

Article

The minerals of the kröhnkite supergroup: structural relations and chemical compositions

Frank C. Hawthorne 

Department of Earth Sciences, University of Manitoba, Winnipeg, MB, Canada

Abstract

The minerals of the kröhnkite, talmessite and fairfieldite groups plus dondoellite, general formula $X_2M^{2+}(TO_4)_2(H_2O)_2$ where $X = Na, Ca$; $M^{2+} = Mg, Fe, Mn, Co, Ni, Zn, Cu$; and $T = S, P, As$; have been consolidated into the IMA-approved kröhnkite supergroup. The cell dimensions and space-group symmetries of the minerals in these three groups and dondoellite are distinct but the structures of these minerals are strongly related as they have topologically identical structural units. Differences in structure between the different groups involve the disposition of adjacent $[M^{2+}(TO_4)_2(H_2O)_2]$ chains and the stereochemical details of the hydrogen bonds that link adjacent $[M^{2+}(TO_4)_2(H_2O)_2]$ chains. The ions that form the interstitial complex of a mineral and the structural unit must satisfy the *principle of correspondence of Lewis acidity–basicity* whereby stable structures will form where the Lewis acidity of the structural unit closely matches the Lewis basicity of the interstitial complex. For pentavalent T cations (P^{5+} or As^{5+}), the Lewis acidity of Ca^{2+} shows the closest match of all cations to the Lewis basicity of the structural unit. For hexavalent T cations (S^{6+}), the Lewis acidity of Na^+ shows the closest match of all cations to the Lewis basicity of the structural unit.

Keywords: kröhnkite supergroup; kröhnkite; talmessite and fairfieldite groups; structural relations; Lewis acidity–basicity; chemical composition

(Received 22 October 2024; revised 2 January 2025; accepted 3 January 2025; Accepted Manuscript published online: 21 January 2025)

Introduction

A mineral supergroup consists of *two or more* groups that have essentially the same structure and are composed of chemically similar elements (Mills *et al.*, 2009). The minerals of the kröhnkite, talmessite and fairfieldite groups have the general formula



where $X = Na$ or Ca ; $M^{2+} = Mg, Fe, Mn, Co, Ni, Zn$ or Cu ; and $T = S, P$ or As . There are currently 17 IMA-approved minerals in these three groups (Table 1) plus a single mineral, dondoellite, with a structure different from but related to the structures of the minerals of these three groups. The Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA–CNMNC) has approved the creation of the kröhnkite supergroup (Bosi *et al.*, 2024). The details of the minerals in the supergroup and their division into three groups are shown in Fig. 1. The currently named **kröhnkite**, **talnessite** and **fairfieldite** groups are retained, and belong to the **kröhnkite supergroup**. Dondoellite is an isolated structure within

the kröhnkite supergroup but cannot form a group until an isotopic mineral is approved whereupon a new group can be proposed.

Structure

All minerals in the kröhnkite supergroup are either monoclinic or triclinic. The cell dimensions and associated space-group symmetries of the minerals in these three groups and dondoellite are distinct (Table 2), but the structures of these minerals are strongly related as they have topologically identical structural units (Lima-de-Faria *et al.*, 1990) that define the c-dimension of each group (Fig. 2). The structural unit is an $[M(TO_4)_2\Phi_2]$ chain (Hawthorne, 1985) as shown idealised in Fig. 2a and as in the structure of brandtite in Fig. 2b. As noted by Hawthorne (1983), the linkage between polyhedra in Fig. 2 maximises the accord with the valence-sum rule (Brown, 2016; Hawthorne, 2012, 2015) for linkage of isolated octahedra and isolated tetrahedra into a chain without octahedron–octahedron or tetrahedron–tetrahedron linkages.

Differences in structure between the different groups involve the disposition of adjacent $[M^{2+}(TO_4)_2(H_2O)_2]$ chains and the details of the hydrogen bonds that link adjacent $[M^{2+}(TO_4)_2(H_2O)_2]$ chains. As indicated by the red arrows in Fig. 3, in the structures of the kröhnkite-group minerals (Fig. 3a), the octahedra of the structural units point alternately

Email: frank.hawthorne@umanitoba.ca

Associate Editor: Anthony R. Kampf

This paper is part of a collection in tribute to the work of Edward Grew at 80

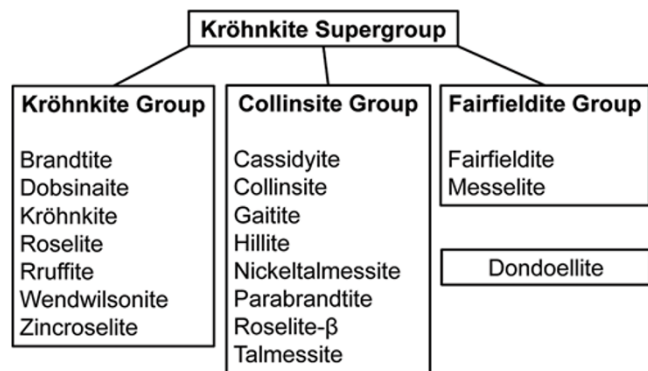
Cite this article: Hawthorne F.C. (2025) The minerals of the kröhnkite supergroup: structural relations and chemical compositions. *Mineralogical Magazine*, 1–5. <https://doi.org/10.1180/mgm.2025.2>

Table 1. Minerals of the kröhnkite supergroup

Name	End-member formula	Reference
Kröhnkite group		
Brandtite	$\text{Ca}_2[\text{Mn}^{2+}(\text{PO}_4)_2(\text{H}_2\text{O})_2]$	(1)
Dobšinaitite	$\text{Ca}_2[\text{Ca}(\text{AsO}_4)_2(\text{H}_2\text{O})_2]$	(2)
Kröhnkite	$\text{Na}_2[\text{Cu}^{2+}(\text{SO}_4)_2(\text{H}_2\text{O})_2]$	(3)
Roselite	$\text{Ca}_2[\text{Co}^{2+}(\text{PO}_4)_2(\text{H}_2\text{O})_2]$	(4)
Ruffite	$\text{Ca}_2[\text{Cu}^{2+}(\text{AsO}_4)_2(\text{H}_2\text{O})_2]$	(5)
Wendwilsonite	$\text{Ca}_2[\text{Mg}(\text{AsO}_4)_2(\text{H}_2\text{O})_2]$	(6)
Zincroselite	$\text{Ca}_2[\text{Zn}(\text{AsO}_4)_2(\text{H}_2\text{O})_2]$	(7)
Talmessite group		
Cassidyite	$\text{Ca}_2[\text{Ni}^{2+}(\text{PO}_4)_2(\text{H}_2\text{O})_2]$	(8)
Collinsite	$\text{Ca}_2[\text{Mg}(\text{PO}_4)_2(\text{H}_2\text{O})_2]$	(9)
Gaitite	$\text{Ca}_2[\text{Zn}(\text{AsO}_4)_2(\text{H}_2\text{O})_2]$	(6)
Hillite	$\text{Ca}_2[\text{Zn}(\text{PO}_4)_2(\text{H}_2\text{O})_2]$	(10)
Nickeltalmessite	$\text{Ca}_2[\text{Ni}^{2+}(\text{AsO}_4)_2(\text{H}_2\text{O})_2]$	(11)
Parabrandtite	$\text{Ca}_2[\text{Mn}^{2+}(\text{PO}_4)_2(\text{H}_2\text{O})_2]$	(12)
Roselite-β	$\text{Ca}_2[\text{Co}^{2+}(\text{PO}_4)_2(\text{H}_2\text{O})_2]$	(13)
Talmessite	$\text{Ca}_2[\text{Mg}(\text{AsO}_4)_2(\text{H}_2\text{O})_2]$	(14)
Fairfieldite group		
Fairfieldite	$\text{Ca}_2[\text{Mn}^{2+}(\text{PO}_4)_2(\text{H}_2\text{O})_2]$	(15)
Messelite	$\text{Ca}_2[\text{Fe}^{2+}(\text{PO}_4)_2(\text{H}_2\text{O})_2]$	(16)
Dondoellite*	$\text{Ca}_2[\text{Fe}^{2+}(\text{PO}_4)_2(\text{H}_2\text{O})_2]$	(17)

*Dondoellite falls within the kröhnkite supergroup but not within the kröhnkite, talmessite and fairfieldite groups; it does not (as yet) have any isostructural minerals and hence cannot form a group, but it is likely that this will happen in due course.

References: (1) Dahlman (1951); (2) Sejkora *et al.* (2021); (3) Hawthorne and Ferguson (1975); (4) Hawthorne and Ferguson (1977); (5) Yang *et al.* (2011); (6) Kolitsch and Fleck (2006); (7) Keller *et al.* (2004); (8) White *et al.* (1967); (9) Brotherton *et al.* (1974); (10) Yakubovich *et al.* (2003); (11) Chukanov *et al.* (2020); (12) Dunn *et al.* (1987); (13) Frondel (1955); (14) Catti *et al.* (1977); (15) Fanfani *et al.* (1970); (16) Fleck and Kolitsch (2003); (17) Yang *et al.* (2022).

**Figure 1.** The classification of the minerals of the kröhnkite supergroup.

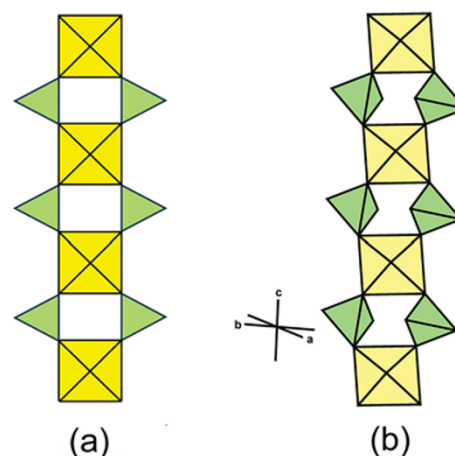
northeast and northwest in adjacent chains; in the structures of the talmessite-group minerals (Fig. 3b), the octahedra of the structural units point southwest in adjacent chains; in the structures of the fairfieldite-group minerals (Fig. 3c), the octahedra of the structural units point northeast in adjacent chains; and in the structure of dondoellite (Fig. 3d), the octahedra of the structural units point southwest in adjacent chains.

In the structures of the minerals of all groups, one H atom of the (H₂O) group hydrogen-bonds to a (TO₄) oxygen of the same chain and the other H atom of the (H₂O) group hydrogen-bonds to a (TO₄) oxygen of an adjacent chain. As indicated in Fig. 3a, in the kröhnkite-group structures, only two chains are involved in this mutual linkage of opposing (H₂O) groups. In the collinsite-group

Table 2. Crystallographic properties of kröhnkite, brandtite, collinsite, fairfieldite and dondoellite

	Kröhnkite	Brandtite	Talmessite	Fairfieldite	Dondoellite
<i>a</i> (Å)	5.807(1)	5.877(1)	5.874(7)	5.795(1)	5.4830(2)
<i>b</i> (Å)	12.656(2)	12.957(2)	6.943(11)	6.576(1)	5.7431(2)
<i>c</i> (Å)	5.517(1)	5.675(1)	5.537(6)	5.496(1)	13.0107(5)
α (°)	90	90	97.3(1)	102.39(3)	98.772(2)
β (°)	108.32(1)	108.00(3)	108.7(1)	108.63(3)	96.209(2)
γ (°)	90	90	108.1(2)	90.29(3)	108.452(2)
<i>V</i> (Å ³)	384	411.05	196.76	193.25	378.71(2)
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>Z</i>	2	2	1	1	2
Reference*	(1)	(2)	(3)	(2)	(4)

*References: (1) Hawthorne and Ferguson (1975); (2) Herwig and Hawthorne (2006); (3) Catti *et al.* (1977); (4) Yang *et al.* (2022).

**Figure 2.** The [M(TO₄)₂Φ₂] chain (Φ = unspecified anion) that forms the structural unit in the minerals of the kröhnkite supergroup; (a) the generalized chain (modified from Hawthorne, 1985); and (b) the [Mn²⁺(PO₄)₂(H₂O)₂] chain in brandtite. Drawn using ATOMS V6.4 (Dowty, 2016).

structures, the fairfieldite-group structures, and in dondoellite, four chains are involved in this mutual linkage of opposing (H₂O) groups (Fig. 3b,c,d).

There is no apparent sorting of structure type by cation radii and there are several compositions that occur as polymorphs that belong to different groups: brandtite–parabrandtite–fairfieldite; roselite–roselite-β; wendwilsonite–talmessite; zincroselite–gaitite; and messelite–dondoellite.

The bond-valence tables for kröhnkite and brandtite are shown in Tables 3 and 4, respectively. The bond topology of the two structures is the same and hence they have a similar pattern of bond valences. The coordination numbers of the anions, omitting the hydrogen bonds, is the same: O(1) = [3], O(2) = [4], O(3) = [2], O(4) = [3], OW = [2], and an unusual feature of each structure is the fact that the OW (H₂O) group has significant incident bond-valence: 0.667 and 0.660 valence units (vu) and hence the associated hydrogen bonds are stronger than usual for bonded (H₂O) groups in minerals. These strong hydrogen bonds compensate for the variation in coordination number of the anions and ensure that the valence-matching principle is satisfied (Tables 3 and 4). The incident bond-valence at the OW (H₂O) group is the same in both kröhnkite and brandtite (~0.67 vu) and yet

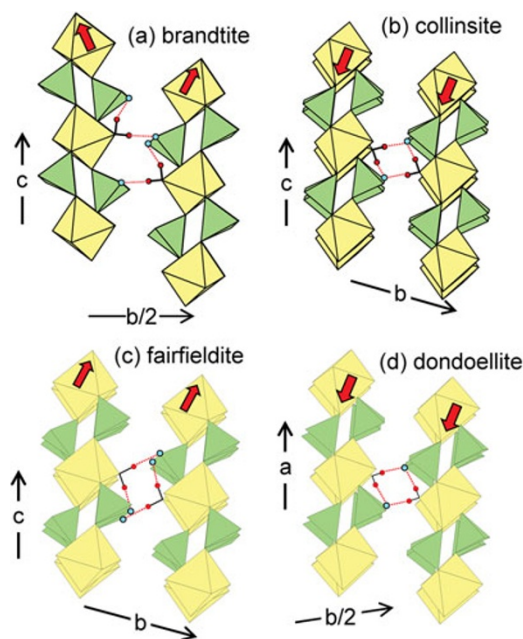


Figure 3. The crystal structures of (a) brandtite; (b) collinsite; (c) fairfieldite; and (d) dondoellite, projected onto (100). *M* octahedra are yellow, *T* tetrahedra are green, and H are small red circles; solid black lines: $O_{\text{donor}}\text{--H}$ bonds; red dotted lines: hydrogen bonds; small blue circles: O_{acceptor} anions. The red arrows show the relative attitude of octahedra in adjacent chains. Drawn using ATOMS V6.4 (Dowty, 2016).

Table 3. Bond-valence (vu) table* for kröhnkite**

	Na	Cu^{2+}	S	H(1)	H(2)	Σ
O(1)	0.161	0.444 ^{x21}	1.385			1.990
O(2)	0.155	0.112 ^{x21}	1.490			1.878
	0.121					
O(3)	0.115		1.527	0.333		1.975
O(4)	0.147		1.475		0.333	1.090
	0.135					
OW	0.173	0.494 ^{x21}		0.667	0.667	2.001
Σ	1.007	2.100	5.877			

*Bond-valence curves from Gagné and Hawthorne (2015);

**O(1) and O(3) have been interchanged to make the site labels consistent in kröhnkite and brandtite.

the oxidation states of the coordinating cations are 1^+ and 2^+ in kröhnkite and 2^+ and 2^+ in brandtite; how can the same incident bond-valence be maintained in these two minerals? The key to this issue is the fact that the divalent cation in kröhnkite is Cu^{2+} . Octahedrally coordinated Cu^{2+} is Jahn-Teller active (Burns and Hawthorne, 1996) and typically shows four short meridional bonds and two long apical bonds (Eby and Hawthorne, 1993; Gagné and Hawthorne, 2020). This is the case in kröhnkite. As the OW (H_2O) group in kröhnkite is a meridional anion, it has a very strong bond incident from Cu^{2+} which compensates for the weaker Na–OW bond in kröhnkite (Table 3) compared to the stronger Ca–OW bond in brandtite (Table 4). This accounts for the absence of mineral compositions with the general formula $\text{Na}_2^{[6]}\text{M}^{2+}(\text{SO}_4)_2(\text{H}_2\text{O})_2$ other than kröhnkite with $\text{M}^{2+} = \text{Cu}^{2+}$.

Table 4. Bond-valence (vu) table* for brandtite

	Ca	Mn^{2+}	As^{5+}	H(1)	H(2)	Σ
O(1)	0.275	0.385 ^{x21}	1.217			1.948
	0.071					
O(2)	0.241	0.290 ^{x21}	1.217			1.964
	0.216					
O(3)	0.319		1.266	0.335		1.920
O(4)	0.222		1.255		0.335	2.075
	0.263					
OW	0.290	0.380 ^{x21}		0.665	0.665	2.000
Σ	1.897	2.110	4.955			

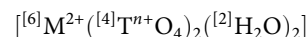
*Bond-valence curves from Gagné and Hawthorne (2015).

Controls on chemical composition in kröhnkite-supergroup structures

The general formula for the kröhnkite-supergroup minerals is $\text{X}_2\text{M}^{2+}(\text{TO}_4)_2(\text{H}_2\text{O})_2$. What ions are possible in this topological structure-type at the various sites in the structure? Inspection of Table 1 shows that $\text{X} = \text{Na}^+$ or Ca^{2+} ; $\text{M}^{2+} = \text{Mg}$, Fe, Mn, Co, Ni, Zn or Cu; and $\text{T} = \text{S}^{6+}$, P^{5+} and As^{5+} . What other ions can feasibly enter a crystal structure with the kröhnkite bond topology? In regard to this question, there has been considerable work on synthetic analogues of these minerals (e.g. Fleck *et al.*, 2002; Fleck and Kolitsch, 2003; Kolitsch and Fleck, 2005, 2006; Wildner and Stoilova, 2003) as they show potential for industrial applications.

To approach this question, we use *binary representation* (Schindler and Hawthorne, 2001; Hawthorne and Schindler, 2008) whereby a structure is divided into a structural unit and an *interstitial complex*. The ions that form the interstitial complex of a mineral and the structural unit must satisfy the *principle of correspondence of Lewis acidity–basicity* (Hawthorne, 2012, 2015; Hawthorne and Schindler, 2008), a mean-field version of the valence-matching principle (Brown, 1981; Hawthorne, 1994) whereby stable structures will form when the Lewis acid strength of the cation closely matches the Lewis base strength of the anion. Thus an ion may enter a structure with the kröhnkite bond topology if the resultant structure accords with the principle of correspondence of Lewis acidity–basicity.

The structural unit with the kröhnkite bond topology may be written as follows:



The number of bonds in the structural unit = $1 \times [6] + 2 \times [4] + 4 \times [2] = 22$. Note that although two of the hydrogen bonds exit the structural unit, they bond to anions in adjacent structural units and the two exident hydrogen-bonds are balanced by the two incident hydrogen-bonds from adjacent structural units. The number of bonds needed for [4]-coordination of all simple anions and [3]-coordination of (H_2O) = $8 \times [4] \times 2 \times [3] = 38$. The number of additional bonds to the structural unit to achieve this coordination = $38 - 22 = 16$ and hence the structural unit needs 16 bonds from the interstitial complex.

The charge on the structural unit $[^{[6]}\text{M}^{2+}(^{[4]}\text{T}^{n+}\text{O}_4)_2(^{[2]}\text{H}_2\text{O})_2] = 2^+ + 2 \times n^+ + 4 \times 1^+ - 2^- \times 10 = 6 + 2n - 20 = 2n - 14$. The Lewis basicity of the structural unit = charge/bonds = $(2n - 14)/14$ vu.

For $n = 5^+$ (P^{5+} , As^{5+}), the Lewis basicity of the structural unit = $4/16 = 0.250$ vu. The Lewis basicity of $\text{Ca}^{2+} = 0.264$ vu (Gagné

and Hawthorne, 2017) is the closest match with the Lewis basicity of the structural unit containing pentavalent cations. The Lewis basicity of $\text{Pb}^{2+} = 0.266$ vu but no Pb-bearing species occur; this may be a steric effect due to the large size of $^{[8]}\text{Pb}^{2+}$ (2.697 Å) compared to that of $^{[8]}\text{Ca}^{2+}$ (2.498 Å) (values from Hawthorne and Gagné, 2024).

For $n = 6^+$ (S^{6+}), the Lewis basicity of the structural unit = $2/16 = 0.125$ vu. The Lewis basicity of Na^+ is 0.159 vu but the coordination of Na^+ in kröhnkite is [7] (Table 3) which reduces the effective Lewis acidity to $1/7 = 0.143$ vu. The Lewis basicity of K^+ is 0.108 vu (Gagné and Hawthorne, 2017). K-bearing kröhnkite-super group minerals have not been found but K-bearing synthetics have been synthesised with a view to their use in alkali-metal batteries (e.g. Barpanda *et al.*, 2014; Marinova *et al.*, 2015; Watcharatharapong *et al.*, 2017) and various possible optical applications (e.g. de Oliveira Neto *et al.*, 2022).

Acknowledgements. I thank Aaron Lussier and two anonymous reviewers for their comments on this paper.

Financial statement: This work was supported by a Discovery Grant from the Natural Sciences and Engineering Research Council of Canada.

Competing interests. The author declares none.

References.

- Barpanda P., Oyama G., Ling C.D. and Yamada A. (2014) Krohnkite-type $\text{Na}_2\text{Fe}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ as a novel 3.25 V insertion compound for Na-ion batteries. *Chemistry of Materials*, **26**, 1297–1299.
- Bosi F., Hatert F., Pasero M. and Mills S.J. (2024) IMA Commission on New Minerals, Nomenclature and Classification (CNMNC) – Newsletter 80. *European Journal of Mineralogy*, **36**, 599–604.
- Brotherton P.D., Maslen E.N., Pryce M.W. and White A.H. (1974) Crystal structure of collinsite. *Australian Journal of Chemistry*, **27**, 653–656.
- Brown I.D. (1981) The bond-valence method: an empirical approach to chemical structure and Bonding. pp. 1–30 in: *Structure and Bonding in Crystals II* (M. O'Keeffe and A. Navrotsky, editors). Academic Press, New York.
- Brown I.D. (2016) *The Chemical Bond in Inorganic Chemistry: The Bond Valence Model*. Oxford University Press, UK.
- Burns P.C. and Hawthorne F.C. (1996) Static and dynamic Jahn-Teller effects in Cu^{2+} -oxysalt minerals. *The Canadian Mineralogist*, **34**, 1089–1105.
- Catti M., Ferraris G. and Ivaldi G. (1977) Hydrogen bonding in the crystalline state. Structure of talnessite, $\text{Ca}_2(\text{Mg},\text{Co})(\text{AsO}_4)_2 \cdot 2(\text{H}_2\text{O})$, and the crystal chemistry of related minerals. *Bulletin de la Société Française de Minéralogie et de Cristallographie*, **100**, 230–236.
- Chukanov N.V., Mukhanov A.A., Möckel S., Belakovskiy D.I. and Levitskaya L.A. (2020) Nickeltalnessite, $\text{Ca}_2\text{Ni}(\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}$, a new mineral species of the fairfieldite group, Bou Azzer, Morocco. *Geology of Ore Deposits*, **52**, 606–611.
- Dahlman B. (1951) The crystal structures of kröhnkite, $\text{CuNa}_2(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ and brandtite, $\text{MnCa}_2(\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}$. *Arkiv för Mineralogi och Geologi*, **1**, 339–366.
- de Oliveira Neto J.G., Lang R., Rodrigues J.A.O., Gutiérrez C.E.O., Murillo M.A.R., de Sousa F.F., Filho J.G.S. and dos Santos A.O. (2022) Kröhnkite-type $\text{K}_2\text{Mn}(\text{SO}_4)_2(\text{H}_2\text{O})_2$ double salt: synthesis, structure, and properties. *Journal of Materials Science*, **57**, 8195–8210.
- Dowty E. (2016) *ATOMS (Version 6.5.0)*. Shape Software, Kingsport, Tennessee, USA.
- Dunn P.J., Sturman D.B. and Nelen J.A. (1987) Wendwilsonite, the Mg analogue of roselite, from Morocco, New Jersey, and Mexico, and new data on roselite. *American Mineralogist*, **72**, 217–221.
- Eby R.K. and Hawthorne F.C. (1993) Structural relations in copper oxysalt minerals. I. Structural hierarchy. *Acta Crystallographica*, **B49**, 28–56.
- Fanfani L., Nunzi A. and Zanazzi P.F. (1970) The crystal structure of fairfieldite. *Acta Crystallographica*, **B26**, 640–645.
- Fleck M. and Kolitsch U. (2003) Natural and synthetic compounds with kröhnkite-type chains. An update. *Zeitschrift für Kristallographie*, **218**, 553–567.
- Fleck M., Kolitsch U. and Hertweck B. (2002) Natural and synthetic compounds with kröhnkite-type chains: an update. *Zeitschrift für Kristallographie*, **217**, 435–443.
- Fronzel C. (1955) Neomesselite and beta-roselite: two new members of the fairfieldite group. *American Mineralogist*, **40**, 828–833.
- Gagné O.C. and Hawthorne F.C. (2015) Comprehensive derivation of bond-valence parameters for ion pairs involving oxygen. *Acta Crystallographica*, **B71**, 562–578.
- Gagné O.C. and Hawthorne F.C. (2017) Empirical Lewis-acid strengths for 135 cations bonded to oxygen. *Acta Crystallographica*, **B73**, 956–961.
- Gagné O.C. and Hawthorne F.C. (2020) Bond-length distributions for ions bonded to oxygen: Results for the transition metals and quantification of the factors underlying bond-length variation in inorganic solids. *IUCr*, **7**, 581–629.
- Hawthorne F.C. (1983) Graphical enumeration of polyhedral clusters. *Acta Crystallographica*, **A39**, 724–736.
- Hawthorne F.C. (1985) Towards a structural classification of minerals: The $^{VI}\text{M}^{IV}\text{T}_2\Phi_n$ minerals. *American Mineralogist*, **70**, 455–473.
- Hawthorne F.C. (1994) Structural aspects of oxides and oxysalt crystals. *Acta Crystallographica*, **B50**, 481–510.
- Hawthorne F.C. (2012) A bond-topological approach to theoretical mineralogy: crystal structure, chemical composition and chemical reactions. *Physics and Chemistry of Minerals*, **39**, 841–874.
- Hawthorne F.C. (2015) Toward theoretical mineralogy: a bond-topological approach. *American Mineralogist*, **100**, 696–713.
- Hawthorne F.C. and Ferguson R.B. (1975) Refinement of the crystal structure of kröhnkite. *Acta Crystallographica*, **B31**, 1753–1755.
- Hawthorne F.C. and Ferguson R.B. (1977) The crystal structure of roselite. *The Canadian Mineralogist*, **15**, 36–42.
- Hawthorne F.C. and Gagné O.C. (2024) New ion radii for oxides and oxysalts, fluorides, chlorides and nitrides. *Acta Crystallographica*, **B80**, 326–339.
- Hawthorne F.C. and Schindler M. (2008) Understanding the weakly bonded constituents in oxysalt minerals. *Zeitschrift für Kristallographie*, **223**, 41–68.
- Herwig S. and Hawthorne F.C. (2006) The topology of hydrogen bonding in minerals of the brandtite, collinsite and fairfieldite groups. *The Canadian Mineralogist*, **44**, 1181–1196.
- Keller P., Lissner F. and Schleid T. (2004) The crystal structures of zincroselite and gaitite: Two natural polymorphs of $\text{Ca}_2\text{Zn}[\text{AsO}_4]_2 \cdot 2\text{H}_2\text{O}$ from Tsumeb, Namibia. *European Journal of Mineralogy*, **16**, 353–359.
- Kolitsch U. and Fleck M. (2005) Second update on compounds with kröhnkite-type chains. *Zeitschrift für Kristallographie*, **220**, 31–41.
- Kolitsch U. and Fleck M. (2006) Third update on compounds with kröhnkite-type chains: the crystal structure of wendwilsonite [$\text{Ca}_2\text{Mg}(\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}$] and the new triclinic structure types of synthetic $\text{AgSc}(\text{CrO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{M}_2\text{Cu}(\text{Cr}_2\text{O}_7)_2 \cdot 2\text{H}_2\text{O}$ (M = Rb, Cs). *European Journal of Mineralogy*, **18**, 471–482.
- Lima-de-Faria J., Hellner E., Liebau F., Makovicky E. and Parthé E. (1990) Nomenclature of Inorganic Structure Types. Report of the International Union of Crystallography Commission on Crystallographic Nomenclature Subcommittee on the Nomenclature of Inorganic Structure Types. *Acta Crystallographica*, **A46**, 1–11.
- Marinova D., Kostov V., Nikolova R., Kukeva R., Zhecheva E., Sendova-Vasileva M., Stoyanova R. (2015) From kröhnkite- to alluaudite-type of structure: novel method of synthesis of sodium manganese sulfates with electrochemical properties in alkali-metal ion batteries. *Journal of Materials Chemistry*, **3A**, 22287–22299.
- Mills S.J., Hatert F., Nickel E.H. and Ferraris G. (2009) The standardisation of mineral group hierarchies: application to recent nomenclature proposals. *European Journal of Mineralogy*, **21**, 1073–1080.
- Schindler M. and Hawthorne F.C. (2001) A bond-valence approach to the structure, chemistry and paragenesis of hydroxy-hydrated oxysalt minerals: I. Theory. *The Canadian Mineralogist*, **39**, 1225–1242.

- Sejkora J., Števko M., Škoda R., Višková E., Toman J., Hreus S., Plášil J. and Dolníček Z. (2021) Dobšináite, $\text{Ca}_2\text{Ca}(\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}$, a new member of the roselite group from Dobšiná (Slovak Republic). *Journal of Geosciences*, **66**, 127–135.
- Watcharatharapong T., Thienprasert J., Barpanda P., Ahuja R. and Chakraborty S. (2017) Mechanistic study of Na-ion diffusion and small polaron formation in kröhnkite $\text{Na}_2\text{Fe}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ based cathode materials. *Journal of Materials Chemistry*, **A5**, 21726–21739.
- White J.S. Jr., Henderson E.P. and Mason B. (1967) Secondary minerals produced by weathering of the Wolf Creek meteorite. *American Mineralogist*, **52**, 1190–1197.
- Wildner M. and Stoilova D. (2003) Crystal structures and crystal chemical relationships of kröhnkite- and collinsite-type compounds $\text{Na}_2\text{Me}^{2+}(\text{XO}_4)_2 \cdot 2\text{H}_2\text{O}$ ($\text{X} = \text{S}$, $\text{Me} = \text{Mn}$, Cd ; and $\text{X} = \text{Se}$, $\text{Me} = \text{Mn}$, Co , Ni , Zn , Cd) and $\text{K}_2\text{Co}(\text{SeO}_4)_2 \cdot 2\text{H}_2\text{O}$. *Zeitschrift für Kristallographie*, **218**, 201–209.
- Yakubovich O.V., Massa W., Liferovich R.P., Gavrilenko P.G., Bogdanova A.N. and Tuisku P. (2003) Hillite, a new member of the fairfieldite group: its description and crystal structure. *The Canadian Mineralogist*, **41**, 981–988.
- Yang H., Jenkins R.A., Downs R.T. and Evans S.H. (2011) Ruffite, $\text{Ca}_2\text{Cu}(\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}$, a new member of the roselite group, from Tierra Amarilla, Chile. *The Canadian Mineralogist*, **49**, 877–884.
- Yang H., Gibbs R.B., Mcglasson J.A., Jenkins R.A. and Downs R.T. (2022) Dondoelite, $\text{Ca}_2\text{Fe}(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$, a new mineral species polymorphic with messelite, from Rapid Creek, Yukon, Canada. *The Canadian Mineralogist*, **60**, 837–847.