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PROOF THAT A DOMINANT ENDMEMBER FORMULA CAN ALWAYS BE WRITTEN FOR A MINERAL OR A CRYSTAL STRUCTURE

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Abstract

An endmember formula must be: (1) conformable with the crystal structure of the mineral, (2) electroneutral (*i.e*., not carry a net electric charge), and (3) irreducible [*i.e*., not capable of being factored into components that have the same bond topology (atomic arrangement) as that of the original formula]. The stoichiometry of an endmember formula must match the "stoichiometry" of the sites in the structure; for ease of expression, I denote such a formula here as a *chemical endmember*. In order for a chemical endmember to be a true endmember, the corresponding structure must obey the valence-sum rule of bond-valence theory. For most minerals, the chemical endmember and the (true) endmember are the same. However, where local order would lead to strong deviation from the valence-sum rule for some local arrangements, such arrangements cannot occur and the (true) endmember differs from the chemical endmember. I present heuristic and algebraic proofs that a specific chemical formula can always be represented by a corresponding dominant endmember formula. That dominant endmember may be derived by calculating the difference between the mineral formula considered and all of the possible endmember compositions; the endmember formula which is closest to the mineral formula considered is the dominant endmember.

Keywords: endmember, component, mineral formula, endmember charge-arrangement.

Introduction

There exists a persistent belief that a mineral cannot always be expressed in terms of a dominant endmember chemical formula. It is easy to see where this belief originated: many minerals are extremely complicated from both chemical and structural perspectives, and analytical difficulties can make the derivation of accurate chemical formulae quite challenging. Moreover, chemical data for an incompletely characterized mineral obviously cannot be correctly interpreted, as all the constituents of that mineral have not been identified or quantitatively measured. However, inadequate characterization does not provide proof that a mineral does not have a dominant endmember formula. Here, I will examine these issues and provide both heuristic and rigorous algebraic proofs that one can always (1) express a chemical formula in terms of a dominant-endmember chemical formula and (2) express a crystal structure in terms of a dominant structural endmember.

Endmembers

The concept of an endmember is central to mineralogy and petrology, and it is also central to the issue to be considered here. Hawthorne (2002) has discussed the properties of endmembers: (1) they must be conformable with the crystal structure of the mineral, (2) they must be neutral (*i.e*., not carry a net electric charge), and (3) they must be irreducible within the system considered [*i.e*., they should not be capable of being factored into components that have the same bond topology (atomic arrangement) as that of the original formula]. It also must be realized that "endmember" is an abstract concept: it corresponds to an ideal chemical formula and an ideal atomic arrangement; it does not correspond to a real mineral sample (although a mineral sample may have a composition that corresponds closely to the formula of the dominant endmember). Point (1) needs further discussion, as there are two separate conditions that are necessary for this requirement.

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TABLE 1. PAULING BOND-STRENGTH (*vu*) TABLE FOR *C*2/*m* AMPHIBOLE OF HYPOTHETICAL COMPOSITION $\square Ca_2Al_5(Si_3Al_5)O_{22}F_2$

	M(1)	*M*(2)	*M*(3)	*M*(4)	*T*(1)	*T*(2)	Sum
Z^+	3	3	3	2	3	3.75	
O(1)	$0.50^{x2\downarrow}$	$0.50^{x2\downarrow}$	$0.50^{x4\downarrow}$		0.75		2.25
O(2)	$0.50^{x2\downarrow}$	$0.50^{x2\downarrow}$		$0.25^{x2\downarrow}$		0.94	2.44
F	$0.50^{x2\downarrow\rightarrow}$		$0.50^{x2\downarrow}$				1.50
O(4)		$0.50^{x2\downarrow}$		$0.25^{x2\downarrow}$		0.94	1.69
O(5)				$0.25^{x2\downarrow}$	0.75	0.93	1.93
O(6)				$0.25^{x2\downarrow}$	0.75	0.93	1.93
O(7)					$0.75^{x2\rightarrow}$		1.50
Sum	3.00	3.00	3.00	2.00	3.00	3.75	

AN ENDMEMBER MUST BE CONFORMABLE WITH THE ATOMIC ARRANGEMENT OF THE MINERAL

For this statement to be true, the following two conditions must hold: (1) the stoichiometry of the endmember formula must match the "stoichiometry" of the sites in the structure (*i.e.*, the ratios of the different occupied sites in the unit cell of the structure) and (2) the atomic arrangement with that endmember chemical formula must be physically possible, *i.e.*, it must accord with the valence-sum rule (Brown 2016, Hawthorne 2012, 2015).

Condition (1)

The stoichiometry of an endmember formula must match the "stoichiometry" of the sites in the corresponding structure; for ease of expression in this paper, I denote such a chemical formula as a *chemical endmember*. Note that this requirement includes vacancies. For example, the general stoichiometry of the *C*2/*m* amphiboles may be written as follows: $AB_2C_5T_8O_{22}W_2$ with the following correspondence to sites in the structure: A = *A*; B = *M*(4), C = *M*(1), *M*(2), *M*(3); T = *T*(1), *T*(2); W = O(3); italics indicate cation sites (Hawthorne *et al*. 2012). The endmember formula for fluoro-edenite is $NaCa_2Mg_5(Si_7Al)O_{22}F_2$ and the endmember formula for tremolite is $\square Ca_2Mg_5Si_8O_{22}(OH)_2$ where □ denotes a vacancy at the *A* site and within the A group of cations.

For the majority of atomic arrangements and chemical formulae, the properties of endmembers (see above) result in endmember formulae which have a single constituent at each site [*e.g.*, diopside, $CaMgSi_2O_6$: $M(1) = Mg^{2+}$, $M(2) = Ca^{2+}$, $T = Si^{4+}$, $O(1) = O(2) = O(3) = O^{2-}$] or group of sites [*e.g.*, forsterite, $Mg_2(SiO_4)$: $M(1)$, $M(2) = Mg^{2+}$, $T = Si^{4+}$, $O(1) = O(2) = O(3) = O(4) = O^{2-}$] in the structure. Where the constituents of the sites are neutral (*e.g.*, in native metals and alloys), the dominant element at a site may be assigned as completely occupying that site and applying this procedure to each site in the structure in turn results in the dominant endmember formula. Where the atoms in a mineral occur as ions, Hawthorne (2002) has shown that the constraint of electroneutrality can require that some endmembers have two constituents of different valence and in a fixed ratio at one site in their structure (the remaining sites having only one constituent each). Thus, the dominant endmember formula for richterite, $Na(NaCa)Mg_5Si_8O_{22}(OH)_2$, has a single ion at each site in the structure except for the *M*(4) site, which is occupied by Ca^{2+} and Na^+ in equal amounts; this double occupancy of one site is necessary for electroneutrality of the endmember formula.

Condition (2)

The stoichiometry of a chemical formula may match with the "stoichiometry" of the sites in a crystal structure, but this does not ensure that the corresponding atomic arrangement with that chemical formula is physically possible. For example, let us consider a rather extreme case. Consider the *C*2/*m* amphibole formulae represented by the composition of endmember fluoro-tremolite: $\square Ca_2Mg_5Si_8O_{22}F_2$, and the unit exchange vector ${}^{C}Al_1{}^{C}Mg_{-1}{}^{T}Al_1{}^{T}Si_{-1}$. Operation of the vector $5({}^{C}Al_1{}^{C}Mg_{-1}{}^{T}Al_1{}^{T}Si_{-1})$ gives the composition $\square Ca_2{}^{C}Al_5{}^{T}(Si_3Al_5)O_{22}F_2$, with site occupancies $M(1) = M(2) = M(3) = 1.0\ Al^{3+}$, $T(1) = 1.0\ Al^{3+}$, $T(2) = 0.75\ Si^{4+} + 0.25\ Al^{3+}$. This formula fits both the general formula and the stoichiometry of the sites in the *C2*/*m* amphibole structure and conforms to condition (1) for the definition of an endmember (see above). Can this set of ions adopt the *C*2/*m* amphibole arrangement? We may test this using the valence-sum rule together with Pauling bond-strengths (Pauling 1929) replacing the bond valences, as we do not have observed bond-lengths from which to calculate bond valences. As is apparent in Table 1, the sums of the Pauling bond-strengths incident at the anions depart strongly from the valence-sum rule, particularly for the

TABLE 2. SITE POPULATIONS (*APFU*) IN HAINITE-(Y)

Site[1]	Site[2]	Assigned site-populations[1] (*apfu*)	Simplified formula[2] (*apfu*)
M4	$M^O(2)$	$Na_{0.87}$ $Ca_{0.13}$	Na
M2	$M^O(3)$	$Na_{1.22}$ $Ca_{0.78}$	NaCa
M3	A^P	$Ca_{2.00}$	Ca_2
M1	M^H	$Ca_{1.06}$ $Y_{0.66}$ $REE_{0.26}$ $Mn_{0.02}$	CaY
M5	$M^O(1)$	$Ti_{0.60}$ $Zr_{0.23}$ $Nb_{0.14}$ $Fe_{0.03}$	Ti
X8	X^O_M	$F_{1.06}$ $O_{0.94}$	FO
F9	X^O_A	$F_{2.00}$	F_2

[1] From Lyalina *et al.* (2015).

[2] From Sokolova & Cámara (2017).

TABLE 3. SHORT-RANGE ION ARRANGEMENTS (A AND B) AND LOCAL BOND-VALENCES* (*vu*) AROUND THE X^O_M SITE IN CHEMICAL ENDMEMBERS [1] AND [2] (SEE TEXT) FOR HAINITE-(Y)

	[1]A		[1]B		[2]A		[2]B	
M^H	Ca^{2+}	0.33	Y^{3+}	0.50	Ca^{2+}	0.33	$Y^{3+}_{0.5}$	0.50
$M^O(3)$	Na^+	0.17	Na^+	0.17	Ca^{2+}	0.33	Ca^{2+}	0.33
$M^O(3)$	Na^+	0.17	Na^+	0.17	Ca^{2+}	0.33	Ca^{2+}	0.33
$M^O(1)$	Ti^{4+}	0.67	Ti^{4+}	0.67	Ti^{4+}	0.67	Ti^{4+}	0.67
	Σ	1.34	Σ	**1.50**	Σ	**1.66**	Σ	1.83
Ideal charge	1		**1**		2		2	

* Using Pauling bond-strengths (Pauling 1929).

anions at the F [≡ O(3)] and O(7) sites. Thus, although the formula $\square Ca_2{}^{C}Al_5{}^{T}(Si_3Al_5)O_{22}F_2$ matches the "stoichiometry" of the *C*2/*m* amphibole structure, it cannot occur as an amphibole because the resultant atomic arrangement is not physically possible, as indicated by the departure of the incident bond-strengths from the valence-sum rule.

Let us now consider a more realistic example. Lyalina *et al*. (2015) refined the crystal structure of a hainite-(Y) from the Sakharjok nepheline syenite pegmatite, Kola Peninsula, Russia. Table 2 lists the site-specific composition and the corresponding ideal structural formula of Sokolova & Cámara (2017). The relevant chemical endmember formulae that correspond to the "stoichiometry" of the structure are as follows:

$$NaNa_2Ca_2(CaY)Ti(Si_2O_7)_2F_2F_2 \qquad \text{(Formula 1)}$$

$$NaCa_2Ca_2(CaY)Ti(Si_2O_7)_2O_2F_2 \qquad \text{(Formula 2)}$$

In Formula (1), the X^O_M site is fully occupied by F^-, whereas in Formula (2), the X^O_M site is fully occupied by O^{2-}. Hawthorne (1997) showed that bond-valence theory can be used to examine short-range (local) arrangements of ions in crystal structures and that local arrangements occur in order to minimize local deviations from the valence-sum rule. Of interest here are the local arrangements of ions at and around the X^O_M site for Formulae (1) and (2), together with the resulting bond-valences. As we do not know interatomic distances in an endmember, we must use Pauling bond-strengths to do this. Table 3 shows the short-range arrangements around the X^O_M site for Formulae (1) and (2). As the M^H site is occupied equally by Ca^{2+} and $(Y+REE)^{3+}$ (Table 3), there are two short-range (local) ion arrangements around X^O_M, one involving Ca^{2+} (arrangement A, Table 3) and one involving Y^{3+} (arrangement B, Table 3). The Pauling bond-strengths are shown, together with the sums around X^O_M for each short-range arrangement in each formula: [1]A, [1]B, [2]A, and [2]B. For Formula (1), the X^O_M site is occupied completely by F^-, and for Formula (2), the X^O_M site is occupied completely by O^{2-}. Inspection of the bond-strength sums shows a major deviation from the valence-sum rule at the X^O_M site (bolded in Table 3): an incident bond-strength sum of 1.50 *vu* for arrangement [1]B where the anion site is occupied by F^-. This indicates that Formula (1) cannot form a physically possible structure of this type, as it shows major violation of the short-range valence-sum rule at the X^O_M site for local arrangement [1]B. Can Formula (2) form a structure of this type? This question is somewhat more involved, as the maximum deviation from the valence-sum rule is considerably less than for arrangement 1[B]: 0.34 *vu* for arrangement [2]A (Table 3), similar to arrangement [1]A (Table 3), and there are many structures in which such deviations from the valence-sum rule for Pauling bond-strengths is compensated by shortening or lengthening of the corresponding bond lengths. Hainite belongs to the rinkite group of the seidozerite-supergroup minerals (Sokolova & Cámara 2017), and inspection of the formulae of these minerals can give us an indication of whether or not Formula (2) can form a possible structure. All rinkite-group minerals except seidozerite (Christiansen *et al*. 2003) and grenmarite (Bellezza *et al*. 2004) have $X^O_M = OF$; seidozerite and grenmarite have $X^O_M = O_2$. Seidozerite, ideally $Na_2Zr_2Na_2MnTi(Si_2O_7)_2O_2F_2$, and grenmarite, ideally $Na_2Zr_2Na_2MnZr(Si_2O_7)_2O_2F_2$, have the anion at X^O_M (= O_2) coordinated by Zr^{4+}, Ti^{4+}, Mn^{2+}, and Na^+ and Zr^{4+}, Zr^{4+}, Mn^{2+}, and Na^+, respectively, for a Pauling bond-strength sum at X^O_M of 1.83 *vu*. Thus, seidozerite and grenmarite have two tetravalent cations bonded to the X^O_M anions for $X^O_M = O_2$, whereas hainite and the other rinkite-group minerals have only one tetravalent cation bonded to the X^O_M anions for $X^O_M = OF$ (see Table 3), indicating that

TABLE 4. SHORT-RANGE ION ARRANGEMENTS (A AND B) AND LOCAL BOND-VALENCES* (*vu*) AROUND THE X^{O}_{M} SITE IN IDEAL HAINITE-(Y)

	A		B	
M^{H}	Ca^{2+}	0.33	Y^{3+}	0.50
$M^{O}(3)$	Na^{+}	0.17	Ca^{2+}	0.33
$M^{O}(3)$	Na^{+}	0.17	Ca^{2+}	0.33
$M^{O}(1)$	Ti^{4+}	0.67	Ti^{4+}	0.67
	Σ	1.34	Σ	1.83
Ideal charge		1		2

* Using Pauling bond-strengths (Pauling 1929).

$X^{O}_{M} = O_2$ is not physically possible where the site is coordinated only by one tetravalent cation. Thus, although the local Pauling bond-strengths of Table 3 are not conclusive, the correlations with the chemical compositions of the minerals of the rinkite group indicate that Formula (2) is also not a possible structure. If arrangement [2]A is not possible, how can arrangement [1]B occur if it shows the same deviation from the valence-sum rule? We may examine this question by looking at the structure of mosandrite (Sokolova & Hawthorne 2013), as mosandrite has $X^{O}_{M} = (OH)_2$ (*i.e.*, is completely occupied by a monovalent anion) and we may examine the coordination of the X^{O}_{M} anion without problems of local (short-range) order. In mosandrite, three of the four bonds to X^{O}_{M} are significantly longer than the mean cation–X^{O}_{M} distances, indicating that for a monovalent X^{O}_{M} anion, the structure can relax by shortening the bonds to that anion. Thus, the structures of the rinkite-group minerals can relax to accommodate the local arrangement [1]B whereas it cannot relax to accommodate the local arrangement [2]A. In conclusion, Formulae (1) and (2) are not physically possible as crystal structures.

Consider the simplified formula of hainite-(Y) given above: $Na(NaCa)Ca_2(CaY)Ti(OF)F_2$ (Table 2). There are two short-range arrangements around the X^{O}_{M} site (Table 4) labelled A and B, and above I have shown that both are possible arrangements with respect to the valence-sum rule: the local atomic arrangements accord with the valence-sum rule and are conformable with the crystal structure of the mineral. This simplified formula of hainite-(Y), $Na(NaCa)Ca_2(CaY)Ti(OF)F_2$, is not a chemical endmember formula, as it has more than one ion at more than one site in the structure. However, Hawthorne (2002) also gave another requirement for an endmember: (3) it must be irreducible within the system considered, *i.e.*, not capable of being factored into components that have the same bond topology (atomic arrangement) as that of the original formula. For hainite-(Y), the endmember formula is constrained by the requirement that the valence-sum rule be obeyed for all short-range arrangements of ions in the structure. There are three sites that have more than one constituent ion, seemingly indicating that the formula is not irreducible. However, there are two valence-sum constraints that remove two of these apparent degrees of freedom, and electroneutrality constrains the third site. Thus, from the perspective of structure stability, the formula $Na(NaCa)Ca_2(CaY)Ti(OF)F_2$ is irreducible and hence is a (true) endmember. This issue was recognized by Sokolova & Cámara (2017), who listed $Na(NaCa)Ca_2(CaY)Ti(OF)F_2$ as the ideal formula for hainite-(Y). It should be noted that there are several other TS-block minerals whose dominant endmember formulae are similarly constrained (Sokolova 2006, Sokolova & Cámara 2017) by such short-range bond-valence requirements.

Heuristic Proof that Every Mineral has a Dominant Chemical Endmember Formula

Consider a crystal structure with *n* ions that may occur in variable amounts. The structure must exert a constraint on the maximum relative amount of each ion in that it cannot exceed the number of sites at which that anion occurs in the unit cell, and the sum of the ions at a specific site cannot exceed the number of those sites in the unit cell. Thus, the relative amount of each ion in the unit cell is bounded in compositional space by a convex polyhedron, the vertices of which are defined by the numbers of sites associated with each specific component. If this were not the case, the mineral would have infinite variation in composition and hence would be infinitely large. The vertices of that polyhedron define the endmember compositions compatible with the structure, *i.e.*, the endpoints of all exchange vectors and combinations of exchange vectors that are compatible with the constituent structural arrangement. Thus, any composition of that mineral must lie within the bounds of that convex polyhedron and all possible variations of the chemical composition of this mineral must be bounded. Moreover, any composition must lie nearer to one vertex than all other vertices (unless it is equally distant from more than one vertex, *i.e.*, it occurs on a compositional boundary). The nearest vertex defines the dominant endmember composition. Any suggestion that a mineral does not have a dominant endmember composition means that the composition must lie outside the bounds of its possible compositional variation, a self-contradiction that invalidates the statement that the mineral does not have a dominant endmember composition.

ALGEBRAIC PROOF THAT ANY MINERAL HAS A DOMINANT CHEMICAL-ENDMEMBER FORMULA

For minerals in which the individual atomic constituents have zero formal charge (*e.g.*, native metals, alloys), endmember compositions may be derived simply by filling each crystallographic site in the structure with the dominant metal observed at that site. However, the situation for structures of ions is (or can be) more complicated, as such a procedure has to conserve electric charge. This issue may be approached using the idea of *endmember charge-arrangements* (Hawthorne 2002). There is some confusion in the literature with regard to the expressions "root-charge arrangement" and "endmember charge arrangement". This is due in part to the occurrence of approved mineral species for which the ideal formulae are not irreducible. As noted by Hawthorne & Oberti (2006, 2007), "the IMA CNMNN has recognized that distinct arrangements of formal charges at the sites (or groups of sites) in the amphibole structure warrant distinct **root names**, and are, by implication, distinct species…[and] the expression 'a distinct arrangement of formal charges' was not defined in previous classifications". However, by inspection, it is apparent that "distinct arrangements of formal charges at the sites (or groups of sites) in the amphibole structure" means that all different combinations of integer charges over three of the four sites or groups of sites for the $C2/m$ structure, A, $M(4)$, $M(1,2,3)$, $T(1,2)$, are considered distinct. Hawthorne *et al*. (2012) state the following: "(1) All distinct arrangements of integral charges over the amphibole formula are considered as *root charge arrangements*. (2) Specific ions [Na^+, Mg^{2+}, Al^{3+}, Si^{4+}, $(OH)^-$] of appropriate charge are associated with sites in the structure, and each distinct chemical composition is a *root composition*. These compositions are assigned trivial names." A root charge-arrangement is a charge arrangement associated with a root composition and is not necessarily an endmember charge-arrangement. For example, the amphibole charge arrangement ${}^{A}0$ ${}^{M(4)}2^+{}_2$ ${}^{M(1,3)}2^+{}_3$ ${}^{M(2)}(2^+3^+)$ $T(3^+4^+{}_7)$ ${}^{O}2^-{}_{22}$ ${}^{O(3)}1^-{}_2$ is a root charge-arrangement and corresponds to the root name magnesio-hornblende with the ideal formula $\square Ca_2(Mg_4Al)(Si_7Al)O_{22}(OH)_2$; however, this formula is not a valid endmember formula, as it is not irreducible. Unfortunately, the tables in Hawthorne *et al*. (2012) list the "endmember formulae" for all species; some of these formulae are root compositions and are not true endmember formulae. Why are such compositions considered as distinct species? These compositions generally correspond to very common (often rock-forming) minerals which are (1) embedded in the mineralogical and petrological literature; and (2) characteristic of specific rock-types, and loss of these species would negatively affect petrology in the extreme. It is desirable to introduce the terms *endmember formula* (or composition) and *ideal formula* (or composition) to be associated with minerals whose associated charge arrangement is endmember (*i.e.*, irreducible) or not endmember (*i.e.*, reducible). Gagné & Hawthorne (2016) use the expression "root charge arrangement" where they are actually deriving endmember charge arrangements, and Bosi *et al*. (2019) use "root charge arrangement" where they are actually dealing with endmember charge arrangements.

Endmember charge-arrangement may be defined as the charge arrangement of an endmember; thus, diopside has the charge arrangement ${}^{M(2)}2^+$ ${}^{M(1)}2^+$ ${}^{T}4^+{}_2$ ${}^{O}2^-{}_6$ (condensing the anions into one term), and both jadeite and spodumene have the charge arrangement ${}^{M(2)}1^+$ ${}^{M(1)}3^+$ ${}^{T}4^+{}_2$ ${}^{O}2^-{}_6$, the latter emphasizing that different endmembers can have the same endmember charge-arrangement. Note that endmember charge-arrangements must obey the same set of criteria as chemical endmember formulae: (1) they are conformable with the crystal structure of the mineral, (2) they do not carry a net electric charge, and (3) they are irreducible within the system considered. Moreover, it must be emphasized that the derivation of endmember charge-arrangements is not synonymous with the derivation of endmember compositions, as is apparent from the example of jadeite and spodumene given above.

Proof that any mineral has a dominant endmember charge-arrangement

Consider a crystal-structure arrangement of the general form S_i ($i = 1,n$) where S_i is any occupied site in the structure, n is the number of symmetrically distinct occupied sites in the structure, m_i is the number of positions of the S_i site per unit cell, and Z_i is the charge at the ith site.

[1] Any appropriate charge can be assigned to each of $(n - 1)$ of these sites, and each of these charges is associated with a single ion. This process of assignment produces a net charge of $\Sigma m_i Z_i$ ($i = 1, n - 1$) that must be neutralized by the charge Z_r assigned to the remaining site, S_r of multiplicity m_r : $m_r Z_r$. For the charge arrangement to be an endmember charge arrangement, the site S_r must be occupied by one or two charges that sum to Z_r:

$$aZ_a + bZ_b = Z_r \qquad \text{(Equation 1)}$$

$$a + b = 1 \qquad \text{(Equation 2)}$$

Both a and b must be positive, and Z_a and Z_b must be integers (*i.e.*, integral charges), and hence $Z_a \leq Z_r \leq Z_b$. Solutions to these equations must involve pairs of charges, Z_a and Z_b, conforming to the requirement $Z_a \leq Z_r \leq Z_b$. There are only a small number of possible pairs of (Z_a, Z_b) conforming to this requirement; these may be listed and Equations (1) and (2) solved simultaneously for each of these pairs. The resultant solutions must conform to the requirement for an endmember charge arrangement.

[2] Step [1] is repeated for all different possible charge arrangements over the same set of sites: S_i (i = 1, n − 1), giving different solutions for Equations (1) and (2).

[3] Steps [1] and [2] are repeated, setting each site in the structure in turn as the S_r site. The result is the complete set of endmember charge-arrangements.

The argument given above is completely general and shows that *any chemical formula compatible with a crystal structure can be resolved into a finite set of endmember charge-arrangements compatible with the atomic arrangement of that structure*. I must emphasize that endmember charge-arrangements are not endmembers—they are arrangements of charges, not specific ions, and hence the dominant endmember charge-arrangement does not necessarily correspond to the dominant endmember formula. However, this result may be used to assign the ions in a specific chemical formula to the endmember charge-arrangements as discussed below.

Examples

Consider richterite: $^{A}Na^{M(4)}(CaNa)_2{}^{M(1,2,3)}Mg_5{}^{T(1,2)}Si_8O_{22}(OH)_2$. I will show some details of the calculation with the M(4) site set as S_r. $\Sigma m_i Z_i$ (i = 1, n − 1) = 6^- and $m_r = 4$ [the number of M(4) positions in the unit cell]; hence $Z_r = 1.5^+$. From above, $Z_a \leq 1.5 \leq Z_b$, and hence the possible distinct combinations of charges are as follows: 0,2; 0,3; 0,4; 1,2; 1,3; 1,4; giving the following solutions:

0,2: $0_{0.25}\ 2^+_{0.75} = (\square_{0.25}\ M^{2+}_{0.75})$
0,3: $0_{0.50}\ 3^+_{0.50} = (\square_{0.50}\ M^{3+}_{0.50})$
0,4: $0_{0.50}\ 4^+_{0.50} = (\square_{0.625}\ M^{4+}_{0.375})$
1,2: $\mathbf{1^+_{0.50}\ 2^+_{0.50} = (M^+_{0.50}\ M^{2+}_{0.50})}$
1,3: $1^+_{0.50}\ 3^+_{0.50} = (M^+_{0.75}\ M^{3+}_{0.25})$
1,4: $1^+_{0.833}\ 4^+_{0.167} = (M^+_{0.833}\ M^{4+}_{0.167})$

All these solutions are formally possible, but once we consider assigning ions to these arrangements, most of them will violate the valence-sum rule and we are left with the endmember charge-arrangement (bolded above) that corresponds to the M(4) occupancy in richterite: (NaCa).

Consider monazite-(Ce): $CePO_4$. I will show some details of the calculation with the *Ce* site set as S_r. $\Sigma m_i Z_i$ (i = 1, n − 1) = 12^- and $m_r = 4$; hence $Z_r = 3^+$ and $Z_a \leq 3 \leq Z_b$. Thus, the possible distinct combinations of charges are as follows: 0,3; 0,4; 0,5; 1,4; 1,5; 2,4; 2,5; giving the following solutions:

0,3: $\mathbf{0_{0.00}\ 3^+_{1.00} = (\square_{0.00}\ M^{3+}_{1.00})}$
0,4: $0_{0.25}\ 4^+_{0.75} = (\square_{0.25}\ M^{4+}_{0.75})$
0,5: $0_{0.40}\ 5^+_{0.60} = (\square_{0.40}\ M^{5+}_{0.60})$
1,4: $1^+_{0.33}\ 4^+_{0.67} = (M^+_{0.33}\ M^{4+}_{0.67})$
1,5: $1^+_{0.50}\ 5^+_{0.50} = (M^+_{0.50}\ M^{5+}_{0.50})$
2,4: $\mathbf{2^+_{0.50}\ 4^+_{0.50} = (M^{2+}_{0.50}\ M^{4+}_{0.50})}$
2,5: $2^+_{0.67}\ 5^+_{0.33} = (M^{2+}_{0.67}\ M^{5+}_{0.33})$

All these solutions are formally possible, and I have bolded the endmember charge arrangements corresponding to monazite-(Ce) and cheralite.

Consider milarite: $^{A}Ca_2{}^{B}\square_2{}^{C}K^{T(2)}(Be_2Al)^{T(1)}Si_{12}O_{30}$. I will show some details of the calculation with the T(2) site set as S_r. $\Sigma m_i Z_i$ (i = 1, n − 1) = 14^- and $m_r = 6$; hence $Z_r = 2.33$, $Z_a \leq 2.33 \leq Z_b$, and the possible combinations of charges are as follows: 0,3; 0,4; 1,3: 1,4; 2,3; 2,4; giving the following solutions:

0,3: $0_{0.223}\ 3^+_{0.777} = (\square_{0.223}\ M^{3+}_{0.777})$
0,4: $0_{0.417}\ 4^+_{0.583} = (\square_{0.417}\ M^{4+}_{0.583})$
1,3: $1^+_{0.223}\ 3^+_{0.777} = (M^+_{0.223}\ M^{3+}_{0.777})$
1,4: $1^+_{0.557}\ 4^+_{0.443} = (M^+_{0.557}\ M^{4+}_{0.443})$
2,3: $\mathbf{2^+_{0.677}\ 3^+_{0.333} = (M^{2+}_{0.677}\ M^{3+}_{0.333})}$
2,4: $2^+_{0.835}\ 4^+_{0.165} = (M^{2+}_{0.835}\ M^{4+}_{0.165})$

All these solutions are formally possible, and I have bolded the endmember charge arrangement corresponding to the T(2) occupancy in milarite (and almarudite) (Be_2Al).

Derivation of the dominant endmember formula from endmember charge-arrangements

Hawthorne (2002) developed the idea of endmember charge-arrangements and used it to determine the dominant endmember formula in several specific minerals; however, never did he suggest that the dominant endmember charge-arrangement corresponds to the dominant endmember chemical formula. A mineral is identified by the ions at its constituent sites, not by the arrangement of charges at those sites, no matter how useful the latter in understanding aspects of the crystal chemistry of that mineral. Moreover, the dominant endmember charge-arrangement does not necessarily correspond to the dominant chemical endmember formula, as the latter corresponds to a formula of specific ions whereas the former corresponds to an arrangement of charges. However, each dominant endmember charge-arrangement allows specific ions to be associated with it, identifying chemical endmember formulae; this is why the idea of endmember charge-arrangements was developed. Hawthorne (2002), Gagné & Hawthorne (2016), and Hawthorne *et al*. (2018) used the following procedure to identify a dominant chemical endmember formula for any chemical formula:

[1] Calculate all possible endmember charge-arrangements for that structure and set of constituent cations.
[2] Calculate the mean charge at each site in the structure for the chemical composition of interest.
[3] Determine which endmember charge-arrangements are closer to the arrangement of mean charges in the mineral by comparing the sums of the squares of the differences between the endmember charge-arrangement of the mineral and each endmember charge-arrangement for that structure.
[4] The endmember charge-arrangements of the structure closer to the mean charge arrangement of the mineral allow assignment of the corresponding ions to one or more possible endmember formulae. The dominant endmember composition is that which is closest in compositional space to the chemical formula of the mineral.

For example, makarochkinite was originally proposed as a distinct species by Yakubovich *et al*. (1990) but was rejected by the IMA. Using the idea of endmember-charge arguments, Hawthorne (2002) showed that makarochkinite is actually a distinct species, and it was subsequently described as such by Grew *et al*. (2005).

Two more examples were given by Hawthorne (2002) involving possible new species belonging to the hyalotekite group and the milarite group. Subsequently, the possibilities for chemical endmembers in these two groups were examined in much more detail *via* the process of *chemographic exploration*, whereby all possible endmember charge-arrangements conformable with a specific structure type are derived and subsequently used to extract all chemical endmember compositions possible for that structure type. Hawthorne *et al*. (2018) did this for the hyalotekite structure type, which led to the discovery of khvorovite, ideally $\mathrm{Pb^{2+}{}_4Ca_2[Si_8B_2(SiB)O_{28}]F}$ (Pautov *et al*. 2015), and recognition of another as-yet undescribed species. Gagné & Hawthorne (2016) examined the milarite structure from this perspective and showed that there are 34 distinct endmember charge-arrangements with Si = 12 *apfu* and 39 distinct endmember charge-arrangements with Si = 8–11 *apfu*. Examination of ~350 chemical analyses from the literature showed that six of these compositions deserve to be described as new mineral species, plus an additional two analyses of what could be new minerals if their site populations from crystal-structure refinement so indicate.

TABLE 5. A PYRALSPITE GARNET* AND ALL POSSIBLE ENDMEMBERS

Components	Formula
Grossular (Gr)	$\mathrm{Ca_3Al_2Si_3O_{12}}$
Andradite (An)	$\mathrm{Ca_3Fe^{3+}{}_2Si_3O_{12}}$
Uvarovite (Uv)	$\mathrm{Ca_3Cr^{3+}{}_2Si_3O_{12}}$
Pyrope (Py)	$\mathrm{Mg_3Al_2Si_3O_{12}}$
Almandine (Al)	$\mathrm{Fe^{2+}{}_3Al_2Si_3O_{12}}$
Spessartine (Sp)	$\mathrm{Mn^{2+}{}_3Al_2Si_3O_{12}}$
1	$\mathrm{Mg_3Fe^{3+}{}_2Si_3O_{12}}$
2	$\mathrm{Mg_3Cr^{3+}{}_2Si_3O_{12}}$
3	$\mathrm{Fe^{2+}{}_3Fe^{3+}{}_2Si_3O_{12}}$
4	$\mathrm{Fe^{2+}{}_3Cr^{3+}{}_2Si_3O_{12}}$
5	$\mathrm{Mn^{2+}{}_3Fe^{3+}{}_2Si_3O_{12}}$
6	$\mathrm{Mn^{2+}{}_3Cr^{3+}{}_2Si_3O_{12}}$

* Formula: $\mathrm{(Mg_{1.82}Fe^{2+}{}_{0.79}Mn_{0.02}Ca_{0.37})(Al_{1.92}Fe^{3+}{}_{0.06}Cr_{0.02})Si_3O_{12}}$; from Deer *et al.* (1992, page 684).

Derivation of the dominant endmember formula: An example

I will consider the calculation of the dominant endmember formula for the garnet example of Deer *et al*. (1992, page 684):

$$\left(\mathrm{Mg_{1.82}Fe^{2+}_{0.79}Mn_{0.02}Ca_{0.37}}\right)\left(\mathrm{Al_{1.92}Fe^{3+}_{0.06}Cr_{0.02}}\right)\mathrm{Si_3O_{12}}$$

I have modified the formula given by them (which was originally normalized on 24 O *apfu*) so that it is now normalized to the more conventional 12 O *apfu*, the site populations sum to the numbers of available sites, and the formula is electroneutral (Table 5). I have listed all the possible endmember formulae in Table 5. Deer *et al*. (1992) chose to express the endmember proportions in terms of pyralspite-ugrandite (Table 5) and I have so labelled the corresponding endmembers; the other possible endmembers I have labelled 1 to 6. The endmember charge-arrangement for this garnet is ${}^{X}2^{+}{}_{3}\ {}^{Y}3^{+}{}_{2}\ {}^{Z}4^{+}{}_{3}\ {}^{O}2^{-}{}_{12}$ and this corresponds to the charge arrangements of all endmembers listed in Table 5. We may calculate the distance (in compositional space) of the garnet composition from each endmember *via* the square root of the sum of the squares of the differences in compositions; note that the compositions need to be expressed in terms of site occupancies (not site populations) and thus the compositional differences for each ion are divided by the multiplicity of the relevant site (see Table 6). Table 6 lists the square-root of the sum of the squares of the differences (RSSD) between each of the endmembers and the mineral

TABLE 6. DIFFERENCES IN SITE OCCUPANCIES FOR EACH ION BETWEEN THE GARNET FORMULA AND THE ENDMEMBER FORMULAE, AND THE RESULTING RSSD* VALUE

	Ca	Mg	Fe^{2+}	Mn	Al	Fe^{3+}	Cr^{3+}	RSSD*
Gr	2.63/3	1.82/3	0.79/3	0.02/3	0.08/2	0.06/2	0.02/2	1.099
An	2.63/3	1.82/3	0.79/3	0.02/3	1.92/2	1.94/2	0.02/2	1.752
Uv	2.63/3	1.82/3	0.79/3	0.02/3	1.92/2	0.06/2	1.98/2	1.763
Py	0.37/3	1.18/3	0.79/3	0.02/3	0.08/2	0.06/2	0.02/2	0.492
Al	0.37/3	1.82/3	2.21/3	0.02/3	0.08/2	0.06/2	0.02/2	0.964
Sp	0.37/3	1.82/3	0.79/3	2.98/3	0.08/2	0.06/2	0.02/2	1.201
1	0.37/3	1.18/3	0.79/3	0.02/3	1.92/2	1.94/2	0.02/2	1.500
2	0.37/3	1.18/3	0.79/3	0.02/3	1.92/2	0.06/2	1.98/2	1.464
3	0.37/3	1.82/3	2.21/3	0.02/3	1.92/2	1.94/2	0.02/2	1.670
4	0.37/3	1.82/3	2.21/3	0.02/3	1.92/2	0.06/2	1.98/2	1.682
5	0.37/3	1.82/3	0.79/3	2.98/3	1.92/2	1.94/2	0.02/2	1.817
6	0.37/3	1.82/3	0.79/3	2.98/3	1.92/2	0.06/2	1.98/2	1.828

* RSSD = Square-Root of the Sum of the Squares of the Differences.

formula of Table 5. The smallest RSSD is for pyrope, and hence this is the dominant endmember. Note that this accords with the calculation of Deer *et al*. (1992), which listed pyrope as the dominant endmember, and also note that the method is not dependent on quantitatively representing the formula as a set of endmember constituents.

SUMMARY

[1] An endmember formula must be: (1) conformable with the crystal structure of the mineral, (2) electroneutral (*i.e*., not carry a net electric charge), and (3) irreducible (*i.e*., not capable of being factored into components that have the same bond topology (atomic arrangement) as that of the original formula).

[2] The stoichiometry of an endmember formula must match the "stoichiometry" of the sites in the structure; for ease of expression, I denote such a formula here as a *chemical endmember*. In order for a chemical endmember to be a true endmember, the corresponding structure must obey the valence-sum rule.

[3] The derivation of a dominant endmember formula for a specific chemical formula is independent of expressing the specific chemical formula as a set of endmember constituents.

[4] I have presented heuristic and algebraic proofs that a specific chemical formula can always be represented by a corresponding dominant endmember formula.

[5] The dominant endmember is that endmember which is closest to the formula of the mineral considered, expressed as the smallest RSSD (square-root of the sum of the squared differences) from the mineral formula.

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