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ORIGINAL PAPER

Structure refinement and hydrogen bonding of ferrinatrite, $Na_3Fe(SO_4)_3 \cdot 3H_2O$

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Abstract

The structure of trigonal ferrinatrite, $Na_3Fe(SO_4)_3 \cdot 3H_2O$, from the Hongshan Cu-Au deposit, Eastern Tianshan, NW China was refined in space group $P\bar{3}$ based on single crystal X-ray diffraction data [$a = 15.553(2)$, $c = 8.6616(17)$ Å, $V = 1814.4(5)$ Å^3, $Z = 6$; $R_1 = 0.0535$]. All hydrogen atoms were located by difference Fourier methods and refined with soft restrictions for distances, but with fixed thermal isotropic displacement parameters. The atomic arrangement in ferrinatrite is based on chains along [001] consisting of isolated FeO_6-octahedra corner-linked with sulfate groups. All vertices of octahedra link to tetrahedra, and half the tetrahedron vertices link to octahedra. These chains are linked by interstitial Na-ions and H_2O groups. All Na atoms are coordinated to four oxygen atoms of sulfate groups and to two oxygen atoms of H_2O molecules within 2.33–2.71 Å; next oxygens are at distances of 2.85–3.00 Å. Among six hydrogen bonds, three acceptor O-atoms of sulfate groups belong to the nearest octahedral-tetrahedral chains, and three acceptor sulfate O-atoms from the neighboring chains, which further strengthen the linkages between octahedral-tetrahedral chains. The O–H···O distances are in the range 2.86–3.13 Å. The O–H stretching frequencies derived from structural data are in good consistence with the known Infrared spectra.

Keywords Ferrinatrite · Hydrated sulfate · Crystal structure · Hydrogen-bonding system

Introduction

Ferrinatrite, $Na_3Fe(SO_4)_3 \cdot 3H_2O$, is a hydrated sulfate of sodium and ferric iron found in arid environments. The mineral was first mentioned by Mackintosh (1889) from Sierra Gorda, Chile, and the chemical composition was verified by Cesbron (1964) who, on the basis of Weissenberg photographs also confirmed trigonal symmetry with $a = 15.57(3)$, $c = 8.67(3)$ Å, $Z = 6$, and probable space group $P\bar{3}$. The structure of ferrinatrite from Sierra Gorda, Chile, was first determined from X-ray intensities measured on a 2-circle diffractometer (Mereiter 1976) and at about the same time independently studied by Scordari (1977) and refined to final values of $R = 0.047$ and 0.068, respectively. The crystal structure of the synthetic phase $Na_3In(SO_4)_3 \cdot 3H_2O$ (Mukhtarova et al. 1979) is isotypic with ferrinatrite, too.

A sample of ferrinatrite found in the Cetine mine, Tuscany (Italy) has been investigated by scanning electron microscope examination and X-ray powder diffraction study by Sabelli and Santucci (1987). The powder X-ray data agree well enough with the data given by Cesbron (1964). A Mössbauer spectrum of ferrinatrite from the Xitieshan Pb-Zn deposit, Qinghai Province, China, was measured to determine the Fe valence state by Zhang and Wang (1998), proving that iron in this mineral belongs to Fe^{3+}, with four independent atomic sites. The infrared and Raman spectra of ferrinatrite from fossil materials were determined by Rouchon et al. (2012).

Upon submission of our manuscript, a new paper (Ventruti et al. 2019) was published describing Infrared and Raman spectra as well as the crystal structure of ferrinatrite from the type locality Sierra Gorda, Chile. It is based on a single-crystal X-ray diffraction experiment ($R_1 = 0.045$) revealing also

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positions of H-sites. In case of H152 given by Ventruti et al. (2019) the position is doubtful.

The structure of ferrinatrite was described with three Na-ions in octahedral arrangement to oxygen ligands within a Na–O bond distance ≤2.70 Å or to form a [7]-coordination up to a sphere of 3 Å. Isolated FeO_6-octahedra form chains along [001] corner-linked with sulfate groups. These chains are further connected by $NaO_5(H_2O)_2$ polyhedra and via their H_2O molecules involved in hydrogen bonding.

In the structures of sulfate minerals, hydrogen bonding can be essential in combining subunits. The substructures in ferrinatrite are linked together by hydrogen bonding and by large low-valence interstitial cations. In the present study on the structure of ferrinatrite from the Hongshan Cu-Au deposit, Eastern Tianshan, NW China, all H-atoms were located by difference Fourier methods and refined from X-ray diffraction data. The hydrogen-bonding system is discussed and compared with the H-bonding scheme given by Ventruti et al. (2019).

Sample and experimental details

The Hongshan Cu-Au deposit is located in the southern margin of the Tu-Ha Basin in the eastern Xinjiang, China. The deposit occurs in the Mesozoic volcanic rocks, which consist of quartz porphyry, rhyolitic porphyry and granitic porphyry. The ore minerals include chalcopyrite, pyrite, bornite, chalcocite, sphalerite and native gold (Xu 2007; Xu et al. 2008). The oxidation zone of the deposit is well developed with a thickness varying from 50 to 60 m. The secondary Fe-bearing sulfates are the dominant minerals in the oxidation zone. The associated minerals include coquimbite, paracoquimbite, parabutlerite, jarosite, ferricopiapite, rhomboclase, metasideronatrite, krausite, yavapaiite, voltaite, ferrinatrite, roemerite, and sideronatrite (Xu et al. 2008).

The sample was obtained from the collection of the Museum of the Institute of Geology and Geophysics, Chinese Academy of Sciences, and originally described by Xu (2007). Ferrinatrite appears as fibrous aggregates, grayish white in color with vitreous luster. The mineral forms transparent prism tabular crystals up to 8–10 mm in size.

The chemical composition, determined by chemical analysis, was reported as (in wt%): SO_3 = 51.26, Fe_2O_3 = 17.33, MgO = 0.09, CaO = 0.01, Na_2O = 19.83, H_2O = 11.26, total = 99.78 (Xu 2007). On the basis of 15 O atoms the empirical formula can be expressed as: $Na_{3.01}(Fe_{1.02}Mg_{0.01})_{\Sigma 1.03}S_{3.01}H_{5.87}O_{15}$ or $Na_{3.01}(Fe_{1.02}Mg_{0.01})_{\Sigma 1.03}(SO_4)_{3.01}(OH)_{0.03}(H_2O)_{2.93}$, close to the ideal formula for ferrinatrite, $Na_3Fe(SO_4)_3{\cdot}3H_2O$. The theoretical chemical composition for ferrinatrite is (in wt%): SO_3 = 51.42, Fe_2O_3 = 17.10, Na_2O = 19.91, H_2O = 11.57, total = 100.00.

Single-crystal X-ray data were collected using monochromatic Mo$K\alpha$-radiation on a Rigaku RA-Micro7HF diffractometer with a Saturn 724+ CCD detector. A total of 660 frames were recorded by a combination of several ω and φ rotation sets with 0.5 ° frame scan width.

Data reduction, including intensity integration, correction for Lorentz and polarization effects, and absorption correction, was done using the software CrystalClear (Rigaku). The starting atomic positions and the labelling scheme in ferrinatrite were taken from Scordari (1977) and Ventruti et al. (2019) as references. The crystal structure was refined with full-matrix least-squares techniques on F^2 using SHELX-97 (Sheldrick 1997). The program uses the neutral atom scattering curves. Refinement of the site occupation factors (sof) for Na1, Na2, Na3, Fe1, Fe2, Fe3 and Fe4, yielded 0.995(7), 0.984(7), 0.995(7), 0.982(6), 0.984(6), 0.987(5) and 0.987(5), respectively, close to the ideal value. Therefore, these sofs were fixed at full occupancy. The positions of the H-atoms of the H_2O groups were identified in difference Fourier maps. The hydrogen atoms were refined with soft restraints (0.89(4) Å for O-H distances) and thermal isotropic displacement parameters related to the parent atom. For all non-H atoms anisotropic displacement parameters were used. The $R_1(F)$ value obtained is 0.0535 for 2666 observed reflections with $I > 2\sigma(I)$. The refined formula is consistent with the ideal one: $Na_3Fe(SO_4)_3{\cdot}3H_2O$.

The crystal data, information on data-collection and refinement details for ferrinatrite are listed in Table 1; the positional, equivalent isotropic displacement and anisotropic displacement parameters are given in Tables 2 and 3, respectively. The relevant bond lengths and angles are shown in Table 4. The unit cell parameters of ferrinatrite [$P\bar{3}$, a = 15.553(2), c = 8.6616(17) Å, V = 1814.4(5) Å^3, Z = 6] are very close to those reported by Mereiter (1976), Scordari (1977) and Ventruti et al. (2019). For $Na_3In(SO_4)_3{\cdot}3H_2O$ (Mukhtarova et al. 1979) the unit cell parameters are larger [a = 15.720(6), c = 8.77216(3) Å, V = 1877.3 Å^3.

Structure description

There are 3 crystallographically independent Na-, 4 Fe-, and 3 S-atom sites present in the structure of ferrinatrite. Except for the Fe sites (symmetry$\bar{3}$ for Fe3, 4 and 3 for Fe1, 2), all atoms are located on general positions. The atomic arrangement is shown in a projection along [110] in Fig. 1. The non-hydrogen atom positions are in close agreement with previous studies on the ferrinatrite structure (Mereiter 1976; Scordari 1977; Ventruti et al. 2019): differences in Na–O bond lengths are ≤0.016 Å, for Fe–O and S–O bond lengths ≤0.006 Å between the model of Ventruti et al. (2019) and the present bond lengths.

Table 1 Crystal data, data collection information and refinement details for ferrinatrite

Formula	$Na_3Fe(SO_4)_3 \cdot 3H_2O$
Formula weight	467.05
Space group	$P\bar{3}$
a (Å)	15.553(2)
c (Å)	8.6616(17)
V (Å^3), Z	1814.4(5), 6
μ (mm^{-1})	1.959
Crystal dimensions (mm^3)	0.31 × 0.12 × 0.09
F (000), ρ_{calc}(g·cm^{-3})	1398, 2.565
λ (Mo$K\alpha$)(A), T(K)	0.71073, 293(2)
θ range for collection	3.52° to 27.47°
Number of frames	660
Scan time (s/°)	8
h,k,l ranges	−19 → 19, −15 → 20, −11 → 11
Total reflections measured	13217
Unique reflections	2772 [R(int) =4.60%]
Reflections used	2666 with $I > 2\sigma(I)$
Refinement on	F^2
$R_1(F)$, w$R_2(F^2)$[I > 2σ(I)]	5.35%, 9.48%
No. of refined parameters	219
GooF on F^2	1.389
$\Delta\rho_{min}$, $\Delta\rho_{max}$ (e/Å^3)	−0.52, 0.40

Rigaku four-circle diffractometer equipped with a Saturn 724+ CCD detector, Mo tube (λ$K\alpha$ = 0.71073 Å), graphite monochromator, φ-scans for distinct ω-angles, Δφ = 0.5°/frame, frame size: binned mode, 34 μm/2048 × 2048 pixels, detector-to sample distance: 45 mm. T(K) = 293(2).Unit-cell parameters were obtained by least-squares refinements of 2θ values

Ferrinatrite is based on infinite $\{Fe[SO_4]_3\}^{3-}$ chains consisting of FeO_6-octahedra linked by corner-sharing with SO_4-tetrahedra such that all octahedron vertices link to tetrahedra, and half the tetrahedron vertices link to octahedra. Two such infinite types of chains, both running along the c-axis, are present in the structure: the chain $\{Fe3[S3O_4]_3Fe4[S3O_4]_3\}$ is centered at 0 0 z; and the chain $\{Fe1[S1O_4]_3Fe2[S2O_4]_3\}$ at 1/3 2/3 z and 2/3 1/3 z. These chains are linked by interstitial Na-ions and H_2O groups (Fig. 2).

All four Fe atoms exhibit quite regular octahedral coordination by oxygen atoms. The average Fe-O distances shown in Table 4 can be well compared with those found for ferric iron e.g. in the monoclinic polytype of sideronatrite $Na_2Fe(SO_4)_2(OH) \cdot 3H_2O$ (2.006 Å, Yang et al. 2015), in the orthorhombic polytype of sideronatrite (1.999 Å, Scordari and Ventruti 2009), in metasideronatrite $Na_2Fe(SO_4)_2(OH) \cdot H_2O$ (2.008 Å, Ventruti et al. 2010), in amarillite $NaFe(SO_4)_2 \cdot 6H_2O$ (1.986 Å, Yang and Giester 2016), in yavapaiite $KFe(SO_4)_2$ (1.988 Å, Graeber and Rosenzweig 1971), or in $Fe^{3+}{}_2Fe^{2+}(SO_4)_4 \cdot 2H_2O$ (1.984 Å, Wildner and Giester 1991). In the isotypic compound $Na_3In(SO_4)_3 \cdot 3H_2O$ (Mukhtarova et al. 1979) respective In-O distances are within 2.125 to 2.141 Å, reflecting the significantly larger cation size of In^{3+} (0.80 Å) as compared to ferric iron (0.65 Å).

Table 2 Atomic coordinates and isotropic atomic displacement parameters (in Å^2) with estimated standard deviations (e.s.d.'s) in parentheses for ferrinatrite

Atom	x	y	z	U_{eq}
Fe1	0.33333	0.66667	0.18660(10)	0.0122(2)
Fe2	0.33333	0.66667	0.68734(10)	0.0116(2)
Fe3	0	0	0	0.0121(3)
Fe4	0	0	0.5	0.0117(3)
Na1	0.08326(13)	0.63634(14)	0.0703(2)	0.0292(4)
Na2	0.10846(14)	0.41593(14)	0.2991(2)	0.0337(5)
Na3	0.21891(13)	0.25032(13)	0.4005(2)	0.0276(4)
S1	0.33706(7)	0.51306(7)	0.42831(10)	0.0128(2)
S2	0.18125(7)	0.50885(7)	0.94441(10)	0.0129(2)
S3	0.14322(7)	0.16494(7)	0.74536(10)	0.0129(2)
O1	0.2536(2)	0.54404(19)	0.8142(3)	0.0168(6)
O2	0.3727(2)	0.5838(2)	0.5607(3)	0.0163(6)
O3	0.28433(19)	0.5452(2)	0.3166(3)	0.0163(6)
O4	0.21202(19)	0.5936(2)	0.0568(3)	0.0156(6)
O5	0.2638(2)	0.4144(2)	0.4811(3)	0.0228(6)
O6	0.4216(2)	0.5164(2)	0.3513(3)	0.0201(6)
O7	0.5155(2)	0.5998(2)	0.8869(3)	0.0232(6)
O8	0.5725(2)	0.7555(2)	0.0222(3)	0.0225(6)
O9	0.0264(2)	0.11732(19)	0.1286(3)	0.0165(6)
O10	0.06017(19)	0.12336(19)	0.6282(3)	0.0150(5)
O11	0.2332(2)	0.1793(2)	0.6694(3)	0.0203(6)
O12	0.1518(2)	0.2557(2)	0.8045(3)	0.0224(6)
O13	0.0336(2)	0.7508(2)	0.1302(4)	0.0286(7)
H131	0.064(4)	0.803(3)	0.077(6)	0.043
H132	−0.026(3)	0.736(4)	0.114(6)	0.043
O14	0.0507(3)	0.6430(3)	−0.1993(4)	0.0302(7)
H141	0.091(4)	0.706(3)	−0.217(6)	0.045
H142	0.078(4)	0.609(4)	−0.225(6)	0.045
O15	0.3905(3)	0.3146(3)	0.4305(4)	0.0299(7)
H151	0.421(4)	0.367(3)	0.384(6)	0.045
H152	0.415(4)	0.281(4)	0.402(6)	0.045

The three SO_4 groups exhibit moderate bond length distortions, each with two shorter and two longer S-O distances, with mean values of 1.450 and 1.499 Å, respectively. The value of Bond-Length Distortion Parameter (BLDP) for tetrahedral coordination in ferrinatrite is 0.39 for S1, 0.46 for S2 and 0.41 for S3, respectively. The value of Bond-Length Distortion Parameter (ELDP) is 0.16 for S1 and 0.17 for S2 and S3, respectively (for definitions of BLDP and ELDP, see Griffen and Ribbe 1979). The longer S–O bonds are those to oxygen atoms shared with ferric iron. The average S-O distances for three SO_4 groups, 1.475, 1.474 and 1.476 Å, fall in the range 1.47–1.48 Å reported for most hydrated sulfates (Palmer et al. 1972; Hawthorne et al. 2000). Bond valences are given in Table 5: the range for S1–O bonds is 1.376–1.592

Table 3 Anisotropic displacement parameters (in Å^2) with estimated standard deviations (e.s.d.'s) in parentheses for ferrinatrite

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Fe1	0.0137(3)	0.0137(3)	0.0092(4)	0	0	0.00683(15)
Fe2	0.0128(3)	0.0128(3)	0.0091(4)	0	0	0.00642(14)
Fe3	0.0140(4)	0.0140(4)	0.0085(6)	0	0	0.0070(2)
Fe4	0.0127(4)	0.0127(4)	0.0098(6)	0	0	0.0063(2)
Na1	0.0248(9)	0.0363(11)	0.0301(10)	−0.0022(8)	−0.0013(7)	0.0179(8)
Na2	0.0277(10)	0.0320(10)	0.0295(10)	0.0036(8)	−0.0011(8)	0.0060(8)
Na3	0.0256(9)	0.0224(9)	0.0305(9)	0.0026(7)	−0.0007(7)	0.0087(8)
S1	0.0152(5)	0.0132(4)	0.0105(4)	0.0002(3)	0.0009(3)	0.0075(4)
S2	0.0133(4)	0.0124(4)	0.0110(4)	−0.0001(3)	0.0002(3)	0.0050(4)
S3	0.0124(4)	0.0132(4)	0.0113(4)	−0.0004(3)	0.0004(3)	0.0051(4)
O1	0.0199(14)	0.0165(14)	0.0126(12)	0.0015(10)	0.0044(11)	0.0080(12)
O2	0.0191(14)	0.0198(14)	0.0114(12)	−0.0032(10)	−0.0015(10)	0.0108(12)
O3	0.0179(14)	0.0177(14)	0.0129(12)	0.0016(10)	−0.0019(10)	0.0085(12)
O4	0.0170(14)	0.0177(14)	0.0126(12)	−0.0057(10)	−0.0027(10)	0.0091(11)
O5	0.0260(16)	0.0143(14)	0.0268(15)	0.0052(11)	0.0037(12)	0.0090(13)
O6	0.0207(15)	0.0266(16)	0.0185(13)	−0.0017(11)	0.0034(11)	0.0159(13)
O7	0.0255(16)	0.0256(16)	0.0254(15)	−0.0028(12)	0.0042(12)	0.0179(13)
O8	0.0179(15)	0.0223(15)	0.0190(14)	−0.0018(11)	−0.0063(11)	0.0038(13)
O9	0.0203(14)	0.0146(13)	0.0134(12)	−0.0010(10)	0.0029(11)	0.0078(12)
O10	0.0172(14)	0.0160(13)	0.0130(12)	−0.0035(10)	−0.0037(10)	0.0092(11)
O11	0.0178(14)	0.0228(15)	0.0173(13)	0.0021(11)	0.0037(11)	0.0079(12)
O12	0.0215(15)	0.0176(15)	0.0268(15)	−0.0075(12)	−0.0022(12)	0.0088(12)
O13	0.0267(17)	0.0260(17)	0.0335(17)	0.0045(13)	0.0021(14)	0.0135(15)
O14	0.0295(18)	0.0306(18)	0.0333(17)	0.0037(15)	0.0020(14)	0.0170(15)
O15	0.0291(18)	0.037(2)	0.0303(17)	0.0077(14)	0.0053(14)	0.0217(16)

v.u. (valence units), 1.357–1.622 *v.u.* in S2–O and 1.357–1.627 *v.u.* in S3–O, according to the bond-valence curve for S–O bonds (1.13–1.92 *v.u.*) given by Brown (1981) and Hawthorne et al. (2000).

In the previous studies on the ferrinatrite structure, the arrangement of the sodium ion to oxygen ligands was described as distorted octahedron (Mereiter 1976) or to exhibit a seven-fold coordination (Scordari 1977). All sodium atoms are coordinated to four oxygen atoms of sulfate groups and to two oxygens of H_2O molecules forming distorted polyhedra, i.e. three O atoms of three SO_4 groups from the nearest octahedral-tetrahedral chain, and one from the neighboring

Table 4 Relevant bond lengths (Å) and angles (°) in ferrinatrite

Fe1-O3 (×3)	1.993(3)	Fe2-O1 (×3)	2.004(3)	Fe3-O9 (×6)	1.997(3)
Fe1-O4 (×3)	1.995(3)	Fe2-O2 (×3)	2.008(3)	Fe4-O10 (×6)	1.998(3)
<Fe1-O>	1.994	<Fe2-O>	2.006		
Na1-O13	2.327(4)	Na2-O14	2.334(4)	Na3-O15	2.350(4)
Na1-O7	2.359(3)	Na2-O15	2.388(4)	Na3-O5	2.389(3)
Na1-O14	2.402(4)	Na2-O3	2.459(3)	Na3-O13	2.391(4)
Na1-O4	2.408(3)	Na2-O11	2.542(3)	Na3-O11#1	2.518(3)
Na1-O6	2.632(3)	Na2-O8	2.630(3)	Na3-O10	2.533(3)
Na1-O8	2.705(4)	Na2-O6	2.679(4)	Na3-O11	2.635(3)
<Na1-O>	2.472	<Na2-O>	2.505	<Na3-O>	2.469
Na1-O7	2.853(3)	Na2-O5	2.895(4)	Na3-O10	3.001(3)
S1-O6	1.452(3)	S2-O8	1.445(3)	S3-O12	1.444(3)
S1-O5	1.453(3)	S2-O7	1.447(3)	S3-O11	1.459(3)
S1-O2	1.490(3)	S2-O1	1.491(3)	S3-O9	1.488(3)
S1-O3	1.506(3)	S2-O4	1.511(3)	S3-O10	1.511(3)
<S1-O>	1.475	<S2-O>	1.474	<S3-O>	1.476
H131-O13-H132	101(5)				
H141-O14-H142	110(5)				
H151-O15-H152	106(6)				
D–H···A	*d*(D–H)	*d*(H···A)	<DHA	*d*(D···A)	
O13–H131 ···O12#2	0.85(3)	2.45(4)	138(5)	3.130(4)	
*O13–H131 ···O9#3	0.85(3)	2.51(5)	129(5)	3.116(4)	
O13–H132 ···O12#4	0.85(3)	2.14(4)	147(5)	2.890(4)	
O14–H141 ···O12#2	0.87(3)	2.13(4)	142(5)	2.869(4)	
O14–H142 ···O7#2	0.85(3)	2.21(5)	133(5)	2.862(5)	
O15–H151 ···O6	0.82(3)	2.33(5)	140(5)	3.005(4)	
*O15–H151 ···O7#5	0.82(3)	2.50(5)	130(5)	3.085(4)	
O15–H152 ···O5#6	0.83(3)	2.26(5)	130(5)	2.860(4)	

Symmetry code for equivalent positions: #1 = x-y, x,1-z; #2 = −x + y,1-x,z-1; #3 = −x + y,1-x,z; #4 = −x,1-y,1-z; #5 = 1-x,1-y,1-z; #6 = y,-x + y,1-z. * = possibly additional H-bond. D = H-bond donor, A = H-bond acceptor

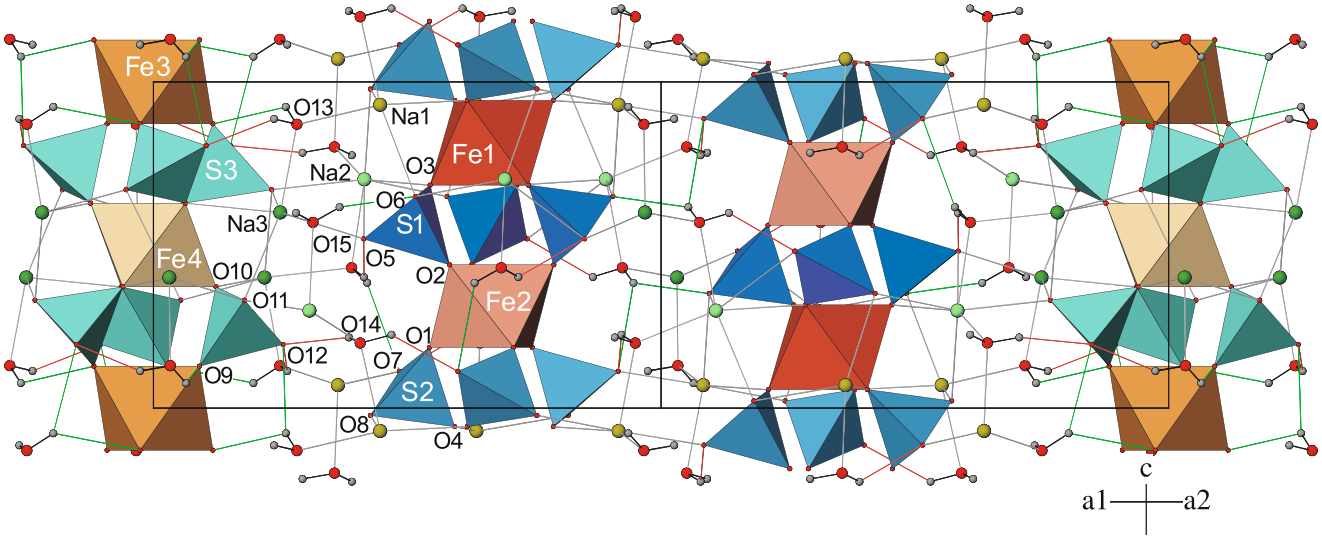

Fig. 1 Octahetral and tetrahedral chains in ferrinatrite viewed along [110] direction. Grey lines = Na-O. Red lines = hydrogen bonds. Green lines = bifurcated hydrogen bonds. All crystal structure drawings were done with ATOMS (Dowty 2016)

chain which strengthen the inter-chains linkages shown in Figs. 1 and 2. The mean $Na^{[6]}$–O bond lengths for Na1 to Na3 are 2.472 Å, 2.505 Å and 2.469 Å, similar to that found in the structure of metasideronatrite (2.451 Å, Ventruti et al. 2010), but larger than those in the structures of monoclinic sideronatrite (2.424 Å and 2.415 Å, Yang et al. 2015) and amarillite (2.426 Å, Yang and Giester 2016). Next nearest oxygen atoms are at distances of 2.85–3.00 Å, resulting in polyhedra with $<Na^{[7]}\text{-O}>$ values of 2.53, 2.56 and 2.55 Å for Na1–3, respectively. However, the valence sums of the bond strengths reaching Na1 and Na3 in distorted octahedra (2.33–2.71 Å, 2.35–2.64 Å) already are equal to 1.04 and 1.02 *v.u.*, while the valence sum of the bond strengths reaching Na2 in a [7]-coordination polyhedron (2.33–2.90 Å, Table 5) is just 0.99 *v.u.* On this basis the coordination of Na1 and Na3 atoms may be described as distorted octahedra, while Na2 atom belongs to a [7]-coordination polyhedron. The [7]-coordination comprises five sulfate oxygen atoms and two H_2O molecules,

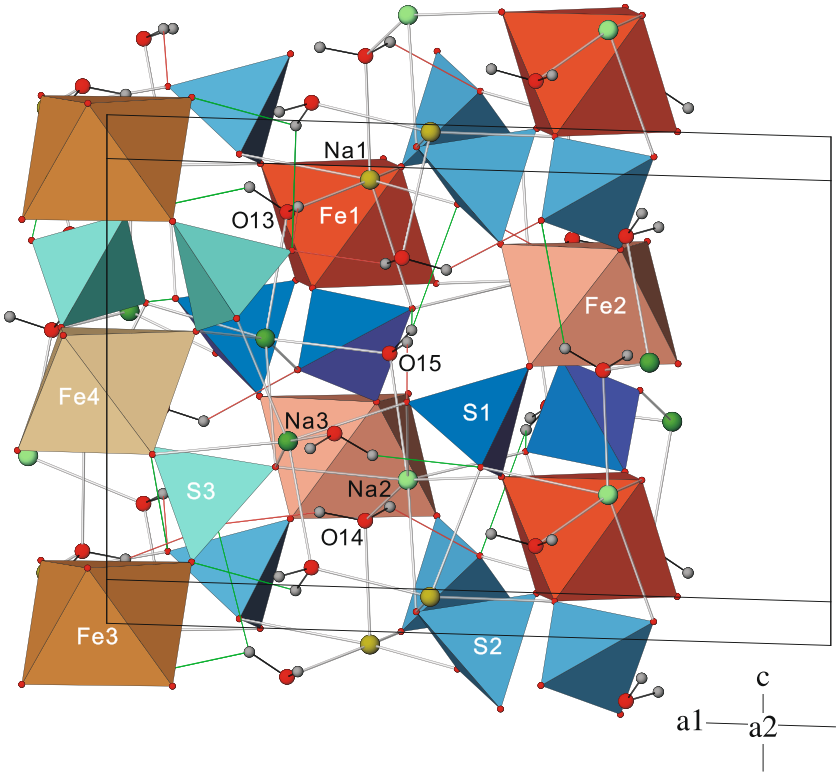

Fig. 2 The $Na(1,3)O_4(H_2O)_2$ distorted octahedra and $Na2O_5(H_2O)_2$ sevenfold polyhedra are linked by their vertices to each other via two H_2O molecules in ferrinatrite

Table 5 Bond valences for ferrinatrite

	O1	O2	O3	O4	O5	O6	O7	O8	O9	O10	O11	O12	O13	O14	O15	
Fe1			0.528 × 3	0.531 × 3												3.18
Fe2	0.516 × 3	0.510 × 3														3.08
Fe3									0.526 × 6							3.15
Fe4										0.524 × 6						3.14
Na1				0.193		0.106	0.221	0.087					0.241	0.197		1.04
Na2			0.168		0.052	0.093		0.106			0.135			0.236	0.204	0.99
Na3					0.204					0.138	0.144,0.105		0.202		0.226	1.02
S1		1.436	1.376		1.588	1.592										5.99
S2	1.433			1.357			1.613	1.622								6.03
S3									1.444	1.357	1.562	1.627				5.99
H131												0.110	0.890			1.00
H132												0.155	0.845			1.00
H141												0.161		0.839		1.00
H142							0.163							0.837		1.00
H151						0.129									0.871	1.00
H152					0.164										0.836	1.00
	1.95	1.95	2.07	2.08	2.01	1.92	2.06	1.81	2.02	2.02	1.94	2.05	2.18	2.11	2.14	

The bond valences were calculated from the curves of Brese and O'Keeffe (1991); Hydrogen bond strengths were calculated from the curves of Ferraris and Ivaldi (1988)

i.e. four O atoms of three SO_4 groups from the nearest octahedral-tetrahedral chain, and one from the neighboring chain. The $NaO_4(H_2O)_2$ distorted octahedra and $NaO_5(H_2O)_2$ sevenfold polyhedra are connected to each other by their vertices via two H_2O molecules shown in Fig. 2.

Hydrogen-bonding system

There are three interstitial H_2O groups shown in Figs. 1–3. The O–H bond distances in ferrinatrite - restrained to values expected for X-ray diffraction experiments - vary between 0.82 and 0.87 Å (Table 4). The hydrogen bond distances (O···H) vary from 2.13 to 2.51 Å (Table 4), and the corresponding hydrogen bond strengths range from 0.110 to 0.163 *v.u.* (Table 5).

The three independent H_2O molecules are shared among $NaO_4(H_2O)_2$ distorted octahedra and $NaO_5(H_2O)_2$ polyhedra which donate 6 hydrogen bonds to six neighboring O-atoms (based on the shortest O···H distance), i.e. four acceptor O-atoms of sulfate groups belonging to the nearest octahedral-tetrahedral chains, O13–H131···O12, O13–H132···O12', O14–H142···O7 and O15–H152···O5, as well as two acceptor sulfate O-atoms from the neighboring chains, O14–H141···O12' and O15–H151···O6 (Fig. 3). The latter two hydrogen bonds further strengthen the linkages between octahedral-tetrahedral chains.

The bond-valence sums including contributions of hydrogen bonds, calculated from the O···O distances as suggested by Ferraris and Ivaldi (1988) (Table 5), show satisfactory agreement with the valence-sum rule (Brown 2002). In common crystal chemistry, each O atom in an (SO_4) tetrahedron receives ~1.5 *v.u.* from the bond involving the S atom. The O–H bond of a hydroxyl group commonly has a bond valence of ~0.8 *v.u.*, and the acceptor anion receives ~0.2 *v.u.* In ferrinatrite, among the oxygen atoms of the SO_4 tetrahedra, those unshared with Fe (O5, O6, O7, O8 and O12, except for O11) receive a sum of electrostatic bond strengths differing significantly from ideal value and may act as hydrogen-bond acceptors. O11 is shared with two Na3 and one Na2 atoms, and receives a sum of electrostatic bond strengths relatively higher than other oxygen atoms unshared with Fe. O12 is strongly bonded to S3 and weakly bonded to three H atoms as a hydrogen-bond acceptor (Table 5). This may represent a weak point from which the structure can destabilize or transform.

The hydrogen bonding pattern observed for O15–H152···O5 is significantly different to that given by Ventruti et al. (2019). The position for H152 found by these authors is doubtful, because it directly points towards the Na3 atom at a distance of only about 1.54 Å, which violates common crystal chemistry rules. For

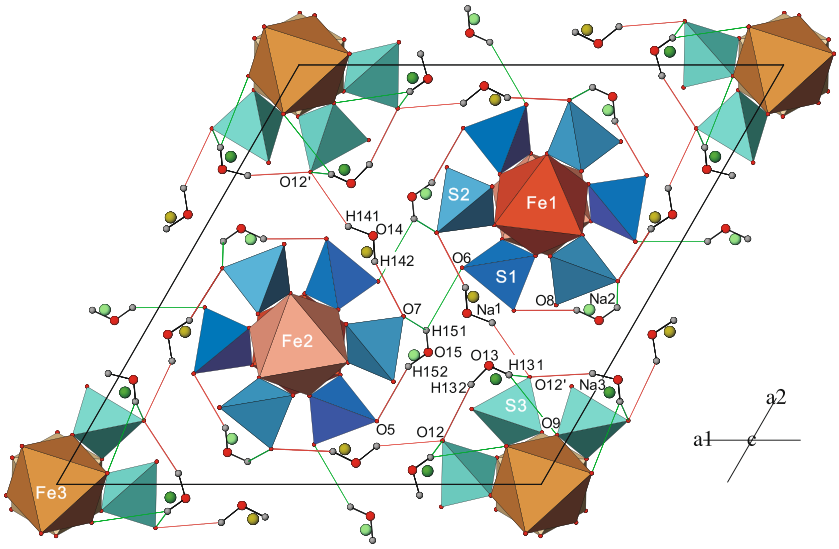

Fig. 3 Hydrogen-bonding system in ferrinatrite viewed down the *c*-direction. Red lines = hydrogen bonds. Green lines = bifurcated hydrogen bonds

H151, a bifurcated hydrogen bond involving O6 and O7 as acceptor atoms can be assumed.

Ventruti et al. (2019) further describe the H_2O molecule of O13 with H131 linked to O8 by hydrogen bonding at a distance (O8···H131) of 2.88 Å. Nevertheless, the angle O13–H131···O8 is rather small (104 °) and there are obviously two additional hydrogen bonds H131···O_{acc} shorter than 2.88 Å, i.e. to O9 and O12 forming a bifurcated hydrogen bond. In the present study, the two possible H-bond acceptors of the bifurcated hydrogen bond are O12···H131 (2.45 Å) and O9···H131 (2.51 Å), respectively. In the structure of ferrinatrite, each of the three independent SO_4 tetrahedra share two oxygen atoms with the FeO_6 octahedra and the remaining two with $Na(1,3)O_4(H_2O)_2$ and $Na2O_5(H_2O)_2$ polyhedra, except for the oxygen atom O12. Since O12 is only linked to sulfur S3, the O12···H131 hydrogen bonding strengthens linkage to the weak point in the structure.

Using the empirical equations correlating the *d*(O···O) and *d*(H···O) lengths in minerals with the O–H stretching frequencies from infrared spectroscopy (Libowitzky 1999), the *d*(O···O) lengths ranging from 2.9 to 3.1 Å and the *d*(H···O) lengths from 2.1 to 2.5 Å in ferrinatrite (Table 4) would be expected to have the O–H stretching energies ranging between ~3500 and ~3620 cm^{-1}. In the room-temperature single-crystal Fourier-Transform Infrared (FTIR) spectrum of ferrinatrite, two very intense peaks at 3530 and 3596 cm^{-1}, respectively, were observed (Ventruti et al. 2019; Majzlan et al. 2011; Ventruti et al. 2013; Della Ventura et al. 2013). The O–H stretching frequencies calculated from structural data are in good consistence with the known FTIR spectrum.

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