinement of type frondelite converged at $R_{wp} = 5.9$, $\chi^2 = 3.8$ and gave the following site occupancies: *M2* = 0.33Mn + 0.466(4)Fe + 0.204□ (□ = vacancy) and *M3* = 0.585(2)Fe + 0.415□.

3.7. Single-crystal studies

Single-crystal diffraction data for ferrirockbridgeite and type rockbridgeite were collected at ambient temperature on a Rigaku R-Axis Rapid II curved-imaging-plate microdiffractometer utilising monochromatised MoKα radiation. The Rigaku CrystalClear software package was used for processing of structure data, including the application of an empirical multi-scan absorption correction using ABSCOR (Higashi, 2001). For the Hagendorf Süd frondelite sample IGC89, single-crystal diffraction data were collected on the microfocus beam line MX2 at the Australian Synchrotron. The collection was made at 100 K using monochromatic radiation with a wavelength of 0.7107 Å. A phi scan was employed over 360° with an exposure time of 36 s. The data were corrected for absorption using SADABS. Further details of the data collections are given in Table 4.

The structure analysis procedure was the same for the three minerals and it closely followed recent published single-crystal refinements of rockbridgeite-group minerals (Grey *et al.*, 2018, 2019; Röska *et al.*, 2018). It is described briefly for ferrirockbridgeite. A structure model was obtained in space group *Cmcm* using SHELXT (Sheldrick, 2015). The cell and coordinates were transformed to space group *Bbmm*, to be consistent with Moore's (1970) rockbridgeite structure. The amount of Mn from the EMP analyses was located with Fe at the *M2* site, while Fe only was located at the *M1* and *M3* sites (except for type rockbridgeite, where a small

Table 2. Analytical data (wt%), standard deviation (SD) in parentheses.

	Ferrorockbridgeite	Type rockbridgeite	Type frondelite	Frondelite	Frondelite
	Palermo	Rockbridge County	Sapucaia	Hagendorf Süd IGC89	IGC14 ^a
No. analyses	8	15	9	47	8
MnO	3.53 (0.26)	0.32 (6)	7.21 (1.22)	6.42 (0.95)	6.9 (0.5)
MgO	0.07 (0.04)	0.03 (7)	0.25 (0.07)	0.02 (0.03)	0.01 (0.02)
ZnO	0.33 (0.13)	0.0	0.91 (0.41)	0.29 (0.15)	2.4 (0.2)
CaO	0.47 (0.11)	0.16 (6)	0.05 (0.07)	0.28 (0.10)	0.24 (0.04)
Al ₂ O ₃	—	0.20 (8)	0.29 (0.38)	0.01 (0.04)	0.03 (0.04)
Fe _{tot} as Fe ₂ O ₃	53.9 (0.9)	57.6 (1.7)	48.7 (3.6)	51.6 (1.7)	48.5 (1.0)
FeO*	0.96	4.66	0.88	0.46	0.9
Fe ₂ O ₃ *	52.8	52.4	47.7	51.1	47.4
P ₂ O ₅	32.2 (0.9)	31.1 (0.5)	32.6 (0.5)	31.8 (0.9)	31.2 (0.3)
H ₂ O	8.7 ^b	9.0 ^b	7.5 ^c	8.9 ^d	8.0 ^b
Total	99.1	97.8	97.3	99.3	97.1
Sample	Empirical formulae				ΣM/P
Ferrorockbridgeite	Mn _{0.31} ²⁺ Fe _{0.08} ²⁺ Mg _{0.01} Zn _{0.03} Ca _{0.05} Fe _{4.18} ³⁺ P _{2.87} O ₁₇ H _{6.11}				1.62
Type rockbridgeite	Mn _{0.03} ²⁺ Fe _{0.42} ²⁺ Ca _{0.02} Al _{0.02} Fe _{4.22} ³⁺ P _{2.82} O ₁₇ H _{6.27}				1.67
Type frondelite	Mn _{0.66} ²⁺ Fe _{0.08} ²⁺ Mg _{0.04} Zn _{0.07} Ca _{0.01} Al _{0.04} Fe _{3.91} ³⁺ P _{3.00} O ₁₇ H _{5.44}				1.60
Frondelite, IGC89	Mn _{0.58} ²⁺ Fe _{0.04} ²⁺ Zn _{0.02} Fe _{4.07} ³⁺ P _{2.85} O ₁₇ H _{6.28}				1.65
Frondelite, IGC14	Mn _{0.67} ²⁺ Fe _{0.08} ²⁺ Zn _{0.20} Ca _{0.03} Fe _{4.07} ³⁺ P _{3.00} O ₁₇ H _{6.05}				1.68

*FeO/Fe₂O₃ from Mössbauer spectroscopy.^aFrom Grey *et al.* (2018).^bFrom TGA.^cFrom Lindberg (1949).^dFrom EK analysis.

Table 3. Unit-cell parameters (Å) from Rietveld refinement of powder diffraction data.

	<i>a</i>	<i>b</i>	<i>c</i>	Reference
Ferrorockbridgeite	13.7996(7)	16.9187(7)	5.1887(2)	This work
Type rockbridgeite	13.8599(7)	16.8196(7)	5.1813(2)	This work
Type frondelite	13.8069(6)	16.9640(6)	5.1827(2)	This work
Hagendorf Süd frondelite IGC89	13.8208(6)	16.9381(9)	5.1817(3)	This work
Hagendorf Süd frondelite IGC14	13.8041(7)	16.9827(7)	5.1823(2)	Grey <i>et al.</i> (2018)

amount of Al from the EMP analysis was included at the *M3* site). The trace to minor amounts of Zn and Mg from the EMP analyses were included in the Mn content of the *M2* site, which was fixed during the refinement, whereas the Fe contents in *M2* and *M3* were allowed to vary. Unambiguous location of H atoms in difference-Fourier maps was not possible. The positions of H-atoms in rockbridgeite-group minerals have been established in two recent powder neutron-diffraction studies (Röska *et al.*, 2018; Grey *et al.*, 2019). Refinement with anisotropic displacement parameters in JANA2006 (Petříček *et al.*, 2014) converged at $R_{\text{obs}} = 0.048$ for 592 unique reflections to a resolution of 0.84 Å. Further details of the refinement for ferro-rockbridgeite, as well as for type rockbridgeite and frondelite sample IGC89, are reported in Table 4. The refined coordinates, equivalent isotropic displacement parameters and calculated bond-valence sums (BVS; Gagné & Hawthorne, 2015) from the three single-crystal refinements are given in Table 5. Polyhedral bond distances are given in Table 6. The refined site occupancies, together with the EMP analyses

for Mn, Zn and Mg, and the Mössbauer results for Fe²⁺ were combined to calculate structural formulae, with adjustment of OH/H₂O for charge balance. The formulae are given in Table 7.

4. Discussion

4.1. Description of structure

The structure of rockbridgeite-group minerals is built of two types of (100) layers, illustrated in Fig. 6. The layer shown in Fig. 6a contains double columns along [001] of face- and corner-connected *M3*-centred octahedra that are interconnected along [010] via corner-connection with PO₄ tetrahedra. All published crystal-structures of rockbridgeite-group minerals have been reported in space group *Bbmm* (or first-setting *Cmcm*) and the *M3* atoms occupy the 16(h) general position. These are labelled in the upper half of Fig. 6a. Full occupation of the 16(h) sites results in unreasonably short (2.4 Å) *M3*–*M3* separations along [001]

Table 4. Single-crystal X-ray data collection and refinement details.

	Ferrorockbridgeite	Type rockbridgeite	Frondelite IGC89
Structural formula (Mn includes minor Zn, Mg)	$(\text{Mn}_{0.35}^{2+}\text{Fe}_{0.08}^{2+}\text{Fe}_{1.04}^{3+}\square_{0.53})_{\Sigma 2}$ $\text{Fe}_{3.19}^{3+}(\text{PO}_4)_3(\text{OH})_{4.55}(\text{H}_2\text{O})_{0.45}$	$(\text{Mn}_{0.03}^{2+}\text{Fe}_{0.44}^{2+}\text{Fe}_{1.01}^{3+}\square_{0.52})_{\Sigma 2}$ $\text{Al}_{0.03}\text{Fe}_{3.05}^{3+}(\text{PO}_4)_3(\text{OH})_{4.21}(\text{H}_2\text{O})_{0.79}$	$(\text{Mn}_{0.60}^{2+}\text{Fe}_{0.04}^{2+}\text{Fe}_{0.90}^{3+}\square_{0.46})_{\Sigma 2}$ $\text{Fe}_{3.18}^{3+}(\text{PO}_4)_3(\text{OH})_{4.52}(\text{H}_2\text{O})_{0.48}$
Data collection	Rigaku R-Axis Rapid II diff.	Rigaku R-Axis Rapid II diff.	Synchrotron microfocus MX2
Wavelength, Å	0.7107 (Mo)	0.7107 (Mo)	0.7107 (synchrotron)
Space group	<i>Bbmm</i>	<i>Bbmm</i>	<i>Bbmm</i>
Cell parameters, Å	$a = 13.853(1)$ $b = 16.928(1)$ $c = 5.1917(5)$	$a = 13.877(1)$ $b = 16.847(2)$ $c = 5.1900(6)$	$a = 13.873(1)$ $b = 16.957(1)$ $c = 5.193(1)$
Volume, Å ³	1217.5(2)	1213.3(2)	1221.6(3)
Z	4	4	4
Absorption coefficient, mm ⁻¹	5.85	5.80	5.89
Crystal size, mm	0.03 × 0.15 × 0.20	0.02 × 0.07 × 0.15	0.05 × 0.10 × 0.30
Theta range, °	2.4–25.0	3.2–25.0	2.4–32.2
Reflections collected	2485	2459	9335
Independent reflections	592 [$R_{\text{int}} = 0.054$]	610 [$R_{\text{int}} = 0.069$]	970 [$R_{\text{int}} = 0.085$]
Reflections $I > 3\sigma(I)$	570	463	780
Data completeness	97%	100%	98%
Refinement method	Full-matrix, least squares on F	Full-matrix, least squares on F	Full-matrix, least squares on F
Restraints/constraints/params.	0/6/84	0/15/83	0/6/83
R indices, $I > 3\sigma(I)$	$R_{\text{obs}} = 0.046$, $wR_{\text{obs}} = 0.068$	$R_{\text{obs}} = 0.045$, $wR_{\text{obs}} = 0.047$	$R_{\text{obs}} = 0.043$, $wR_{\text{obs}} = 0.053$
R indices, all data	$R_{\text{obs}} = 0.048$, $wR_{\text{obs}} = 0.069$	$R_{\text{obs}} = 0.064$, $wR_{\text{obs}} = 0.051$	$R_{\text{obs}} = 0.070$, $wR_{\text{obs}} = 0.055$
Largest ΔF peaks	+0.68, −0.65 e Å ⁻³	+0.80, −0.82 e Å ⁻³	+0.99, −0.93 e Å ⁻³

and in practice these sites are statistically half-occupied to avoid this situation. Recent studies (Grey *et al.*, 2018; Röska *et al.*, 2018) have reported weak diffuse reflections that violate the extinction conditions of *Bbmm* and these have been interpreted as being due to local ordering of Fe atoms and vacancies in the *M3* sites. An example of this local ordering, described in space group *Pnma* (Grey *et al.*, 2018), is shown in the lower half of Fig. 6a. The local-ordering is important in order to be able to describe H-bonding, because neutron-diffraction studies (Röska *et al.*, 2018; Grey *et al.*, 2019) show that the H atoms are located in the spaces corresponding to vacant *M3* sites, as shown in Fig. 6a. The local order is confined to very small regions of a few nm in size and the reflections corresponding to the local order are extremely diffuse and difficult to integrate; consequently, refinements of rockbridgeite-group minerals have been limited to the average structure in *Bbmm*.

The second type of layer (Fig. 6b) contains the *M1*- and *M2*-centred octahedra, which form face-sharing trimers, called *h*-clusters by Moore (1970). The trimers connect into chains along [010] by edge-sharing between the *M2*-centred octahedra. The chains are interconnected along [001] by corner-sharing with PO₄ tetrahedra. In ferrockbridgeite, Fe₂²⁺Fe₃(PO₄)₃(OH)₄(H₂O) (Grey *et al.*, 2019), the *M2* sites are fully occupied by Fe²⁺ and the stoichiometric (100) layer is as shown in the upper half of Fig. 6b. A feature of the oxidized rockbridgeite-group minerals reported here is that the *M2* sites contain high vacancy concentrations, in the range ~17 to 27%, as shown in Table 7. The lower half of Fig. 6b shows this situation, with 25% of the *M2* sites vacant. This breaks up the *h*-clusters so that on average only half of the clusters remain intact. The

influence of the oxidation on the metal atom environments is seen by a comparison of the polyhedral bond lengths of three oxidised rockbridgeite-group minerals with those in ferrockbridgeite in Table 6. The largest effect is seen for the distances involving O5, which forms a corner-connection between *M2*- and *M3*-centred octahedra in adjacent layers. There is a large decrease in *M2*–O5 upon oxidation, from 2.11 Å to ~2.02 Å, whereas the *M3*–O5 distance increases upon oxidation from 1.98 Å to ~2.01 Å. Previous neutron-diffraction studies on ferrockbridgeite (Röska *et al.*, 2018; Grey *et al.*, 2019) have shown that H₂O is localised at the O5 site (shown in Fig. 6a). Creation of a vacancy at an *M2* site is accompanied by oxidation of Fe²⁺ to Fe³⁺ in two occupied *M2* sites. Thus, although H₂O will be retained at O5 when it is associated with a vacant *M2* site, it would be expected that H₂O would be replaced by OH[−] at the two O5 sites coordinated to *M2* containing Fe³⁺. Such an anion configuration is consistent with the observed changes in *M2*–O5 and *M3*–O5 distances upon oxidation.

4.2. Mechanism of oxidation

Table 7 reports the structural formulae for the four oxidized rockbridgeite-group minerals studied here, as well as for a non-stoichiometric frondelite specimen, IGC14, from Hagendorf Süd (Grey *et al.*, 2018). The results for the five minerals show a consistent relationship, with the amount of Fe³⁺ in the site being close to twice the vacancy content. The results suggest that the oxidized minerals have formed from more reduced precursors by a reaction of the type:

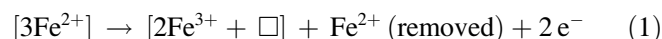
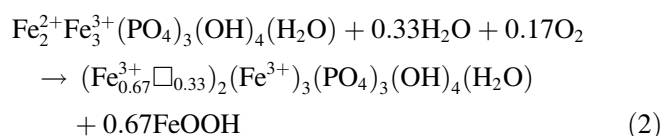


Table 5. Atom coordinates, equivalent isotropic displacement parameters ($\text{\AA}^2$) and bond-valence sums (BVS).

	Occupancy	x	y	z	U_{eq}	BVS
<i>Ferrorockbridgeite</i>						
M1	1	0	0	0	0.0236(5)	3.00
M2	0.558(6)Fe + 0.175Mn	0.06937(10)	0.15715(7)	0	0.0232(6)	2.36
M3	0.548(4)Fe	0.32151(9)	0.13870(7)	0.2368(3)	0.0241(6)	2.94
P1	1	0.14198(11)	0.04348(8)	0.5	0.0155(6)	5.06
P2	1	0.48325(19)	0.25	0	0.0216(8)	5.09
O1	1	0.0455(4)	0.25	0.2561(12)	0.043(2)	1.87
O2	1	0.0804(3)	0.0582(2)	0.2577(6)	0.0249(12)	2.01
O3	0.5	0.3143(6)	0.25	0.3906(19)	0.024(3)	0.91
O4	1	0.3207(4)	0.0399(3)	0	0.037(2)	1.80
O5	1	0.2140(4)	0.1722(3)	0	0.0314(16)	0.91
O6	1	0.4236(3)	0.1032(3)	0.5	0.0243(15)	1.16
O7	1	0.4201(3)	0.1758(3)	0	0.0290(17)	1.94
O8	1	0.2226(3)	0.1056(2)	0.5	0.0223(14)	1.81
<i>Type rockbridgeite</i>						
M1	1	0	0	0	0.0251(7)	2.95
M2	0.723(6)Fe + 0.015Mn	0.06806(12)	0.15698(10)	0	0.0242(7)	2.36
M3	0.513(4)Fe + 0.0075Al	0.32068(11)	0.13888(9)	0.2350(3)	0.0214(6)	2.93
P1	1	0.14203(16)	0.04410(13)	0.5	0.0181(7)	5.12
P2	1	0.4816(2)	0.25	0	0.0248(12)	4.98
O1	1	0.0449(4)	0.25	0.2526(14)	0.043(3)	1.83
O2	1	0.0804(3)	0.0589(2)	0.2588(8)	0.0237(14)	2.02
O3	0.5	0.3130(8)	0.25	0.386(2)	0.030(4)	0.99
O4	1	0.3200(5)	0.0396(3)	0	0.040(3)	1.79
O5	1	0.2119(4)	0.1716(3)	0	0.028(2)	0.89
O6	1	0.4233(4)	0.1041(3)	0.5	0.0208(19)	1.13
O7	1	0.4190(5)	0.1761(3)	0	0.030(2)	1.95
O8	1	0.2224(4)	0.1058(3)	0.5	0.024(2)	1.80
<i>Frondelite IGC89</i>						
M1	1	0	0	0	0.0295(3)	2.95
M2	0.447(5)Fe + 0.30Mn	0.07027(6)	0.15708(5)	0	0.0308(3)	2.36
M3	0.546(3)Fe	0.32178(6)	0.13890(5)	0.23721(17)	0.0302(3)	2.92
P1	1	0.14270(7)	0.04355(5)	0.5	0.0232(3)	5.05
P2	1	0.48354(11)	0.25	0	0.0277(4)	4.94
O1	1	0.0468(3)	0.25	0.2531(8)	0.0478(12)	1.84
O2	1	0.08049(15)	0.05834(13)	0.2586(4)	0.0295(6)	2.00
O3	0.5	0.3142(5)	0.25	0.3922(14)	0.0352(17)	0.99
O4	1	0.3199(3)	0.03994(18)	0	0.0412(11)	1.79
O5	1	0.2150(2)	0.17319(17)	0	0.0370(10)	0.92
O6	1	0.4244(2)	0.10404(19)	0.5	0.0310(9)	1.16
O7	1	0.4211(2)	0.17582(18)	0	0.0324(9)	1.93
O8	1	0.2229(2)	0.10577(17)	0.5	0.0291(8)	1.80

This mechanism involves diffusion of Fe^{2+} through the crystal structure to a surface, where it is released. The loss of Fe^{2+} is charge-compensated by the oxidation of 2Fe^{2+} to 2Fe^{3+} in the structure, and the anion framework remains unchanged. This type of mechanism was proposed in the 1970s for the alteration of ilmenite to pseudorutile (Grey & Reid, 1975), where it was considered as an electrochemical corrosion reaction, analogous to the reactions involved in oxidation of sulphide ore bodies (Sato, 1960). More recently, Kondoh *et al.* (1985) invoked a similar mechanism for the low-temperature oxidation of fayalite, $\text{Fe}_2^{2+}\text{SiO}_4$, to laihunite, $\text{Fe}_{2-3x}\text{Fe}_{2x}^{3+}\square_x\text{SiO}_4$. Their experiments were conducted on synthetic samples, but subsequent studies have characterised the same reaction in natural fayalite (Martin *et al.*, 2015). Hamelet *et al.* (2011) have demonstrated that the oxidation of synthetic $\text{LiFe}^{2+}\text{PO}_4$ with the triphylite structure undergoes low-temperature oxidation to $\text{LiFe}_{0.67}^{3+}\square_{0.33}\text{PO}_4$, analogous to the fayalite-to-laihunite oxidation.

On the basis of the proposed oxidation mechanism, the oxidation of ferrockbridgeite to ferrorockbridgeite can be described by the reaction:



where the surface-removed iron is considered to be oxidized to goethite, as shown by the goethitic limonite attached to type rockbridgeite in Fig. 2. The formula of the oxidation product, $(\text{Fe}_{0.67}^{3+}\square_{0.33})_2(\text{Fe}^{3+})_3(\text{PO}_4)_3(\text{OH})_4(\text{H}_2\text{O})$, represents the ideal end-member formula for ferrorockbridgeite.

The $\text{Fe}^{3+}/\square$ ratios in the M2 site are generally very close to 2 (1.94 to 2), although the ratio for type frondelite is lower, 1.80. This may be because the site occupancies for this specimen were determined from refinement of PXRD

Table 6. Polyhedral bond distances (Å) for oxidized rockbridgeite-group minerals and for ferrockbridgeite.

	Ferrorockbridgeite	Type rockbridgeite	Frondelite IGC89	Ferrorockbridgeite IGC29 ^a
M1–O2 x4	2.001(3)	2.008(3)	2.007(2)	2.012(4)
M1–O6 x2	2.043(5)	2.052(6)	2.053(3)	2.049(7)
Av.	2.015	2.023	2.022	2.024
M2–O1 x2	2.085(4)	2.068(5)	2.078(3)	2.085(5)
M2–O2 x2	2.149(4)	2.137(4)	2.151(2)	2.114(7)
M2–O5	2.023(5)	2.011(6)	2.027(3)	2.150(5)
M2–O6	2.217(5)	2.197(6)	2.215(3)	2.218(6)
Av.	2.118	2.103	2.117	2.128
M3–O3	2.048(4)	2.032(5)	2.051(3)	2.028(5)
M3–O5	2.009(4)	2.018(5)	2.012(3)	1.984(6)
M3–O4	2.074(4)	2.070(5)	2.082(3)	2.061(6)
M3–O6	2.056(3)	2.064(5)	2.058(2)	2.079(5)
M3–O7	1.945(4)	1.935(5)	1.952(3)	1.942(6)
M3–O8	2.015(3)	2.015(4)	2.015(2)	2.038(5)
Av.	2.024	2.022	2.028	2.022
P1–O4	1.503(5)	1.506(6)	1.508(3)	1.496(7)
P1–O8	1.534(5)	1.525(6)	1.533(3)	1.542(7)
P1–O2 x2	1.540(4)	1.537(6)	1.543(2)	1.535(5)
Av.	1.529	1.526	1.532	1.527
P2–O1 x2	1.531(6)	1.555(7)	1.554(4)	1.550(7)
P2–O7 x2	1.527(5)	1.518(6)	1.527(3)	1.520(7)
Av.	1.529	1.536	1.540	1.535

^aGrey *et al.* (2019).

Table 7. Structural formulae for oxidized rockbridgeite-group minerals.

	M2	M1	M3	ΣM/P	Calc. %H ₂ O
Ferrorockbridgeite	(Mn _{0.31} Zn _{0.03} Mg _{0.01} Fe _{0.08} ²⁺ Fe _{1.04} ³⁺ □ _{0.53})Σ2	Fe ³⁺	(Fe _{2.19} ³⁺ □ _{1.81})Σ4(PO ₄) ₃ (OH) _{4.55} (H ₂ O) _{0.45}	1.55	7.6
Type rockbridgeite	(Mn _{0.03} ²⁺ Fe _{0.44} ²⁺ Fe _{1.01} ³⁺ □ _{0.52})Σ2	Fe ³⁺	(Fe _{2.05} ³⁺ Al _{0.03} □ _{1.92})Σ4(PO ₄) ₃ (OH) _{4.21} (H ₂ O) _{0.79}	1.52	8.3
Frondelite, IGC89	(Mn _{0.58} ²⁺ Zn _{0.02} Fe _{0.04} ²⁺ Fe _{0.90} ³⁺ □ _{0.46})Σ2	Fe ³⁺	(Fe _{2.18} ³⁺ □ _{1.82})Σ4(PO ₄) ₃ (OH) _{4.52} (H ₂ O) _{0.48}	1.57	7.8
Type frondelite	(Mn _{0.66} ²⁺ Zn _{0.07} Mg _{0.04} Fe _{0.08} ²⁺ Fe _{0.74} ³⁺ □ _{0.41})Σ2	Fe ³⁺	(Fe _{2.34} ³⁺ □ _{1.66})Σ4(PO ₄) ₃ (OH) _{4.94} (H ₂ O) _{0.06}	1.64	7.1
Frondelite IGC14 Grey <i>et al.</i> (2018)	(Mn _{0.67} ²⁺ Zn _{0.20} Fe _{0.08} ²⁺ Fe _{0.70} ³⁺ □ _{0.35})Σ2	Fe ³⁺	(Fe _{2.31} ³⁺ □ _{1.69})Σ4(PO ₄) ₃ (OH) _{4.93} (H ₂ O) _{0.07}	1.65	7.0

data and will be less well determined than those for the other four samples, obtained from single-crystal refinement. The higher vacancy concentration for this sample may also be due to a minor contribution from proton exchange for cations, $[M^{n+} + nO^{2-}] + nH^+ \rightarrow [nOH^-] + M^{n+}$, as reported to occur in hydrogarnets (Lager *et al.*, 1987), hydrohematite (Wolska, 1981), MnO₂ (Reutschi & Giovanoli, 1988) and pseudorutile (Grey & Li, 2003).

The formula given above for ferrockbridgeite is ideal because reaction (2) does not take into account any variation in the occupancy of the M3 site during oxidation. As shown in Table 7, the composition of the M3 site varies from 2.05 to 2.34 Fe³⁺ *pfu*, compared to a value of 2.00 obtained in refinement of ferrockbridgeite (Röska *et al.*, 2018; Grey *et al.*, 2019). The increase in M3 site occupancy is most likely due to the trapping of diffusing Fe²⁺ cations at vacant M3 sites. From Table 7 it is seen that for type frondelite and the frondelite specimen IGC14 (Grey *et al.*, 2018), the increase in M3 site occupancy accounts for over 80% of the decrease in M2 site occupancy, and the overall stoichiometry, given by ΣM/P in Table 7, is only slightly below the stoichiometric

value of 1.667. In contrast, for type rockbridgeite, the Fe³⁺ content per formula unit in the M3 site, 2.05(2) Fe³⁺, is not significantly different from 2.00 and, therefore, the Fe lost from the M2 site has been removed from the crystal structure, and most likely precipitated as goethite (Fig. 2). Ferrockbridgeite and frondelite specimen IGC89 represent intermediate cases where about one third of the Fe removed from the M2 site appears to have transferred to the M3 site. It is interesting to note that, although the ΣM/P ratio for the latter three samples is in the range 1.52–1.57 from the structure analysis, the corresponding ratios from the EMP analyses are considerably higher, 1.60–1.67 (Table 2). This suggests that the Fe removed from the crystal has precipitated on internal surfaces, most likely micropores, on a very fine scale and is therefore included in the EMP analyses.

4.3. General formula for oxidized rockbridgeite-group minerals

A general formula for rockbridgeite-group minerals needs to take account of reaction (1) for oxidized species, as well as a

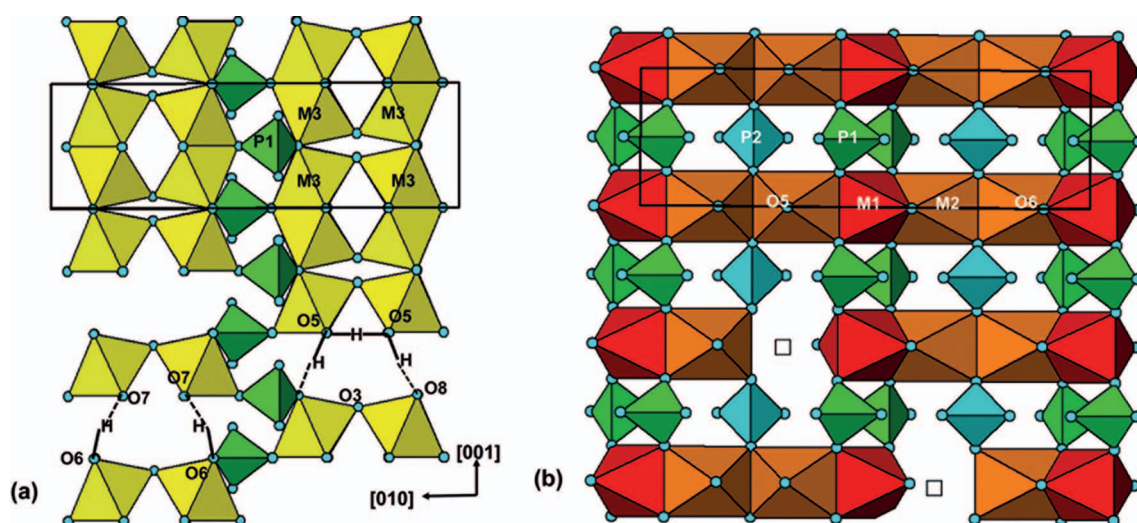
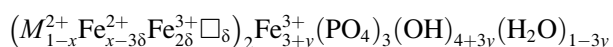


Fig. 6. (a) (100) layer containing double columns of $M3$ -centred octahedra, interconnected *via* corner-shared PO_4 . The upper half of the diagram shows the average structure in space-group $Bbmm$, with 50% occupancy of the $M3$ sites. The lower half shows a local ordering of alternately filled and empty $M3$ sites along $[001]$. The H-bonding spans the vacant $M3$ -centred octahedra. (b) (100) layer containing $[010]$ chains of face- and edge-shared $M1$ and $M2$ octahedra, interconnected along $[001]$ by corner-sharing with PO_4 tetrahedra. In the lower half of the diagram, two vacant $M2$ sites are shown by $\square$.

variable occupation of the $M3$ site. Grouping the divalent cations Mn, Zn and Mg as M^{2+} , the stoichiometric $A_2B_3(PO_4)_3(OH)_4(H_2O)$ formula can be generalised as:



where 3δ corresponds to the amount of oxidation of Fe^{2+} in the $M2$ site and y represents the increase in the Fe^{3+} content of the $M3$ site above $2Fe^{3+}$ *pfu*. This formula reproduces the structural formulae given in Table 7. From this study and Grey *et al.* (2018, 2019) the observed ranges of x , y and δ are $0 < x < 0.98$, $0 < y < 0.34$ and $0 < \delta < 0.265$. The relative amounts of OH^- and H_2O are affected only by the value of y . As seen from Table 7, the calculated total H_2O is lowest for the two samples that have the highest value of y , and the calculated trends agree with the measured H_2O contents in Table 2.

Röska *et al.* (2018) have also proposed a general formula for rockbridgeite-type minerals, based on their neutron-diffraction study on a single ferrorockbridgeite specimen from Hagendorf Süd. Their formula is $Fe^{2+}Fe_{4-x}^{3+}(Mn^{2+}, Zn)_x(PO_4)_3(OH)_{5-x}(H_2O)_x$. For their case of $x = 1$, Röska *et al.*'s formula reduces to $(Fe^{2+}, Mn^{2+}, Zn)_2Fe_3^{3+}(PO_4)_3(OH)_4(H_2O)$, which is identical to our formula for stoichiometric ferrorockbridgeite with δ and $y = 0$. For oxidized specimens, however, with their $x < 1$, Röska *et al.*'s formula deviates from our general formula because they did not take account of vacancy formation accompanying oxidation as per reaction (1).

4.4. Identification of rockbridgeite-group species

The non-stoichiometry associated with oxidation processes described above presents potential difficulties for the identification of rockbridgeite-group species in museum

collections, etc., where it is not always possible to conduct single-crystal diffraction studies to determine the contents of the $M2$ and $M3$ sites. In practice, however, the problem is tractable because the Fe removed from the $M2$ site during oxidation is found to be either trapped within the crystal structure at the $M3$ site, or else is distributed very finely in internal surfaces in the mineral, so that the chemical analyses give close to stoichiometric compositions, as shown by the $\Sigma M/P$ ratios in Table 2. To a good approximation, the identity of the species can then be established simply from a chemical analysis, including, importantly, the FeO content. Assigning all divalent cations, including Fe^{2+} , to the $M2$ site and completing the occupation of $M2$ with Fe^{3+} (no vacancies) allows the $M2$ composition to be plotted on a phase diagram, as shown in Fig. 7. This diagram applies to species

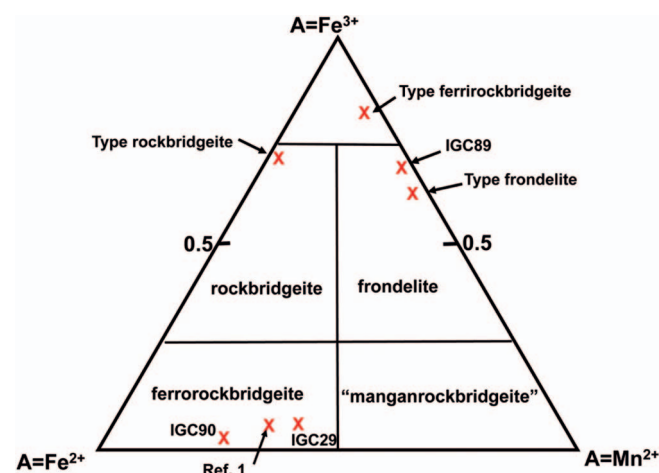


Fig. 7. Rockbridgeite-group mineral phase fields, based on the occupation of the $M2$ site by Mn^{2+} , Fe^{2+} and Fe^{3+} . Ref. 1 = Redhammer *et al.* (2006).

where Zn is not dominant in the *M2* site. Zn and Mg have to be removed from the *M2* site composition to give the Mn-Fe²⁺-Fe³⁺ points plotted in Fig. 7. Included in Fig. 7 is the *M2* composition reported by Redhammer *et al.* (2006) for a manganoan rockbridgeite from Hagendorf, which is seen to be a ferrockbridgeite. An almost identical *M2* composition is calculated from the results reported by Röska *et al.* (2018) for a specimen from Hagendorf Süd.

The type rockbridgeite plots at the upper limit of the rockbridgeite phase-field. The point for type rockbridgeite is based on the original analyses reported by Frondel (1949). Using our EMP analyses for type rockbridgeite (Table 2), the results plot in the ferrockbridgeite phase-field. The original analyses reported by Frondel were made in 1880 and so it is possible that further oxidation of the type specimen has occurred over the last 138 years. Consideration should be given to establishing a new type rockbridgeite that is closer to the ideal composition.

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