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 NaFe$^{3+}$,Fe$^{3+}$_2(Si$_6$O$_{18}$)(BO$_3$)$_3$(OH)$_3$, whereas the correct end-member formula is NaFe$^{3+}$(Fe$^{3+}$,Mg$^2$)$_2$(Si$_6$O$_{18}$)(BO$_3$)$_3$(OH)$_3$. 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 K(CaY)[Be$_3$Si$_8$O$_{28}$F]. There are seven accredited [4](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.

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) Elle 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 éclairer 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 NaFe$^{3+}$,Fe$^{3+}$_2(Si$_6$O$_{18}$)(BO$_3$)$_3$(OH)$_3$, tandis que la formule correcte du pôle serait NaFe$^{3+}$(Fe$^{3+}$,Mg$^2$)$_2$(Si$_6$O$_{18}$)(BO$_3$)$_3$(OH)$_3$. 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 K(CaY)[Be$_3$Si$_8$O$_{28}$F]. Il y a sept membres homologués de ce groupe contenant [4](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 beryllium, 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 distinctes: (1) Ba$_4$Ca$_2$Si$_8$(BeB)(SiB)O$_{28}$F et (2) Ba$_4$Ca$_2$Si$_8$(B$_2$)O$_{28}$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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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 \[ \text{Fe}^{2+}_{3.2} \text{Al}^{3+} \] Al \(_6\) (Si \(_6\) O \(_{18}\)) (BO \(_3\))\(_3\) (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: \[ \text{Fe}^{2+}_{3.2} \text{Al}^{3+} \] Al \(_6\) (Si \(_6\) O \(_{18}\)) (BO \(_3\))\(_3\) (OH)\(_4\) and \[ \text{Fe}^{2+}_{3.2} \text{Fe}^{3+} \] Al \(_6\) (Si \(_6\) O \(_{18}\)) (BO \(_3\))\(_3\) (OH)\(_4\).

2. An end-member composition must be compatible with the crystal structure of the associated mineral species. Forsterite, Mg\(_2\)SiO\(_4\), can be decomposed into the two components 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: Na \([\text{Li}_{1.5} \text{Al}_{1.5}] \text{Al}_6 (\text{Si}_6 \text{O}_{18}) (\text{BO}_3)_3 (\text{OH})_4\), a common mineral of the tourmaline group. In the crystal structure, \(X = \text{Na}, Z = \text{Al}, T = \text{Si}_6, B = \text{B}, V = (\text{OH})_3\) and \(W = (\text{OH})_2\) (atomic formula unit); 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 \(Y = \text{Mg}_5\), 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 Na \([\text{Li}_{1.5} \text{Al}_{1.5}] \text{Al}_6 (\text{Si}_6 \text{O}_{18}) (\text{BO}_3)_3 (\text{OH})_4\) can be resolved into the end-member compositions 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 Na \([\text{Li}_{1.5} \text{Al}_{1.5}] \text{Fe}^{3+}_5 (\text{Si}_6 \text{O}_{18}) (\text{BO}_3)_3 (\text{OH})_4\).

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 [≡ O(3)] site can be occupied by O and (OH), and the W [≡ 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 monoanion-anion content of tourmaline can vary in the range (OH) 3 (OH) to (OH) 3 F; the former by F. Thus the monovalent-anion content of tourmaline occupied by O], and hence this (OH) cannot be replaced.

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

\[
\text{Na}_3\text{Fe}^{3+}_{13}\text{Fe}^{3+}_6\text{Si}_6\text{O}_{18}\text{BO}_3\text{O}_3\text{OH}_{12}
\]

and the ideal end-member formula as

\[
\text{NaFe}^{3+}_{1}\text{Fe}^{3+}_{1}\text{Si}_6\text{O}_{18}\text{BO}_3\text{O}_3\text{OH}_{4}
\]

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 38 (OH) 12. This latter composition is very close to the following ordered arrangement of anions: V = (OH) 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:

\[
\text{NaFe}^{3+}_{1}\text{Fe}^{3+}_{1}\text{Mg}_2\text{Si}_6\text{O}_{18}\text{BO}_3\text{O}_3\text{OH}_3
\]

There is binary occupancy at 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, K Ca₂[Be₂ Al Si₁₂ O₃₀](H₂O)ₓ, has a complicated but elegant structure (Černý 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 (SiO₄) tetrahedra are arranged at the vertices of a 6̅3 plane net (Fig. 1a) and are linked by (BeO₄) 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 (BeO₄) 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 [Si₁₂ O₃₀] 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, Fe³⁺, Sn⁴⁺, Fe²⁺, Mg, Zr, Ca, Na, Y, REE, Sc
- \( B = \) Na, (H₂O), ☐, Ca?, K?
- \( C = \) K, Na, Ba, ☐, Ca?
- \( D = \) ☐, ?
- \( T(2) = \) Li, Be, B, Mg, Al, Si, Mn³⁺, 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 osmiumite 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 osmiumite structure (and also has priority).

Yttrian milarite: Černý et al. (1991) described milarite crystals from Strange Lake (Labrador, Canada) and the Jaguaraçu 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:

\[ ^4Y + ^{T(2)}Be \leftrightarrow ^4Ca + ^{T(2)}Al \]  
(1)

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

\[ ^{(B,C)}(Na,K) + ^{T(2)}Be \leftrightarrow ^{(B,C)}☐ + ^{T(2)}Al \]  
(2)

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

Consider the effect of substitution (1) on the endmember formula of milarite, K Ca₂[(Be₂ Al) (Si₁₂ O₃₀)], omitting (H₂O) 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 [Si₁₂O₃₀] cages.](image)
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.% Sc2O3. 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)[Be$_3$(Si$_{12}$O$_{30}$)].

$^4$(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) (= Si$_{12}$) 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:

1. $A_2 = M^{4+}$, $B_2 = \square_2$
2. $A_2 = M^{3+}$, $B_2 = M^{*}_2$
3. $A_2 = M^{2+}, M^{4+}$, $B_2 = M^{*}_2$
4. $A_2 = M^{2+}, M^{3+}, B_2 = M^{*}_2$

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 occupants of the A and B sites are as follows:

1. $A_2 = M^{2+}$, $B_2 = M^{*}_2$
2. $A_2 = M^{3+}, M^{4+}$, $B_2 = M^{*}_2$

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

(6) \( A_2 = M^{2+} \quad B = M^{4+} \)

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 \( M^{4+} \). 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 K Na\(_2\) Li (Mn\(_2\),Zn\(_2\)) Zr Si\(_{12}\) 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 [Li\(_{1.54}\) Zn\(_{1.15}\) 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) = Li\(_3\) and T(2) = Li\(_2\) Zn, respectively. As shown above, end-member arrangements are not possible for T(2) = Li\(_2\) Zn, and hence, according to their view, the ideal end-member composition for darapiosite must have T(2) = 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) = Li\(_3\) (Table 3). However, one may consider the alternative possibility of Li not dominant at T(2); here, the possibilities are T(2) = Zn\(_3\) and T(2) = Li Zn\(_2\). These site populations 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) = [Li\(_{1.26}\) 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 [Li\(_{0.72}\) Zn\(_{2.28}\)], suggesting that the appropriate end-member composition should have T(2) = 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) = 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 are 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 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 (K,Na\(_2\) Li\(_2\) (Li,Fe,Al,Ti\(_{1.8}\) (Zr,Ti) [Si\(_{12}\) O\(_{30}\)]. Bakakin et al. (1975) refined the crystal structure of sogdianite and wrote the formula to accord with the milarite structure as K (Zr\(_{0.8}\) Fe\(^{3+}\)0.6 Ti\(_{0.4}\) Fe\(^{2+}\)0.2) (Li\(_{2.55}\)

| TABLE 3. END-MEMBER FORMULAE FOR LI- AND Zn-BEARING MINERALS WITH THE Milarite-TYPE STRUCTURE |
|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| A     | B     | T(1) |
|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| (1)  | Sn\(^{4+}\) | K | Li\(_3\) | Si\(_{12}\) | Brannockite |
| (1)  | Ti\(^{4+}\) | K | Li\(_3\) | Si\(_{12}\) | Berezanskite |
| (1)  | Zr\(^{4+}\) | K | Li\(_3\) | Si\(_{12}\) | Sugilite |
| (2)  | Fe\(^{3+}\) | Na | Li\(_3\) | Si\(_{12}\) | Darapiosite |
| (3)  | Mn\(^{2+}\) | Na | Li | Zn | Si\(_{12}\) | Shibkovite |
| (4)  | Mn\(^{2+}\) | K | Li | Zn | Si\(_{12}\) | — |
| (5)  | Ca | K | Zn | Si\(_{12}\) | Dusmatovite |
| (6)  | Ca | K | Zn | Si\(_{12}\) | Dusmatovite |

| TABLE 4. CHEMICAL COMPOSITIONS AND UNIT FORMULAE FOR DARAPIOSITE |
|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| (1)  | NaO | 2.96 | 3.32 | 3.05 | Na | 1.09 | 1.22 | 1.35 |
| (2)  | CaO | 0.57 | — | — | Ca | 0.12 | — | 0.09 |
| (3)  | K\(_2\)O | 5.14 | 6.63 | 5.05 | K | 0.24 | 0.36 | 0.22 |
| (4)  | FeO | 100.43** | 99.57 | 100.02 | Fe | 0.55 | 0.42 | 0.36 |
| (5)  | MnO | 2.00 | 2.00 | 2.00 | Mn | 2.00 | 2.00 | 2.00 |

1. Semenov et al. (1975); 2. Ferraris et al. (1999); 3. This work.
4. Reported as REE\(_{0.6}\).
**. Includes 1.74 wt% loss on ignition.
A₀.₁₅ [O₃₀.₃₀] [Si₁₂  O₉₀] (Na₀.₉₅ K₀.₀₅). Cooper et al. (1999) refined the structure of sogdianite and assigned the site populations as follows: (Z₁₀.₇₆ T₁₅.₇₃  Fe⁺₁.₀₇₃  Al₀.₁₃) (Na₀.₈₅  K₁.₁₀₅) [Li₁  Si₁₂  O₀.₆₅]. In this composition, tetravalent and trivalent cations occur at the A site, in accord with the presence of Li₁ 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 = □ and the composition of sogdianite has B₁ = (□₁.₁₀₅ Na₀.₈₅). However, if the above sogdianite composition is resolved into its end-member components, it becomes Sogdianite₀.₁₈ Sugilite₀.₃₇ Berezanskite₀.₁₉ “Al-sugilite”₀.₉₆, 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 (BO₃) and (SiO₄) 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 [Si(1)–O] distance is 1.597 Å, which is very short for a [Si–O] distance; the other [Si–O] distances in hyalotekite are 1.613, 1.610 and 1.613 Å. Now Be [Be(1) = 0.27 Å] is marginally larger than Si (Si = 0.26 Å), and substitution of Be cannot account for the small [Si(1)–O] 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 [Si(1)–O] distance would be shorter than the distance characteristic of [Si–O], and the [B–O] distance should be longer than the distance characteristic of [B–O] (≈ 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 the 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

(1) Ba₄  Ca₂  Si₈  (Be,B)₂  (Si,B)₂  O₂₈  F
(2) Ba₄  Ca₂  Si₈  (Be,B)₂  (Si,B)₂  O₂₈  F

Their chemical data show that Ba is in many cases dominant over Pb²⁺, and Ca is dominant over Y, and hence a simplified formula can be written as

Ba₄  Ca₂  Si₈  (Be,B)₂  (Si,B)₂  O₂₈  F

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

(1) Ba₄  Ca₂  Si₈  (Be)₂  (Si)₂  O₂₈  F
(2) Ba₄  Ca₂  Si₈  (B)₂  (Si)₂  O₂₈  F

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):

(1) Ba + Be ↔ K + B
(2) 2Ba + Be ↔ 2K + Si
(3) Ba + B ↔ K + Si

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 Ba + B ↔ K + Si, indi-

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

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>T(2)</th>
<th>T(1)</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dusmatovite end-member Mn⁺²</td>
<td>□ Na</td>
<td>K</td>
<td>Zn</td>
<td>Si₂</td>
<td>0.76</td>
<td></td>
</tr>
<tr>
<td>Sogdianite end-member Zr₂</td>
<td>□ 2</td>
<td>K</td>
<td>Li</td>
<td>Si₂</td>
<td>0.12</td>
<td></td>
</tr>
<tr>
<td>Unnamed end-member Y₃</td>
<td>Na₂</td>
<td>K</td>
<td>Li</td>
<td>Si₂</td>
<td>0.12</td>
<td></td>
</tr>
<tr>
<td>Dusmatovite Mn⁺²₆  Y₆  Zr₁₂  Na</td>
<td>□ Na</td>
<td>K</td>
<td>Li₂</td>
<td>Zn₂</td>
<td>Si₂</td>
<td>1.00</td>
</tr>
</tbody>
</table>

* Sokolova & Pautov (1995).*
Figure 3. Variation in the chemical composition of hyalotekite. (a) Proportion of B versus (Si – 8); the compositions (1) \( \text{Ba}_4 \text{Ca}_2 \text{Si}_8 \left[ \text{B}_2 \text{B}_2 \text{O}_{28} \right] \text{F} \) and (2) \( \text{Ba}_4 \text{Ca}_2 \text{Si}_8 \left( \text{B}_2 \right) \left( \text{SiB} \right) \text{O}_{28} \text{F} \) are marked by filled squares and are joined by a line representing the substitution \( \text{B} + \text{B} \leftrightarrow \text{Be} + \text{Si} \); 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 \( \text{Ba} + \text{B} \leftrightarrow \text{K} + \text{Si} \).

“Makarochkinite”

“Makarochkinite” is a non-accredited Be-bearing aenigmatite-like phase. The structure contains decorated chains of \((\text{BeO}_4)\), \((\text{SiO}_4)\) and \((\text{AlSi})_2\) tetrahedra: the basic chain resembles a pyroxenoid-like \([\text{T}_0 \text{O}_3]\) chain consisting of alternating dimers of \((\text{Be}_0.5 \text{Si}_0.5 \text{O}_4)\) tetrahedra and \((\text{SiO}_2)\) tetrahedra, and it is decorated with side-groups of \((\text{SiO}_4)\) tetrahedra attached to each of the \((\text{Be}_0.5 \text{Si}_0.5)\) 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 \((\text{Fe}^{2+} \text{O}_6)\) and \((\text{Fe}^{3+} \text{O}_6)\) octahedra (with minor substitution of \(\text{Ti}^{4+}\) and \(\text{Mg}\)), and between these ribbons in the layer of octahedra are interstitial sites containing \([7]\)-coordinated \(\text{Ca}\) (with minor substitution of \(\text{Na}\)).

It is of interest to examine the compositional relations between “makarochkinite” and høgtuvaite, as Grauch et al. (1994) stated that “makarochkinite” is the same as høgtuvaite. 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 \(\text{Na}_2 \text{M}_6 \text{T}_6 \text{O}_{22}\). In aenigmatite (Cannillo et al. 1971), \(\text{Ti}^{4+}\) is strongly ordered at the \(M(7)\) site and \(\text{Fe}^{2+}\) occurs at the \(M(1)\) to \(M(6)\) sites to give the end-member formula \(\text{Na}_2 \left(\text{Fe}^{2+}_5 \text{Ti}^{4+}\right) \text{Si}_6 \text{O}_{20}\). In the present case, homovalent substitutions may be ignored in order to focus on “makarochkinite” and høgtuvaite, the chemical compositions and formulae of which are shown in Table 6.
Following aenigmatite, Ti$^{4+}$ is assumed to be ordered at the $M(7)$ site. In “makarochkinite”, Ti$^{4+}$ > 0.50 apfu and hence the $M(7)$ site is dominated by Ti$^{4+}$ (i.e., Ti$^{4+}$ is an essential constituent of “makarochkinite”). In høgtuvaite, Ti$^{4+}$ < 0.50 apfu and hence does not predominate at the $M(7)$ site (i.e., Ti$^{4+}$ is not an essential constituent of høgtuvaite). Are “makarochkinite” and høgtuvaite distinct? Yes, according to the data currently available, as Ti$^{4+}$ is an essential constituent of “makarochkinite” and is not an essential constituent of høgtuvaite. 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: ($Si_4$ Be Al) in “makarochkinite” and ($Si_5$ Be) in høgtuvaite. The $M$ content of each may be written as follows: ($Fe^{2+}_4Fe^{3+}Ti^{4+}$) for “makarochkinite” (where Fe$^{2+}$ ≡ Fe$^{2+}$ + Mg + Mn) and ($Fe^{2+}_4Fe^{3+}Ti^{4+}$) for høgtuvaite (where Fe$^{2+}$ ≡ Fe$^{2+}$ + Mg + Mn). Thus the end-member formulae may be written as follows:

“makarochkinite” $Ca_2(Fe^{2+}_4Fe^{3+}Ti^{4+})(Si_4BeAl)O_{20}$

høgtuvaite $Ca_2(Fe^{2+}_4Fe^{3+}Ti^{4+})(Si_5Be)O_{20}$

These are distinct species, and the statement of Grauch et al. (1994) that the “informally proposed new mineral” (viz. “makarochkinite”) “is the same as høgtuvaite” is not correct according to the published data [although note that the formula for “makarochkinite” is unsatisfactory because of the excess amount of (Ca + Na + 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

(1) $Ca_2(Fe^{2+}_4Fe^{3+}Ti^{4+})(Si_4BeAl)O_{20}$
(2) $Ca_2(Fe^{2+}_5Ti^{4+})(Si_5Be)O_{20}$

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

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