



Comment

A brief comment on Hawthorne (2023): “On the definition of distinct mineral species: A critique of current IMA-CNMNC procedures”

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Abstract

In this communication we present a brief response to Hawthorne (2023) who, in a paper in volume 87, doi.org/10.1180/mgm.2023.8 (this journal), claims evidence for violations of the electroneutrality principle in mineral formulae derived through IMA–CNMNC procedures: i.e. the dominant-constituent rule, the valency-imposed double site-occupancy, the dominant-valency rule, and the site-total-charge approach (STC).

His statement is not correct as the STC method is based on the end-member definition; thus, it cannot violate the requirements of an end-member, particularly the laws of conservation of electric charge. The STC was developed to address the shortcomings in the previous IMA–CNMNC procedures.

The real question is: which method to use to define an end-member formula? Currently, there are two approaches: (1) STC, which first identifies the dominant *end-member* charge arrangement and then leads to the dominant *end-member composition*; (2) the dominant end-member approach.

Keywords: IMA–CNMNC, mineral formula, end-member, site total charge

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Introduction

We are commenting on a paper (Hawthorne, 2023) in which the author expressed criticisms about the procedures of the Commission on New Minerals, Nomenclature and Classification (CNMNC) of the International Mineralogical Association (IMA) for the definition of a new mineral species. Hawthorne (2023) stated that the dominant-constituent rule, the valency-imposed double site-occupancy, the dominant-valency rule, and the site-total-charge (STC) approach can violate the laws of conservation of electric charge. Thus, according to this author, the chemical formulae resulting from application of the IMA–CNMNC rules can violate the requirements of an end-member, particularly that of electroneutrality, and these cannot derive end-member formulae for some groups of minerals.

In this discussion, we will show that such a statement is incorrect.

Discussion

The STC method (Bosi *et al.*, 2019a, 2019b) is based on the end-member definition, thus it cannot violate the requirements of an end-member, particularly the laws of conservation of electric

charge, by definition. The application of the STC method is divided in two steps: one, identifying the dominant *end-member charge arrangement* from the empirical formula, and two, deriving the dominant *end-member formula* from this end-member charge arrangement. There are several examples where the STC method was successfully applied to obtain end-member formulae, including those related to the complex chemistry of pyrochlore-supergrout minerals (Bhattacharjee *et al.*, 2022).

Hawthorne (2023) nicely discusses specific examples where the dominant-constituent rule and dominant-valency rule lead to non-electroneutral formulae, thus violating the conservation of electric charge. However, the application of the dominant-constituent rule, the valency-imposed double site-occupancy, and the dominant-valency rule generally leads to valid end-member formulae (Hatert and Burke, 2008). Moreover, it is important to note that the deficiency in these IMA–CNMNC rules was already noted by Bosi (2018) and successively addressed by the CNMNC with the paper by Bosi *et al.* (2019a). In fact, Hawthorne (2023) could show only examples of minerals with end-member formulae derived from the STC method.

In this regard, it is instructive to show a misunderstanding by Hawthorne (2023) on the STC method. This author states that “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 $K^M(Li_{1.49}Mn_{1.02}^{3+}Al_{0.49})Si_4O_{10}^A(O_{1.02}F_{0.98})$ intermediate between norrishite, ideally $K^M(LiMn_2^{3+})Si_4O_{10}^AO_2$, and polyolithionite, ideally $K^M(Li_2Al)Si_4O_{10}^AF_2$. The relevant sums of the STC are

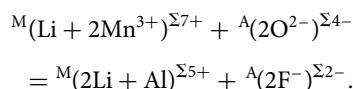
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$M^{6.02+}$ and $A^{3.02-}$, and Bosi *et al.* (2019b) arbitrarily pick the alternative values M^{7+} and A^{4-} and assign the end-member as norrishite. However, according to the explanation of the STC method that they provide, they could also have picked the STC pair M^{5+} and A^{2-} to give the end-member as polyolithionite. The STC values of the empirical formula are slightly closer to those of norrishite than those of polyolithionite, but this is not given as a criterion in the rule”.

However, reading the papers by Bosi (2019a, 2019b), it becomes clear that there is no arbitrariness in picking integer numbers, instead of this is a mathematically-driven procedure: an integer number must be selected for which possible charge and atomic arrangements can be identified in accord with mineral composition. If (*and only if*) those arrangements satisfy all the criteria of an *end-member*, the mineral formula may be defined. Note that if the integer number closest to the STC is not consistent with an end-member, because of lack of consideration of all the potential end-members involved in the chemical substitution and/or the degree of atom disorder over structural sites, another integer number in line with the end-member definition must be selected.

To complete the information on the mica example given above, we report what is written in Bosi *et al.* (2019b). Minerals occurring between norrishite, $K^M(LiMn_2^{3+})Si_4O_{10}^A(O)_2$, and polyolithionite, $K^M(Li_2Al)Si_4O_{10}^A(F)_2$, are related by the substitution:



The boundary between these two minerals lies at the composition $K^M(Li_{1.5}Mn_{1.0}Al_{0.5})^{\Sigma 6+}Si_4O_{10}^A(OF)^{\Sigma 3-}$, corresponding to the sum of charges M^{6+} and A^{3-} . Thus, mineral compositions with $M > +6$ and $A < -3$ belong to the norrishite compositional field, whereas those with STC for the $M < +6$ and $A > -3$ belong to the polyolithionite field. Consider the hypothetical norrishite composition $K^M(Li_{1.49}Mn_{1.02}Al_{0.49})Si_4O_{10}^A(O_{1.02}F_{0.98})$ with $M^{6.02+}$ and $A^{3.02-}$, very close to the integer numbers +6 and -3. These numbers are compatible with the atomic arrangements $M^{6+}(Li_{1.50}R_{1.50})^{\Sigma 6+}$ and $A^{3-}(O_{1.00}F_{1.00})^{\Sigma 3-}$, but such arrangements are inconsistent with the end-member definition (double occupancy of two sites). In order to identify the end-member formula, we need to consider integer numbers next to +6 and -3, that is, +7 and -4 which are compatible with $M^{7+}(Li_{1.00}R_{2.00})^{\Sigma 7+}$ and $A^{4-}(O_{2.00})^{\Sigma 4-}$, leading to the end-member $K(LiMn_2^{3+})Si_4O_{10}(O)_2$, that is norrishite.

What can we learn from this example?

(1) The STD method always leads to a charge-balanced mineral formula, which in this case corresponds to that defined by the end-member approach (51% norrishite and 49% polyolithionite).

(2) The end-member formula is an *overriding* condition to identify minerals, something that Bosi *et al.* (2019a, 2019b) mentioned in their papers but which seems to have been overlooked by Hawthorne (2023) who cited their results.

Other inconsistencies are reported by Hawthorne (2023), but they need a separate paper to be addressed. The purpose of this discussion is (1) to point out that Hawthorne (2023) criticises things already known in the mineralogical literature, and (2) to reiterate that the STC method does not violate any fundamental law of Physics.

Real discussion point

As already pointed out by Bosi *et al.* (2019a, 2019b), the real discussion is how to define the end-member formula of minerals,

and this can be achieved through two different approaches: (1) the STC approach, and (2) the dominant end-member approach. Graphically, figure 1 from Bosi *et al.* (2019a), which is also repeated by Hawthorne (2023) for the feldspar system, shows the fundamental differences between these two approaches, and how they are relevant only for particular intermediate compositions.

The next step is to decide which of these two approaches best reflects the mineral properties. Currently, the CNMNC recommends the STC approach (coupled with the dominant-constituent and dominant-valency rules) as it overcomes the fundamental flaw introduced in some cases by the previous IMA–CNMNC rules.

The simple example by Hawthorne (2023), on the hypothetical compound with a composition $(Ca_{0.40}Sc_{0.35}Y_{0.25})(S_{0.4}P_{0.6})O_4$, perfectly demonstrates the essential differences between the two approaches. With respect to the root composition $ScPO_4$ (arbitrarily chosen), the relations between end-member constituents in terms of ion replacements are as follows: $Y^{3+} \rightarrow Sc^{3+}$ gives YPO_4 and $Ca^{2+} + P^{5-} \rightarrow Y^{3+} + S^{6-}$ gives $CaSO_4$. By applying the *end-member approach*, the following end-member compositions may be obtained: 40% $CaSO_4$, 35% $ScPO_4$ and 25% YPO_4 , thus leading to $CaSO_4$ as the dominant end-member. However, the dominant cation at the tetrahedrally-coordinated sites is P^{5+} , so why should we not consider this sample as a phosphate? By applying the *dominant-valency rule*, the larger trivalent REE cations are dominant at non-tetrahedrally coordinated sites, and among them, Sc^{3+} is the dominant cation. This mineral may consequently be regarded as $[(Sc,Y),Ca](P,S)O_4$, a Y-, Ca- and S-bearing $ScPO_4$: a phosphate, indeed. In this regard, it is also interesting to consider the effect of homovalent and heterovalent substitutions on the bond-valence variations that correlate with some mineral properties such as thermal expansion and force constant (Brown, 2016). Homovalent substitutions generally introduce only slight changes in bond valences due to relaxation of bond distances, whereas heterovalent substitutions produce significant changes in the pattern of bond valences due to the different arrangements of formal charges in the structure (Gagné and Hawthorne, 2016). Hence, a homovalent substitution such as $Sc^{3+} \rightarrow Y^{3+}$ is expected to produce a smaller variation in the mineral properties than a heterovalent substitution such as $Ca^{2+} + P^{5-} \rightarrow (Y,Sc)^{3+} + S^{6-}$.

As a final comment, it should be noted that the CNMNC does not aim at imposing an arbitrary set of rigid rules on the mineralogical community, but rather at defining a set of coherent guidelines that provide a reasonably consistent approach for the introduction of new minerals and the application of mineral nomenclature (Nickel and Grice, 1998). Exceptions to the CNMNC rules are possible and welcome if soundly argued, as Nature does not read mineralogical papers. In this regard, it is important to note that CNMNC welcomes proposals that may improve existing procedures, mineral classification and mineral nomenclature. Constructive proposals for alternative improved procedures are always desirable. CNMNC is an IMA Commission with elected representatives from national mineralogical societies. The proper places for constructive discussions on matters handled by the CNMNC would primarily be those societies and through their representatives in CNMNC.

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