

Structure and crystal chemistry of vivianite-type compounds: Crystal structures of erythrite and annabergite with a Mössbauer study of erythrite

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Abstract: The crystal structures of erythrite from Schneeberg, Saxony, and annabergite from Lavrion, Attika, were refined using single crystal X-ray diffraction data [space group $C2/m$, $Z = 2$; $a = 10.251(3) \text{ \AA}$, $b = 13.447(4) \text{ \AA}$, $c = 4.764(1) \text{ \AA}$, $\beta = 104.98(1)^\circ$, $V = 634.4 \text{ \AA}^3$ (erythrite) and $a = 10.179(2) \text{ \AA}$, $b = 13.309(3) \text{ \AA}$, $c = 4.725(1) \text{ \AA}$, $\beta = 105.00(1)^\circ$, $V = 618.2 \text{ \AA}^3$ (annabergite)]; X-ray data measured up to $2\theta = 65, 70^\circ$; 1199, 1434 unique reflections; $R = 0.027, 0.015$]. Both minerals crystallize in the vivianite structure type, formed by $\text{Me(1)O}_2(\text{H}_2\text{O})_4$ octahedra and $\text{Me(2)}_2\text{O}_6(\text{H}_2\text{O})_4$ double octahedral groups, which are linked via XO_4 tetrahedra to complex sheets in (010), further interconnected by hydrogen bonds only. Chemical compositions of the investigated samples, obtained from EDX- and microprobe analyses, are $\text{Co}_{2.01}\text{Fe}_{0.74}\text{Ni}_{0.25}(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$ for erythrite and $\text{Ni}_{2.48}\text{Mg}_{0.50}\text{Fe}_{0.02}(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$ for annabergite. The Me^{2+} cation distribution on the Me(1) and Me(2) sites in erythrite and annabergite is discussed based on Mössbauer spectroscopy and site occupancy refinements, respectively. The refinement of the Ni/Mg-ratio in annabergite leads to the formula $\text{Ni}_{2.64}\text{Mg}_{0.36}(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$ and yields a strong preference of Mg^{2+} for the Ni(2) site. Mössbauer spectroscopy of erythrite reveals an analogous preference of Fe^{2+} on the Co(2) site. These findings are further confirmed by crystal chemical considerations.

Key-words: erythrite, annabergite, vivianite group minerals, crystal structure, crystal chemistry, Mössbauer spectroscopy.

Introduction

Most minerals and synthetic compounds with the general formula $\text{Me}_3(\text{XO}_4)_2 \cdot 8\text{H}_2\text{O}$ (Me = Mg, Fe, Co, Ni, Zn; X = P, As) crystallize in the monoclinic ($C2/m$) structure type of vivianite, $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$, first determined by Mori & Ito (1950) and subsequently refined by Fejdi *et al.* (1980), Dörmann *et al.* (1982) (oxidized vivianite) and Bartl (1989). Structure investigations on the following vivianite-type compounds have been done so far: parasymplectite, $\text{Fe}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$, (Mori & Ito, 1950, but denoted as symplectite); köttigite, ideally $\text{Zn}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$, (Hill, 1979); 'cabrerite', $(\text{Ni,Mg})_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$, a Mg-rich variety of an-

nabergite, (Giuseppetti & Tadini, 1982); synthetic $\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ -II (Takagi *et al.*, 1986); synthetic $\text{Co}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ (Riou *et al.*, 1989). In order to provide further structural information on vivianite-type minerals, this study reports the crystal structure of erythrite, not investigated so far, and of annabergite with significantly lower Mg content compared with 'cabrerite'. Special attention is drawn to the Co/Fe and Ni/Mg cation distributions on two Me(II) sites by means of Mössbauer spectroscopy and single crystal X-ray refinement, respectively. For short preliminary notes on these subjects as well as on Rietveld refinements of several synthetic arsenate end-members cf. Wildner *et al.* (1994a, b).

Experimental procedures

Crystals of erythrite (Schneeberg, Sachsen, FRG) and annabergite (Lavrion, Attika, Greece) from the collection of the Institut für Mineralogie und Kristallographie der Universität Wien were used for the investigations. The chemical composition was obtained by EDX- and microprobe analyses (EDX: Jeol JSM-6400, program system LINK eXL10, operating voltage 20 kV, automatical correction for attenuation and enhancement effects, internal standards used. Microprobe: ARL-SEMQ, 15 kV acceleration voltage, 15 nA sample current). The empirical formulas obtained are $\text{Co}_{2.01}\text{Fe}_{0.74}\text{Ni}_{0.25}(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$ and $\text{Ni}_{2.48}\text{Mg}_{0.50}\text{Fe}_{0.02}(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$ for erythrite and annabergite, respectively.

Single crystal X-ray diffraction intensities were measured on a Stoe AED2 four-circle diffractometer with graphite monochromatized $\text{MoK}\alpha$ -radiation (2θ - ω scans; 42/38 steps per reflection, increased for α_1 - α_2 splitting, $2 \times 6/5$ steps for background correction; 0.03° and 0.5 – 2.0 sec per step; three standard reflections each 120 min; lattice parameters refined from 30 accurate reflections in the range $28^\circ < 2\theta < 34^\circ$). Corrections for Lorentz- and polarization effects as well as an empirical absorption correction by ψ -scans were applied to the data. The structure refinements on F^2 were done with the program SHELXL-93 (Sheldrick, 1993), starting with the atomic coordinates of vivianite (Mori & Ito, 1950). Hydrogen atoms were located by difference Fourier syntheses; their refined positions correspond to the hydrogen system found for köttigite (Hill, 1979), 'cabrerite' (Giuseppetti & Tadini, 1982), and vivianite (Bartl, 1989). In the refinement procedure of erythrite, Co scattering curves only were employed for the Me^{2+} sites due to similar scattering curves of Co, Fe and Ni; on the other hand, in annabergite the Ni/Mg-ratio could be refined separately for the two positions, resulting in the structural formula $[\text{Ni}(1)_{0.99}\text{Mg}(1)_{0.01}][\text{Ni}(2)_{1.65}\text{Mg}(2)_{0.35}](\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$. Residual electron densities in the final difference Fourier maps were less than $0.9/0.5 \text{ e}\text{\AA}^{-3}$. Further details of the structure refinements and important crystal data are summarized in Table 1.

For the Mössbauer investigation of erythrite, crystals from the same vug as used for the X-ray study were gently ground with acetone. No colour change was noted during the grinding. 22 mg of the powder was mixed with benzophenone and

Table 1. Crystal data and details of the intensity measurements and structure refinements of erythrite and annabergite.

erythrite	annabergite	
space group	$C2/m$	$C2/m$
a [$\text{\AA}$]	10.251(3)	10.179(2)
b [$\text{\AA}$]	13.447(4)	13.309(3)
c [$\text{\AA}$]	4.764(1)	4.725(1)
β [$^\circ$]	104.98(1)	105.00(1)
V [$\text{\AA}^3$]	634.4	618.2
Z	2	2
ρ_{calc} [gcm^{-3}]	3.135	3.146
$\mu(\text{MoK}\alpha)$ [cm^{-1}]	91.4	94.1
$2\theta_{\text{max}}$ [$^\circ$]	65	70
measured reflections	2637	3035
unique data set	1199	1434
data with $F_o > 4\sigma(F_o)$	914	1264
variables	72	76
absorption correction	ψ -scans	ψ -scans
min/max transmission	0.19/0.26	0.06/0.16
extinction coefficient	0.0018(4)	0.0057(3)
$R1$ [for $F_o > 4\sigma(F_o)$]	0.027	0.015
$wR2$ [for all F_o^2]	0.064	0.037

$$R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{1/2}$$

$$w = 1 / [\sigma^2(F_o^2) + 0.0348 (\text{erythrite}), 0.0178 (\text{annabergite}) \times P^2]$$

$$P = ([\max \text{ of } (0 \text{ or } F_o^2)] + 2F_c^2) / 3$$

Table 2. Mössbauer data for erythrite: IS (isomer shift), QS (quadrupole splitting), FWHM (full width at half maximum), RA (relative area), and RA_{corr} (relative area corrected for thickness effects).

	$\text{Fe}(1)^{2+}$	$\text{Fe}(2)^{2+}$	Fe^{3+}
IS [mm/s]	1.183(5)	1.199(5)	0.30(2)
QS [mm/s]	2.287(8)	3.208(5)	0.79(3)
FWHM [mm/s]	0.236(13)	0.236(5)	0.64(5)
RA [%]	13.3(7)	67.9(13)	18.8(10)
RA_{corr} [%]	12.9	69.0	18.1

loaded in a plexiglass holder (12 mm diameter). The effective sample thickness was 1.6 mg Fe/cm^2 . The spectrum (Fig. 1) was recorded in transmission mode at 293 K using a conventional Mössbauer spectrometer. The velocity scale was calibrated relative to α -Fe. Three Lorentzian doublets (corresponding doublet components constrained to equal line widths and areas) were the

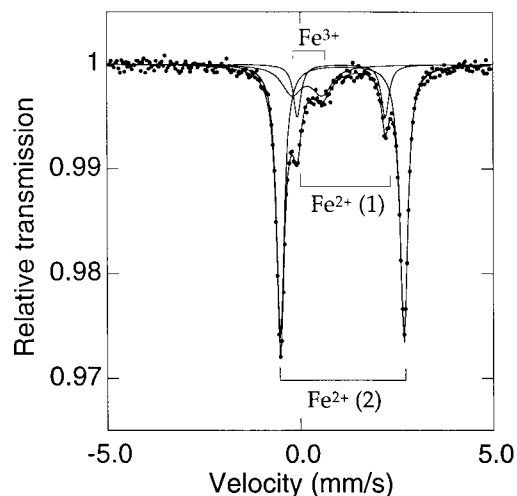


Fig. 1. Mössbauer spectrum of erythrite from Schneeberg, Sachsen.

minimum required to fit the spectral envelope adequately. Results are presented in Table 2.

Results and discussion

Final atomic coordinates and displacement parameters of erythrite and annabergite are listed in Table 3, and important interatomic distances and bond angles are compiled in Table 4. The present study confirms, as expected for a long time from powder diffraction and single-crystal data, that erythrite belongs to the vivianite structure type. Furthermore, it provides new structural data for annabergite with significantly lower Mg-content compared with the variety 'cabrerite' (Giuseppetti & Tadini, 1982). Generally, vivianite-type structures are built by $\text{Me}(1)\text{O}_2(\text{H}_2\text{O})_4$ octahedra and $\text{Me}(2)_2\text{O}_6(\text{H}_2\text{O})_4$ octahedral dimers, which are linked via XO_4 tetrahedra and hydrogen bonds to complex layers parallel to (010). These layers are interconnected only by hydrogen bonds (Fig. 2).

Description of coordination polyhedra

The geometry of the AsO_4 tetrahedron is very similar in both compounds. The mean As–O distances (1.69 Å) comply well with average values given in

Table 3. Atomic coordinates and anisotropic displacement parameters [pm^2] in erythrite (upper row) and annabergite (lower row) with e.s.d.'s in parentheses. The anisotropic displacement parameter is defined as $\exp(-2\pi^2 \sum_i \sum_j U_{ij} h_i h_j a_i^* a_j^*)$.

	x	y	z	U_{11}/iso	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co1	0	0	0	112(3)	170(3)	80(3)	0	-5(2)	0
Ni1 ^a				112(1)	135(2)	109(1)		23(1)	
Co2	0	.38512(3)	0	136(2)	156(2)	99(2)	0	10(2)	0
Ni2 ^a		.38583(2)		128(1)	124(1)	114(1)		31(1)	
As	.31621(3)	0	.37235(7)	100(2)	146(2)	71(1)	0	-2(1)	0
	.31620(1)		.37558(3)	102(1)	122(1)	95(1)		23(0)	
O1	.1493(2)	0	.3748(5)	97(10)	227(12)	94(10)	0	5(8)	0
	.1491(1)		.3807(2)	102(4)	210(6)	128(4)		28(3)	
O2	.4057(3)	0	.7226(5)	166(11)	176(11)	58(9)	0	-25(8)	0
	.4072(1)		.7287(2)	155(4)	145(6)	102(4)		-3(3)	
O3	.3433(2)	.1067(1)	.2087(4)	157(8)	151(8)	140(7)	-5(6)	35(6)	27(6)
	.3429(1)	.1076(1)	.2104(2)	153(3)	135(4)	147(3)	-2(3)	52(2)	15(3)
Ow1	.0978(2)	.1137(2)	.8067(4)	156(8)	227(9)	139(8)	-19(7)	10(7)	-11(7)
	.0961(1)	.1135(1)	.8126(2)	155(3)	196(5)	153(3)	-7(3)	39(3)	-2(3)
Ow2	.3995(2)	.2273(2)	.7133(5)	279(10)	221(10)	169(9)	21(8)	37(7)	20(7)
	.4001(1)	.2253(1)	.7183(2)	245(4)	180(5)	173(4)	24(3)	48(3)	18(3)
H11	.119(4)	.091(3)	.657(7)	156(76)					
	.118(2)	.085(1)	.674(4)	229(43)					
H12	.163(4)	.127(3)	.902(9)	306(109)					
	.164(2)	.128(2)	.924(5)	414(59)					
H21	.368(5)	.208(3)	.536(11)	464(124)					
	.372(2)	.205(2)	.545(6)	466(62)					
H22	.448(4)	.282(3)	.714(9)	416(119)					
	.446(2)	.275(2)	.711(5)	457(64)					

^a refined occupancy factors: Ni1: 0.99Ni+0.01Mg; Ni2: 0.83Ni+0.17Mg

		erythrite		annabergite	
Me1-O1	2×	2.029(2)		2.031(1)	
Me1-Ow1	4×	2.160(2)		2.114(1)	
<Me1-O>		2.116		2.086	
O1-Me1-Ow1	4×	87.3(1)	[2.893(2)]	87.1(0)	[2.858(1)]
O1-Me1-Ow1	4×	92.7(1)	[3.033(3)]	92.9(0)	[3.004(1)]
Ow1-Me1-Ow1	2×	89.9(1)	[3.053(2)]	88.8(0)	[2.960(1)]
Ow1-Me1-Ow1	2×	90.1(1)	[3.058(3)]	91.2(0)	[3.020(1)]
<O-Me1-O>			[2.994]		[2.951]
Me2-O2	2×	2.099(1)		2.054(1)	
Me2-O3	2×	2.100(2)		2.092(1)	
Me2-Ow2	2×	2.118(2)		2.072(1)	
<Me2-O>		2.106		2.073	
O2-Me2-O2	1×	85.3(1)	[2.843(3)]	84.6(0)	[2.763(1)]
O2-Me2-O3	2×	87.0(1)	[2.890(2)]	87.5(0)	[2.868(1)]
O2-Me2-O3	2×	88.6(1)	[2.932(3)]	88.9(0)	[2.903(1)]
O2-Me2-Ow2	2×	92.9(1)	[3.057(2)]	93.3(0)	[3.000(1)]
O2-Me2-Ow2	2×	178.0(1)		177.7(0)	
O3-Me2-O3	1×	174.0(1)		175.2(0)	
O3-Me2-Ow2	2×	92.1(1)	[3.036(2)]	91.9(0)	[2.993(1)]
O3-Me2-Ow2	2×	92.2(1)	[3.039(3)]	91.5(0)	[2.984(1)]
Ow2-Me2-Ow2	1×	88.9(1)	[2.966(3)]	88.9(0)	[2.902(1)]
<O-Me2-O>			[2.976]		[2.930]
As-O1	1×	1.714(2)		1.707(1)	
As-O2	1×	1.683(2)		1.686(1)	
As-O3	2×	1.690(2)		1.686(1)	
<As-O>		1.694		1.691	
O1-As-O2	1×	106.4(1)	[2.721(3)]	106.3(0)	[2.715(1)]
O1-As-O3	2×	106.6(1)	[2.730(2)]	106.7(0)	[2.723(1)]
O2-As-O3	2×	110.2(1)	[2.766(3)]	110.2(0)	[2.765(1)]
O3-As-O3	1×	116.2(1)	[2.870(2)]	116.2(0)	[2.864(1)]
<O-As-O>		109.38	[2.764]	109.38	[2.759]
Ow1-H11		0.85(3)		0.84(2)	
Ow1-H12		0.73(4)		0.77(2)	
H11...O1		1.90(3)		1.88(2)	
H12...O3		2.06(4)		1.99(2)	
Ow1-H11...O1		160(3)	[2.723(3)]	169(2)	[2.703(1)]
Ow1-H12...O3		157(4)	[2.742(2)]	157(2)	[2.721(1)]
H11-Ow1-H12		103(4)	[1.24(6)]	106(2)	[1.29(3)]
Ow2-H21		0.86(5)		0.84(3)	
Ow2-H22		0.89(4)		0.81(2)	
H21...O3		2.04(5)		2.01(3)	
H22...Ow1		2.04(4)		2.10(2)	
Ow2-H21...O3		153(4)	[2.833(3)]	157(2)	[2.798(1)]
Ow2-H22...Ow1		164(4)	[2.904(3)]	163(2)	[2.885(1)]
H21-Ow2-H22		108(4)	[1.42(6)]	106(2)	[1.32(3)]

Table 4. Selected interatomic distances [Å] and angles [°] (with corresponding O—O or H—H distances in brackets) in erythrite and annabergite.

the literature (*e.g.* Baur, 1981, gives 1.682 Å as mean As^[4]—O distance). The bond angle distortions of the arsenate tetrahedra in erythrite and annabergite are identical within the limits of error and correspond closely with the analogous distortions in other arsenate members of the vivianite series. These bond angle distortions can be correlated with polyhedral connections in this structure

type: with their O3—O3 edges, spanning the large O3—As—O3 angle, two AsO₄ tetrahedra each link mirror-related corners within one Me(2)₂O₆(H₂O)₄ dimer, consequently, the opposite angle, O1—As—O2, is the smallest one within the tetrahedron. The corresponding O1—O2 edge links an octahedral dimer with an isolated Me(1)O₂(H₂O)₄ octahedron (*cf.* Fig. 2).

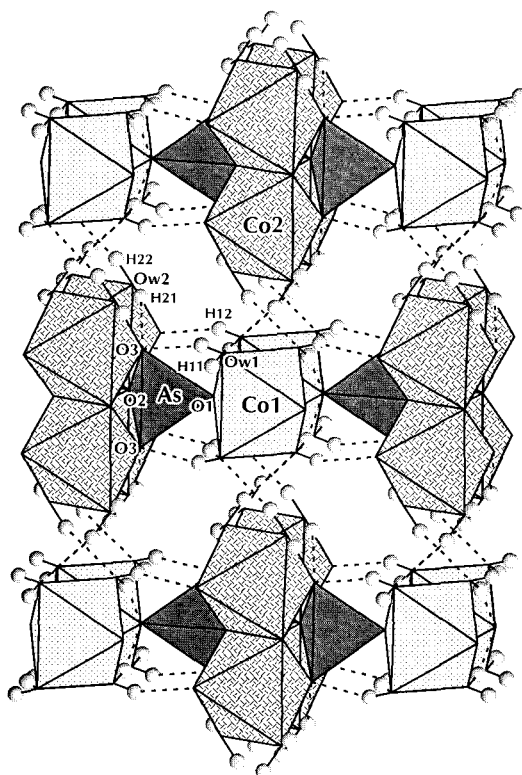


Fig. 2. Crystal structure of erythrite in a projection slightly inclined to [001]. The drawing was done with the program ATOMS (Dowty, 1993).

The Me^{2+} cations occupy two crystallographically different sites with point symmetries $2/m$ (Me1) and 2 (Me2). The Me1 atoms are coordinated to two O1 atoms (shared with the AsO_4 tetrahedra) and to four Ow1 atoms of H_2O molecules. The lengths of the short Me1–O1 bonds are very similar in both title compounds and also remarkably constant within all vivianite-type arsenates and phosphates [2.015 Å in synthetic $\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O-II}$ (Takagi *et al.*, 1986) to 2.032 Å in synthetic $\text{Co}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$ (Giester *et al.*, in prep.)]. In contrast, the longer Me1–Ow1 bonds are clearly correlated with the respective radii of the Me^{2+} ions. The mean Me1–O bond distance in erythrite, 2.116 Å, is very close to literature data for $\text{Co}^{6\text{L}}\text{O}$ bonds (2.111 Å; Wildner, 1992), while the corresponding mean value in annabergite, 2.086 Å, is somewhat higher than the expected one (2.064 Å; Trömel, 1984). The Me2 atoms are coordinated to each two O2 and O3 oxygen atoms and to two

H_2O molecules (Ow2). The shortest edge, O2–O2, links two of these octahedra, forming a $\text{Me}(2)_2\text{O}_6(\text{H}_2\text{O})_4$ dimer. The bond length distortion within the $\text{Me}(2)\text{O}_4(\text{H}_2\text{O})_2$ octahedron is smaller compared with the $\text{Me}(1)\text{O}_2(\text{H}_2\text{O})_4$ octahedron. The average Co2–O and Ni2–O bond lengths, 2.106 and 2.073 Å in erythrite and annabergite, are significantly shorter than the respective mean Me1–O distances, a characteristic structural feature of all vivianite-type arsenates and phosphates.

The hydrogen bonding system in erythrite and annabergite corresponds to the general arrangement reported for other vivianite-type compounds. The observed O–H...O distances (2.703 to 2.904 Å) are in a range typical for water molecules (*cf.* *e.g.* Chiari & Ferraris, 1982). Including the H atoms, the oxygen atoms in erythrite and annabergite are coordinated to three cations in nearly planar (O2 by As and two Me2) resp. pyramidal configurations (Ow2 by Me2, H21, and H22) or in distorted tetrahedral environments (O1 by As, Me1, and two H11; O3 by As, Me2, H12 and H21; Ow1 by Co1, H11, H12, and H22).

X-ray refinement of cation distribution and Mössbauer spectroscopy

The refinement of the Ni / Mg-ratio at the Me(II) sites in annabergite revealed that – within limits of error – Mg is entirely incorporated at the Me2 position, yielding the structural formula $[\text{Ni}(1)_{0.99}\text{Mg}(1)_{0.01}][\text{Ni}(2)_{1.65}\text{Mg}(2)_{0.35}](\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$. This strong preference of the slightly larger Mg^{2+} ion for the Me2 site is remarkable in view of the fact that this octahedron shows the smaller average Me–O bond distance. Nevertheless, for ‘cabrerite’ Giuseppetti & Tadini (1982) report an analogous cation distribution, namely $[\text{Ni}(1)_{0.976}\text{Mg}(1)_{0.024}][\text{Ni}(2)_{1.392}\text{Mg}(2)_{0.608}](\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$. Accordingly, it is plausible that the Me1–O distances are identical in both compounds as well as in synthetic $\text{Ni}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$ (Giester *et al.*, in prep.), while the individual Me2–O bond lengths differ slightly, with a significant decrease of the mean Me2–O distance in the synthetic compound.

As stated above, it was not possible to refine the Co/Fe cation distribution in erythrite. However, nearly identical Me1–O bond lengths in erythrite and in synthetic $\text{Co}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$ (Giester *et al.*, in prep.) combined with a smaller mean Me2–O bond length in the synthetic compound indicate an analogous preference of the larger Fe^{2+} ion on the Me2 site.

This assumption is substantiated by analysis of the Mössbauer spectrum of erythrite (Fig. 1, Table 2). The line-widths of the two Fe^{2+} doublets are narrow, indicating that each doublet corresponds to a single site, likely representing the two different octahedral sites, Co1 and Co2. An unambiguous assignment of each doublet to a distinct site is difficult, but, by analogy with vivianite (McCammon & Burns, 1980) it seems reasonable that the $\text{Fe}^{2+}(1)$ doublet corresponds to the isolated Co(1) octahedron and that the $\text{Fe}^{2+}(2)$ doublet belongs to the edge-sharing Co(2) octahedron. As the ratio of $\text{Fe}^{2+}(2) : \text{Fe}^{2+}(1) = 5.3$ is higher than the expected value for a random distribution ($= 2$), this assignment establishes that the Fe^{2+} ions preferably occupy the Co(2) site in erythrite. The line-width of the Fe^{3+} doublet is extremely broad without any resolvable fine structure, indicating a range of environments. Therefore it is likely that Fe^{3+} ions occupy both types of octahedral sites in erythrite.

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