

THE USE OF END-MEMBER CHARGE-ARRANGEMENTS IN DEFINING NEW MINERAL SPECIES AND HETEROVALENT SUBSTITUTIONS IN COMPLEX MINERALS*

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ABSTRACT

The characteristics of an end-member formula are defined as follows: (1) the chemical formula must be fixed; no variable chemical components are possible; (2) the end-member formula must be compatible with the crystal structure of the mineral (or putative mineral); (3) the chemical composition at each site in the crystal structure must be fixed; an end-member formula may have two types of cation or anion (in a fixed ratio) at *one* site in the structure if required for electroneutrality; two cations or anions at more than one site are not allowed. Combining these characteristics of end-member formulae with aspects of their crystal structures can lead to unambiguous definition of end-member compositions of complex minerals, and can give considerable insight into coupled heterovalent substitutions. Several examples are given. The end-member formula of the tourmaline-group mineral povondraite was originally written as $\text{Na Fe}^{3+}_3 \text{Fe}^{2+}_6 (\text{Si}_6 \text{O}_{18}) (\text{BO}_3)_3 (\text{O}, \text{OH})_4$, whereas the correct end-member formula is $\text{Na Fe}^{3+}_3 (\text{Fe}^{3+}_4 \text{Mg}_2) (\text{Si}_6 \text{O}_{18}) (\text{BO}_3)_3 (\text{OH})_3 \text{O}$. The yttrium-rich milarite described by Černý *et al.* (1991) is shown to be a new mineral of the milarite group, with the end-member formula $\text{K} (\text{CaY}) [\text{Be}_3 (\text{Si}_{12} \text{O}_{30})]$. There are seven accredited ¹⁴(Li,Zn)-bearing minerals of the milarite group, and there has been some ambiguity over the end-member compositions of darapiosite, dusmatovite and sogdianite; end-member formulae for these minerals are unambiguously defined with the approach used here. The complex Be-bearing borosilicate mineral hyalotekite has been somewhat elusive with regard to unambiguous definition of its solid-solution behavior. The ideal formula of Christy *et al.* (1998) can be resolved into two distinct end-member formulae: (1) $\text{Ba}_4 \text{Ca}_2 \text{Si}_8 (\text{BeB}) (\text{Si}_2 \text{O}_{28} \text{F})$, and (2) $\text{Ba}_4 \text{Ca}_2 \text{Si}_8 (\text{B}_2) (\text{SiB}) \text{O}_{28} \text{F}$; note that one end-member has essential Be and the other end-member does not. Thus the competing views on whether hyalotekite is a Be mineral or not are both correct, and there are two distinct minerals buried in the chemical compositional data for hyalotekite. "Makarochkinite" is a non-accredited phase described by Yakubovich *et al.* (1990) that has been identified as identical to høgtuvaite by Grauch *et al.* (1994). Application of the approach developed here shows that, according to the published chemical data, "makarochkinite" and høgtuvaite have distinct end-member formulae, $\text{Ca}_2 (\text{Fe}^{2+}_4 \text{Fe}^{3+} \text{Ti}) (\text{Si}_4 \text{BeAl}) \text{O}_{20}$ and $\text{Ca}_2 (\text{Fe}^{2+}_4 \text{Fe}^{3+}_2) (\text{Si}_5 \text{Be}) \text{O}_{20}$, respectively. These examples show that the very simple approach developed here, using the characteristics of an end-member formula with aspects of the crystal structure, can simply and easily resolve many quite complicated problems in mineral chemistry.

Keywords: end member, crystal structure, new mineral species, heterovalent substitution.

SOMMAIRE

La formule chimique d'un pôle, dans une solution solide, possède les caractéristiques suivantes. (1) Elles doit être fixe, sans variabilité dans les composants chimiques. (2) Elle doit être compatible avec la structure cristalline du minéral (ou du minéral supposé). (3) La composition chimique à chaque site de la structure cristalline doit être invariable. La formule d'un pôle peut avoir deux types de cation ou d'anion (dans un rapport fixe) à *un seul* site dans la structure pour satisfaire à l'électroneutralité; deux cations ou deux anions ne peuvent pas occuper plus d'un site dans la structure. Une combinaison de ces caractéristiques des formules proposées avec les aspects des structures cristallines de ces pôles peut mener à une définition non ambiguë de la composition des pôles de minéraux complexes, et éclaircir les substitutions couplées hétérovalentes. Plusieurs exemples servent à illustrer ces principes. La formule de la povondraïte, membre du groupe de la tourmaline, a d'abord été écrite $\text{Na Fe}^{3+}_3 \text{Fe}^{2+}_6 (\text{Si}_6 \text{O}_{18}) (\text{BO}_3)_3 (\text{O}, \text{OH})_4$, tandis que la formule correcte du pôle serait $\text{Na Fe}^{3+}_3 (\text{Fe}^{3+}_4 \text{Mg}_2) (\text{Si}_6 \text{O}_{18}) (\text{BO}_3)_3 (\text{OH})_3 \text{O}$. Le membre riche en yttrium du groupe de la milarite, décrit par Černý *et al.* (1991), serait en fait un nouveau membre de ce groupe, avec comme pôle $\text{K} (\text{CaY}) [\text{Be}_3 (\text{Si}_{12} \text{O}_{30})]$. Il y a sept membres homologués de ce groupe contenant ¹⁴(Li,Zn), mais il y a une certaine ambiguïté à propos de la composition de la darapiosite, la dusmatovite et la sogdianite. La formule de ces pôles est ici définie sans ambiguïté en utilisant les démarches proposées. La formule de la hyalotékite, borosilicate complexe à béryllium, est restée quelque peu floue par rapport à son statut comme solution solide. La formule idéale de Christy *et al.* (1998) peut se résoudre en deux formules de pôles distincts: (1) $\text{Ba}_4 \text{Ca}_2 \text{Si}_8 (\text{BeB}) (\text{Si}_2 \text{O}_{28} \text{F})$ et (2) $\text{Ba}_4 \text{Ca}_2 \text{Si}_8 (\text{B}_2) (\text{SiB}) \text{O}_{28} \text{F}$. Un de ces pôles possède le Be comme composant essentiel, tandis que l'autre n'en a pas. C'est donc dire que les deux points de vue concernant le statut de la

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hyalotékite comme minéral de Be (ou non) sont tous deux corrects, et il existe deux minéraux distincts à déceler dans les données sur la composition chimique de la hyalotékite. Enfin, la "makarochkinite" est une phase non approuvée décrite par Yakubovich *et al.* (1990); Grauch *et al.* (1994) l'ont considéré synonyme de la høgтуvaite. L'application des démarches préconisées ici montre que selon les données chimiques publiées, la "makarochkinite" et la høgтуvaite seraient des pôles possédant des compositions distinctes, $\text{Ca}_2 (\text{Fe}^{2+}_4 \text{Fe}^{3+} \text{Ti}) (\text{Si}_4 \text{Be Al}) \text{O}_{20}$ et $\text{Ca}_2 (\text{Fe}^{2+}_4 \text{Fe}^{3+}_2) (\text{Si}_5 \text{Be}) \text{O}_{20}$, respectivement. Ces exemples montrent qu'avec ces principes très simples, développés en utilisant les caractéristiques de la formule d'un pôle avec les aspects de la structure cristalline, on peut simplement et facilement résoudre plusieurs problèmes compliqués à propos de la composition chimique des minéraux.

(Traduit par la Rédaction)

Mots-clés: pôle, structure cristalline, nouvelle espèce minérale, substitution hétérovalente.

INTRODUCTION

End-member mineral compositions are often used in petrology, particularly when examining compositional variations in the more simple of the rock-forming minerals (*e.g.*, garnets, olivines, feldspars). However, mineralogy does not make use of end-member mineral compositions as much as it could. When combined with knowledge of the crystal structure of a mineral, approaching chemical variations in minerals from the perspective of end-member compositions can often lead to the solution of otherwise quite intractable problems concerning the uniqueness of a mineral composition or the character of complex heterovalent substitutions in minerals. This lack of use of end-member compositions is compounded by the fact that the Commission on New Minerals and Mineral Names of the International Mineralogical Association does not require definition of the end-member composition of a new mineral. Hence the appropriate end-member composition is often not in the literature, and erroneous "end-member compositions" abound, adding further confusion to the chemistry of complex minerals. Moreover, there is a lot of confusion about what are the necessary characteristics of an end-member composition. Here, I discuss the criteria required for an end member, and then apply these to several aspects of the definition of new mineral species, and how the use of end members can clarify the nature of chemical substitutions in minerals of complex structure and chemistry. I do not apologize for focusing primarily on my own previous work in finding examples of errors that can be discovered using the ideas presented here; I considered that finding errors in my own work might be more popular than finding errors in the work of other people.

DEFINITION OF AN END-MEMBER COMPOSITION

There are several characteristics that are essential for an end-member composition.

(1) An end-member composition must be fixed. If a supposed end-member is expressed with variable components, it can be factored into (at least) two distinct components that are of fixed composition. For example,

MacDonald *et al.* (1993) defined the end-member composition of foitite as $\square [\text{Fe}^{2+}_2 (\text{Al}, \text{Fe}^{3+})] \text{Al}_6 (\text{Si}_6 \text{O}_{18}) (\text{BO}_3)_3 (\text{OH})_4$. This definition of an end-member is wrong because the composition is variable and can be expressed in terms of two fixed (true end-member) compositions: $\square [\text{Fe}^{2+}_2 \text{Al}] \text{Al}_6 (\text{Si}_6 \text{O}_{18}) (\text{BO}_3)_3 (\text{OH})_4$ and $\square [\text{Fe}^{2+}_2 \text{Fe}^{3+}] \text{Al}_6 (\text{Si}_6 \text{O}_{18}) (\text{BO}_3)_3 (\text{OH})_4$.

(2) An end-member composition must be compatible with the crystal structure of the associated mineral species. Forsterite, $\text{Mg}_2 \text{SiO}_4$, can be decomposed into the two components $\text{MgO} (\times 2)$ and SiO_2 . These are chemical components, but they are not end-members because they do not have the same crystal-structure arrangement as the initial mineral.

(3) An end member *may* have more than one type of cation or anion at *one site if required by the electroneutrality principle*. Perhaps the best known example is elbaite: $\text{Na} [\text{Li}_{1.5} \text{Al}_{1.5}] \text{Al}_6 (\text{Si}_6 \text{O}_{18}) (\text{BO}_3)_3 (\text{OH})_3 (\text{OH})$, a common mineral of the tourmaline group. In the crystal structure, $X = \text{Na}$, $Z = \text{Al}_6$, $T = \text{Si}_6$, $B = \text{B}$, $V = (\text{OH})_3$ and $W = (\text{OH})$ *apfu* (atoms per formula unit); thus each site is completely ordered (*i.e.*, occupied by only one type of cation or anion). The aggregate charge of these sites, together with the anion sites, is 6^- , and hence the electroneutrality principle requires that the total cation charge at the Y site is 6^+ . This can be satisfied by $Y = \text{Mg}_3$, giving rise to the species dravite. Where $Y = (\text{Li}, \text{Al})_3$, the requirement that the aggregate charge at Y be 6^+ is satisfied only by the composition $Y = [\text{Li}_{1.5} \text{Al}_{1.5}]$. The elbaite end-member composition cannot be resolved into completely ordered components that have the tourmaline structure.

Note that an end-member can have more than one species at only one site. If more than one cation or anion is introduced to another site in elbaite, the resulting composition may be resolved into two end-member compositions. Thus the composition $\text{Na} [\text{Li}_{1.5} \text{Al}_{1.5}] [\text{Al}, \text{Fe}^{3+}]_6 (\text{Si}_6 \text{O}_{18}) (\text{BO}_3)_3 (\text{OH})_4$ can be resolved into the end-member compositions $\text{Na} [\text{Li}_{1.5} \text{Al}_{1.5}] \text{Al}_6 (\text{Si}_6 \text{O}_{18}) (\text{BO}_3)_3 (\text{OH})_4$ and $\text{Na} [\text{Li}_{1.5} \text{Al}_{1.5}] \text{Fe}^{3+}_6 (\text{Si}_6 \text{O}_{18}) (\text{BO}_3)_3 (\text{OH})_4$.

(4) Anions are just as important as cations in defining end-members (and the associated mineral species). This is of particular importance with regard to the an-

ions (OH) and F, as the difficulty in analyzing for hydrogen and the cation-centric view of mineral chemistry has tended to downplay the importance of this issue. This is unfortunate, as although (OH) and F have the same formal charge, they can play very different roles in a crystal structure, particularly where strong hydrogen-bonding is present. Moreover, the presence of (OH) versus F can reflect very different conditions of crystallization, and recognition of this type of compositional variation can be important from a petrogenetic perspective.

(5) A group of similar anions can occupy more than one crystallographically distinct site in a crystal structure. Thus in the tourmaline structure, the $V [\equiv O(3)]$ site can be occupied by O and (OH), and the $W [\equiv O(1)]$ site can be occupied by O, (OH) and F. As shown by Robert *et al.* (1997), this difference in site preference is the result of weak hydrogen-bonding at the O(1) site and strong hydrogen-bonding at the O(3) site; F can replace (OH) at O(1) because the hydrogen bonding involving this (OH) is not an essential part of the structure. However, the hydrogen bonding involving the (OH) group at the O(3) site is essential to the bond-valence requirement of the neighboring O(5) anion [where O(3) is not occupied by O], and hence this (OH) cannot be replaced by F. Thus the monovalent-anion content of tourmaline can vary in the range $(OH)_3(OH)$ to $(OH)_3F$; the former will constitute the hydroxyl end-member, and the latter will constitute the fluor end-member.

(6) A group of similar cations can occupy more than one site in a crystal structure. Thus in the olivine structure, there are two octahedrally coordinated sites, $M(1)$ and $M(2)$, that can be occupied by a wide range of monovalent to trivalent cations. Consider the case of forsterite and fayalite: their end-member compositions are Mg_2SiO_4 and $Fe^{2+}_2SiO_4$, respectively. Although olivines intermediate between these two compositions are fairly disordered, this disorder is not complete. An exact description of the end-members would involve the compositions Mg_2SiO_4 , $MgFe^{2+}SiO_4$, $Fe^{2+}MgSiO_4$ and $Fe^{2+}_2SiO_4$, and these have been used for some thermodynamic descriptions of order-disorder processes in olivine. However, the two intermediate compositions and their implied arrangements are not approached in Nature, and recognition of only two species is appropriate.

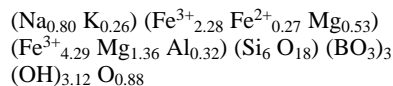
USES OF END-MEMBER COMPOSITIONS:
DEFINING NEW MINERAL SPECIES AND ANALYSIS
OF COMPLEX SOLID-SOLUTIONS

When describing a new mineral, the idea of an end-member composition is extremely useful. In fact, it is only by using this idea that a mineral can be identified as a new mineral, and yet there are very few descriptions of new minerals that explicitly state the end-member composition corresponding to the new mineral described. The reason for this may be associated with

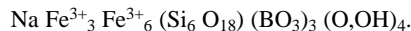
the process for the approval of new minerals by the Commission on New Minerals and Mineral Names of the International Mineralogical Association. In this procedure, one is required to give the empirical formula and the *simple formula* of the mineral; the regulations do not explicitly require that the end-member composition be stated. Most published descriptions of new minerals give a simplified empirical formula rather than an end-member formula. Both types of formulae are preferable, particularly when dealing with compliant structure-types that can accommodate a wide variety of cations and anions in heterovalent substitutions.

The end-member composition of povondraite

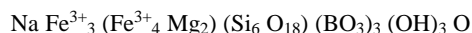
A good example of the confusion that can arise from too much simplification is that of the tourmaline mineral *povondraite*. Grice *et al.* (1993) gave the structural formula of the holotype sample as



and the ideal end-member formula as



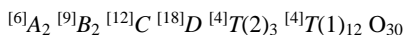
The latter is not an end-member formula, as the anion contents of the V and W sites are not fixed. However, the anion content of V and W must be fixed as the rest of the formula is fixed. In the above formula, the electroneutrality principle requires that $(O,OH)_4$ is actually $O_3(OH)$. Note that this content is not in accord with the empirical formula given above, in which the anion content is $O_{0.88}(OH)_{3.12}$. This latter composition is very close to the following ordered arrangement of anions: $V = (OH)_3$ and $W = O$. The above "end-member" formula has an excess cation charge of 2^+ with this new ordered composition at the V and W sites. Inspection of the above empirical formula shows that Na is dominant at the X site, Fe^{3+} is dominant at the Y site (with minor Mg), and Fe^{3+} is dominant at the Z site (with significant Mg). The above end-member formula has an excess charge of 2^+ , but the formula does not take into account the presence of 1.36 Mg *apfu* (atoms per formula unit) at the Z site. By considering the presence of Mg at the Z site, an appropriate composition for the end member emerges:



There is binary occupancy of one site (Z), and all other sites have a single occupying species. Moreover, the occurrence of a divalent anion at W [the O(1) site] is in accord with the bond-valence requirements of that site where the Y site is completely occupied by a trivalent cation (Hawthorne 1996).

The milarite-group minerals

Milarite, $KCa_2 [Be_2 Al Si_{12} O_{30}] (H_2O)_x$, has a complicated but elegant structure (Cerný *et al.* 1980, Armbruster *et al.* 1989) and is the type structure for a large group of minerals (Hawthorne *et al.* 1991). Six-membered rings of (SiO_4) tetrahedra are arranged at the vertices of a 6^3 plane net (Fig. 1a) and are linked by (BeO_4) tetrahedra. Note that there are pairs of six-membered rings at each vertex of the net, one rotated by 30° relative to the other such that the (BeO_4) tetrahedra also link the two rings in the c direction (Fig. 1b). These sheets then stack along the c direction such that six-membered rings from adjacent sheets link vertices to form an $[Si_{12} O_{30}]$ cage (Fig. 1b). In the interstices of the resulting framework, [6]-coordinated Ca and [12]-coordinated K balance the framework charge. The chemical formula can be written as



where $A = Al, Fe^{3+}, Sn^{4+}, Fe^{2+}, Mg, Zr, Ca,$
 Na, Y, REE, Sc

$B = Na, (H_2O), \square, Ca?, K?$

$C = K, Na, Ba, \square, Ca?$

$D = \square, ?$

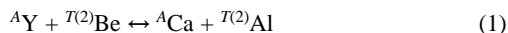
$T(2) = Li, Be, B, Mg, Al, Si, Mn^{2+}, Zn$

$T(1) = Si, Al$

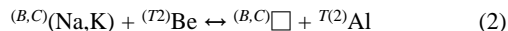
and the question marks (?) indicate possible substitutions that have not yet been substantiated. There are some twenty species in this group, many of which have been discovered in the last 20 years, and the flexibility

of the structure suggests that others remain to be discovered. This group is called the osumilite group in the United States and the milarite group in the rest of the world. The latter name is to be preferred as the milarite structure has more sites occupied than the osumilite structure (and also has priority).

Yttrian milarite: Cerný *et al.* (1991) described milarite crystals from Strange Lake (Labrador, Canada) and the Jaguaracú granitic pegmatite (Minas Gerais, Brazil) with Y contents of up to 0.72 *apfu*. Figure 2a and 2b show the variation of (Y + REE) as a function of the other principally varying cations. Figure 2a shows that Y (+ REE) substitute for Ca at the A site, and Figure 2b shows that the principal charge-compensating substitution involves Al for Be at the T(2) site:



The variation in the Be content is also affected by the substitution



but the dominance of substitution (1) is shown by Figure 2b.

Consider the effect of substitution (1) on the end-member formula of milarite, $KCa_2 [(Be_2 Al) (Si_{12} O_{30})]$, omitting (H_2O) for simplicity. This substitution replaces Ca and Al (in the same proportion) by Y and Be. However, milarite has twice as much Ca as Al, and hence the maximum extent of this substitution results in the A site being half-occupied by both Ca and Y:

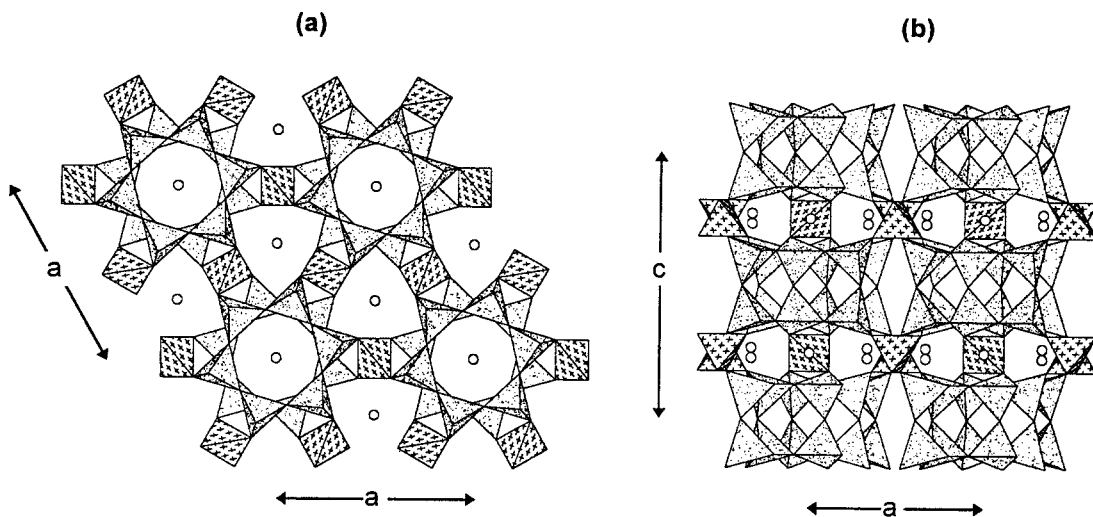


FIG. 1. The crystal structure of milarite: (a) projected onto (001); circles are Ca atoms; (b) projected onto (010); note the $[Si_{12} O_{30}]$ cages.

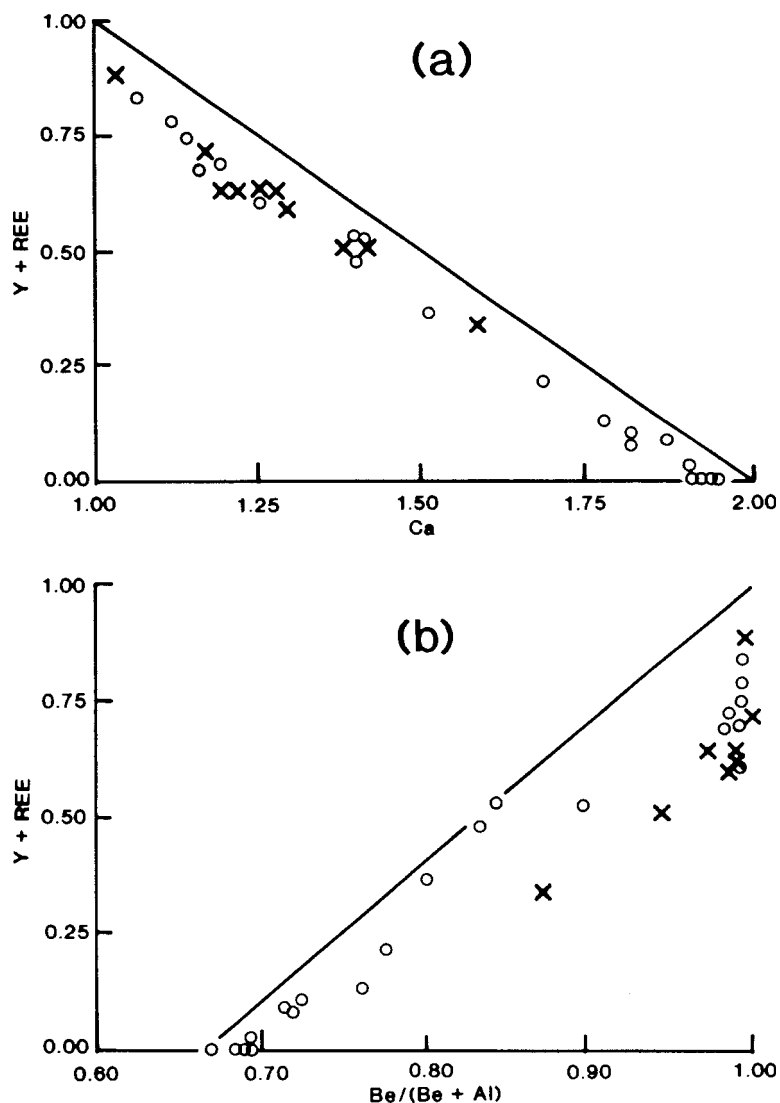
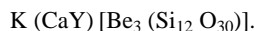


FIG. 2. (a) Proportions of Ca versus $(Y + \sum REE)$ (apfu) in yttrian milarite. Circles: Jaguaraçu; X: Strange Lake. (b) Proportion of $(Y + \sum REE)$ in apfu versus $Be/(Be + Al)$ apfu in yttrian milarite. Note that the data plot below the line that marks the ideal substitution. Symbols as in Figure 2a. From Černý *et al.* (1991).



Note that this composition has all the characteristics of an end-member: one site contains two cations in a fixed ratio, and all other sites contain just one cation or anion. Table 1 shows the chemical composition of the most $(Y + REE)$ -rich milarite from Strange Lake (Černý *et al.* 1991). The unit formula contains 2.99 Be and 1.05 $(Y + REE)$ apfu, and hence this specific sample of Černý *et*

al. (1991) warrants description as a new mineral of the milarite group.

Raade & Kristiansen (2000a, b) reported the occurrence of Sc-rich minerals from the Heftetjern granitic pegmatite, Tørdal, Norway. In particular, they noted the presence of milarite with 5–7 wt.% Sc_2O_3 . Although a complete analysis has not yet been published, this amount of Sc suggests that this could be a new milarite-group mineral, the Sc equivalent of the Y-rich milarite

discussed above: end-member K (CaSc) [Be₃ (Si₁₂ O₃₀)].

^[4](Li,Zn)-bearing minerals of the milarite group:

They are currently seven of these minerals known; these are listed in Table 2, together with some of the chemical formulae written for them. All of these minerals have K dominant at the C site and Si dominant at the T(1) site, and hence these sites can be considered as fixed in the following discussion. The total anion charge is 60⁻, the charge at the C (= K) and T(1) (= Si₁₂) is 49⁺, and hence the electroneutrality principle requires that the aggregate charge at the A, B and T(2) sites is 11⁺.

The possibilities for occupancy of the T(2) site and the resulting charge-constraints on the A and B sites are as follows:

- (A) $T(2)_3 = \text{Li}_3 = 3^+ \quad A_2 + B_2 = 8^+$
 (B) $T(2)_3 = \text{Li}_2 \text{Zn} = 4^+ \quad A_2 + B_2 = 7^+$
 (C) $T(2)_3 = \text{Li Zn}_2 = 5^+ \quad A_2 + B_2 = 6^+$
 (D) $T(2)_3 = \text{Zn}_3 = 6^+ \quad A_2 + B_2 = 5^+$

The charge at the A site is assumed to be greater than the charge at the B site, i.e., B is occupied only by monovalent cations or vacancies. For composition (A), the T(2) site is singly occupied and hence either the A or the B sites can be multiply occupied. The sum of the charges at the A and B sites is even, and this means that the charges at these sites are either [even + even] or [odd + odd]. The latter requires that each site has multiple occupancy, and hence is not possible for an end-member composition. Thus the possibilities for the A and B sites are as follows:

- (1) $A_2 = M^{4+}_2 \quad B_2 = \square_2$
 (2) $A_2 = M^{3+}_2 \quad B_2 = M^+_2$
 (3) $A_2 = M^{2+} M^{4+} \quad B_2 = M^+_2$

For composition (B), the T(2) site is multiply occupied and hence the A and B sites must each be singly occupied. As the A and B sites occur in pairs, the sum of their charges cannot be odd, and hence there are no possibilities for composition (B). Again, for composition (C), the A and B sites must each be singly occupied. Their aggregate charge is even, and the possible occupancies of the A and B sites are as follows:

- (4) $A_2 = M^{2+}_2 \quad B_2 = M^+_2$
 (5) $A_2 = M^{3+}_2 \quad B_2 = \square_2$

For composition (D), the T(2) site is singly occupied, and hence one of the A and B sites can be multiply occupied. The sum of the charges at the A and B sites is odd, and thus the charges at these sites are either [even + odd] or [odd + even]. The odd aggregate charge at a pair of sites requires that this pair of sites has multiple

TABLE 1. CHEMICAL COMPOSITION* AND UNIT FORMULA (apfu) FOR SAMPLE 71-2 FROM ČERNÝ *et al.* (1991)

	wt. %		apfu	end-member
SiO ₂	70.20	Si	12.07	12
Al ₂ O ₃	0.04			
BeO	7.24	Be	2.99	3
CaO	5.60	Al	0.01	
K ₂ O	4.50			
Y ₂ O ₃	7.90	K	0.99	1
Ce ₂ O ₃	0.40			
Nd ₂ O ₃	0.30	Ca	1.03	1
Dy ₂ O ₃	0.90			
Er ₂ O ₃	0.80	Y	0.72	
Yb ₂ O ₃	0.50	Ce	0.03	
Σ	98.38	Nd	0.18	
		Dy	0.05	
		Er	0.04	
		Y	0.03	
		Y + ZREE	1.05	1

* Na not detected

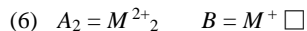
TABLE 2. ASSIGNED SITE-POPULATIONS (apfu) AND CALCULATED AND OBSERVED DISTANCES FOR Li- AND Zn-BEARING MINERALS OF THE MILARITE-TYPE STRUCTURE

Mineral	A site			B site		T(2) site	
	Site-population	<A-O> _{calc} *	<A-O> _{obs}	Site-population	Site-population	<T(2)-O> _{calc} *	<T(2)-O> _{obs}
Brannockite ¹	Sn ⁴⁺ ₂	2.05	2.013	□ _{2,0}	Li ₃	1.95	1.922
Berezanskite ²	Ti ⁴⁺ _{1.94} Nb _{0.04} Fe _{0.02}	-	-	□ _{1.94} Na _{0.06}	Li _{2.95} Al _{0.02}	-	-
Sogdianite ³	Zr _{0.76} Fe ³⁺ _{0.73} Ti _{0.38} Al _{0.13}	2.03	2.019	□ _{1.15} Na _{0.85}	Li ₃	1.95	1.957
Sogdianite ⁴	Zr ₂	2.08	2.077	□ _{2,0}	Li ₃	1.95	1.947
Sugilite ¹	Fe ³⁺ _{1.66} Al ³⁺ _{0.34}	1.97	1.972	Na _{1.96} □ _{0.04}	Li ₃	1.95	1.97
Daraposite ⁵	Mn ²⁺ _{1.47} Zr _{0.28} Y _{0.22} Mg _{0.03}	2.18	2.151	Na _{1.22} K _{0.36} □ _{0.42}	Li _{1.54} Zn _{1.15} Fe ²⁺ _{0.31}	1.95	1.976
Dusmatovite ⁶	Mn ²⁺ _{1.52} Zr _{0.24} Y _{0.24}	2.18	2.120	□ _{1,0} Na _{0.64} K _{0.36}	Zn _{2.28} Li _{0.72}	1.96	1.971
Shibkovite ⁷	Ca _{1.26} Mn ²⁺ _{0.40} Na _{0.34}	2.33	2.300	□ _{0.74} K _{1.26}	Zn ₃	1.96	1.959

* Calculated by summing the constituent ionic radii; values from Shannon (1976); O = O(3);

¹ Armbruster & Oberhänsli (1988); ² Pautov & Agakhanov (1997); ³ Cooper *et al.* (1999); ⁴ Sokolova *et al.* (2000); ⁵ Semenov *et al.* (1975), Ferraris *et al.* (1999); ⁶ Sokolova & Pautov (1995); ⁷ Pautov *et al.* (1998), Sokolova *et al.* (1999).

occupancy. This is possible for an end-member composition in this particular case; the possibilities for the *A* and *B* sites are as follows:



The possible general end-member compositions are summarized in Table 3.

Brannockite (berezanskite) has Sn^{4+} (Ti^{4+}) at *A*, the *B* site is vacant, and Li is dominant at *T*(2). These minerals are close to an ordered composition that satisfies all the criteria of an end member; their end-member arrangement is (1) in Table 3. Sugilite has Fe^{3+} dominant at *A*, *B* occupied by Na, and *T*(2) completely occupied by Li. This composition corresponds to end-member arrangement (2) in Table 3. Shibkovite has Ca dominant at *A*, Zn dominant at *T*(2), and *B* is half-occupied by K and half-occupied by \square . This composition corresponds to that of end-member arrangement (5) in Table 3.

Darapiosite, dusmatovite and sogdianite are somewhat more complicated, as there are significant amounts of more than two cations at the *A*, *B* and *T*(2) sites, and there has been some confusion in the literature as to their end-member compositions. Darapiosite was originally described by Semenov *et al.* (1975) as $\text{K Na}_2 \text{Li} (\text{Mn,Zn})_2 \text{Zr Si}_{12} \text{O}_{30}$, a formula that is ambiguous with regard to site assignments for the milarite-type structure. Ferraris *et al.* (1999) reported the crystal structure and the results of a new chemical analysis (Table 4) of darapiosite. They derived a *T*(2) site-population of $[\text{Li}_{1.54} \text{Zn}_{1.15} \text{Fe}^{2+}_{0.31}]$ and stated that "darapiosite is characterized by Li... dominant at *T*(2)...". There are two possibilities for "Li dominant at *T*(2)", $T(2) = \text{Li}_3$ and $T(2) = \text{Li}_2 \text{Zn}$, respectively. As shown above, end-member arrangements are not possible for $T(2) = \text{Li}_2 \text{Zn}$, and hence, according to their view, the ideal end-member composition for darapiosite must have $T(2) = \text{Li}_3$. However, the chemical composition and site populations (Table 4) are not in accord with the necessary charge arrangements at the *A* and *B* sites for $T(2) = \text{Li}_3$ (Table 3). However, one may consider the alternative possibility of Li *not* dominant at *T*(2); here, the possibilities are $T(2) = \text{Zn}_3$ and $T(2) = \text{Li Zn}_2$. These site populations

TABLE 3. END-MEMBER FORMULAE FOR LI- AND ZN-BEARING MINERALS WITH THE MILARITE-TYPE STRUCTURE

	<i>A</i>	<i>B</i>	<i>C</i>	<i>T</i> (2)	<i>T</i> (1)	
(1)	Sn^{4+}_2	\square_2	K	Li_3	Si_{12}	Brannockite
(1)	Ti^{4+}_2	\square_2	K	Li_3	Si_{12}	Berezanskite
(1)	Zr_2	\square_2	K	Li_3	Si_{12}	Sogdianite
(2)	Fe^{3+}_2	Na_2	K	Li_3	Si_{12}	Sugilite
(3)	Mn^{2+}_2	Na_2	K	Li Zn_2	Si_{12}	Darapiosite
(4)	M^{2+}_2	\square_2	K	Li Zn_2	Si_{12}	—
(5)	Mn^{2+}_2	$\square \text{Na}$	K	Zn_3	Si_{12}	Dusmatovite
(5)	Ca_2	$\square \text{K}$	K	Zn_3	Si_{12}	Shibkovite

allow the end-member arrangements (3) and (4) in Table 3; charge arrangement (3) corresponds with the site populations indicated in Table 4. The results of a new electron-microprobe analysis (Table 4) of darapiosite (sample courtesy of Bill Pinch) is more in accord with this new formulation of the end-member composition, with $T(2) = [\text{Li}_{1.26} \text{Zn}_{1.74}]$. Thus Li is *not* dominant at *T*(2) in darapiosite, and the correct end-member formula is given in Table 3.

Dusmatovite was well characterized by Sokolova & Pautov (1995). The observed *T*(2) site-population is $[\text{Li}_{0.72} \text{Zn}_{2.28}]$, suggesting that the appropriate end-member composition should have $T(2) = \text{Li Zn}_2$. However, the half-occupancy of the *B* site is not in accord with this suggestion [see charge arrangements (3) and (4) above]. In interpreting this composition, the key issue is that trivalent and tetravalent cations can only occur at the *A* site if $T(2) = \text{Li}_3$, and also the amounts of Y and Zr at the *A* site are equal. Moreover, the sum of the trivalent and tetravalent cations at the *A* and *B* sites is two-thirds the amount of Li at the *T*(2) site, indicating that the trivalent and tetravalent cations at the *A* and *B* sites are associated with Li_3 at the *T*(2) site. Thus the composition of dusmatovite may be resolved into end members as indicated in Table 5, and the end-member composition of dusmatovite corresponds to charge-arrangement (5) in Table 3.

Sogdianite was described by Dusmatov *et al.* (1968) as $(\text{K,Na})_2 \text{Li}_2 (\text{Li,Fe,Al,Ti})_{1.8} (\text{Zr,Ti}) [\text{Si}_{12} \text{O}_{30}]$. Bakakin *et al.* (1975) refined the crystal structure of sogdianite and wrote the formula to accord with the milarite structure as $\text{K} (\text{Zr}_{0.8} \text{Fe}^{3+}_{0.6} \text{Ti}_{0.4} \text{Fe}^{2+}_{0.2}) (\text{Li}_{2.55}$

TABLE 4. CHEMICAL COMPOSITIONS AND UNIT FORMULAE FOR DARAPIOSITE

	(1)	(2)	(3)	(1)	(2)	(3)	
SiO_2	63.65	63.19	62.92	Si	12.06	11.98	11.98
Li_2O	1.74	2.01	1.65	Li	1.33	1.54	1.26
ZnO	7.85	8.22	12.35	Zn	1.10	1.15	1.74
				Fe^{2+}	<u>0.27</u>	<u>0.31</u>	—
				$\Sigma T(2)$	2.70	3.00	3.00
MnO	8.25	9.58	8.72	Mn^{2+}	1.33	1.54	1.40
FeO	1.67	1.96	1.60	Fe	—	—	0.25
MgO	—	0.12	0.27	Mg	—	0.03	0.07
Y_2O_3	0.96*	2.26	2.32	Y	0.10	0.23	0.23
ZrO_2	5.00	3.28	1.05	Zr	0.46	0.30	0.10
Nb_2O_5	0.90	—	—	Nb	<u>0.08</u>	—	—
				ΣA	1.97	2.10	2.05
Na_2O	2.96	3.32	3.65	Na	1.09	1.22	1.35
CaO	0.57	—	0.44	Ca	0.12	—	0.09
K_2O	<u>5.14</u>	<u>5.63</u>	<u>5.05</u>	K	0.24	0.36	0.22
Σ	100.43**	99.57	100.02	\square	<u>0.55</u>	<u>0.42</u>	<u>0.36</u>
				ΣB	2.00	2.00	2.00
				K	1.00	1.00	1.00

(1) Semenov *et al.* (1975); (2) Ferraris *et al.* (1999); (3) this work.

* reported as REE_2O_3

** includes 1.74 wt.% loss on ignition

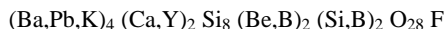
$\text{Al}_{0.15} \square_{0.30} [\text{Si}_{12} \text{O}_{30}] (\text{Na}_{0.95} \text{K}_{0.05})$. Cooper *et al.* (1999) refined the structure of sogdianite and assigned the site populations as follows: $(\text{Zr}_{0.76} \text{Ti}_{0.38} \text{Fe}^{3+}_{0.73} \text{Al}_{0.13}) (\square_{1.105} \text{Na}_{0.85}) \text{K} [\text{Li}_3 \text{Si}_{12} \text{O}_{30}]$. In this composition, tetravalent and trivalent cations occur at the A site, in accord with the presence of Li_3 at T(2). As there are more tetravalent than trivalent cations at the A site, the end-member charge arrangement must be (1) above. There seems to be a problem, as this composition has $B = \square_2$ and the composition of sogdianite has $B_2 = (\square_{1.105} \text{Na}_{0.85})$. However, if the above sogdianite composition is resolved into its end-member components, it becomes Sogdianite_{0.38} Sugilite_{0.37} Berezanskite_{0.19} "Al-sugilite"_{0.06}, and the Na at the B site is seen as due to solid solution of sugilite and its Al-equivalent. Sokolova *et al.* (2000) recently reported the crystal structure of a sample of sogdianite very close to the ideal end-member composition (Table 4), in accord with the argument of Cooper *et al.* (1999). Thus the end-member composition of sogdianite corresponds to charge-arrangement (1) in Table 3.

Hyalotekite

Hyalotekite (Moore *et al.* 1982) is a complex framework of (BO_4) and (SiO_4) tetrahedra. In the crystal-structure refinement, one of the tetrahedral sites with T–O distances fairly typical of Si–O [*Si*(1)] showed lower-than-expected scattering; Moore *et al.* (1982) assigned Be to this site. Thus Be and Si occur at the *Si*(1) site, according to this assignment. Another possible arrangement can be suggested. The $\langle \text{Si}(1)\text{--O} \rangle$ distance is 1.597 Å, which is very short for a $\langle \text{Si--O} \rangle$ distance; the other $\langle \text{Si--O} \rangle$ distances in hyalotekite are 1.613, 1.610 and 1.613 Å. Now Be ($r = 0.27$ Å) is marginally larger than Si ($r = 0.26$ Å), and substitution of Be cannot account for the small $\langle \text{Si}(1)\text{--O} \rangle$ distance. However, if Be were to substitute for B at the B site and the displaced B were to substitute for Si at the *Si*(1) site, then the $\langle \text{Si}(1)\text{--O} \rangle$ distance would be shorter than the distance characteristic of $\langle \text{Si--O} \rangle$, and the $\langle \text{B--O} \rangle$ distance should be longer than the distance characteristic of $\langle \text{B--O} \rangle$ (= 1.476 Å, Hawthorne *et al.* 1996). Moreover, Be substitutes for B and B substitutes for Si, as is observed

in many other structures, rather than Be substituting for Si, which tends not to occur. Christy *et al.* (1998) re-refined the data of Moore *et al.* (1982) and came to this same conclusion.

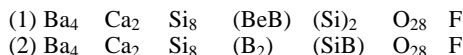
Consider the possible end-member compositions of hyalotekite from the viewpoint of the above discussion of the site occupancies of Be, B and Si. Christy *et al.* (1998) wrote the general formula of hyalotekite as



Their chemical data show that Ba is in many cases dominant over Pb^{2+} , and Ca is dominant over Y, and hence a simplified formula can be written as

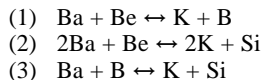


This is not an end-member formula as there is multiple occupancy at more than one site in the structure, and the formula is not fixed. This formula can be resolved into two simpler components



These are true end-members in that neither can be resolved into more simple compositions that retain the hyalotekite structure and remain neutral.

Christy *et al.* (1998) provided chemical data for a range of compositions of hyalotekite. In Figure 3a, these data are shown from the perspective of the above two end-members. The data extend between the two end-member compositions, in accord with the above discussion. Moreover, the displacement of the data from the ideal line correlates closely with the amount of K substituting for Ca, indicating the presence of a significant additional substitution. Next, consider the character of this substitution. There are three possible ways to incorporate K into the hyalotekite structure (ignoring replacement of Ca by Y):



The directions of these three substitutions relative to the axes of Figure 3a are shown in Figure 3b. If the data were to lie exactly along the line between compositions (1) and (2) in Figure 3a, the Be content should vary along this line from 1.0 *apfu* at composition (1) to 0.0 *apfu* at composition (2). Next, the data points are joined to the corresponding points with the same Be contents along the line between compositions (1) and (2) (Fig. 3b). For clarity, not all data are shown in Figure 3b. However, what is apparent is that the lines joining the observed data-points with their Be content along the (1)–(2) join are all subparallel to the substitution direction defined by the substitution $\text{Ba} + \text{B} \leftrightarrow \text{K} + \text{Si}$, indi-

TABLE 5. SITE POPULATIONS AND COMPOSITION OF DUSMATOVITE* IN TERMS OF END-MEMBER COMPOSITIONS

	A	B	C	T(2)	T(1)	Amount
Dusmatovite end-member	Mn^{2+}_2	$\square \text{Na}$	K	Zn_3	Si_{12}	0.76
Sogdianite end-member	Zr_2	\square_2	K	Li_3	Si_{12}	0.12
Unnamed end-member	Y_3	Na_2	K	Li_3	Si_{12}	0.12
Dusmatovite	$\text{Mn}^{2+}_{1.52} \text{Y}_{0.24} \text{Zr}_{0.24}$	$\square \text{Na}$	K	$\text{Li}_{0.72} \text{Zn}_{1.28}$	Si_{12}	1.00

* Sokolova & Pautov (1995).

cating that this is the substitution whereby K is incorporated into the hyalotekite structure.

Figure 3b also shows that *both* species (1) and (2) are represented in the compositional data of Christy *et al.* (1998). The situation for hyalotekite may be summarized as follows: there are two distinct end-members (1) and (2) (see above), and compositions fall into both compositional fields. Thus there are two distinct "hyalotekite minerals", one of which [composition (1)] contains essential Be, and the other of which [composition (2)] does not contain essential Be. In this regard, kapitsaite-(Y), ideally $Ba_4 Y_2 Si_8 [B_2 B_2 O_{28}] F$, is Be-

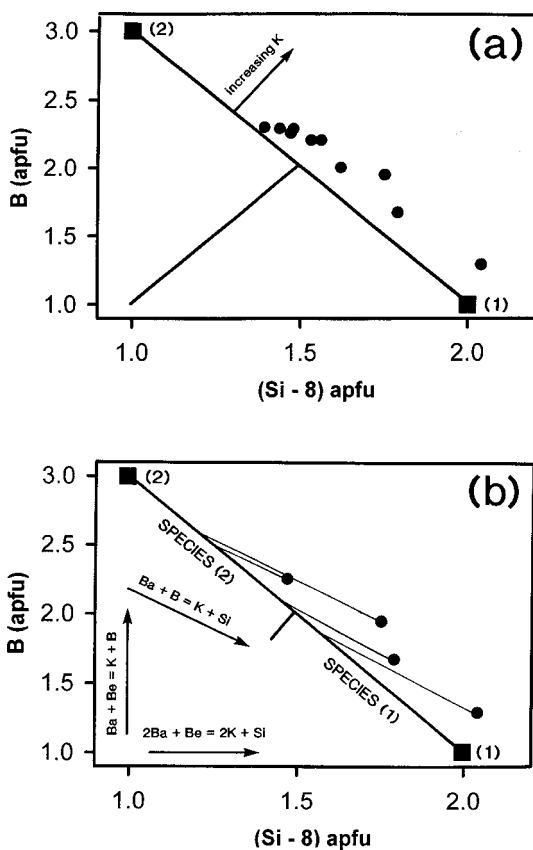


FIG. 3. Variation in the chemical composition of hyalotekite. (a) Proportion of B versus (Si - 8); the compositions (1) $Ba_4 Ca_2 Si_8 (BeB) (Si_2) O_{28} F$ and (2) $Ba_4 Ca_2 Si_8 (B_2) (SiB) O_{28} F$ are marked by filled squares and are joined by a line representing the substitution $B + B \leftrightarrow Be + Si$; data from Christy *et al.* (1998) are shown as filled circles. (b) Proportion of B versus (Si - 8); the arrows represent the directions of the substitutions involving K, the lines join selected data-points to points on the (1) - (2) line with the same Be content. Note that these lines are parallel to the substitution $Ba + B \leftrightarrow K + Si$.

free and isostructural with hyalotekite (Sokolova *et al.* 2000).

"Makarochkinite"

"Makarochkinite" is a non-accredited Be-bearing aenigmatite-like phase. The structure contains decorated chains of (BeO_4) , (SiO_4) and $(\{Si,Al\}O_4)$ tetrahedra; the basic chain resembles a pyroxenoid-like $[TO_3]$ chain consisting of alternating dimers of $(Be_{0.5} Si_{0.5} O_4)$ tetrahedra and $(Si_{0.75} Al_{0.25} O_4)$ tetrahedra, and it is decorated with side-groups of (SiO_4) tetrahedra attached to each of the $(Be_{0.5} Si_{0.5} O_4)$ tetrahedra. These chains extend along the *a* axis (Fig. 4a), forming layers of tetrahedra orthogonal to $[011]$ (Fig. 4b). The layers of tetrahedra are linked by ribbons of edge-sharing $(Fe^{2+} O_6)$ and $(Fe^{3+} O_6)$ octahedra (with minor substitution of Ti^{4+} and Mg), and between these ribbons in the layer of octahedra are interstitial sites containing [7]-coordinated Ca (with minor substitution of Na).

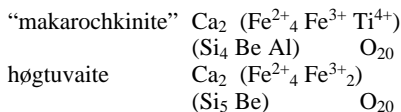
It is of interest to examine the compositional relations between "makarochkinite" and høgтуvaite, as Grauch *et al.* (1994) stated that "makarochkinite" is the same as høgтуvaite. Details of the structure of aenigmatite were given by Cannillo *et al.* (1971). It is triclinic, space group $P\bar{1}$, with six [4]-coordinated sites, designated *T*(1) to *T*(6), seven [6]-coordinated sites designated *M*(1) to *M*(7), and two [8]-coordinated sites designated *Na*(1) and *Na*(2). Two of the *M* sites, *M*(1) and *M*(2), occur at centers of symmetry, and thus one can write the resulting structural formula as $Na_2 M_6 T_6 O_{22}$. In aenigmatite (Cannillo *et al.* 1971), Ti^{4+} is strongly ordered at the *M*(7) site and Fe^{2+} occurs at the *M*(1) to *M*(6) sites to give the end-member formula $Na_2 (Fe^{2+}_5 Ti^{4+}) Si_6 O_{20}$. In the present case, homovalent substitutions may be ignored in order to focus on "makarochkinite" and høgтуvaite, the chemical compositions and formulae of which are shown in Table 6.

TABLE 6. CHEMICAL COMPOSITION AND UNIT FORMULA OF "MAKAROCHKINITE" (M) AND HØGTUVAITE (H)

	M	H		M	H
SiO ₂ wt.%	30.09	31.60	Si apfu	4.39	4.60
Al ₂ O ₃	3.55	2.64	Al	0.61	0.45
BeO	2.32	2.65	Be	0.81	0.93
TiO ₂	6.02	2.77	ΣT	5.81	5.98
Fe ₂ O ₃	11.12	19.03			
FeO	26.91	28.06	Fe ³⁺	1.22	2.09
MnO	1.26	0.27	Fe ²⁺	3.28	3.42
MgO	2.74	0.42	Mn	0.16	0.03
SnO ₂		0.53	Mg	0.60	0.09
CaO	13.38	10.44	Ti ⁴⁺	0.66	0.30
Na ₂ O	1.35	1.52	ΣM	5.92	5.96*
K ₂ O	0.30				
Total	99.04	99.93	Ca	2.09	1.63
			Na	0.38	0.43
			K	0.06	-
			Σ	2.53	2.06

Data on chemical compositions from Yakubovich *et al.* (1990) and Grauch *et al.* (1994). * includes 0.03 apfu Sn.

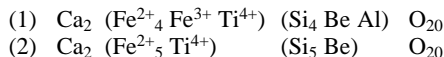
Following aenigmatite, Ti^{4+} is assumed to be ordered at the $M(7)$ site. In "makarochkinite", $\text{Ti}^{4+} > 0.50 \text{ apfu}$ and hence the $M(7)$ site is dominated by Ti^{4+} (*i.e.*, Ti^{4+} is an essential constituent of "makarochkinite"). In høgтуvaite, $\text{Ti}^{4+} < 0.50 \text{ apfu}$ and hence does not predominate at the $M(7)$ site (*i.e.*, Ti^{4+} is *not* an essential constituent of høgтуvaite). Are "makarochkinite" and høgтуvaite distinct? Yes, according to the data currently available, as Ti^{4+} is an essential constituent of "makarochkinite" and is *not* an essential constituent of høgтуvaite. The problem is most easily resolved by writing the end-member formula of each of these species, following what we have discussed above. The T contents of both are very close (Table 6), but fall on either side of the boundary between two distinct arrangements: ($\text{Si}_4 \text{ Be Al}$) in "makarochkinite" and ($\text{Si}_5 \text{ Be}$) in høgтуvaite. The M content of each may be written as follows: ($\text{Fe}^{2+}_4 \text{ Fe}^{3+} \text{ Ti}^{4+}$) for "makarochkinite" (where $\text{Fe}^{2+} \equiv \text{Fe}^{2+} + \text{Mg} + \text{Mn}$) and ($\text{Fe}^{2+}_4 \text{ Fe}^{3+}_2$) for høgтуvaite (where $\text{Fe}^{2+} \equiv \text{Fe}^{2+} + \text{Mg} + \text{Mn}$). Thus the end-member formulae may be written as follows:



These are distinct species, and the statement of Grauch *et al.* (1994) that the "informally proposed new mineral" (*viz.* "makarochkinite") "is the same as høgтуvaite" is not correct according to the published data [although note that the formula for "makarochkinite" is unsatisfactory because of the excess amount of ($\text{Ca} + \text{Na} + \text{K}$) (Table 6)].

Very recently, Barbier *et al.* (2001) reported a refined crystal structure of "makarochkinite". Although

full details of the structure are not yet available, they stated that Ti^{4+} is dominant at $M(7)$ and Be is disordered over two T sites, but did not report site populations for $M(1)$ – $M(6)$. Moreover, the Al content is slightly less than that reported by Yakubovich *et al.* (1990); however, the Ca (1.77 *apfu*) and Na (0.20 *apfu*) contents of the [7]-coordinated sites are much more satisfactory than the previously reported values. Thus the "makarochkinite" reported by Barbier *et al.* (2001) is almost exactly half-way between the compositions



Composition (1) corresponds to that derived above for the "makarochkinite" of Yakubovich *et al.* (1990), and composition (2) is new. Both compositions (1) and (2) are *bona fide* end-member compositions of the aenigmatite structure, provided they show ordered distributions of cations at the $M(1)$ – $M(6)$ or $T(1)$ – $T(6)$ sites, or both.

SUMMARY

There are several characteristics that are essential for an end-member composition:

- (1) An end-member composition must be fixed.
 - (2) An end-member composition must be compatible with the crystal structure of the associated mineral species.
 - (3) An end member *may* have more than one type of cation or anion at *one* site if required by the electro-neutrality principle.
 - (4) Anions are just as important as cations in defining end members (and their associated mineral species).
- Using the characteristics of an end-member formula in combination with aspects of the crystal structure can

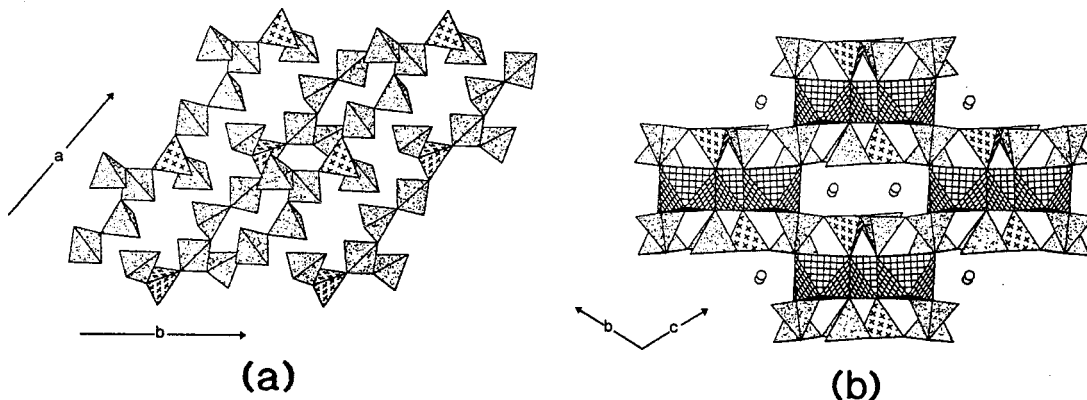


FIG. 4. The crystal structure of "makarochkinite": (a) projected onto (001); note the chains of (BeO_4) (cross-shaded) and ($\{\text{Si,Al}\}\text{O}_4$) (random-dot shaded) tetrahedra extending parallel to the a axis; (b) projected onto (100); circles in (b) represent interstitial Ca atoms.

often simply and easily resolve many quite complicated problems in mineral chemistry.

ACKNOWLEDGEMENTS

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