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## Article

# On the definition of distinct mineral species: A critique of current IMA–CNMNC procedures

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**Abstract**

The criteria for the definition of a new mineral species currently used by the Commission on New Minerals Nomenclature and Classification (CNMNC) of the International Mineralogical Association are critically examined. In particular, the rule of the dominant constituent can violate the laws of conservation of electric charge. A series of additional rules: (1) valency-imposed double site-occupancy; (2) the dominant-valency rule; and (3) the site-total-charge approach, have been developed in an attempt to correct this error. However, none of these rules can overcome the fundamental flaw introduced by the rule of the dominant constituent, and the chemical formulae resulting from application of these rules can violate the requirements of an end-member, particularly that of electroneutrality. As a result, the IMA–CNMNC rules cannot derive end-member formulae for some groups of minerals, giving rise to many *ad hoc* decisions in defining distinct mineral species.

## Introduction

The approval of a new mineral species by IMA–CNMNC has three distinct parts: (1) definition of the end-member composition and structure; (2) consideration of the classification of the new species; and (3) assignment of a name. These are independent processes and should proceed in the above sequence. Thus (1) is independent of (2) and (3) and should not be influenced by (2) and/or (3), and yet in practice, criteria of classification often conflate these processes, whereas they are distinct and should be kept separate.

The criteria for the definition of a new mineral species currently used by the Commission on New Minerals Nomenclature and Classification (CNMNC) of the International Mineralogical Association (IMA) are based on what is called the "rule of the dominant constituent" (Hatert and Burke, 2008; page 717): "a mineral is a distinct species if the set of dominant constituents (ions or neutral species) at the sites in the crystal structure is distinct from that of any other mineral with the same structural arrangement". Note that this definition concerns mineral species and is distinct from the formal definition of a mineral (e.g. Nickel, 1995). The rule of the dominant constituent has been very successful in defining mineral species across the complete range of chemical compositions encountered in Nature. However, there are two problems with this approach: there are minerals for which this criterion and its later modifications do not work,

and there are demonstrable errors associated with the operation of these rules. Here, I critically examine these issues and the examples that IMA–CNMNC has used in attempts to justify the introduction of a series of modifications to the rule of the dominant constituent.

## Defining mineral species

Bosi *et al.* (2019a; page 628) made the following statement: "Usually, two approaches could be used to distinguish mineral species: (1) the dominant-valency approach, which identifies mineral species by determining the dominant root-charge arrangement (e.g. Hawthorne, 2002); (2) the dominant-end-member approach, which identifies species by determining the most abundant end-member component (e.g. Bulakh, 2010; Dolivo-Dobrovol'sky, 2010)". Although the rule of the dominant constituent does not explicitly use the expression 'end-member', Nickel (1992), Nickel and Grice (1998), Hatert and Burke (2008) and Bosi *et al.* (2019a, 2019b) all implicitly assumed that a mineral has a unique end-member chemical formula, and Bosi *et al.* (2019a; page 627) explicitly state: "Mineral species should be identified by an end-member formula…". Summarising the above quotes in a more straightforward manner: **there are two approaches to determining the end-member chemical formula of a mineral: the dominant-valency method, and the dominant-end-member method**. Which is correct? Here, I will consider the issues associated with defining an end-member formula *via* the rules of the IMA–CNMNC and will show that the examples purportedly used to explain the need for each of these rules can be interpreted in a straightforward

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manner using the dominant end-member approach. Elsewhere I will consider issues associated with defining an end-member formula of a mineral species by its dominant end-member as there are also unresolved issues associated with this approach.

## Definitions

Before I consider these issues, I will define various terms so that there is no confusion arising from their use in the following considerations.

### Valence and oxidation state

IUPAC (2019) (the International Union of Pure and Applied Chemistry) defines valence as follows: "The maximum number of univalent atoms (originally hydrogen or chlorine atoms) that may combine with an atom of the element under consideration, or with a fragment, or for which an atom of this element can be substituted". Two other widely accepted versions are as follows: "…the number of hydrogen atoms that can combine with an element in a binary hydride or twice the number of oxygen atoms combining with an element in its oxide or oxides" (Greenwood and Earnshaw, 1997; page 27), and "…the number of electrons that an atom uses in bonding" (Parkin, 2006; page 791). IUPAC (2019) defines oxidation state as follows: "the charge on an atom after ionic approximation of its heteronuclear bonds". Whichever definition one accepts for valence, it is clear that valence does not have a sign whereas oxidation state (number) does have a sign (or is 0).

### Electric charge and electroneutrality

A neutral atom has equal numbers of protons and electrons. By extension, a set of neutral atoms has equal numbers of protons and electrons. Where the atoms in this set form a solid, some of the electrons are shared between atoms to form chemical bonds, but the total numbers of electrons and protons remain the same, and this set of bonded atoms, e.g. a crystal, is electroneutral. Electric charge is a continuously differentiable function and hence is subject to a conservation law as required by Noether's first theorem (Quigg, 2013), and the global gauge invariance of the electromagnetic field results in the conservation of electric charge. Thus the electroneutrality of an assemblage of atoms in a crystal structure must be conserved, irrespective of the oxidation states of the constituent ions. Any deviation from conservation of electric charge violates one of the most fundamental laws of Physics.

### End-member

An end-member is defined as one end of a range or series made up of similar members; more specifically in Mineralogy, a mineral that occurs at one end in a range of solid solutions (https://en.wiktionary.org/wiki/endmember). At least with respect to minerals, this definition is wrong. As the concept of an end-member is central to Mineralogy and Petrology, and also central to the issues to be considered here, some discussion is desirable.

Let us consider the experimental data on a set of minerals: a set of chemical analyses, a set of unit-cell dimensions, etc. In detail, all of these chemical analyses are different from each other, and all of these unit-cell dimensions are different from each other; how do we know whether these sets of data correspond to the same mineral species?

In order to decide whether objects belong to the same set, one needs a set of properties that are the same for all these objects in this set, and this set of properties constitutes the definition of an abstract object with which we can compare real objects and decide if the real objects belong to that same set, i.e. are the same as each other (or not). Properties of objects may be divided into intrinsic properties and extrinsic properties: an intrinsic property is a property that is characteristic of the object itself and is independent of anything else; an extrinsic property is a property that depends on the relation between the object itself and other things. The chemical analyses (and associated chemical formulae) and the unit-cell dimensions mentioned above are extrinsic properties: they differ from sample to sample, and the unit-cell dimensions also vary with changing temperature and pressure. Hence chemical analyses, chemical formulae and unit-cell dimensions are extrinsic properties and cannot be used to define the mental object with which we can compare our data. Intrinsic properties that may be used to define this mental object, which henceforth I will call an end-member, are as follows: (1) the end-member formula (including Z, the number of formula units in the unit cell); (2) the space group and bond topology of the end-member structure; and (3) the name of the end-member. This set of intrinsic properties constitutes a set of universals that are associated with the archetype of a mineral species. This archetype is an abstract object and all real mineral samples corresponding to this archetype are imperfect copies of that archetype but have the set of intrinsic properties identical to the corresponding set of universals. This correspondence allows us to say that the different mineral samples are the same mineral species (or not). So, to summarise: **An end-member is not a mineral, it is an abstract concept that we use to identify minerals and a particular mineral species** (Hawthorne *et al.*, 2021).

## General properties of end-members

Hawthorne (2002) has discussed the properties of an end-member: (1) an end-member formula must be irreducible (fixed) within the system considered (i.e. it should not be capable of being factored into components that have the same bond topology (atomic arrangement) as that of the original composition); (2) it must be compatible with the crystal structure of the associated mineral species; and (3) it must be electroneutral (i.e. not carry an electric charge).

Hawthorne (2021a) has examined the concept of end-members in more detail. In particular, condition (2): the end-member must be conformable with the crystal structure of the mineral. There are two requirements for this condition to hold: first, the end-member chemical formula must match the 'stoichiometry' of the sites in the structure, and second, the resultant atomic arrangement must be capable of existence. For some minerals, what seem to be valid chemical end-member formulae strongly violate the valence-sum rule (Brown, 2002, 2016; Brown and Shannon, 1973) and atomic arrangements cannot exist for these compositions.

### A hypothetical amphibole

Consider the root formula of pargasite (Hawthorne *et al.*, 2012): $NaCa_2(Mg_4Al)(Si_6Al_2)O_{22}(OH)_2$. The following substitution maintains the general stoichiometry of the amphibole structure

$(AB_2C_5T_8O_{22}W_2)$: $^A\square + {}^CMg + {}^W\square_2 \rightarrow {}^ANa + {}^CAl + {}^W(OH)_2 \rightarrow \square Ca_2Mg_5(Si_6Al_2)O_{22}\square_2$; this formula is electroneutral and fits the general stoichiometry of the amphiboles. However, it cannot exist as a crystal structure as it violates several requirements for a stable structure. The occurrence of a vacancy at the W position of the general formula may maintain electroneutrality of the formula, but it means that the O(3) site is occupied by a vacancy which, in turn, means that the $M(1)$ and $M(2)$ sites are [4]-coordinated, in particular imparting a one-sided coordination to the cation(s) at the $M(1)$ site, leading to major violations of the valence-sum rule (Brown, 2016; Hawthorne, 2012, 2015) and non-stability of the amphibole-type arrangement of ions implied by the formula $\square Ca_2Mg_5(Si_6Al_2)O_{22}\square_2$. In this regard, it must be emphasised that the algebraic fit of a formula to the general stoichiometry of a mineral structure is a necessary but not sufficient condition for stability. The arrangement of ions implied by the formula must also be a stable structure (Hawthorne, 2021a).

### A real example: Y-rich hainite

Lyalina *et al.* (2015) refined the crystal structure of Y-rich hainite of approximate chemical formula $Na(NaCa)Ca_2(CaY)Ti(Si_2O_7)_2(OF)F_2$. This formula may be split into two chemical formulae as follows: $NaNa_2Ca_2(CaY)Ti(Si_2O_7)_2F_2F_2$ and $NaCa_2Ca_2(CaY)Ti(Si_2O_7)_2O_2F_2$. Using bond-valence theory, Hawthorne (2021a) showed that these formulae are not structurally stable atomic arrangements and hence cannot be end-members. The formula $Na(NaCa)Ca_2(CaY)Ti(Si_2O_7)_2(OF)F_2$ has various local (short-range) arrangements of cations that are stable with regard to the valence-sum rule of bond-valence theory. In the formula $Na(NaCa)Ca_2(CaY)Ti(Si_2O_7)_2(OF)F_2$, there are three sites that contain more than one constituent ion, apparently 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 (Hawthorne, 2021a). Thus, the formula $Na(NaCa)Ca_2(CaY)Ti(Si_2O_7)_2(OF)F_2$ is irreducible, it accords with the valence-sum rule (Brown, 2016), and is a true end-member. This point was recognised by Sokolova and Cámara (2017) who wrote the ideal formula for hainite-(Y) as $Na(NaCa)Ca_2(CaY)Ti(Si_2O_7)_2(OF)F_2$. Other TS-block minerals have dominant end-member formulae (Sokolova, 2006; Sokolova and Cámara, 2017) that are likewise constrained by such short-range bond-valence requirements; it is not by accident that these minerals have the empirical formulae that they do. The number of minerals for which this situation occurs is quite small, but mineralogists need to be aware of this issue.

### Calculation of the proportions of end-member constituents in minerals

The ostensible reason for not using dominant end-member formulae to define distinct mineral species was invoked by Grew *et al.* (2013) and stated by Bosi *et al.* (2019a; page 627) as follows: "As demonstrated for garnet-supergroup minerals, for example, the end-member approach is ambiguous, as end-member proportions strongly depend on the calculation sequence". This calculation involves the solution of a set of simultaneous equations relating the amount of each end-member constituent to the amount of each ion in the chemical formula of the mineral. The operative word here is 'simultaneous'; there is no sequence in finding a solution to these equations, they are solved

simultaneously. Hawthorne (2021b) examined the data of Rickwood (1968) on which these statements are based, and showed that his sequence-dependent results arise because of the use of non-stoichiometric and non-electroneutral formulae, something that Rickwood (1968) mentioned in his paper but which seems to have been overlooked by those who have cited his results. If that garnet formula is adjusted slightly such that it exactly fits the general formula of a garnet, $^{[8]}X_3^{[6]}Y_2^{[4]}Z_3O_{12}$, and is electroneutral, the simultaneous equations relating its chemical formula to a particular set of end-member constituents have a single unique solution.

We tend to treat minor deviations in stoichiometry and electroneutrality in chemical formulae as trivial issues. However, they are not trivial issues. If the number of ions exceeds the number of sites available, a structure of that composition is physically impossible. Furthermore, if the chemical formula has a net electric charge, it is violating the conservation of electric charge, one of the most fundamental laws of Physics. Adjusting the composition of a mineral, normally within the noise of the data, seems a small price to pay for removing such fundamental physical errors from the data (Hawthorne, 2021b). Thus the 'sequence argument' that has been used to ostensibly justify avoiding use of the dominant end-member in the definition of a mineral species is specious, and the reason given for not using the rule of the dominant constituent is invalid.

### The IMA–CNMNC rules for determining distinct mineral species

It is instructive to follow the sequence of work sanctioned by IMA on determining distinct mineral species. Nickel (1992) assumed that distinct mineral species have end-member compositions and the thrust of his paper is on how one determines the boundary between distinct mineral species. Boundaries between different end-members of a solid-solution series were expressed in terms of mol.% of the end-member compositions and did not explicitly involve the amounts of ions at particular sites in a mineral. The result was the 50% rule, stated by Nickel (1992; page 231) as follows: "For purposes of nomenclature, a complete solid-solution series without structural order of the ions defining the end-members is *arbitrarily* [my emphasis] divided at 50 mole %, and the two portions are given different names, with each name applying to the compositional range from the end-member to the 50% mark. For the sake of brevity, this will be called the 50% rule. Analogously, the 50% rule applied to members of ternary solid-solutions series implies that mineral names should be given only to the three end-members; each name should apply to the compositional range from the end-member to the nearest right bisectors of the sides of the composition triangle". There are two important points here:

(1) As the end-members are expressed as mol.% of the end-member compositions, electric charge is always conserved in the derivation of compositional boundaries in this procedure.

(2) The description of the division at 50% between the two parts of the solid solution is hardly arbitrary; it ensures that the assigned end-member composition corresponds to that of the dominant end-member belonging to each part of the solid solution.

Nickel (1992; page 232) goes on to state: "According to the same principle, in a multicomponent solid-solution series, *different names can be given to isostructural or isotypic phases that have different chemical elements dominant in specified structural sites*"

[my emphasis in italics]. This is not the same principle as expressed by the first quote which considers the compositions of the solid solutions in terms of the constituent end-members, ensuring electroneutrality in the system. The second quote considers the compositions of the solid solutions in terms of the constituent elements at the structural sites, and the expression "different chemical elements dominant in specified structural sites" does not ensure electroneutrality if only single chemical elements are considered. Thus ambiguity is introduced into this issue as may be seen in the following example.

Consider a compound with the general formula $A_1B_2O_4$, a structure $A_1B_2O_4$ where A, B denote groups of cations and $A$, $B$ denote sites in the crystal structure, and two end-member formulae: $^A\text{Ca}\ ^B\text{Al}_2\text{O}_4$ and $^A\text{Y}\ ^B(\text{MgAl})\text{O}_4$. In the following intermediate composition in a solid solution involving these two end-members: $^A(\text{Y}^{3+}_{0.6}\text{Ca}^{2+}_{0.4})\ ^B(\text{Al}^{3+}_{1.4}\text{Mg}^{2+}_{0.6})\text{O}_4$, Y is dominant at the $A$ site and Al is dominant at the $B$ site. Hence according to the second quote of Nickel (1995) given above, a specific name should be applied to this composition and the corresponding end-member with $A = \text{Y}^{3+}$ and $B = \text{Al}^{3+}$ is $\text{Y}^{3+}\text{Al}_2\text{O}_4$; however, this composition is not an end-member as an end-member formula must be electroneutral by definition (Hawthorne, 2002) and this formula has a net positive charge of $3^+ + 6^+ = 9^+$ whereas $\text{O}_4^{2-}$ provides only $8^-$: it is not electroneutral. In this example, treating the sites as independent in deriving the end-member composition violates the principle of conservation of electric charge, and hence this procedure fails.

### The rule of the dominant constituent

The following statement is taken from Nickel and Grice (1998; page 917): "In multiple solid-solution series, the 50% rule is interpreted to mean predominant occupancy of a particular structural site. Thus, if there are two types of atom in a structural site, the species is to be defined by the atom comprising at least 50% of that site. If there are more than two substituting atoms in the site, the species is defined by the predominant atom occupying the site". This statement reinforces the second quote from Nickel (1992) given above, a procedure which does not necessarily conserve electric charge if the atoms concerned are ions of different oxidation state.

Hatert and Burke (2008; page 717) christened the method of Nickel and Grice (1998) the "rule of the dominant constituent", where the word 'constituent' "may designate atoms (cations or anions), molecular groups, or vacancies". As noted above, the problem with the rule of the dominant constituent is that its operation may violate the law of conservation of electric charge. This problem is apparent in many places in Hatert and Burke (2008) where one commonly meets the statement "but its idealized end-member formula…is not charge-balanced". This statement is nonsensical as an end-member formula is electroneutral by definition (Hawthorne, 2002). The situation is correctly summarised as follows: **in many cases, operation of the rule of the dominant constituent fails to produce an end-member chemical formula**.

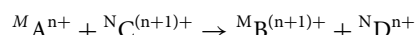### Valency-imposed double site-occupancy

Hatert and Burke (2008; page 719) introduced "valency-imposed double site-occupancy" to deal with the type of issue raised by the occurrence of richterite, end-member formula Na(CaNa) $\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$ (Hawthorne *et al.*, 2012), i.e. occupancy of a site by two ions of different oxidation state in the end-member

formula. As noted above, the use of the word 'valency' here is incorrect; according to the IUPAC definition, valency has no sign (see 'Definitions' section above); the correct term is oxidation state. However, to avoid complicating matters any further, I will retain the word 'valence' when discussing these various rules. The idea of valency-imposed double site-occupancy is correct, and occurs in many mineral species (Hawthorne, 2002). However, it should be realised that valency-imposed double site-occupancy directly contradicts the rule of the dominant constituent, something that has been ignored in the development of these rules.
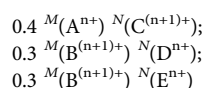
### The dominant-valency rule

Hatert and Burke (2008; page 721) also introduced what they called the "dominant-valency rule" to compensate for the fact that in minerals with mixed-valence ions at more than one site, if one of the constituents is substituted by another constituent of the same valence, the valency-imposed double site-occupancy rule fails to derive an end-member formula.

I will consider the example that they give to justify this rule. Consider two sites in a structure: $M$ and $N$. Hatert and Burke (2008, figure 3) label the constituents at these sites in the relevant substitutions by writing the sites $M$ and $N$ as post-subscripts, e.g. $\text{D}^{n+}_N$, which are easily confused with stoichiometric coefficients. Here I have modified their notation for clarity by noting the sites as pre-superscripts, e.g. $^N\text{D}^{n+}$. They consider the following substitution:

$$^M\text{A}^{n+} + {}^N\text{C}^{(n+1)+} \rightarrow {}^M\text{B}^{(n+1)+} + {}^N\text{D}^{n+}$$

where $\text{A}^{n+}$, $\text{B}^{(n+1)+}$, $\text{C}^{(n+1)+}$ and $\text{D}^{n+}$ are different constituents. They focus on the specific composition $^M(\text{A}^{n+}_{0.4}\ \text{B}^{(n+1)+}_{0.6})\ ^N(\text{C}^{(n+1)+}_{0.4}\ \text{D}^{n+}_{0.6})$ and allow the substitution $^N\text{E}^{n+} \rightarrow {}^N\text{D}^{n+}$ to replace half of $^N\text{D}^{n+}$; the result is the composition $^M(\text{A}^{n+}_{0.4}\ \text{B}^{(n+1)+}_{0.6}){}^N(\text{C}^{(n+1)+}_{0.4}\ \text{D}^{n+}_{0.3}\ \text{E}^{n+}_{0.3})$. According to Hatert and Burke (2008; page 721): "The strict application of the dominant-constituent rule would indicate that this composition corresponds to a new species with $\text{C}^{(n+1)+}$ instead of $\text{D}^{n+}$ as the dominant constituent at the $N$ site. However, the end-member formula for this supposedly new species, $[\text{B}^{(n+1)+}]_M\ [\text{C}^{(n+1)+}]_M$ is impossible because it is not charge-balanced. The valency-nomenclature problem can be solved by considering the elements of the homovalent substitution $\text{E}^{n+}_N \rightarrow \text{D}^{n+}_N$ as a whole, so that the group of cations with n+ valency are still dominant at the $N$ site, in spite of the majority $\text{C}^{(n+1)+}$. Consequently, species with such coupled heterovalent–homovalent substitutions must be defined by the most abundant amongst the cations with the same valency state at this site, here n+. This rule is called the dominant-valency rule, as it is necessary to preserve charge balance in any end-member formula". Hatert and Burke (2008) fail to recognise that end-member formulae are electroneutral by definition (Hawthorne, 2002) and need no such arbitrary rules to ensure this property. In this example, the three end-member constituents may be read directly from the composition $^M(\text{A}^{n+}_{0.4}\ \text{B}^{(n+1)+}_{0.6}){}^N(\text{C}^{(n+1)+}_{0.4}\ \text{D}^{n+}_{0.3}\ \text{E}^{n+}_{0.3})$:

0.4 $^M(\text{A}^{n+})\ ^N(\text{C}^{(n+1)+})$;
0.3 $^M(\text{B}^{(n+1)+})\ ^N(\text{D}^{n+})$;
0.3 $^M(\text{B}^{(n+1)+})\ ^N(\text{E}^{n+})$

and the dominant end-member formula is $^M(\text{A}^{n+})\ ^N(\text{C}^{(n+1)+})$. Again, the situation is correctly summarised by the following

statement: **in many cases, operation of the rule of the dominant valency fails to produce an end-member chemical formula**.

### Specific examples of the dominant-valency rule

Hatert and Burke (2008) and Bosi *et al.* (2019a) have given several examples of the operation of the dominant-valency rule to justify its use. I will consider the validity of (some of) these examples below.

### Ternary feldspars

Hatert and Burke (2008; page 722) considered a feldspar with the chemical formula $(Ca_{0.4}Na_{0.35}K_{0.25})(Al_{1.4}Si_{2.6})O_8$ and noted that "According to the current dominant-constituent rule, this mineral is Ca-dominant and would thus be anorthite. But its idealized end-member formula, $CaAlSi_3O_8$ is not charge-balanced. Application of the dominant-valency rule, however, clearly shows that the monovalent cations are dominant at the large crystallographic site, not Ca. Amongst these monovalent cations, Na is the dominant one, and this sample is thus simply a Ca- and K-rich albite". What is wrong with this statement?

(1) A crystallographic site is a point, and a (zero-dimensional) point does not have a size.
(2) The formula $CaAlSi_3O_8$ is not an end-member formula (idealised or not), it is merely the formula given by the dominant-constituent rule.
(3) There are three end-member formulae in this simple feldspar system: $KAlSi_3O_8$, $NaAlSi_3O_8$ and $CaAl_2Si_2O_8$. The composition $(Ca_{0.4}Na_{0.35}K_{0.25})(Al_{1.4}Si_{2.6})O_8$ is denoted by the red circle labelled X on the ternary-feldspar composition diagram (Fig. 1). According to the dominant-valency rule, the alkali feldspars lie in the compositional field KNCD and composition X lies in the compositional field of albite: NCFB, and the compositional field of anorthite is ADC. However,
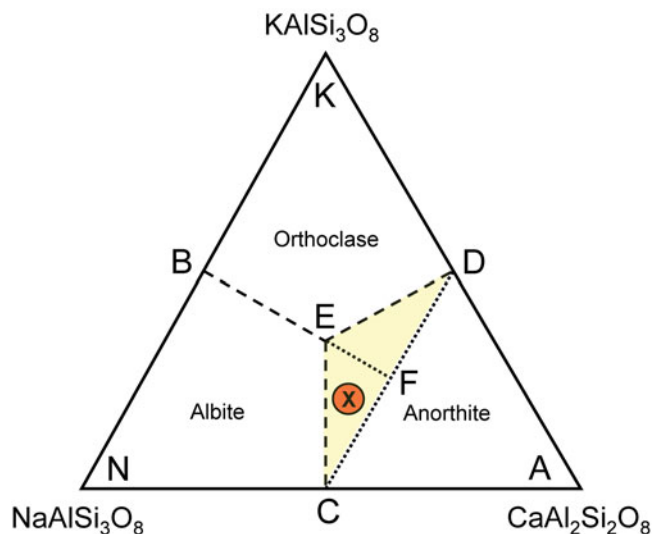
dividing the diagram on the basis of the dominant end-member, the field is divided into three equal areas: KBED, NCEB and ADEC for orthoclase, albite and anorthite. The difference in the two schemes involves the yellow-shaded triangle CED in Fig. 1: this area is classed as anorthite according to the dominant end-member, and classed as albite and orthoclase according to the dominant-valency rule. The problem with the latter scheme is that the compositions CEF and DEF are called albite and orthoclase, but the highest component activity (according to Raoult's Law; Spear, 1993; Anderson, 2005) is that of anorthite. Although the feldspar system is strongly non-ideal from a thermodynamic perspective, it does not seem logical to name a mineral albite where the highest (ideal) component activity is that of anorthite.

### Li,Fe²⁺MgMn²⁺Al-bearing tourmaline

Hatert and Burke (2008; page 722) state the following: "The *Y*-site composition $(Fe^{2+}_{1.5}Li_{0.75}Al_{0.75})$ is the boundary between schorl and elbaite series in their solid-solution series (see above). A composition $(Fe^{2+}_{1.60}Li_{0.70}Al_{0.70})$ represents thus schorl, but what about the composition $(Fe^{2+}_{0.60}Mg_{0.50}Mn_{0.50}Li_{0.70}Al_{0.70})$ caused by a multiple homovalent substitution? Application of the current dominant-constituent rule would lead to the name elbaite (as Li and Al are now the dominant elements at the site). But this is erroneous: the divalent ions (Fe + Mg + Mn) are still dominant (S = 1.60), with $Fe^{2+}$ as the dominant ion, and the composition corresponds to schorl".

One cannot say that the name elbaite is erroneous based on the dominant-valency rule as it is the dominant-valency rule that is erroneous, i.e. it has no scientific basis. Using the end-members listed in Table 1, we may write the relation between the end-member constituents and the formula as a set of simultaneous equations as shown in Table 2. We may solve for *a*, *b*, *c* and *d*, and the resultant values are listed in the bottom row of Table 2: elbaite is the dominant end-member.

### Epidote

Hatert and Burke (2008; page 722) state the following: "Also, the many coupled heterovalent–homovalent substitutions in the epidote-group minerals require the application of the dominant-valency rule in the solid-solution series. This is necessary because strict adherence to the rule based on the dominant ionic species leads to inconsistencies and unbalanced formulae (Armbruster *et al.*, 2006)". However, the examples they gave are mainly concerned with assigning names, and as noted in the Introduction, assigning end-member formulae is independent of naming the resulting species. In the example that follows, I write the site constituents as elements or ions with the amounts indicated by postsubscripts (as in Hatert and Burke, 2008).

Armbruster *et al.* (2006; page 560) stated the following (including section in italics): "*Example: An allanite-subgroup mineral where M3 is not dominated by a single divalent cation but by several, so that a trivalent cation is the most abundant*



**Fig. 1.** The compositional field for the system orthoclase–albite–anorthite. Dashed lines BE, CE and DE are the compositional boundaries using the dominant end-member formulae to define the species. The dotted lines CFD and BEF are the compositional boundaries using the dominant-valency rule to define the species. X denotes a composition that is considered as anorthite using the dominant end-member formulae to define the species, and considered as albite using the dominant-valency rule to define the species.

**Table 1.** End-member formulae for the *Y*-site of a tourmaline-supergroup group mineral of composition $Na[Fe^{2+}_{0.6}Mg_{0.5}Mn^{2+}_{0.5}Li_{0.7}Al_{0.7}]Al_6[Si_6O_{18}][BO_3]_3O_3(OH)$.

| | | |
|---|---|---|
| 1 | Schorl | $NaFe^{2+}_3Al_6Si_6O_{18}(BO_3)_3(OH)_4$ |
| 2 | Elbaite | $Na(Li_{1.5}Al_{1.5})Al_6Si_6O_{18}(BO_3)_3(OH)_4$ |
| 3 | Dravite | $NaMg_3Al_6Si_6O_{18}(BO_3)_3(OH)_4$ |
| 4 | Tsilaisite | $NaMn^{2+}_3Al_6Si_6O_{18}(BO_3)_3(OH)_4$ |

**Table 2.** Simultaneous equations expressing the Y-site composition $[Fe^{2+}_{0.6}Mg_{0.5}Mn_{0.5}Li_{0.7}Al_{0.7}]$ in a tourmaline.

| Y-site component | Schorl | Elbaite | Dravite | Tsilaisite | Σ |
|---|---|---|---|---|---|
| $Fe^{2+}$ | $3a$ | | | | 0.60 |
| Mg | | | $3c$ | | 0.50 |
| Mn | | | | $3d$ | 0.50 |
| Li | | $1.5b$ | | | 0.70 |
| Al | | $1.5b$ | | | 0.70 |
| Σ | 0.20 | 0.46 | 0.17 | 0.17 | |

$a = 0.60 / 3 = 0.20$; $b = 0.70 \times 2 / 3 = 0.46$; $c = 0.50 / 3 = 0.17$; $d = 0.50 / 3 = 0.17$.

one: e.g. $Ca(La_{0.6}Ca_{0.4})Al_2(Fe^{2+}_{0.3}Mg_{0.2}Mn^{2+}_{0.1}Al_{0.4})[Si_2O_7][SiO_4]O(OH)$ [*One might be tempted to write a meaningless, non-charge-balanced end-member* $CaLaAl_3[Si_2O_7][SiO_4]O(OH)]$".

First, an end-member formula is neutral by definition; the supposed 'end-member formula' produced above just shows that the procedure "one might be tempted" to use does not work.

Second, one may write the following end-member formulae involving the cations at the A2 and M3 sites (and omitting $^{A1}Ca^{M1}Al^{M2}Al[Si_2O_7][SiO_4]O(OH)$, the fixed part of the formulae) as shown in Table 3. Using the numbered end-members listed in Table 4, we may write the relation between the end-member constituents and the formula of a mineral as a set of simultaneous equations as shown in Table 5. One may solve this set of equations and the resultant amount of each constituent is shown on the bottom line of Table 5. Armbruster et al. (2006) assign the end-member formula as $CaLaAl_2Fe^{2+}[Si_2O_7][SiO_4]O(OH)$ whereas the dominant end-member formula is $CaCaAl_2Al[Si_2O_7][SiO_4]O(OH)$. These conflicting results arise because the former formula conflates classification and calculation of end-member formulae whereas the latter formula results solely from determining the dominant end-member.

### The fallacy of the dominant-valency rule

As noted above, the dominant-valency rule was introduced to compensate for the fact that in minerals with mixed-valence ions at more than one site, if one of the constituents is substituted by another constituent of the same valence, the valency-imposed double site-occupancy rule fails to derive an end-member formula. It must be emphasised the dominant-valency rule has no basis in Physics or Chemistry; it is an arbitrary 'rule' introduced in an attempt to compensate for the failure of the rule of the dominant constituent and the valency-imposed double site-occupancy rule to always accord with the conservation of electric charge (Hawthorne, 2021a). Moreover, the dominant-valency rule leads to some compositions within particular mineral groups being assigned a name that is different from the component in the mineral that has the highest concentration and the highest (ideal) thermodynamic activity, e.g. as in the ternary feldspar system, hardly an ideal situation.

**Table 3.** Constituents of the A2 and M3 sites in epidote.

| Label | A2 | M3 |
|---|---|---|
| 1 | La | $Fe^{2+}$ |
| 2 | La | Mg |
| 3 | La | $Mn^{2+}$ |
| 4 | Ca | Al |

**Table 4.** End-member formulae* for an epidote-group mineral of composition $Ca(La_{0.6}Ca_{0.4})Al_2(Fe^{2+}_{0.3}Mg_{0.2}Mn^{2+}_{0.1}Al_{0.4})[Si_2O_7][SiO_4]O(OH)$.

| Label** | Amount | A2 | M3 |
|---|---|---|---|
| 1 | $a$ | La | $Fe^{2+}$ |
| 2 | $b$ | La | Mg |
| 3 | $c$ | La | $Mn^{2+}$ |
| 4 | $d$ | Ca | Al |

*Omitting the fixed $^{A1}Ca^{M1}Al^{M2}Al[Si_2O_7][SiO_4]O(OH)$ part of the formula.
**Labels from Table 3.

### The dominant-valency rule and rare earth elements in minerals:

Consider the hypothetical compound $(Ca_{0.40}Sc_{0.35}Y_{0.25})(S_{0.4}P_{0.6})O_4$. We may factor this into the following end-members: $CaSO_4$ (0.40), $ScPO_4$ (0.35) and $YPO_4$ (0.25), and on this basis, we may identify the dominant end-member as $CaSO_4$. This is formally correct but has the counter-intuitive result that a mineral with $P^{5+}$ dominant over $S^{6+}$ has a dominant end-member composition with $S^{6+}$ dominant over $P^{5+}$ and would be classified as a sulfate even though phosphate is the dominant oxyanion. However, counter-intuitive does not necessarily mean wrong. Conversely, we may use the dominant-valency rule and identify the end-members as $CaSO_4$ (0.40) and $R^{3+}PO_4$ (0.60) where $R^{3+}$ = $Sc^{3+}$ + $Y^{3+}$, and on this basis, we may identify the dominant end-member composition as $R^{3+}PO_4$. However, $R^{3+}$ is a formal charge and P is an element, and hence $R^{3+}PO_4$ is neither a formula of formal charges nor a formula of elements and cannot be considered either as an end-member chemical formula or as an end-member charge arrangement. If $R^{3+}PO_4$ were to be considered a chemical formula with $R^{3+}$ = $REE^{3+}$, the definition of $R^{3+}PO_4$ as the dominant end-member composition would contradict the definition of an end-member: it is not irreducible as $R^{3+}$ may be resolved into individual REEs. However, the IMA appends the dominant REE as a post-script to the formal name of the dominant-valency and recognises this as a distinct mineral species. This is a procedure that contradicts itself: a name is given to a dominant-valency end-member, and the dominant-valency end-member is then reduced to a series of chemical components that are considered as distinct mineral species. Either one recognises a dominant charge-arrangement by not distinguishing between REEs, or one recognises a dominant end-member chemical formula by distinguishing between REEs. Coupling these things together is a self-contradictory process that is incompatible both with the formal definition of an end-member and with the procedure of summing the dominant-valence ions and treating them as an irreducible quantity in defining the initial 'end-member'. For convenience and utility, one might use the dominant-valency rule to produce a root formula (as distinct from an end-member formula) and assign it a name so that, for

**Table 5.** Simultaneous equations expressing the formula for the A2 and M3 sites in terms of the end-members 1–4 for the epidote-group mineral of Table 1.

| | 1 | 2 | 3 | 4 | Σ |
|---|---|---|---|---|---|
| La | $a$ | $b$ | $c$ | 0 | 0.6 |
| Ca | 0 | 0 | 0 | $d$ | 0.4 |
| $Fe^{2+}$ | $a$ | 0 | 0 | 0 | 0.3 |
| Mg | 0 | $b$ | 0 | 0 | 0.2 |
| $Mn^{2+}$ | 0 | 0 | $c$ | 0 | 0.1 |
| Al | 0 | 0 | 0 | $d$ | 0.4 |
| | 0.3 | 0.2 | 0.1 | 0.4 | |

example, $(Ca_{0.40}Sc_{0.35}Y_{0.25})(S_{0.4}P_{0.6})O_4$ may be designated as a phosphate mineral, but then it is logically inconsistent to divide it up into REE-containing components (and potential end-members).

### The site-total-charge approach:

Bosi *et al.* (2019a; page 629) define the charge constraint as follows: "The charge constraint can be defined as an integer number close (or next) to the observed site total charge (STC)". There are three problems with this 'definition':

(1) This statement is not a definition. A number is not a constraint until it is used in some fashion in an argument, and then the constraint is the kernel of that argument rather than the number itself.
(2) Wherever the integer defined in this process is not that closest to the observed site-total-charge but just a number close to it, the site-total-charge approach violates the rule of the dominant constituent on which all of the IMA procedures are based.
(3) There is a degree of arbitrariness in picking the integer number close or next to the observed site total. For example, Bosi *et al.* (2019b) consider the composition $K$ $^M(Li_{1.49}Mn^{3+}_{1.02}Al_{0.49})$ $Si_4O^A_{10}(O_{1.02}F_{0.98})$ intermediate between norrishite, ideally $K$ $^M(LiMn^{3+}_2)Si_4O^A_{10}O_2$, and polylithionite, ideally $K$ $^M(Li_2Al)Si_4O^A_{10}F_2$. The relevant sums of the STC are $^M6.02^+$ and $^A3.02^-$, and Bosi *et al.* (2019b) arbitrarily pick the alternative values $^M7^+$ and $^A4^-$ and assign the end-member as norrishite. However, according to the explanation of the STC method that they provide, they could also have picked the STC pair $^M5^+$ and $^A2^-$ to give the end-member as polylithionite. The STC values of the empirical formula are slightly closer to those of norrishite than those of polylithionite, but this is not given as a criterion in the rule (Bosi *et al.*, 2019a).

Bosi *et al.* (2019a; page 629) noted that Hatert and Burke "... have not considered the case ... of coupled heterovalent substitutions at two sites along with the heterovalent substitution at a single site. This more complex case is now clarified (Fig. 2)" and give the following cases of a hypothetical feldspar composition: the Sc-bearing pyroxene jervisite, and a garnet from Magnet Cove as examples. I will consider each of these examples below.

### Hypothetical Pb-bearing feldspar

This hypothetical feldspar has the composition: $^{[8]}(Na_{0.36}Pb^{2+}_{0.12}\square_{0.12}Ca_{0.40})^{[4]}(Al_{1.40}Si_{2.60})O_8$. The possible root-charge arrangements are as follows where the charges are written first for [8]-coordinated ions and then for [4]-coordinated ions: 0 $(4^+_4)$; $1^+$ $(3^+4^+_3)$; $2^+$ $(3^+_24^+_2)$. We may read the constituent end-members directly from the possible root-charge arrangements and the above chemical formula:

| | |
|---|---|
| $NaAlSi_3O_8$ | 0.36 |
| $Pb^{2+}Al_2Si_2O_8$ | 0.12 |
| $\square Si_4O_8$ | 0.12 |
| $CaAl_2Si_2O_8$ | 0.40 |

The dominant end-member formula is $CaAl_2Si_2O_8$ and there is no reason to resort to the overly complicated procedures used by Bosi *et al.* (2019a).

### Jervisite

Bosi *et al.* (2019a) consider jervisite (Mellini *et al.*, 1982), the empirical formula of which is $^{M(2)}(Na_{0.43}Ca_{0.31}Fe^{2+}_{0.14}\square_{0.12})$ $^{M(1)}(Sc_{0.66}Mg_{0.19}Fe^{2+}_{0.15})Si_2O_6$. The net charge at each $M$ site is $M(1) = 1.33^+$, $M(2) = 2.66^+$, which when combined with the composition of the mineral indicates the following possible ideal charge arrangements at the $M(2)$ and $M(1)$ sites: $1^+3^+$, $2^+2^+$ and $(0_{0.5}2^+_{0.5})3^+$. The end-member constituents may be read immediately from these charge arrangements by assigning the cations accordingly:

| | |
|---|---|
| $(1^+\ 3^+) = NaScSi_2O_6$ | 0.43 |
| $(2^+\ 2^+) = CaFe^{2+}Si_2O_6$ | 0.15 |
| $(2^+\ 2^+) = CaMgSi_2O_6$ | 0.05 |
| $(2^+\ 2^+) = Fe^{2+}MgSi_2O_6$ | 0.14 |
| $(2^+\ 2^+) = (Ca_{0.5}\square_{0.5})ScSi_2O_6$ | 0.23 |

The dominant end-member in jervisite is thus $NaScSi_2O_6$ without resorting to any of the complicated procedures used in Bosi *et al.* (2019a).

### Magnet Cove garnet

Bosi *et al.* (2019a; page 631) also considered a garnet from Magnet Cove (Table 6) and stated that "The dominant-valency rule is able to identify this garnet if the concepts of site total charges and charge constraints, dictated by the mineral composition and the electroneutrality principle, are taken into account". However, it is straightforward to rigorously assign the dominant end-member composition to this garnet by examining all possible charge arrangements (Hawthorne, 2021a) and subsequently assigning the cations of the formula to the dominant root-charge arrangements without any complicated arguments. I define site total charge as the sum of the charges of the ions at a site and constituent site charge as the charges of the individual ions at a site.

All possible site-total-charge arrangements for a garnet structure with this composition are listed in Table 6; thus $(2_21_1)^{5+}$ denotes two cations of charge $2^+$ and one cation of charge $1^+$ in the X group (denoted as 2 and 1, respectively) with a site total charge of $5^+$. The sum of the charges of the various arrangements must sum to $24^+$ to satisfy electroneutrality, giving the possible combinations of charges at the various sites in Table 6. There are six site-total-charge arrangements that satisfy this criterion, but three of these do not conform to the end-member requirement of a maximum of one site occupied by more than one charge (ignoring valence-sum restrictions associated with short-

**Table 6.** Possible charge arrangements and corresponding end-members for a garnet from Magnet Cove*. $^X[Ca^{2+}_{2.907}Fe^{2+}_{0.043}Mn^{2+}_{0.035}Na^+_{0.015}]$ $^Y[Ti^{4+}_{1.069}Zr^{4+}_{0.055}Fe^{3+}_{0.517}Fe^{2+}_{0.204}Mg^{2+}_{0.155}]$ $^Z[Si^{4+}_{2.250}Fe^{3+}_{0.588}Al^{3+}_{0.162}]O_{12}$

| Charges at X | Charges at Y | Charges at Z | Possible combinations of site total charges for electroneutrality** | | | |
|---|---|---|---|---|---|---|
| | | | Number | X | Y | Z |
| $(2_31_0)^{6+}$ | $(4_23_02_0)^{8+}$ | $(4_33_0)^{12+}$ | [1] | $6^+$ | $8^+$ | $10^+$ |
| $(2_21_1)^{5+}$ | $(4_13_12_0)^{7+}$ | $(4_23_1)^{11+}$ | – | $6^+$ | $7^+$ | $11^+$ |
| $(2_11_2)^{4+}$ | $(4_13_02_1)^{6+}$ | $(4_13_2)^{10+}$ | [2] | $6^+$ | $6^+$ | $12^+$ |
| $(2_01_3)^{3+}$ | $(4_03_12_1)^{5+}$ | $(4_03_3)^{9+}$ | – | $5^+$ | $8^+$ | $11^+$ |
| | $(4_03_22_0)^{6+}$ | | – | $5^+$ | $7^+$ | $12^+$ |
| | $(4_03_02_2)^{4+}$ | | [3] | $4^+$ | $8^+$ | $12^+$ |

*From Chakhmouradian and McCammon (2005).
**Site-total-charge combinations in italics cannot be end-members as they involve more than one charge species at more than one site.

**Table 7.** Simultaneous equations for the site total charges in terms of the possible arrangements of site total charges.

|   | [1] | [2] | [3] | Site total charge |
|---|-----|-----|-----|-------------------|
| $X$ | $6a$ | $6b$ | $4c$ | 5.985 |
| $Y$ | $8a$ | $6b$ | $8c$ | 6.765 |
| $Z$ | $10a$ | $12b$ | $12c$ | 11.250 |
| S* | 0.375 | 0.6175 | 0.0075 | |

*Solution, giving the amounts $a$, $b$ and $c$ of the distinct site-total-charges at each site in arrangements [1], [2] and [3] (see Table 6).

range order, see above discussion of Y-rich hainite and Hawthorne, 2021a); these arrangements are italicised in Table 6. Only $6^+8^+10^+$, $6^+6^+12^+$ and $4^+8^+12^+$ (Table 6) are end-member charge arrangements. We may use the site total charge at each site in the Magnet Cove garnet to solve for the amounts of these three end-member site-total-charge arrangements. This is done in Table 7 which lists the relevant simultaneous equations and their solution in terms of $a$, $b$ and $c$, the amounts of each end-member site-total-charge arrangement corresponding to the composition of Magnet Cove garnet (Table 5).

The site-total-charge arrangement $6^+6^+12^+$ corresponds to the two end-member constituent-site-charge arrangements $(2_3 1_0)^{6+}$ $(4_1 3_0 2_1)^{6+} (4_3 3_0)^{12+}$ and $(2_3 1_0)^{6+} (4_0 3_3 2_0)^{6+} (4_3 3_0)^{12+}$ (Table 8) and the amounts of these two arrangements can be derived by dividing the amount of that site-total-charge arrangement (0.6175, Table 9) into two parts according to the ratio $^Y[Ti_{0.359}^{4+}Fe_{0.204}^{2+}$ $Mg_{0.155}]$: $^Y[Fe_{0.517}^{3+}]$; $^Y[Ti_{0.359}^{4+}Fe_{0.204}^{2+}Mg_{0.155}] = 0.6175 \times 0.718$ / $(0.718 + 0.517) = 0.3590$ and $^Y[Fe_{0.517}^{3+}] = 0.6175 \times 0.517$ / $(0.718 + 0.517) = 0.2585$ (Table 9, Amount of constituent-site-charge arrangements). There is $(Fe^{2+},Mg)$ occupancy of the $Y$ site and $(Fe^{3+},Al)$ occupancy of the $Z$ site, and the corresponding end-members may be derived by partitioning the amounts of the constituent-site-charge arrangements according to the amounts of the homovalent substituents. This is done in Table 9 ('Amounts of end-members') where it can be seen that the dominant end-member is $Ca_3(Ti_2^{4+})(SiFe_2^{3+})O_{12}$: schorlomite. This contrasts with the end-member assignment of Bosi *et al.* (2019a) which assigns the end-member formula as $Ca_3(Ti^{4+}Fe^{2+})Si_3O_{12}$: morimotoite.

Which is the correct end-member, schorlomite or morimotoite? Morimotoite is derived by a procedure (the rule of the dominant constituent and its additional rules) that has been shown above to be scientifically flawed. Schorlomite has been rigorously shown to be the dominant end-member constituent, and it is difficult to logically justify giving this garnet any other name.
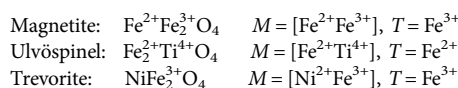
## Some current problems with the IMA procedure to assign end-member compositions

Consider the spinel-group minerals, the general formula for which is written as $AB_2O_4$ where A and B cover a wide range

**Table 9.** Amounts of end-members in Magnet Cove garnet.

| End-members | Amount of site-total-charge arrangements | Amount of constituent-site-charge arrangements | Amounts of end-members |
|-------------|------------------------------------------|-----------------------------------------------|------------------------|
| $Ca_3(Ti_2^{4+})$ $(SiFe_2^{3+})O_{12}$ | 0.3750 | 0.3750 | 0.294 |
| $Ca_3(Ti_2^{4+})$ $(SiAl_2)O_{12}$ | | | 0.081 |
| $Ca_3(Ti^{4+}Fe^{2+})$ $Si_3O_{12}$ | 0.6175 | 0.3590 | 0.204 |
| $Ca_3(Ti^{4+}Mg)$ $Si_3O_{12}$ | | | 0.155 |
| $Ca_3(Fe_2^{3+})$ $Si_3O_{12}$ | | 0.2585 | 0.2585 |
| $(CaNa_2)(Ti_2^{4+})$ $Si_3O_{12}$ | 0.0075 | 0.0075 | 0.0075 |

of formal charge. The cubic ($Fd\bar{3}m$) spinel structure contains two cation sites, $M$ and $T$: $M$ is octahedrally coordinated and $T$ is tetrahedrally coordinated, and there are twice as many $M$ sites as $T$ sites. There are two distinct types of cation arrangements in the $Fd\bar{3}m$ spinel structure: (1) normal spinels in which the B cations occupy the $M$ site and the A cation occupies the $T$ site, e. g. spinel: $^T Mg\ ^M Al_2 O_4$; and (2) inverse spinels in which the A cation and one of the B cations occupy the $M$ site and the other B cation occupies the $T$ site. Consider the formulae of the following minerals that have the inverse spinel structure:

| Magnetite: | $Fe^{2+}Fe_2^{3+}O_4$ | $M = [Fe^{2+}Fe^{3+}]$, $T = Fe^{3+}$ |
|------------|----------------------|----------------------------------------|
| Ulvöspinel: | $Fe_2^{2+}Ti^{4+}O_4$ | $M = [Fe^{2+}Ti^{4+}]$, $T = Fe^{2+}$ |
| Trevorite: | $NiFe_2^{3+}O_4$ | $M = [Ni^{2+}Fe^{3+}]$, $T = Fe^{3+}$ |

These minerals have the $M$ site occupied by two cations (in square brackets) in the ratio 1:1, and the $T$ site occupied by one cation. There is no doubt about the validity of these minerals, and the formulae given above involve no solid solution. According to the rule of the dominant constituent, these are not distinct minerals. Any attempt to make one of the cations at $M$ singularly dominant fails due to the requirement that the formula be neutral. These minerals are dealt with in Hatert and Burke (2008; page 720) by the following sentence: "For the sake of nomenclatural simplicity, divalent and trivalent cations are kept separate in spinels, regardless of their (double) site occupancies as these are not imposed by valency considerations". **This is a cryptic way of stating that the rule of the dominant constituent does not work and is completely ignored for the inverse spinels.** However, the chemical formulae given above for magnetite, ulvöspinel and trevorite conform to the definition of an end-member: (1) they are stoichiometrically conformable with the general spinel formula and crystal-chemically compatible with the spinel structure; (2) they do not carry an electric charge; and (3) they are

**Table 8.** End-member site-total-charge arrangements and possible constituent-site-charge arrangements in Magnet Cove garnet.

| End-member site-total-charge arrangements | Possible constituent-site-charge arrangements at each site | | | Simplified notation of constituent site charges at each site | | | Possible arrangement of ions at each site* | | |
|---|---|---|---|---|---|---|---|---|---|
| [1] $6^+ 8^+ 10^+$ | $(2_3 1_0)^{6+}$ | $(4_2 3_0 2_0)^{8+}$ | $(4_1 3_2)^{10+}$ | $2_3$ | $4_2$ | $4_1 3_2$ | $Ca_3$ | $Ti_2^{4+}$ | $Si_1 M_2^{3+}$ |
| | $(2_3 1_0)^{6+}$ | $(4_1 3_0 2_1)^{6+}$ | $(4_3 3_0)^{12+}$ | $2_3$ | $4_1 2_1$ | $4_3$ | $Ca_3$ | $Ti_1^{4+} M_1^{2+}$ | $Si_3$ |
| [2] $6^+ 6^+ 12^+$ | $(2_3 1_0)^{6+}$ | $(4_0 3_3 2_0)^{6+}$ | $(4_3 3_0)^{12+}$ | $2_3$ | $3_3$ | $4_3$ | $Ca_3$ | $Fe_3^{3+}$ | $Si_3$ |
| [3] $4^+ 8^+ 12^+$ | $(2_1 1_2)^{4+}$ | $(4_2 3_0 2_0)^{8+}$ | $(4_3 3_0)^{12+}$ | $2_1 1_2$ | $4_2$ | $4_3$ | $CaNa_2$ | $Ti_2^{4+}$ | $Si_3$ |

*$M^{2+} = Fe^{2+}$ and Mg; $M^{3+} = Fe^{3+}$ and Al.

irreducible within the system considered (i.e. they cannot be factored into components that have the bond topology of the spinel structure). These minerals with the inverse spinel structure are distinct mineral species based on their dominant end-member formulae.

Consider oftedalite, $(CaSc)KBe_3Si_{12}O_{30}$ (Cooper *et al.*, 2006) in which $Ca^{2+}$ and $Sc^{3+}$ occupy the $A$ site in the milarite structure-type (Gagné and Hawthorne, 2016). This is a valid mineral species as for the structure to be electroneutral, the cations at the rest of the sites in the milarite structure require a net charge of 5+ at the $A$ site (multiplicity 2 in the general formula $A_2B_2CT(2)_3T(1)_{12}$ $O_{30}(H_2O)_x$), which is satisfied by $A = (Ca^{2+}Sc^{3+})$. A similar situation occurs in richterite, ideally $Na(NaCa)Mg_5Si_8O_{22}(OH)_2$ (Hawthorne *et al.*, 2012) in which $Na^+$ and $Ca^{2+}$ occupy the $M(4)$ site. The rest of the sites in richterite are occupied by single ion species and for the structure to be electroneutral, the $M(4)$ site (multiplicity 2 in the general formula $AB_2C_5T_8O_{22}(OH)_2$) requires a net charge of 3+ which is satisfied by $M(4) = (Na^+Ca^{2+})$.

## Conclusions from the above discussion

(1) There is a fundamental error in the operation of the rule of the dominant constituent, and the introduction of a string of complicated procedures to try and correct for this error (i) does not make the error disappear, (ii) still cannot result in the definition of end-member formulae for some mineral species, and (iii) complicates the naming of minerals and clarification of their end-member formulae for mineralogists and petrologists.

(2) The rule of the dominant constituent was introduced by Hatert and Burke (2008) as an arbitrary procedure with no justification whatsoever. Grew *et al.* (2013) justified this rule *a posteriori*, stating that the results of end-member calculations depend on the sequence of the calculations. However, Hawthorne (2021b) showed that this argument is wrong, removing any justification for the rule of the dominant constituent.

(3) Any stoichiometric electroneutral mineral formula can be represented in terms of end-members. The dominant end-member approach gives the formula of the associated end-member as that of the dominant end-member. The IMA–CNMNC rules do not necessarily give the formula of the associated end-member as that of the dominant end-member. Where these rules give an end-member different from that given by the dominant end-member approach, one must ask the following question: which of the non-dominant end-members has its formula associated with that mineral and what is the scientific justification for doing so?

## The role of utility in mineral classification

A scientific classification is a distillation of our knowledge concerning the nature of the objects under consideration (Hawthorne, 1985). That being said, it must also be recognised that scientific rigor can conflict with convenience of use, and with the different requirements of the various groups of people who use the classification. Crystallographers, mineralogists and petrologists will generally have different expectations of a classification (Hawthorne *et al.*, 2012): crystallographers will want a classification that encompasses all aspects of the crystal chemistry of minerals in as concise a way as possible, whereas petrologists will

be more concerned with utility from a petrological perspective. The following factors affect such nomenclatures: (1) longevity and widespread use of common mineral names; (2) convenience of use in Petrology; and (3) use as components of rock names.

### End-member names and root names

Some supergroups of common minerals, particularly those involving more complicated minerals such as amphiboles (Hawthorne *et al.*, 2012) and micas (Rieder *et al.*, 1999), are not organised strictly according to the rule of the dominant constituent and are unlikely ever to be organised rigorously on the basis of end-member formulae. This situation arises because the names of many common minerals occur extensively in the scientific literature and have done so for many (sometimes hundreds of) years, and many of these minerals are involved in rock nomenclature and as petrogenetic indicators. For example, the root composition of magnesio-hornblende: $\square Ca_2(Mg_4Al)(Si_7Al)$ $O_{22}(OH)_2$ is intermediate between the end-member compositions of tremolite: $\square Ca_2Mg_5Si_8O_{22}(OH)_2$ and tschermakite: $\square Ca_2(Mg_3Al_2)(Si_6Al_2)O_{22}(OH)_2$, and the root composition of pargasite: $NaCa_2(Mg_4Al)(Si_6Al_2)O_{22}(OH)_2$ is intermediate between the end-member compositions of edenite: $NaCa_2Mg_5$ $(Si_7Al)O_{22}(OH)_2$ and sadanagaite: $NaCa_2(Mg_3Al_2)(Si_5Al_3)$ $O_{22}(OH)_2$ (Hawthorne *et al.*, 2012).

The classification of the amphiboles is based on the following rules:

(1) All distinct arrangements of integral charges over the amphibole formula are considered as root-charge arrangements.

(2) For a given root-charge arrangement, specific ions of appropriate charge are associated with sites in the structure, and each distinct chemical formula is a root formula.

Root-charge arrangements and root formulae should not be confused with end-member charge arrangements and end-member formulae. In the amphibole examples given above, tremolite, magnesio-hornblende and tschermakite are all root names but only tremolite and tschermakite are (also) end-member names. Deleting magnesio-hornblende, pargasite and the associated prefixed names (e.g. ferro-pargasite) would not be acceptable to the Petrology community. Moreover, the loss of such intermediate species would decrease the petrological utility of amphibole names; for example, tremolite would become much more common and would occur in a far wider spectrum of rocks than it does at present.

Nickel (1992) states that mineral names or definitions already in the literature that contravene recommendations should not be changed unless there are compelling reasons to do so. This seems an eminently sensible approach to the issue of rigorously applying principles of mineral nomenclature to all minerals and mineral groups/supergroups without consideration of the utility of the nomenclature. However, this does not void the requirement that the method of defining mineral species be rigorous and free of scientific error.

### Mineral ecology

Work on mineral ecology needs to account for the fact that some common mineral 'species' do not actually conform to formally unique single species. In particular, when defining numbers of formal mineral species (as distinct from species plus varieties),

either overall or at any particular stage of Earth or planetary evolution, this issue of what (and what is not) a distinct mineral species is of significance, as utility of use should not be a criterion for whether a particular mineral composition is a distinct species. A good historical example of this is found in the plagioclase feldspars where the names albite, 'oligoclase', 'andesine', 'labradorite', 'bytownite' and anorthite were of sufficient utility in Mineralogy and Petrology to persist for hundreds of years in the scientific literature before being reduced to albite and anorthite in more recent times. Should mineral kinds be associated with the names albite and anorthite, or albite, 'oligoclase', 'andesine', 'labradorite', 'bytownite' and anorthite?

## Coda

(1) The approval of a new mineral species by the IMA–CNMNC has three distinct and separate parts: (i) definition of the end-member composition; (ii) consideration of the classification of the new end-member composition; and (iii) assignment of a name. These are independent processes and should proceed in the sequence (i) then (ii) then (iii). In practice, the process of classification often conflates these parts and introduces problems into the processes of end-member recognition and definition.

(2) The operation of the rule of the dominant constituent can violate the conservation of electric charge, one of the most fundamental laws of Physics.

(3) A series of additional rules: (i) valency-imposed double site-occupancy; (ii) the dominant-valency rule; and (iii) the site-total-charge approach, were introduced by the IMA–CNMNC in an attempt to correct for the violation of conservation of electric charge in the rule of the dominant constituent. However, none of these rules can overcome the fundamental error introduced by the rule of the dominant constituent, and the chemical formulae resulting from application of these rules can violate the requirements of an end-member, particularly that of electroneutrality.

(4) As a result, the IMA–CNMNC rules cannot derive end-member formulae for some groups of minerals, giving rise to many *ad hoc* decisions in defining distinct mineral species.

(5) Although there is no mention of 'end-member' in the rule of the dominant constituent, by implication the "set of dominant constituents at the sites in the crystal structure" (Hatert and Burke, 2008; page 717) is consonant with the definition of end-member (Hawthorne, 2002, 2021a). Indeed, the term 'end-member' is used 47 times in Hatert and Burke (2008) although a definition of 'end-member' is not given by these authors. In turn, Bosi *et al.* (2019a, 2019b) use the term 'end-member' 67 and 41 times, respectively. Indeed, Bosi *et al.* (2019a; page 627) explicitly state: "Mineral species should be identified by an end-member formula…". Rewording the above in a more straightforward manner: **there are two approaches to determining the end-member chemical formula of a mineral: the dominant-valency method, and the dominant-end-member method**.

(6) Any stoichiometric electroneutral mineral formula can be represented in terms of end-members. The dominant end-member approach gives the formula of the associated end-member as that of the dominant end-member. The IMA–CNMNC rules do not necessarily give the formula of the associated end-member as that of the dominant end-member. Where these rules give an end-member different from that given by the dominant end-member approach, one must ask the following question: which of the non-dominant end-members has its formula associated with that mineral and what is the scientific justification for doing so?

(7) Here I have examined the problems with the rule of the dominant constituent and its associated procedures for defining an end-member composition, and have shown that these rules are neither adequate nor scientifically based. In particular, the sequence argument that has been used to avoid using the dominant end-member in the definition of a mineral species is wrong, and thus the justification for using the rule of the dominant constituent to define an end-member formula (e.g. Hatert and Burke, 2008; Bosi *et al.*, 2019a) is invalid.

(8) Elsewhere, I shall examine the dominant-end-member method and identify the significant problems that currently exist for this method.

(9) The collective issues addressed above are extremely important as they are the basis on which individual mineral species are defined, and as such, affect many scientific issues across the breadth of Earth and Planetary Sciences.

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