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Metasideronatrite: Crystal structure and its relation with sideronatrite

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ABSTRACT

Metasideronatrite was obtained as the first dehydration product of sideronatrite, $Na_2Fe(SO_4)_2(OH)\cdot 3H_2O$, from Sierra Gorda, Chile. The crystal structure of metasideronatrite was solved by direct methods and refined by full-matrix least-squares to $R = 0.039$, using 574 independent reflections with $I > 3.0\sigma(I)$. It is orthorhombic, space group *Pbnm*, with $a = 7.3959(8)$, $b = 16.0979(15)$, $c = 7.1607(8)$ Å, $V = 852.5(2)$ Å^3, $Z = 4$. The crystal-chemical formula derived from this structural study is $Na_2Fe(SO_4)_2(OH)\cdot H_2O$. The backbone of the structure is the same as that in sideronatrite: infinite $[Fe^{3+}(SO_4)_2(OH)]^{2-}$ chains of interconnected octahedra and tetrahedra parallel to the *c* axis. These chains are linked primarily by Na atoms to build a 3-dimensional network of strong (Fe-O-S) and weak (Na-O) bonds. Another prominent feature of the structure is the arrangement of distorted (NaO_5H_2O) octahedra, which alternately share one edge and one face to form columns parallel to the $[Fe^{3+}(SO_4)_2(OH)]$ chains. Subsidiary intra-chain bonds are provided by H atoms belonging to OH^- groups shared by adjacent Fe octahedra, and to the unique water molecule shared between two adjacent (NaO_5H_2O) octahedra. At normal conditions of relative humidity (RH) and temperature (i.e., RH > 60% and $T < 40$ °C), metasideronatrite rehydrates rapidly to sideronatrite.

The structure solution has allowed us to: (1) investigate the strong relation between sideronatrite and metasideronitrite; (2) elucidate the mechanism involved in the transformation of metasideronatrite into the order/disorder (OD) structure of sideronatrite; and (3) get insight into the stability of this mineral from the valence-matching principle applied to the main structural unit $[Fe^{3+}(SO_4)_2(OH)]^2$ and Na^+ interstitial species. The weak hydrogen bonds and the particular arrangement of the face-sharing adjacent $[NaO_5(H_2O)]$ octahedra are the main factors affecting the stability of metasideronatrite.

Keywords: Metasideronatrite, structure, crystal chemistry, dehydration, sideronatrite

INTRODUCTION

Bandy (1938) described a new basic hydrated sulfate of sodium and ferric iron, from Chuquicamata (Chile), as metasideronatrite to stress the lower water content relative to the related mineral sideronatrite, $Na_2Fe^{3+}(SO_4)_2(OH)\cdot 3H_2O$. According to this author, metasideronatrite is orthorhombic dypiramidal, with an observed density of 2.46 g/cm^3. Chemical analysis (Bandy 1938) led to the following chemical formula: $Na_2Fe^{3+}(SO_4)_2(OH)\cdot 1.5H_2O$. For metasideronatrite, Césbron (1964) proposed a substantially identical chemical formula with less water content, $Na_2Fe^{3+}(SO_4)_2(OH)\cdot H_2O$. Depending on humidity, metasideronatrite rehydrates quickly to sideronatrite. From this observation, Césbron (1964) inferred that the analysis quoted in Bandy (1938) was likely made on material in the course of rehydration/dehydration. Structural data for metasideronatrite are limited and low quality. Using Weissenberg, precession, and powder diffraction data, Finney (1973) confirmed metasideronatrite as orthorhombic, $a = 7.357(3)$, $b = 16.002(4)$, $c = 7.102(8)$ Å, space group *Pbnm* or $Pbn2_1$, with the formula proposed by Bandy (1938). On the basis of new DTA and TGA data combined with X-ray single-crystal Weissenberg photographs, Scordari and Milella (1982) concluded that Césbron's formula corresponds to a mixture of two metasideronatrite-like compounds of different water contents. Powder-diffraction data (Scordari et al. 1982) of differently hydrated metasideronatrite-like compounds support this hypothesis.

The exact structure and correct chemical formula of metasideronatrite is still unsolved. We report here for the first time: (1) the determination and refinement of the crystal structure of metasideronatrite; (2) the correct water content deduced from the structure; (3) the factors that influence the stability of the compound; and (4) the structural relation with sideronatrite.

EXPERIMENTAL AND STRUCTURE DETERMINATION

The crystals investigated here were obtained by spontaneous dehydration on a dry and hot day from sideronatrite from Sierra Gorda (Chile). A Bruker AXS X8 APEX II four-circle Kappa diffractometer equipped with a CCD area detector (Bruker 2003) was used for the structure data collection. A total of 1340 frames was recorded by a combination of several ω and ϕ rotation sets with 0.5° scan width. Data reduction, including intensity integration, correction for Lorentz, polarization, and background effects, and scale variation, was done using the package SAINT-IRIX (Bruker 2001). A semi-empirical absorption correction (Blessing 1995) was done using SADABS (Sheldrick 2004), and equivalent reflections were merged. Subsequent analysis of the intensity data, by XPREP (Sheldrick 2003), confirmed Finney's results (1973) and indicated the centrosymmetric distribution of the normalized structure factors, allowing assignment of the unique space group *Pbnm*. The final unit-cell parameters were obtained from the measured reflections after integration and are reported in Table 1, together with other crystallographic details. The crystal structure was solved by direct methods using SIR2004 (Burla et al. 2005), obtaining a satisfactory structural model for all independent non-H atoms. The structure was refined using the program CRYSTALS (Betteridge et al. 2003). Reflections with $I > 3\sigma(I)$ were considered suitable for the structure refinement, in which scattering curves for neutral chemical species were used. Refined parameters were scale factor, atom positions, cation oc-

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TABLE 1. Refined cell parameters, data collection and structure refinements details for metasideronatrite

Crystal dimensions (mm)	0.160 × 0.060 × 0.020
X-ray radiation/power	MoKα (l = 0.71073 Å)/50 kV, 30 mA
Temperature (K)	298
Crystal system	Orthorhombic
Space group	*Pbnm*
Unit-cell dimensions *a* (Å)	7.3959(8)
b (Å)	16.0979(15)
c (Å)	7.1607(8)
Volume (Å^3)	852.5(2)
θ range for data collection (°)	3–30.4
Index range	$-10 \le h \le 10$; $-22 \le k \le 22$; $-6 \le l \le 10$
Frame number/width/time	1340/0.5° in ω/30 s
Reflections collected/unique/	9985/1382/
R merging (R_{int}*) (%)	4.87
Reflections used	574 with $I > 3\sigma(I)$
No. of refined parameters	58
S†	0.856
R_1‡ (on *F*)/ wR_2^d (on F^2)	0.0388/0.0430
Completeness to θ = 30.4	98.6
Redundancy	6.50
$(\Delta/\sigma)_{max}$	0.001
$\Delta\rho_{min}/\Delta\rho_{max}$ (e/Å^3)	−0.45/+0.67

* $R_{int} = \Sigma |F_o^2 - F_o^2 \text{ (mean)}|/\Sigma[F_o^2]$; $R_{all} = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
† *S* = Goodness-of-fit = $\{\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)\}^{0.5}$, where *n* is the number of reflections and *p* is the total number of parameters refined.
‡ $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; d = $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

cupancies and isotropic atomic displacement factors. In the final refinement cycles, introduction of anisotropic displacement parameters for Fe and S reduced reliability indices to $R = 0.039$ and $R_W = 0.043$.

A difference-Fourier synthesis at this stage showed some peaks with significant density near two O atoms, labeled Oh and Ow, that were assigned as H atoms. Final atom coordinates and displacement parameters for all the non-H atoms are given in Table 2 and bond distances and angles in Table 3.

DESCRIPTION OF THE STRUCTURE

A complete view of the structure along [100] is shown in Figure 1. In terms of polyhedral linkage and general topology, the structure is made up of $[Fe^{3+}(SO_4)_2(OH)]^{2-}$ infinite chains, cross-linked by Na and H bonds. These chains, parallel to the *c* axis, consist of Fe^{3+} octahedra, with composition $[FeO_4(OH)_2]$, linked via *trans* (OH) vertices. Pairs of symmetrically independent $(S1O_4)^{2-}$ and $(S2O_4)^{2-}$ groups, mutually opposed with respect to the $[FeO_4(OH)_2]$ octahedra chain, bridge adjacent $[FeO_4(OH)_2]$ octahedra (hereafter Fe^{3+} octahedra) by corner-sharing, providing further intra-chain linkage to complete the main $[Fe^{3+}(SO_4)_2(OH)]^{2-}$ structural unit. Finally, Na atoms provide inter-chain linkage, as shown in Figures 1 and 2. Bond-valence calculations, discussed later in this section, clearly suggest that

TABLE 2. Atomic coordinates and atomic displacement parameters (Å^2) for metasideronatrite

Atom	*x*	*y*	*z*	$U_{iso/eqiv}$	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Fe	0.0000	0.0000	0.0000	0.014(1)	0.0138(5)	0.0181(6)	0.0092(5)	0.0001(6)	0.0006(7)	0.0006(6)
S1	0.9843(4)	0.1653(2)	0.75	0.016(1)	0.017(1)	0.016(1)	0.014(1)	0.0000	0.0000	0.001(1)
S2	0.6314(3)	0.0142(2)	0.25	0.014(1)	0.014(1)	0.018(1)	0.0102(9)	0.0000	0.0000	−0.000(1)
Na	0.5512(4)	0.1598(2)	0.5225(4)	0.028(2)	–	–	–	–	–	–
O1	0.7889(9)	0.1735(5)	0.75	0.027(2)	–	–	–	–	–	–
O2	0.0703(9)	0.2478(5)	0.75	0.021(2)	–	–	–	–	–	–
O3	0.0464(6)	0.1192(3)	0.9194(7)	0.018(1)	–	–	–	–	–	–
O4	0.7452(7)	0.0337(3)	0.4191(7)	0.019(1)	–	–	–	–	–	–
O5	0.4782(1)	0.0719(4)	0.25	0.019(2)	–	–	–	–	–	–
O6	0.4216(9)	0.0714(5)	0.75	0.022(2)	–	–	–	–	–	–
Oh	0.0953(9)	0.0286(4)	0.25	0.010(6)	–	–	–	–	–	–
Ow	0.4439(9)	0.2589(5)	0.75	0.030(2)	–	–	–	–	–	–

TABLE 3. Selected bond distances (Å) and angles (°) in metasideronatrite

Fe-Oh (×2)	1.978(3)	S1-O1	1.452(8)	S2-O4 (×2)	1.508(5)	Na-O1	2.406(6)
Fe-O3* (×2)	2.032(5)	S1-O2‡	1.472(8)	S2-O5	1.465(8)	Na-O2‖	2.458(5)
Fe-O4† (×2)	2.045(5)	S1-O3‡ (×2)	1.495(5)	S2-O6§	1.432(8)	Na-O4	2.593(6)
						Na-O5	2.470(5)
<Fe-O>	2.008	<S1-O>	1.479	<S2-O>	1.478	Na-O6	2.366(6)
						Na-Ow	2.415(7)
						<Na-O>	2.451
Oh-Fe-O3	88.7(2)	O1-S1-O2‡	110.4(5)	O4-S2-O4‡‡	106.9(4)	O2‖-Na-O4	102.4(2)
Oh-Fe-O3#	91.3(2)	O1-S1-O3‡	110.5(3)	O4-S2-O6§	110.7(3)	O1-Na-O4	82.0(2)
Oh-Fe-O4	90.6(2)	O2‡-S1-O3‡	108.4(3)	O4-S2-O5	107.4(3)	O2‖-Na-O5	74.5(2)
Oh-Fe-O4**	89.4(2)	O3‡-S1-O3††	108.5(4)	O5-S2-O6§	113.5(4)	O5-Na-O4	56.4(2)
O3-Fe-O4	90.8(2)					O1-Na-O6	83.4(2)
O3-Fe-O4**	89.2(2)					O6-Na-O4	87.1(2)
						O5-Na-O6	96.4(2)
						O2‖-Na-Ow	98.9(2)
						O1-Na-Ow	73.9(3)
						O5-Na-Ow	147.1(3)
						O6-Na-Ow	78.5(2)
						O2‖-Na-O1	116.1(3)

* = *x*, *y*, *z* − 1.
† = −1 + *x*, *y*, −*z* + 0.5.
‡ = *x* + 1, *y*, *z*.
§ = 1 − *x*, −*y*, *z* − 0.5.
‖ = 0.5 + *x*, 0.5 − *y*, 1 − *z*.
= −*x*, −*y*, 1 − *z*.
** = 1 − *x*, −*y*, *z* − 0.5.
†† = 1 + *x*, *y*, 1.5 − *z*.
‡‡ = *x*, *y*, *z* − 0.5.

Na is surrounded by five O atoms and one water molecule, resulting in a distorted octahedral geometry. The $NaO_5(H_2O)$ octahedra share alternately one face and one edge, forming columns parallel to the Fe-O-S chains (Fig. 3). Each $[Fe^{3+}(SO_4)_2(OH)]^{2-}$ chain is encircled by six columns of $NaO_5(H_2O)$ polyhedra, and each Na-column, in turn, is surrounded by three Fe-chains to form a three-dimensional network of Fe-O-S strong bonds and Na-O-Na

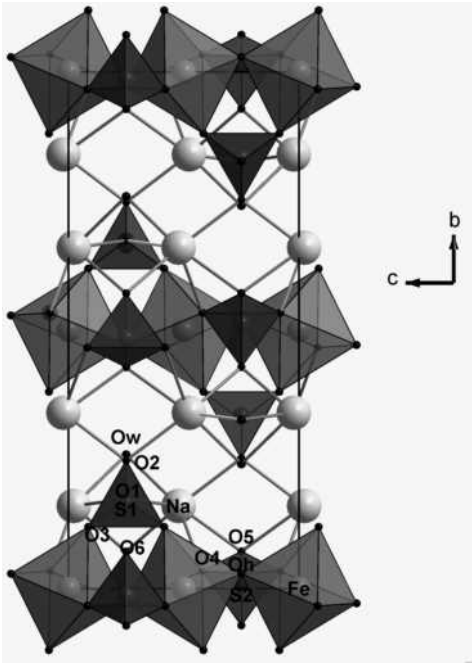

FIGURE 1. The metasideronatrite structure viewed down the **a** direction. $[Fe^{3+}(SO_4)_2OH)]^{2-}$ chains run parallel to **c** and are linked together by [6]-coordinate Na atoms.

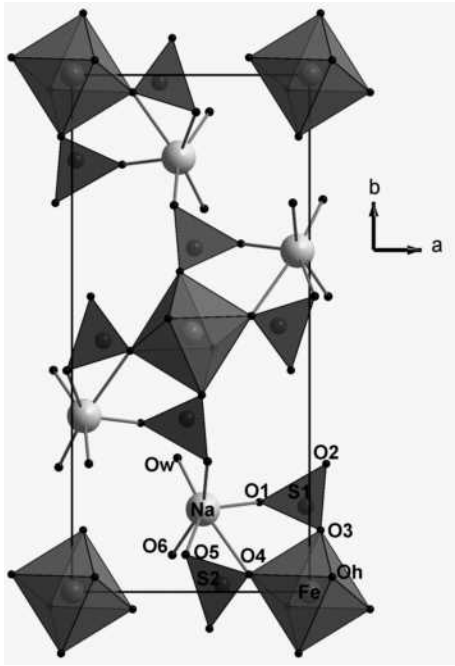

FIGURE 2. View of the metasideronatrite structure down the **c** direction. The $[Fe^{3+}(SO_4)_2OH)]^{2-}$ chains are shown end-on.

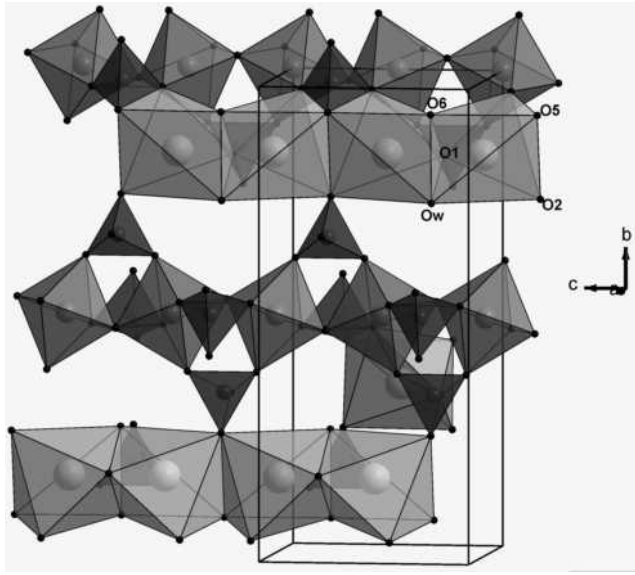

FIGURE 3. A view of the $Na_2Fe(SO_4)_2(OH)\cdot H_2O$ structure down the **a** direction, emphasizing the connections between Na octahedra (...edge-face-edge...).

weak bonds. The $[FeO_4(OH)_2]$ octahedron has point symmetry $\bar{1}$ and is nearly regular, with <Fe-O> = 2.008(4) Å. The $[S1O_4]^{2-}$ and $[S2O_4]^{2-}$ tetrahedra have point symmetry *m* and the usual variation in S-O bond lengths [from 1.432(8) to 1.508(5) Å] and angles [from 106.9(4) to 110.7(3)°]. The S-O distances depend on the type and number of cations sharing the sulfur ligands: S2 forms the two longer distances [S2-O4 = 1.508(5) Å] with the participating O atoms (O4 and its mirror-related O4′), which are shared with Fe and Na, while the S1 tetrahedron shares two symmetrically equivalent O3 and O3′ O atoms with distinct Fe octahedra [S1-O3 = 1.495(5) Å]. The shorter S-O bond distances involve the remaining tetrahedral O1, O2, O5, and O6 O atoms, shared with two mirror-related neighboring Na atoms. The distorted $[NaO_5(H_2O)]$ octahedron has <Na-O> = 2.451 Å, with individual distances ranging from 2.366(6) to 2.593(6) Å.

On the basis of the crystal chemistry and topology, sulfate minerals have been extensively reviewed and classified (Hawthorne et al. 2000). According to the classification of $^{VI}M^{IV}T_2\phi_n$ minerals, the metasideronatrite structure is built of $[M(TO_4)_2\phi]$ chains with ~7 Å period (Moore 1970), involving ^{VI}M and ^{IV}T high bond-valence-cation polyhedra and anion ϕ, cross-linked by large low-valence cations and hydrogen bonds. Metasideronatrite has the same structural unit topology as sideronatrite (Scordari and Ventruti 2009), i.e., the building block of composition $[Fe^{3+}(SO_4)_2(OH)]^{2-}$ that polymerizes via *trans* OH^- groups to form chains with a 7 Å repeat distance. From a topological point of view, metasideronatrite $[M(TO_4)_2\phi]$ chains are similar to those in sulfate minerals such as guildite (Wan et al. 1978), and in phosphate phases such as tancoite (Hawthorne 1983). The symmetry of these structures depends on the arrangement of the chains around the interchain cations balancing the charge on the chains. Hawthorne (1983) suggested consideration of these structures as derivatives of the *Acmm* tancoite-substructure, and metasideronatrite can be derived from tancoite with $[M(TO_4)_2(OH)]$ chains shifted alternately by 1/2**a**.

Hydrogen bonding

Bond-valence theory allows testing of the goodness of the structural model proposed, and can also distinguish O^{2-} from $(OH)^-$ and H_2O in the structure of inorganic compounds (Brown 2002; Schindler and Hawthorne 2001). To locate the H atoms, this last feature is particularly useful. The bond-valence incident at each oxygen ($\Sigma_c v$) was calculated according to Breese and O'Keeffe (1991) for all cations and anions of the metasideronatrite structure (Table 4). The results confirm that the O atoms labeled Oh and Ow are a hydroxyl group and a water molecule, respectively. Thus, the present study establishes unambiguously the chemical formula of metasideronatrite: $Na_2Fe(SO_4)_2(OH)\cdot H_2O$. This result settles the question of the water content of metasideronatrite (Bandy 1938; Césbron 1964; Finney 1973; Scordari and Milella 1982; Scordari et al. 1982), confirming the DTA and TGA results of Césbron (1964).

The O2, O3, and O5 anions show low-incident bond valence, and were designated as possible hydrogen-bond acceptors. There is a strong hydrogen bond from the $(OH)^-$ group to the corner (O5) of the S2 tetrahedron of an adjacent Fe-O-S chain, as observed also in sideronatrite (Scordari and Ventruti 2009). Inspection of the structure (Table 5) shows that possible hydrogen-bond acceptors in the vicinity of the water group Ow are O2 and O3. The difference-Fourier map shows a maximum of electron density between OH and O5 at about 1.0 Å from the hydroxyl oxygen. This value agrees reasonably well with the expected proton position (H1) directed toward O5. Two peaks of significant density far away ~0.92 Å (H2: 0.32, 0.26, 0.75) and ~0.71 Å (H3: 0.48, 0.30, 0.75) from the water molecule suggest one hydrogen bond toward O2, and one bifurcated hydrogen bond to two mirror-related O3 atoms (Fig. 4). The bond-valence sums incorporating these hydrogen bondings, calculated from the O···O distances as suggested by Ferraris and Ivaldi (1988) (Table 4), show satisfactory agreement with the valence-sum rule (Brown 2002).

Stability of the metasideronatrite and sideronatrite structures

As observed by Césbron (1964) and confirmed by us, the solid-state transformation from the OD-structure of sideronatrite to the ordered structure of metasideronatrite by dehydration occurs easily and reversibly, starting at about 35 °C, according to the following reaction:

$$Na_2Fe(SO_4)_2(OH)\cdot 3H_2O \leftrightarrow Na_2Fe(SO_4)_2(OH)\cdot H_2O + 2H_2O.$$

At normal conditions of relative humidity and temperature, metasideronatrite rehydrates quickly to sideronatrite. Comparison of the structures of metasideronatrite and sideronatrite (Scordari and Ventruti 2009) explains the easy transformation from sideronatrite to metasideronatrite, when sideronatrite is exposed to higher temperature, dehydrating agents, or low humidity, and vice versa. Hawthorne (1992, 1994) proposed a method based on the valence-matching principle (Brown 1981) to give an "a priori" estimate of the structural stability of any oxysalt mineral through the comparison of Lewis base strength of the structural unit and the Lewis acid strengths of the interstitial species. Sideronatrite and metasideronatrite are based on the same structural unit, $[Fe^{3+}SO_4)_2(OH)]^{2-}$, but involve different interstitial water contents, 3 H_2O and 1 H_2O, respectively. Following the guidelines of Hawthorne (1992) and taking into account the bonds from the interstitial species to complete the ideal coordination (CN = 3) of the O anions of the structural unit (see Table 6), the Lewis basicity of the structural unit, $[Fe^{3+}SO_4)_2(OH)]^{2-}$, is 0.18 v.u. Twelve additional bonds from the interstitial species must reach the structural unit to satisfy the requirement. One of these bonds is the hydrogen bond from the hydroxyl group to an adjacent structural unit. Thus, 11 essential bonds must be provided from the interstitial cations. We observe that in metasideronatrite, Na is surrounded by five O atoms and one water molecule. According to the procedure

TABLE 4. Bond valences for metasideronatrite, calculated from the curves of Breese and O'Keeffe (1991) and of Ferraris and Ivaldi (1988)

	O1	O2	O3	O3*	O4	O4†	O5	O6	Oh	Ow	Σ_c
Na	0.196	0.170			0.118		0.165	0.218		0.191	1.058
Na*	0.196	0.170				0.118	0.165	0.218		0.191	
Fe			0.478	0.478	0.462	0.462			0.553$^{(\times 2)}$		2.986
S1	1.592	1.508	1.417	1.417							5.934
S2					1.368	1.368	1.537	1.680			5.953
$\Sigma_a v$	1.984	1.848	1.895	1.895	1.948	1.948	1.867	2.116	1.106	0.382	
H1							0.15		0.85		1.000
H2			0.10	0.10						0.80	1.000
H3		0.20								0.80	1.000
Σ_{aH}	1.984	2.048	1.995	1.995	1.948	1.948	2.017	2.116	1.956	1.982	

Note: Symmetry code for equivalent positions: * = *x*, *y*, 1.5 – *z*; † = *x*, *y*, 0.5 – *z*.

TABLE 5. O···O distances (Å) and hydrogen bond strengths (v.u.)

	O··O (Å)	v.u.
Ow-O3*	3.19	0.10
Ow-O2	2.77	0.20
Oh-O5	2.92	0.15

Notes: In each pair of hydrogen bonded O atoms, the first one is the donor, the second one is the acceptor. Atom at: * = ½ + *x*, ½ – *y*, –0.5 + *z*.

TABLE 6. Lewis basicity of the structural unit, $[Fe^{3+}(SO_4)_2(OH)]^{2-}$, in metasideronatrite, sideronatrite, and guildite

Bonded atoms	Number of O^{2-}	Ideal coord. no. (CN)	Bonds needed for ideal CN
S^{6+}	4	3	2·4 = 8
$S^{6+}+Fe^{3+}$	4	3	1·4 = 4
$2Fe^{3+}+H^+$	1	3	0

Notes: Bonds needed to structural unit = 2·4 + 1·4 = 12. No. of H bonds to structural unit = 1. No. of additional bonds needed = 12 – 1 = 11. Charge on structural unit = 2^-. Lewis basicity of structural unit = 2/11 = 0.18 v.u.

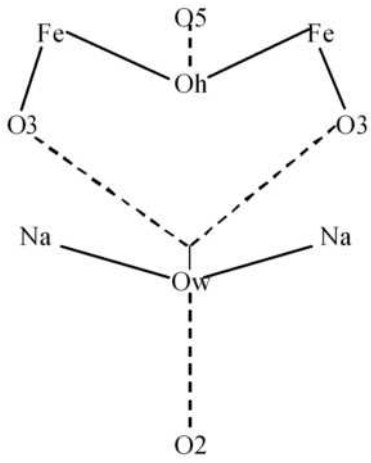

FIGURE 4. Sketch of the proposed hydrogen-bond system for metasideronatrite.

suggested by Hawthorne (1992), additional (H_2O) groups linked to the interstitial cation behave as a bond-valence transformer between the interstitial cation and the structural unit, moderating its Lewis acidity. Therefore, the presence of one H_2O in metasideronatrite lowers the Lewis acidity of the interstitial Na^+ cation from 0.16 to 0.14 v.u., violating the valence-matching principle. Sideronatrite differs from metasideronatrite by its higher water content, increasing further the gap between the Lewis acidity for interstitial Na^+ cation (~0.11 v.u.) and the basicity of the structural unit (0.18 v.u.). Thus the valence-matching principle should favor metasideronatrite to sideronatrite as far as stability is concerned.

Actually, the prediction in this case fails because sideronatrite is the more stable structure, whereas metasideronatrite, at standard conditions, quickly converts into sideronatrite. As emphasized by Hawthorne himself, erroneous predictions by this procedure are mainly due to deviations of the effective anion coordination numbers from the a priori assumed ideal value. Moreover, we observe that the way the interstitial polyedra are interconnected within the framework strongly affects the success of the method proposed by Hawthorne. In metasideronatrite, a striking feature of the structure is the Na octahedra sharing alternately one face (O1, O6, Ow) and one edge (O2, O5) to give rise to columns running along **c**. As a consequence of the Ow shared between two Na^+ cations, the acidity of the interstitial cation is substantially unchanged and close to the basicity of the structural unit (0.18 v.u.). In sideronatrite, the $[NaO_4(H_2O)_2]$ polyhedra are connected through edges with a common water molecule. Moreover, the three water groups participate in a more complicated hydrogen bonding system involving some proton bridging between two water molecules. This particular configuration does not increase the number of bonds between the cation and the structural unit, and so the acidity of the interstitial Na is almost the same as in metasideronatrite. As a consequence, both structures have similar stability behavior, explaining the easy phase transformation sideronatrite ↔ metasideronatrite. It is worthwhile to emphasize that in other cases, the straightforward application of the Hawthorne procedure works successfully. For example, guildite has the same structural unit, $[Fe^{3+}(SO_4)_2(OH)]^{2-}$, as sideronatrite and metasideronatrite and so the same Lewis basicity (0.18 v.u.). The interstitial cation in this mineral is Cu^{2+} and has the characteristic Lewis acidity strength of 0.39 v.u., apparently violating the valence-matching principle. However, the greater content of water in guildite compared to metasideronatrite is about the amount necessary to moderate the Lewis acidity of Cu^{2+} from 0.39 to 0.20 v.u., so that the valence-matching principle holds and guildite is a stable mineral. In guildite, isolated $[CuO_2(H_2O)_4]$ polyhedra form bridges between $[Fe^{3+}(SO_4)_2(OH)]^{2-}$ infinite chains, so in this case, water groups play an effective role as bond-valence transformers, moderating the Lewis acidity of the interstitial cation.

Another important feature is apparent from examination of the metasideronatrite structure. It is known, from Pauling's third rule, that the sharing of faces between coordination polyhedra reduces the stability of the structure. This connection between Na polyhedra is uncommon in the literature (Corazza et al. 1967). The Na-Na separation (3.27 Å) in metasideronatrite is significantly shorter than in sideronatrite, (3.56 Å), in which only octahedral edges are shared. The transformation of metasideronatrite to sideronatrite can be considered as starting from the breaking of such face-sharing connections. This same mechanism has been observed also in the reversible reaction tincalconite ↔ borax during the conversion process (Giacovazzo et al. 1973).

As described above, in metasideronatrite it is possible to identify the same structural unit present in sideronatrite. Thus, the relatively fast rate of this transition arises from the slight reorganization of the structure, which involves only the breaking and building of a few weak bonds involving Na, H, and O atoms. The removal of two water molecules, during the dehydration process of sideronatrite, induces the following structural changes in metasideronatrite: (1) alternate chains shift by **c**/4; (2) the separation distance between adjacent chains shortens (~2 Å) along the **b** direction; (3) shift of Na toward the mirror plane; and (4) disruption of the hydrogen-bond system of sideronatrite, and establishment of a more suitable system in the new structure, i.e., metasideronatrite.

Points 1 and 2 indicate that the corrugated sheet parallel to the **a-c** plane, present in sideronatrite, behaves as a rigid unit during the phase transition. The loss of two water molecules causes the reduction of the sheet separation along the **b** direction and the *b* cell parameter becomes shorter, whereas *a* and *c* remain constant. Owing to the **c**/4 shift between adjacent sheets, the OD character of sideronatrite is not preserved in the transformation. Sodium atoms approach the shared face involving O1, O6, and the water group, Ow, decreasing the Na1-Na2 distance (3.27 Å) with respect to the analogous distance in sideronatrite (3.56 Å). The consequence of points 2 and 3, is that in metasideronatrite, the Na atoms link the infinite Fe-O-S chains not only along the *x* direction, as in sideronatrite, but also along *y* direction, giving rise to a three-dimensional framework. Points 3 and 4 involve a reorganization of bonds from the interstitial atom and the hydrogen bonds to satisfy the bond-valence requirements of the structural unit.

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REFERENCES CITED

Bandy, M.C. (1938) Mineralogy of three sulfate deposits of Northern Chile. American Mineralogist, 23, 669–759.

Betteridge, P.W., Carruthers, J.R., Cooper, R.I., Prout, K., and Watkin, D.J. (2003) Crystals version 12: software for guided crystal structure analysis. Journal of Applied Crystallography, 36, 1487.

Blessing, R.H. (1995) An empirical correction for absorption anisotropy. Acta Crystallographica, A51, 33–38.

Breese, N.E. and O'Keeffe, M. (1991) Bond-valence parameters for solids. Acta Crystallographica, B47, 192–197.

Brown, I.D. (1981) The bond-valence method: An empirical approach to chemical bonding and structure. In M. O'Keefe and A. Navrotsky, Eds., Structure and Bonding in Crystals, 2, p. 1–30. Academic Press, New York.

——— (2002) The Chemical Bond in Inorganic Chemistry: The Bond Valence Model, 288 p. Oxford Scientific Publication, U.K.

Bruker (2001) SAINT. Bruker AXS Inc., Madison, Wisconsin.

——— (2003) APEX2. Bruker AXS Inc., Madison, Wisconsin.

Burla, M.C., Caliandro, R., Camalli, M., Carrozzini, B., Cascarano, G., De Caro, E., Giacovazzo, C., Polidori, G., and Spagna, R. (2005) SIR2004: An improved tool for crystal structure determination and refinement. Journal of Applied Crystallography, 38, 381–388.

Césbron, F. (1964) Contribution à la minéralogie des sulphates de fer hydratés. Bulletin Societe Francais de Mineralogie et Crystallographie, 87, 125–143.

Corazza, E., Sabelli, C., and Giuseppetti, G. (1967) The crystal structure of lecontite, $NaNH_4SO_4.2H_2O$. Acta Crystallographica, 22, 683–687.

Ferraris, G. and Ivaldi, G. (1988) Bond valence vs. bond length in O···O hydrogen bonds. Acta Crystallographica, B44, 341–344.

Finney, J.J. (1973) Unit cell and X-ray powder data for metasideronatrite. American Mineralogist, 58, 1080–1081.

Giacovazzo, C., Menchetti, S., and Scordari, F. (1973) The crystal structure of tincalconite. American Mineralogist, 58, 523–530.

Hawthorne, F.C. (1983) The crystal structure of tancoite. Tschermaks Mineralogische und Petrographische Mitteilungen, 31, 121–135.

——— (1992) The role of OH and H_2O in oxide and oxysalt minerals. Zeitschrift für Kristallographie, 201, 183–206.

——— (1994) Structural aspect of oxide and oxysalts crystals. Acta Crystallographica, B50, 481–510.

Hawthorne, F.C., Krivovichev, S.V., and Burns, P.C. (2000) The crystal chemistry of sulfate minerals. In C.N. Alpers, J.L. Jambor, and B.K. Nordstrom, Eds., Sulfate Minerals—Crystallography, Geochemistry, and Environmental Significance, 40, p. 1–112. Reviews in Mineralogy and Geochemistry, Mineralogical Society of America, Chantilly, Virginia.

Moore, P.B. (1970) Structural hierarchies among minerals containing octahedrally coordinating oxygen: I. Stereoisomerism among corner-sharing octahedral and tetrahedral chains. Neues Jahrbuch für Mineralogie, Monatshefte, 163–173.

Schindler, M. and Hawthorne, F.C. (2001) A bond-valence approach to the structure, chemistry and paragenesys of hydroxyl-hydrated oxysalt minerals. 1. Theory. The Canadian Mineralogist, 39, 1225–1242.

Scordari, F. and Milella, G. (1982) Metasideronatrite: A mixture of coexisting compounds. Neues Jahrbuch für Mineralogie, Monatshefte, 255–264.

Scordari, F. and Ventruti, G. (2009) Sideronatrite, $Na_2Fe(SO_4)_2(OH)\cdot 3H_2O$: Crystal structure of the orthorombic polytype and OD character analysis. American Mineralogist, 94, 1679–1686.

Scordari, F., Stasi, F., and Milella, G. (1982) Concerning metasideronatrite. Neues Jahrbuch für Mineralogie, Monatshefte, 341–347.

Sheldrick, G.M. (2003) XPREP. Bruker-Nonius AXS, Madison, Wisconsin.

——— (2004) SADABS. Program for Empirical Absorption Correction of Area Detector Data. University of Göttingen, Germany.

Wan, C., Ghose, S., Rossmann, G.R. (1978) Guildite, a layer with a ferric hydrous-sulfate chain and its optical absorption spectra. American Mineralogist, 63, 478–483.

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