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

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Running title: Minerals of the kröhnkite supergroup

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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+}, 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.

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Keywords: Kröhnkite supergroup, kröhnkite, talmessite and fairfieldite groups, structural relations, Lewis acidity-basicity, chemical composition.

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, Ca; M^{2+} = Mg, Fe, Mn, Co, Ni, Zn, Cu; and T = S, P, 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 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**, **talmessite** 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 idealized 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 maximizes 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 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 structures, the fairfieldite-group structures, and in dondoellite, four chains are involved in this mutual linkage of opposing (H₂O) groups (Figs. 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; messelite-dondoellite.

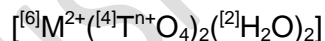
The bond-valence tables for kröhnkite and brandtite are shown in Table 3. The bond topology of the two structures is the same and hence they have a similar pattern of bond valences. The coordination numbers of the anions, omitting the hydrogen bonds, is the same: O(1) = [3], O(2) = [4], O(3) = [2], O(4) = [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 *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 (Table 3). The incident bond-valence at the OW (H₂O) group is the same in both kröhnkite and brandtite (~0.67 *vu*) and yet 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 divalence cation in kröhnkite is Cu²⁺. Octahedrally coordinated Cu²⁺ 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 (H₂O) group in kröhnkite is a meridional anion, it has a very strong bond incident from Cu²⁺ which compensates for the weaker Na–OW bond in kröhnkite (Table 3a) compared to the stronger Ca–OW bond in brandtite (Table 3b). This accounts for the absence of mineral compositions with the general formula Na₂^[6]M²⁺(SO₄)₂(H₂O)₂ other than kröhnkite with M²⁺ = Cu²⁺.

Controls on chemical composition in kröhnkite-supergroup structures

The general formula for the kröhnkite-supergroup minerals is $X_2M^{2+}(TO_4)_2(H_2O)_2$. What ions are possible in this topological structure-type at the various sites in the structure? Inspection of Table 1 shows that $X = Na^+, Ca^{2+}$; $M^{2+} = Mg, Fe, Mn, Co, Ni, Zn, Cu$; and $T = S^{6+}, P^{5+}$ 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 $[{}^{[6]}M^{2+}({}^{[4]}T^{n+}O_4)_2({}^{[2]}H_2O)_2] = 2^+ + 2 \times n^+ + 4 \times 1^- - 2^- \times 10 = 6 + 2n - 20 = 2n - 14$. 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 $Ca^{2+} = 0.264$ *vu* (Gagné and Hawthorne, 2017) is the closest match with the Lewis basicity of the structural unit containing pentavalent cations. The Lewis basicity of $Pb^{2+} = 0.266$ *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 = $2 / 16 = 0.125 \text{ vu}$. The Lewis basicity of Na^+ is 0.159 *vu* but the coordination of Na^+ in kröhnkite is [7] (Table 3a) which reduces the effective Lewis acidity to $1/7 = 0.143 \text{ vu}$. The Lewis basicity of K^+ is 0.108 *vu* (Gagné and Hawthorne, 2017). K-bearing kröhnkite-supergroup minerals have not been found but K-bearing synthetics have been synthesized 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).

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Competing interests. The author declares none.

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Figure captions

Fig. 1. The classification of the minerals of the kröhnkite supergroup.

1

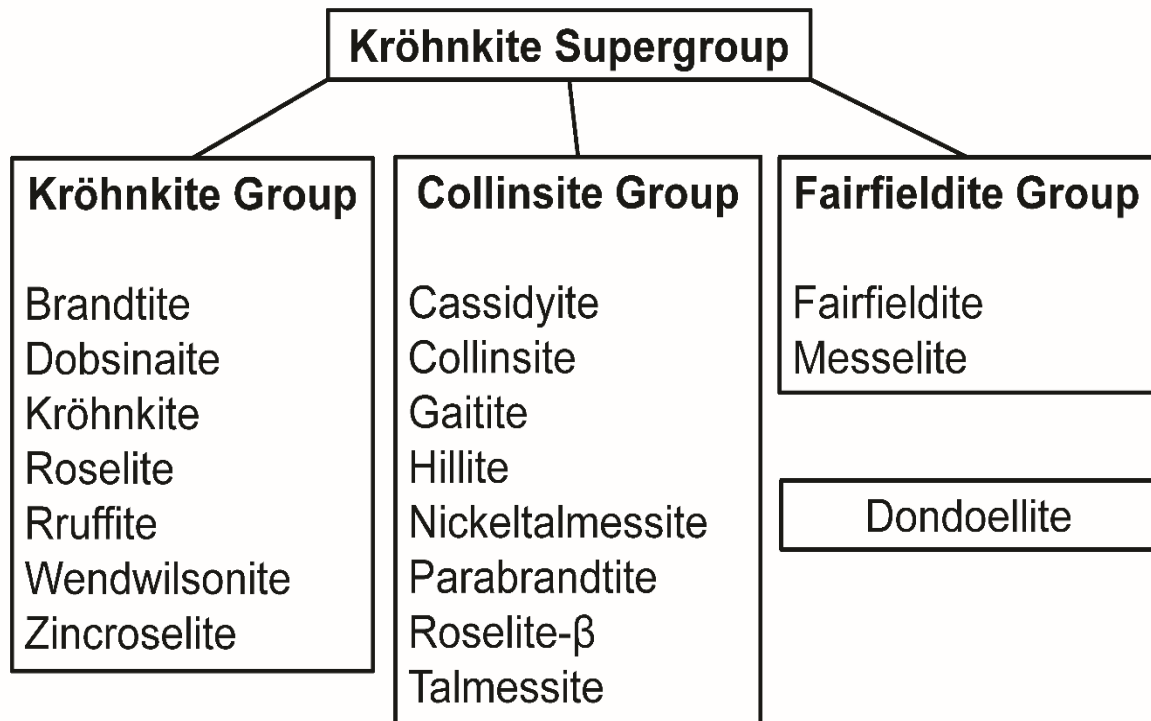


Fig. 2. The $[M(\text{TO}_4)_2\Phi_2]$ chain (Φ = unspecified anion) that forms the structural unit in the minerals of the kröhnkite supergroup; (a) the generalized chain (modified from Hawthorne, 1985), and (b) the $[\text{Mn}^{2+}(\text{PO}_4)_2(\text{H}_2\text{O})_2]$ chain in brandtite.

2

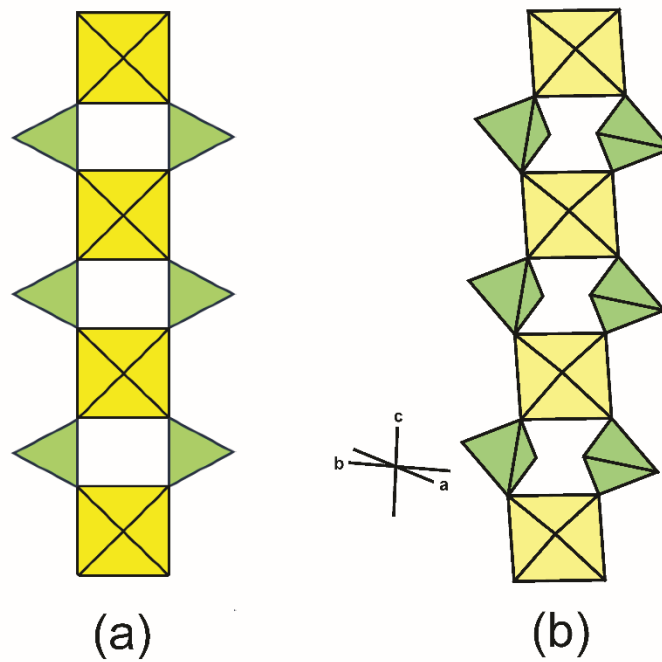
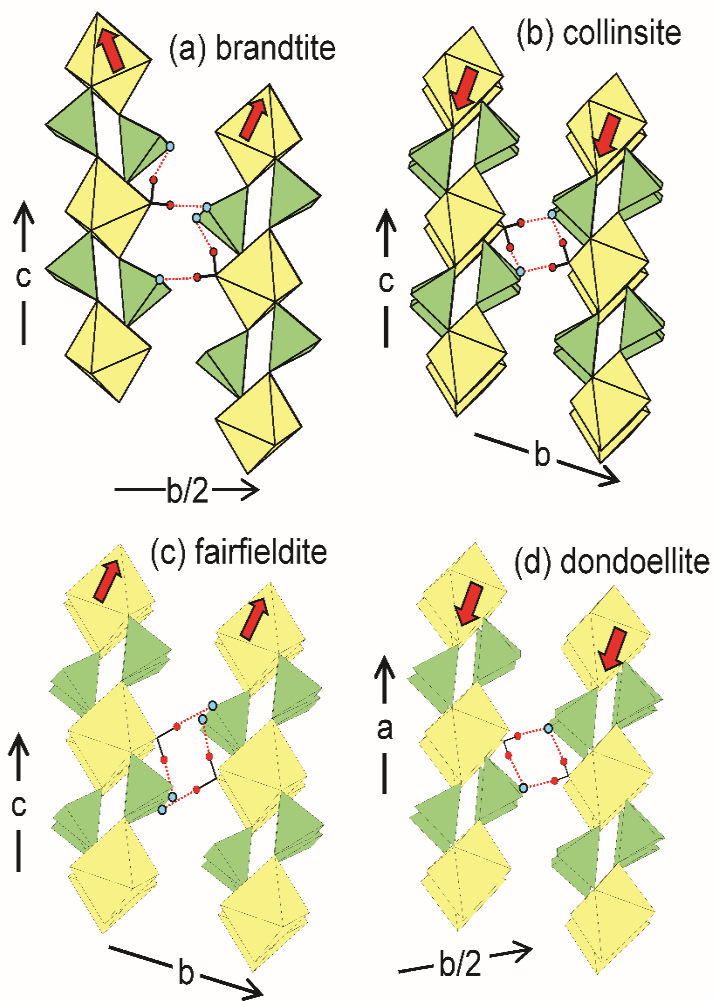


Fig. 3. The crystal structures of (a) brandtite; (b) collinsite; (c) fairfieldite; and (d) dondoellite, projected onto (100). *M* octahedra are yellow, *T* tetrahedra are green, and H are small red circles; solid black lines: $O_{\text{donor}}\text{--H}$ bonds; red dotted lines: hydrogen bonds; small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



3

Table 1. Minerals of the kröhnkite supergroup

Name	End-member formula	Ref.
Kröhnkite Group		
Brandtite	$\text{Ca}_2[\text{Mn}^{2+}(\text{PO}_4)_2(\text{H}_2\text{O})_2]$	(1)
Dobsinaite	$\text{Ca}_2[\text{Ca}(\text{AsO}_4)_2(\text{H}_2\text{O})_2]$	(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)
Rruffite	$\text{Ca}_2[\text{Cu}^{2+}(\text{AsO}_4)_2(\text{H}_2\text{O})_2]$	(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	$\text{Ca}_2[\text{Ni}(\text{PO}_4)_2(\text{H}_2\text{O})_2]$	(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	$\text{Ca}_2[\text{Ni}(\text{AsO}_4)_2(\text{H}_2\text{O})_2]$	(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).

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)	384.91	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
Ref.*	(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).

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

	Na	Cu ²⁺	S	H(1)	H(2)	Σ
O(1)	0.161	0.444 ^{x2↓}	1.385			1.990
O(2)	0.155 0.121	0.112 ^{x2↓}	1.490			1.878
O(3)	0.115		1.527	0.333		1.975
O(4)	0.147 0.135		1.475		0.333	1.090
OW	0.173	0.494 ^{x2↓}		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.

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

	Ca	Mn ²⁺	As ⁵⁺	H(1)	H(2)	Σ
O(1)	0.275 0.071	0.385 ^{x2↓}	1.217			1.948
O(2)	0.241 0.216	0.290 ^{x2↓}	1.217			1.964
O(3)	0.319		1.266	0.335		1.920
O(4)	0.222 0.263		1.255		0.335	2.075
OW	0.290	0.380 ^{x2↓}		0.665	0.665	2.000
Σ	1.897	2.110	4.955			

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