THE IMA–CNMNC DOMINANT-CONSTITUENT RULE REVISITED AND EXTENDED

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Abstract

Mineralogical nomenclature in solid-solution series follows a system that has been called the 50% rule, more correctly the $100\%/n$ rule or the dominant-constituent rule, in which the constituents are atoms (cations or anions), molecular groups, or vacancies. Recently developed systems of nomenclature for the arrojadite and epidote groups have shown that a group of atoms with the same valency state must also be considered as a single constituent to avoid the creation of impossible end-member formulae. The extension with this dominant-valency rule is imposed by all cases of coupled heterovalent–homovalent substitutions. End members with a valency-imposed double site-occupancy may result from single-site heterovalent substitutions and from coupled heterovalent substitutions at two sites where there is a disparity in the number of these two sites.

Keywords: mineral nomenclature, solid-solution series, dominant-constituent rule, dominant-valency rule, IMA–CNMNC.

Sommaire

La nomenclature minéralogique au sein des solutions solides suit une règle généralement connue sous le nom de "règle des 50%", mais qui devrait plus exactement s'appeler "règle des $100\%/n$" ou "règle du constituant dominant". Le terme "constituant" peut désigner des atomes (cations ou anions), des groupements moléculaires ou des lacunes. Récemment, les révisions de nomenclature au sein des groupes de l'arrojadite et de l'épidote ont démontré que des groupes d'atomes homovalents devaient également être considérés comme un seul et unique constituant, de manière à éviter l'apparition de formules chimiques aberrantes pour les termes extrêmes. Cette extension vers une "règle de valence dominante" est absolument nécessaire lorsque des substitutions couplées homovalentes et hétérovalentes sont impliquées. Des termes extrêmes présentent une occupation double de sites cristallographiques peuvent résulter soit d'une substitution hétérovalente affectant un seul site, soit de substitutions hétérovalentes couplées affectant deux sites, lorsqu'il existe une différence de multiplicité entre ces deux sites.

Mots-clés: nomenclature des minéraux, solutions solides, règle du constituant dominant, règle de valence dominante, IMA–CNMNC.

Introduction

The Commission on New Minerals, Nomenclature and Classification (CNMNC) of the International Mineralogical Association (IMA) has defined the nature of minerals (Nickel 1995). The IMA–CNMNC considers the terms "mineral species" and "mineral" to be identical (Dunn & Mandarino 1987, Nickel & Grice 1998). The criteria for the definition of a new mineral (species) currently used by the IMA–CNMNC (Nickel 1992, Nickel & Grice 1998) involve what should now be called the ***rule of the dominant constituent***: a mineral is a distinct species if the set of dominant constituents at the sites in the crystal structure is distinct from that of any other mineral with the same structural arrangement. Nickel (1992) called this rule for the sake of brevity the ***50% rule***, a name that unfortunately is a source of confusion, as this name can of course only be applied in binary systems: the predominant occupancy of a site in multicomponent (three and higher) systems is of course

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much lower than 50%. Wenk & Bulakh (2004) proposed, therefore, to use the name *100%/n rule* (with *n* being the number of components). But it is recommended to use the more descriptive name *dominant-constituent rule*, in which the term "constituent" may designate atoms (cations or anions), molecular groups, or vacancies.

The earlier guidelines for mineral nomenclature recommended by the then Commission on New Minerals and Mineral Names (CNMMN) of the IMA, as published by Nickel & Mandarino (1987), did not cover the nomenclature problems related to solid-solution series. There was only a general guideline for compositional criteria: "*At least one major structural site* should be occupied by a different chemical component than that which occurs in the equivalent site in an existing mineral."

Nickel (1992) published the current CNMMN–CNMNC guidelines for mineral nomenclature within three categories of solid-solution series (complete solid solutions without structural order, solid solutions with structural order and partial solid solutions). These guidelines focused mainly on the general influence of compositional ranges, not on the occupancies of individual crystallographic sites.

In the more recent CNMMN procedures and guidelines on mineral nomenclature, Nickel & Grice (1998) broadened the general guideline for compositional criteria by omitting the word "major" from the previous ones: "*At least one structural site* in the potential new mineral should be predominantly occupied by a different chemical component than that which occurs in the equivalent site in an existing mineral species." Nickel & Grice (1998) also regarded site vacancies as a component in the dominant-constituent rule, prescribed crystal-structure analysis to apply this rule for sites in minerals with complex structures, and suggested the grouping of sites in such structures.

The current dominant-constituent rule is applied in most approved new-mineral proposals. On the one hand, this rule has in some instances been applied rigorously, thus leading to some (substantiated) proliferation of new mineral species as, *e.g.*, in the complex labuntsovite and eudialyte groups (Chukanov *et al.* 2002, Johnsen *et al.* 2003). However, on the other hand, besides the well-known problems in the nomenclature system in the complex amphibole group (Hawthorne & Oberti 2006), new nomenclature systems for minerals of the arrojadite and epidote groups have recently been approved by the CNMNC that do not follow the current definition of the dominant-constituent rule (Cámara *et al.* 2006, Chopin *et al.* 2006, Armbruster *et al.* 2006). *In these systems, the dominant-constituent rule has been extended by considering "a group of atoms with the same valency state" as a single constituent.*

Moreover, Hawthorne (2002, and pers. commun.) had already pointed out several problems in the nomenclature of certain end-members in complex mineral groups (*e.g.*, tourmaline and milarite).

Our aim in this paper is to clarify, revise and extend the dominant-constituent rule, taking into account the recent problems encumbering or prohibiting a strict application of the rule. Mineralogists wishing to define members of known solid-solution series are required to follow the recommendations set out in this paper. However, mineral names previously accepted by the IMA–CNMMN–CNMNC that contravene the recommendations should not be changed without a formal vote of members of the CNMNC.

COMPLETE SOLID-SOLUTIONS WITHOUT STRUCTURAL ORDER

Homovalent substitutions at a single site

The simplest binary case is where an atom B^{n+} replaces the atom A^{n+} at a defined crystallographic M site, according to the substitution mechanism $A^{n+}_M \leftrightarrow B^{n+}_M$. Such a solid-solution series, which involves mutual substitution of only two kinds of atoms, leads to two different mineral names for each compositional range from the end members to the 50 mol.% mark (Fig. 1a).

Example 1: Mg $\leftrightarrow$ Fe^{2+} in the series diopside–hedenbergite, $CaMgSi_2O_6 \leftrightarrow CaFeSi_2O_6$.

Example 2: As $\leftrightarrow$ Sb in the series luzonite–famatinite, $Cu_3AsS_4 \leftrightarrow Cu_3SbS_4$.

The example usually given for this type of solid solution, $Mg_2SiO_4 \leftrightarrow Fe_2SiO_4$ (forsterite–fayalite in the olivine series), is not appropriate, as the substitution takes place at two different crystallographic sites (see below).

Where more than two kinds of homovalent atoms occur at a single crystallographic site, the predominant atom has to be considered in defining the mineral species. Consequently, the 50% mark is not applicable any longer, and instead the limit becomes 33.3% (three atoms, Fig. 1b), 25% (four atoms) or 20% (five atoms) marks in the dominant-constituent rule.

Example 1: In the preisingerite group, mutual substitution of the anionic groups (AsO$_4$), (VO$_4$) and (PO$_4$) leads to three fields in the composition triangle, with the end-members preisingerite, $Bi_3(AsO_4)_2OOH$, schumacherite, $Bi_3(VO_4)_2OOH$, and petitjeanite, $Bi_3(PO_4)_2OOH$.

Example 2: In the structure of schoenfliesite-group minerals, with formula XSn(OH)$_6$, one octahedral site can be dominated by six different homovalent cations, whereby X = Mg is dominant in schoenfliesite, Fe^{2+} in natanite, Mn^{2+} in wickmanite, Cu^{2+} in mushistonite, Zn in vismirnovite, and Ca in burtite.

Independent homovalent substitutions at several sites

The simple binary case (Fig. 1a) of homovalent substitution can take place at more than one site in a crystal structure.
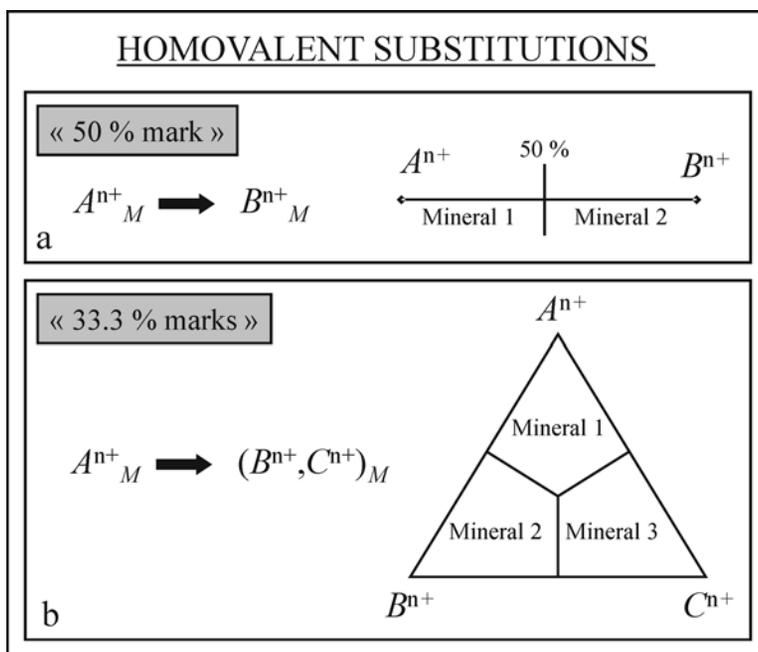
FIG. 1. Diagrammatic representations of homovalent substitutions. a. Complete binary solid-solution series. b. Complete ternary solid-solution series.

Example: The substitutions $Mn^{2+} \leftrightarrow Fe^{2+}$ at the A site and $Nb^{5+} \leftrightarrow Ta^{5+}$ at the B site in the columbite group lead to four end members (using the new nomenclature: Burke 2008): columbite-(Fe) ($FeNb_2O_6$), tantalite-(Fe) ($FeTa_2O_6$), columbite-(Mn) ($MnNb_2O_6$), and tantalite-(Mn) ($MnTa_2O_6$).

Coupled heterovalent substitutions at a single site

In a coupled heterovalent substitution at a single crystallographic site (Fig. 2), the A^{n+} atom, located at an M site, is progressively replaced by an equal amount of $B^{(n+1)+}$ and $C^{(n-1)+}$, according to the substitution mechanism $A^{n+}_M \leftrightarrow 0.5 \, B^{(n+1)+}_M + 0.5 \, C^{(n-1)+}_M$. The composition of one end member contains only A^{n+} at the M site, but the other end member contains an equal amount of $B^{(n+1)+}$ and $C^{(n-1)+}$ at this site. The dominant-constituent rule in such a series leads to the boundary mark $[A^{n+}_{0.5}B^{(n+1)+}_{0.25}C^{(n-1)+}_{0.25}]^{n+}_M$ between the two end members.

Example 1: The substitution $Ce^{3+} \rightarrow 0.5 \, Ca^{2+} + 0.5 \, Th^{4+}$ in monazite-(Ce), $Ce(PO_4)$, leads to the end member cheralite (formerly called "brabantite"), $(Ca^{2+}_{0.5}Th^{4+}_{0.5})(PO_4)$ (Linthout 2007).

Example 2: The substitution $Fe^{2+} \rightarrow 0.5 \, Li^{1+} + 0.5 \, Al^{3+}$ at the Y sites of the tourmaline mineral schorl, $NaFe^{2+}_3Al_6(Si_6O_{18})(BO_3)_3(OH)_4$, leads to

the end member elbaite, $Na(Li_{1.5}Al_{1.5})Al_6(Si_6O_{18})(BO_3)_3(OH)_4$.

Single-site heterovalent substitutions lead thus to end members with (disordered) sites occupied by two constituents, imposed by the differences in valency of the two constituents: this is ***valency-imposed double site-occupancy***.

Coupled heterovalent substitutions at two sites

Where a heterovalent substitution occurs at a given crystallographic site, the charge balance can also be maintained by coupling this substitution to another heterovalent substitution at a different site (Fig. 3a). At the M site, the atom A^{n+} is progressively replaced by $B^{(n+1)+}$, and to maintain charge balance, the atom $C^{(n+1)+}$ is progressively replaced by D^{n+} at the N site. The substitution mechanism is $A^{n+}_M + C^{(n+1)+}_N \leftrightarrow B^{(n+1)+}_M + D^{n+}_N$, and the boundary site-occupancies between the two members of the series are $[A^{n+}_{0.5}B^{(n+1)+}_{0.5}]_M$ $[C^{(n+1)+}_{0.5}D^{n+}_{0.5}]_N$.

Example 1: The two-site coupled substitution $Na^{1+} + Si^{4+} \leftrightarrow Ca^{2+} + Al^{3+}$ leads to the end members albite, $Na(AlSi_3O_8)$, and anorthite, $Ca(Al_2Si_2O_8)$, in the plagioclase series.

Example 2: The two-site coupled substitution $Cu^{1+} + As^{5+} \leftrightarrow Zn^{2+} + Ge^{4+}$ leads to the compositional

variation $Cu_{11}GeAsFe_4S_{16} \leftrightarrow Cu_{10}ZnGe_2Fe_4S_{16}$ in the mineral renierite (for which no separate names for the end members have been used or proposed).

Example 3: The two-site coupled substitution $Mn^{2+}_A + Sn^{4+}_B \leftrightarrow Li^{1+}_A + Ta^{5+}_B$ leads to the end members wodginite, $MnSnTa_2O_8$, and lithiowodginite, $LiTaTa_2O_8$.

Coupled heterovalent substitutions at two sites lead to end members with ***valency-imposed double site-occupancy*** (see above) where there is a disparity in the multiplicity of these two sites.

Example 1: The substitution $\square_A + Ca^{2+}_B \leftrightarrow Na^{1+}_A + Na^{1+}_B$ in the amphibole mineral tremolite, $\square Ca_2Mg_5(Si_8O_{22})(OH)_2$, leads to a valency-imposed double occupancy of the B site in the end member richterite, $Na(CaNa)Mg_5(Si_8O_{22})(OH)_2$ (Hawthorne & Oberti 2006) because there are two atoms at the B site, but only one at the A site.

Example 2: The substitution $Ti^{4+}_Z + Ca^{2+}_X \rightarrow Al^{3+}_Z + REE^{3+}_X$ in the hellandite-group mineral tadzhikite-(Ce), $Ca_4Ce_2Ti\square_2(Si_4B_4O_{22})(OH)_2$, leads to a valency-imposed double occupancy of the X sites in hellandite-(Ce), $(Ca_3REE)_{\Sigma4}Ce_2Al\square_2(Si_4B_4O_{22})(OH)_2$ (Oberti *et al.* 2002) because there are four atoms at the X sites, but only one at the Z site. The hellandite group has more examples of such heterovalent pairs at a single site.

Hawthorne (2002) has extensively discussed such valency-imposed double site-occupancy for some end members, notably in the milarite group.

Example: The end-member formula of milarite (omitting H_2O for simplicity) is $Ca_2K[(Be_2Al)Si_{12}O_{30}]$. The coupled substitution $Ca^{2+} + Al^{3+} \rightarrow Sc^{3+} + Be^{2+}$ leads to the end member $(ScCa)K[Be_3Si_{12}O_{30}]$ in which the A site must have a double occupancy (ScCa) because there is only one Al that can be replaced by

Be at the $T2$ site. This end member is to be named oftedalite. On the basis of the strict application of the current dominant-constituent rule, however, the IMA–CNMNC approved in 2004 the mineral oftedalite as being Sc-dominant at the A site with the formula $(Sc,Ca,Mn)_2K[(Be,Al)_3Si_{12}O_{30}]$ (Cooper *et al.* 2006). But milarite can only become Sc-dominant (and thus be named oftedalite, according to the rules valid in 2004) if some Ca is partly replaced by a third cation at that site; otherwise Ca will usually have more than 50% occupancy, and such specimens are then simply Sc-rich milarite. The adoption of the new dominant-valency rule, however, causes additional problems about the current definition of oftedalite (see below).

Remark: Spinel-group (AB_2O_4) and thiospinel-group (AB_2S_4) minerals occur in "normal" and "inverse" spinel structures. End-member magnesiochromite has a normal spinel site-occupancy, $Mg^{2+}Cr^{3+}_2O_4$; end-member magnetite has an inverse spinel site-occupancy, $Fe^{3+}(Fe^{2+}Fe^{3+})O_4$. There is a complete solid-solution series between magnesiochromite and magnetite, but without certainty about the cation distribution in the intermediate members. For the sake of nomenclatural simplicity, divalent and trivalent cations are kept separate in (thio-)spinels, regardless of their (double) site occupancies, as these are not imposed by valency considerations.

Coupled heterovalent–homovalent substitutions

Coupled heterovalent substitutions, at a single site or at two sites, become more complex if an additional homovalent substitution takes place. In the case of a coupled heterovalent substitution at two sites, a homovalent substitution at one of these sites causes the following problem (Fig. 3b). Starting from a composi-
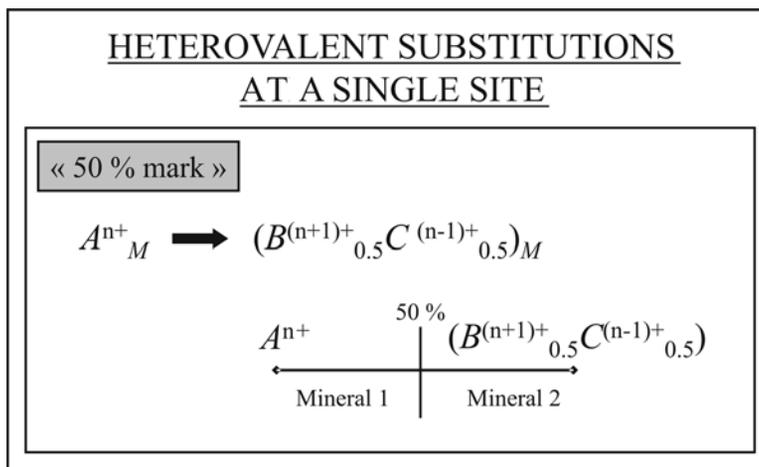

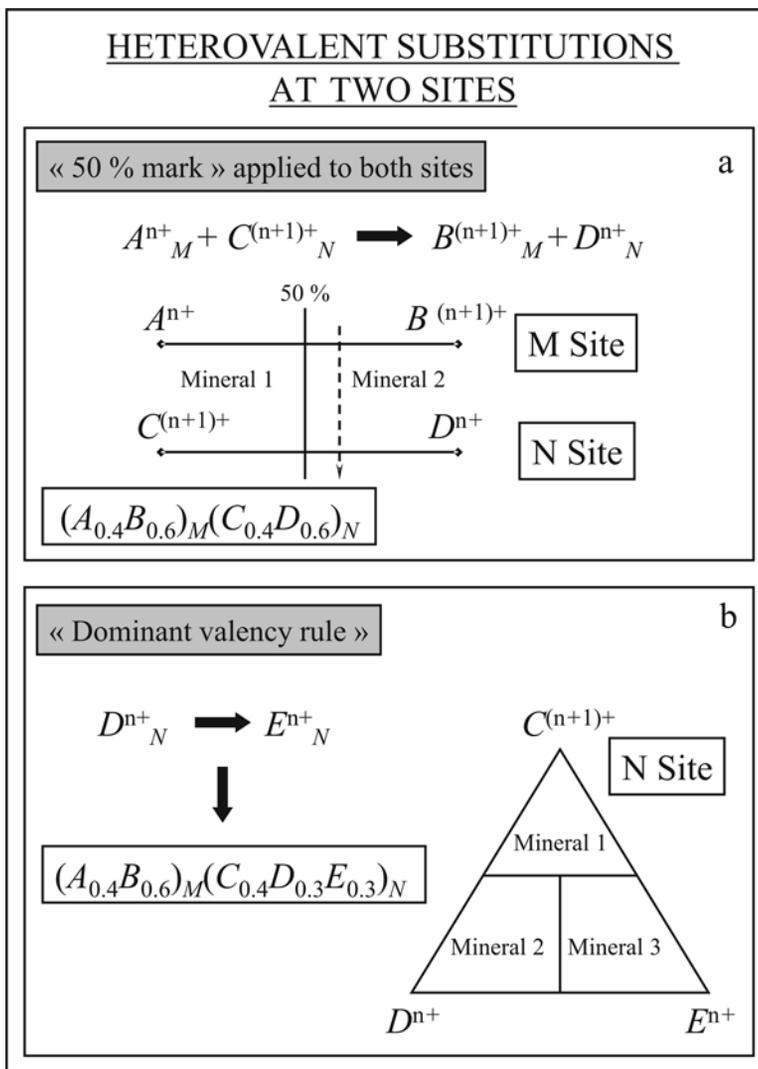Fig. 2. Diagrammatic representation of heterovalent substitution at a single site.

Fig. 3. Diagrammatic representations of heterovalent substitutions involving two sites. a. Coupled heterovalent substitution at two sites. b. Coupled heterovalent–homovalent substitution, leading to the dominant-valency rule.

tion $[A^{n+}_{0.4}B^{(n+1)+}_{0.6}]_M[C^{(n+1)+}_{0.4}D^{n+}_{0.6}]_N$, the homovalent substitution $E^{n+}_N \rightarrow D^{n+}_N$ could progressively take place, leading to an eventual composition $[A^{n+}_{0.4}B^{(n+1)+}_{0.6}]_M$ $[C^{(n+1)+}_{0.4}D^{n+}_{0.3}E^{n+}_{0.3}]_N$. The strict application of the dominant-constituent rule would indicate that this composition corresponds to a new species, with $C^{(n+1)+}$ instead of D^{n+} as the dominant constituent at the N site. However, the end-member formula for this supposedly new species, $[B^{(n+1)+}]_M[C^{(n+1)+}]_N$, is impossible because it is not charge-balanced.

This valency-nomenclatural problem can be solved by considering the elements of the homovalent substitution $E^{n+}_N \rightarrow D^{n+}_N$ as a whole, so that the group of cations with n+ valency are still dominant at the N site, in spite of the majority of $C^{(n+1)}$. 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. ***This rule is thus an extension of the***

current dominant-constituent rule, brought about by considering a group of atoms with the same valency state as a single constituent.

An important implication of this valency rule becomes evident if compositions of such minerals are plotted in a triangular diagram. As shown in Figure 3b, the usual boundaries crossing at the center of the diagram (33.3% of each component, Fig. 1b) are significantly displaced, and atom C needs dominance over the group $(D + E)$ at the N site to allow the definition of a new species.

This dominant-valency rule is not new, as it was already applied (albeit without this specific name) by the CNMMN for rare-earth minerals (Nickel & Grice 1998): "An example of a situation that may arise is one in which a mineral with a particular structural site is occupied by both Ca and REE, and the sum of the REE elements (in molar proportions) is greater than that of Ca, but individual REE elements are subordinate to that of Ca. In such a case, the mineral is regarded as a rare-earth mineral, with a Levinson modifier specifying the predominant REE."

The dominant-valency rule should also be applied to minerals with coupled heterovalent–homovalent substitutions at a *single site*.

Example: 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 ($\Sigma = 1.60$), with Fe^{2+} as the dominant ion, and the composition corresponds to schorl.

A number of examples illustrate the application of the dominant-valency rule to coupled heterovalent–homovalent substitutions at *two sites*.

Example 1: A simple case is given by the plagioclase feldspars. Albite, $NaAlSi_3O_8$, is related to anorthite, $CaAlSi_2O_8$, by the substitution mechanism $Na^{1+} + Si^{4+} \rightarrow Ca^{2+} + Al^{3+}$. This coupled heterovalent substitution at two sites of the feldspar structure may lead to an empirical composition $(Na_{0.6}Ca_{0.4})Al_{1.4}Si_{2.6}O_8$, which is clearly albite. A second, homovalent substitution $Na^{1+} \rightarrow K^{1+}$ may lead to a (high-temperature) composition $(Ca_{0.4}Na_{0.35}K_{0.25})Al_{1.4}Si_{2.6}O_8$. 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.

More complex examples of minerals for which this dominant-valency rule has to be applied have recently been provided by Cámara *et al*. (2006) and Chopin *et al*. (2006) in the arrojadite group. The application of this dominant-valency rule has been approved by the CNMNC.

Example 2: On considering a solution for the nomenclature problems in the arrojadite group, the dominant-constituent rule is implemented as follows: in a relevant site, the *dominant cation of the dominant valency state* is considered for nomenclature. Note that in case of multiple occupancy of a site involved in a heterovalent–homovalent exchange, the dominant cation of the dominant valency state may not be the site-predominant cation.

An arrojadite-group mineral has a formula: $A1A2B_2CaNa_{2+x}M_{13}Al(PO_4)_{11}(PO_3OH)_{1-x}W_2$. The mineral arrojadite-(KNa) is thus $KNaNa_2CaNa_2$ $Fe_{13}Al(PO_4)_{11}(PO_3OH)(OH)_2$. Substitutions at the $A1$ site lead to $(Ba_{0.40}K_{0.35}Na_{0.25})(Na_{0.6}\square_{0.4})Na_2CaNa_2Fe_{13}$ $Al(PO_4)_{11}(PO_3OH)(OH)_2$. This specimen does not receive the name arrojadite-(BaNa), but remains arrojadite-(KNa) because K is the dominant cation of the dominant valency at site $A1$.

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). The application of this dominant-valency rule has been approved by the CNMNC.

Example 3: In the clinozoisite subgroup, the dominant trivalent cation at the $M3$ site determines the name, whereas the cation at the $A2$ site appearing in the suffix has to be selected from among the divalent cations. An epidote-group mineral has the generic formula: $A1A2M1M2M3(T_2O_7)(TO_4)(O,F)(OH,O)$. Following this sequence, clinozoisite is $CaCaAlAlAl(Si_2O_7)(SiO_4)$ $O(OH)$. Consider now the $A2$ occupancy $(Ce_{0.35}La_{0.05}$ $Ca_{0.30}Sr_{0.20}Pb_{0.10})$. Because $(REE)^{3+} < 0.5$, the mineral belongs to the clinozoisite subgroup. Although Ce is the dominant cation at $A2$, the critical cation is Ca, the dominant divalent cation. No suffix is needed because a suffix is only added for a dominant $A2$ cation other than Ca. The $A2$ occupancy $(Ce_{0.35}La_{0.05}Sr_{0.30}Ca_{0.20}Pb_{0.10})$ would thus lead to the name clinozoisite-(Sr). Similarly, with the $M3$ occupancy $(Mg_{0.40}Al_{0.35}Fe^{3+}_{0.25})$, the dominant M^{3+} ion (*i.e.*, Al, not Mg) is decisive for the root name of the species, again clinozoisite (with Ca dominant in $A2$). The $M3$ occupancy $(Mg_{0.40}Fe^{3+}_{0.35}Al_{0.25})$ would thus lead to the name epidote.

Example 4: In the allanite and dollaseite subgroups, for the sites involved in the charge compensation of a heterovalent–homovalent substitution involving $A2$ and $O4$ (*i.e.*, $M3$ in the allanite subgroup; $M3$ and also

$M1$ in the dollaseite subgroup), identification of the relevant end-member formula must take into account *the dominant divalent charge-compensating octahedral cation (M^{2+})* and not the dominant cation at these sites (Armbruster *et al.* 2006).

An epidote-group mineral has the generic formula: $A1A2M1M2M3(T_2O_7)(TO_4)(O,F)(OH,O)$.

Following this sequence, allanite-(Ce) is $CaCe^{3+}AlAlFe^{2+}(Si_2O_7)(SiO_4)O(OH)$. For 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 one, *e.g.*, $Ca(Ce_{0.6}Ca_{0.4})$ $AlAl(Al_{0.4}Fe^{2+}_{0.3}Mg_{0.2}Mn^{2+}_{0.1})(Si_2O_7)(SiO_4)O(OH)$, Fe^{2+} is dominant among the M^{2+} cations, *i.e.*, Fe^{2+} is the dominant *charge-compensating* cation. Thus the mineral would properly be named allanite-(Ce). The $M3$ occupancy $(Al_{0.4}Mg_{0.3}Fe^{2+}_{0.2}Mn^{2+}_{0.1})$ leads to the name dissakisite-(Ce).

The dominant-valency rule is also valid for anionic sites.

Example 1: Oxidation of iron in annite, $KFe^{2+}_3(AlSi_3O_{10})(OH)_2$, evolves along the reaction Fe^{2+} + $(OH)^- \rightarrow Fe^{3+} + O^{2-}$ (Dercourt *et al.* 2001). Partial oxidation of iron and some substitution of (OH) by F could lead to a composition $K(Fe^{2+}_{2.2}Fe^{3+}_{0.8})(AlSi_3O_{10})$ $[O_{0.8}(OH)_{0.7}F_{0.5})]$. In spite of oxygen dominance at the anion A site, this specimen cannot be called "oxyannite", as the sum of monovalent anions at the A site is higher than the oxygen occupancy. The name is thus still annite or, using some modifiers of Bayliss *et al.* (2005), iron(3+)-enriched F-bearing annite. On the other hand, using the same dominant-valency rule for the composition $K(Fe^{2+}_{2.2}Fe^{3+}_{0.8})(AlSi_3O_{10})[O_{0.8}F_{0.7}(OH)_{0.5}]$ would result in the name fluorannite. The end-member formula of "oxyannite" is $K(Fe^{3+}_2Fe^{2+})AlSi_3O_{10}O_2$, an example of "valency-imposed double site-occupancy".

Example 2: The end-member formula of staněkite is $Mn^{2+}Fe^{3+}(PO_4)O$, and that of triploidite is $Mn^{2+}_2(PO_4)(OH)$. The composition $(Mn^{2+}_{1.60}Fe^{3+}_{0.40})(PO_4)$ $[O_{0.40}(OH)_{0.35}F_{0.25}]$ has oxygen as the dominant constituent at the additional anion site. Nevertheless, the specimen does not get a new mineral name ("oxytriploidite"); it is simply triploidite because the sum of the monovalent additional anions is higher than that of the divalent ones. The end-member formula of staněkite is also an example of "valency-imposed double site-occupancy".

The adoption of the extension of the dominant-constituent rule with the dominant-valency rule for the description of new minerals in the future has possible implications for minerals that have been approved in the past on the basis of the old dominant-constituent rule.

Example 1: The pumpellyite series consists of five end members [pumpellyite-(Mg), pumpellyite-(Fe^{2+}), pumpellyite-(Mn^{2+}), pumpellyite-(Fe^{3+}) and pumpellyite-(Al)], based on the dominant cation at the $M1$ site. The dominant presence of trivalent ions at that site is balanced by the replacement of the H_2O

molecule by (OH), *e.g.*, $Ca_2AlAl_2(SiO_4)(Si_2O_7)(OH)_3$. The empirical formula of the IMA–CNMNC-approved pumpellyite-(Al) is $(Ca_{1.99}Na_{0.01})_{\Sigma2.00}(Al_{0.42}Fe^{2+}_{0.33}$ $Mg_{0.24}Mn_{0.01})_{\Sigma1.00}Al_{2.00}(SiO_4)(Si_2O_7)(OH)_{2.42}\bullet0.58H_2O$ (Hatert *et al.* 2007). Aluminum as a single element is dominant at the $M1$ site (0.42 *apfu* Al), but the sum of the divalent ions (Fe + Mg + Mn) is greater (0.58 *apfu*). If the dominant-valency rule is applied, the name of this mineral is not pumpellyite-(Al) but pumpellyite-(Fe^{2+}), because Fe^{2+} is the dominant cation of the dominant valency at that site. Crystal-structure refinement of the same pumpellyite-(Al) specimen showed, however, that the occupancy of the $M1$ site is 75% Al, 12.5% Mg and 12.5% Fe^{2+}. A similar discrepancy between chemical and crystal-structure-derived $M1$ site occupancies has been described for a sample of pumpellyite by Yoshiasha & Matsumoto (1985), $(Al_{0.47}Mg_{0.33}Fe^{2+}_{0.23})_{\Sigma1.03}$ and (80% Al, 20% Fe^{2+}), respectively; on the basis of its chemical composition, this specimen would now be named pumpellyite-(Mg). Several chemical compositions of pumpellyite-group minerals (*e.g.*, Passaglia & Gottardi 1973), however, show Al to be dominant at the $M1$ site; these are examples of real pumpellyite-(Al) specimens.

Example 2: Ganterite has been approved as the Ba-dominant analogue of muscovite (Graeser *et al.* 2003). The empirical formula is $(Ba_{0.44}K_{0.28}Na_{0.27})_{\Sigma0.99}$ $(Al_{1.84}Mg_{0.09}Fe^{2+}_{0.04}Ti_{0.04})_{\Sigma2.01}[Si_{2.72}Al_{1.28}O_{10}](OH)_{1.89}$. Barium is indeed the dominant constituent at the I site (0.44 *apfu*), but the sum of the monovalent ions (K + Na) is greater (0.55 *apfu*). Application of the dominant-valency rule in the scheme of mica nomenclature would not lead to a new mineral, but its name would be a Ba-rich muscovite, although the amount of ^{IV}Si and ^{VI}Al in *apfu* fall outside the range indicated for muscovite by Rieder *et al.* (1998).

As stated in the introduction, it is not our aim in this paper to automatically change mineral names previously accepted by the IMA–CNMNC, even where this new dominant-valency rule is to be applied in the future. There is even an example where the old dominant-constituent rule is to be maintained because application of the dominant-valency rule would make the existence of the mineral almost impossible.

Example: This very special case is oftedalite. It is unique, perhaps with the exception of the hypothetical Y-dominant analogue of milarite and oftedalite, which may also exist in nature (Hawthorne 2002). It has been stated (see above) that milarite can only become Sc-dominant at the A site (and thus be named oftedalite following the old dominant-constituent rule) if some Ca is replaced by a third cation at that site, otherwise Ca will usually have more than 50% occupancy, such specimens are then simply milarite. But if that third cation also is divalent, then the application of the dominant-valency rule changes oftedalite back to milarite! The empirical formula of oftedalite is $(Sc_{0.96}$ $Ca_{0.79}Mn^{2+}_{0.18}Fe^{2+}_{0.04}Y_{0.03})_{\Sigma2.00}K_{0.98}(Be_{2.91}Al_{0.09})_{\Sigma3.00}$

$Si_{11.98}O_{30}$ (Cooper *et al.* 2006). It is true that Sc is dominant as a single element at the *A* site, but the sum of divalent ions (Ca+Mn+Fe) is greater (1.01 *apfu*) than the sum of the trivalent ions (Sc+Y = 0.99 *apfu*). The new valency-dominant rule implies that in oftedalite Sc must be the dominant cation of the dominant valency at the *A* site (except for the end member, which has a valency-imposed double site-occupancy; see above). Current samples of "oftedalite", as previously defined by the old constituent rule, are thus simply Sc-rich milarite as defined by the new constituent rule. It is of course possible, however, that Ca is replaced by a monovalent ion, *e.g.* Na^{1+}, so that Sc is the dominant cation of the then dominant trivalent ions, in that case producing an oftedalite specimen that obeys both the dominant-constituent and the dominant-valency rules.

Grouping of crystallographic sites

It is frequently observed that a group of similar cations or anions can occupy more than one crystallographically distinct site. Such sites with similar crystal-chemical roles may be considered as a whole in nomenclature proposals.

Example 1: The olivine structure has two octahedral sites, *M*1 and *M*2, which in the forsterite–fayalite series are occupied by Mg and Fe^{2+}, in a not completely disordered way. However, recognition of only two species is deemed to be appropriate, as the two intermediate compositions and their implied arrangements are not approached in nature (Hawthorne 2002).

Example 2: In the structure of wiluite, a vesuvianite-group mineral, there are four *T*1 sites and one *T*2 site. Ideally, only one of these sites needs to be more than half-occupied by boron to give rise to a new mineral species; thus there are four potential end-members involving the *T* sites. However, some of the resulting species can only be identified *via* crystal-structure refinement to derive B occupancies at the *T*1 and *T*2 sites. This is obviously not practical, and therefore wiluite was defined as containing > 2.5 B *apfu*, such that the *T*1 and *T*2 sites have an aggregate occupancy of greater than 0.5 (Groat *et al.* 1998).

Example 3: The nomenclature of the amphibole group is based on the formula $AB_2C_5T_8O_{22}W_2$, where *C* represents the group of five *apfu* in the three *M*(1), *M*(2) and *M*(3) crystallographic sites (Leake *et al.* 1997). Grouping these sites had to be done to avoid an unnecessary proliferation of mineral species in this complex group, which would have been caused by the strict application of the dominant-constituent rule to each crystallographic site. The 1997 amphibole nomenclature is based on the *A*, *B* and *T* groups of sites. Hawthorne & Oberti (2006) argued that a nomenclature based on the *A*, *B* and *C* groups of sites is to be preferred, as it is in these groups that the maximum variation in chemical composition occurs, and this scheme would thus also be more in accord with the IMA-sanctioned dominant-

constituent principle. In their proposed scheme, Hawthorne & Oberti (2006) deviate considerably from the end-member rules of Hawthorne (2002), as most of their proposed amphibole end-members need more than one type of cation at more than one group of sites, even up to three groups of sites, *e.g.*, $Na(CaNa)(Fe^{2+}_4Al)$ $(Si_7Al)O_{22}(OH)_2$ for katophorite. The *C*-site group may have four different cations in the end-member formula, *e.g.*, $NaNa_2(MgMn^{3+}_2LiTi^{4+})Si_8O_{22}O_2$ for dellaventuraite; for valency reasons, this end-member formula must have Mn^{3+}_2 although the empirical formula has only 0.85 *apfu* Mn^{3+} (Tait *et al.* 2005). The amphibole subcommittee of the CNMNC is working to establish an acceptable scheme of nomenclature for this important, but very complex group of minerals.

According to the current CNMNC rules (Nickel 1992, Nickel & Grice 1998), all crystallographically distinct sites, even minor ones, may play a role in mineral nomenclature. It might be a matter of discussion whether it is desirable to return to the restriction in the Nickel & Mandarino (1987) guidelines of using only "major" structural sites. Meanwhile, there are examples of both views in our nomenclature systems.

Example 1: The mineral stornesite-(Y) has recently been described by Grew *et al.* (2006). This mineral belongs to the fillowite group of phosphates, characterized by the general formula (M^{2+},Y,REE,Na) $(Na,K,\square)_2(Na,K)_6(M^{2+},Na,K)_8(M^{2+},M^{3+})_{43}(PO_4)_{36}$. Depending on the dominant divalent cation at the 43 *M* sites, the three minerals fillowite ($M^{2+} = Mn^{2+}$), johnsomervilleite ($M^{2+} = Fe^{2+}$), and chladniite ($M^{2+} = Mg^{2+}$) are defined. The main difference between chladniite and stornesite-(Y) is the presence, in the latter, of small amounts of Y and Yb occurring at the (0,0,0) position. This position has a multiplicity of 3, whereas the other *M* sites have generally multiplicities between 6 and 18. As a consequence, the amount of Y is 0.460–0.870 *apfu* or 0.97–1.85 wt.% Y_2O_3, and the amount of Yb is 0.056–0.105 *apfu* or 0.20–0.39% Yb_2O_3. A better knowledge of the crystal chemistry of the fillowite group is now required to confirm that the substitution of divalent cations by Y and REE at the (0,0,0) position really plays a significant role.

Example 2: In order to restrict the number of species in the eudialyte group, it was decided to ignore the *X* anion sites in nomenclature as a rule. To assist in the evaluation of future proposals of these complicated eudialyte-group minerals, however, it was recommended that refined site-scattering data and a table of site assignments for all sites relevant to the space group in question should be submitted with the proposal.

Example 3: The fundamental structural formula for arrojadite-group minerals is $A_2B_2CaNa_{2+x}M_{13}Al$ $(PO_4)_{11}(PO_3OH)_{1-x}W_2$. If the content of each site is considered for nomenclature, the number of independent cation sites in the formula unit has the potential to yield a wealth of mineral names in the arrojadite group. Regardless of whether or not such proliferation would

be a service to Mineralogy, the mixed occupancy of most sites (by Fe, Mn, Mg, and Li in the M sites; by Ca, Na, Fe, and vacancies in the A, B, Ca and Na sites) makes a unique assignment of site population impossible in most instances, even if individual site-scattering values are known through crystal-structure refinement. Therefore, some sites were grouped, and in others, the dominant-constituent rule was adapted to a dominant-valency rule, as above.

There are thus divergent tendencies in establishing systems of nomenclature for mineral groups, especially in complex ones. On the one hand, crystal-structure refinement allows in principle to determine occupancies of all sites, and thus to use all of these in a system of nomenclature. On the other hand, there is a definite need for practical systems of nomenclature, *i.e.*, systems that can be applied on the basis of chemical data (usually obtained by electron microprobe) or X-ray powder diffraction alone, without having to resort to structure refinement (which, as shown by the arrojadite-group example, is not unequivocal in every case). To assist the mineralogical community in its work, nomenclature systems enabling mineral identifications with relatively simple methods are certainly to be preferred.

PARTIAL SOLID-SOLUTION
WITHOUT STRUCTURAL ORDER

Binary partial solid-solution series

The case of partial solid-solution series has already been addressed in detail by Nickel (1992), and only an overview of the issue will be given here. If there is limited solid-solution in the vicinity of one or both end-members, and the solid solution does not extend to the 50% boundary (in a binary system), then the dominant-constituent rule is generally applied (Fig. 4a). For purposes of nomenclature, it does not matter whether or not both end-members are isostructural.

Example: Solid solution in the system hematite–ilmenite, $Fe^{3+}_2O_3 - Fe^{2+}Ti^{4+}O_3$, at low temperatures is limited to small ranges near the end members.

If the miscibility gap in a binary solid-solution series between non-isostructural phases is to one side of the 50% mark, the composition of one of the two members will extend beyond the 50% mark (Fig. 4b). Nickel (1992) made a distinction in these ranges beyond 50% between a "small" one and a "substantial" one, the dividing line between these being "about 10 mol. %, although each situation should be regarded on its own merits". Only "substantial" ranges would merit a separate name. A new name, however, should be given to any range beyond the 50% mark if it can be satisfactorily demonstrated that a given composition exceeds the 50% mark. There is, after all, not such a 10% "no-name-land" for members around the 50% mark in complete solid-solution series.

Example: The system ZnS (sphalerite) – FeS is a partial solid-solution series, with solution of FeS in ZnS ending at 66 mol.% FeS. The Fe-dominant phase with a sphalerite-type structure and compositions between $Zn_{0.5}Fe_{0.5}S$ and $Zn_{0.34}Fe_{0.66}S$ has been approved as the mineral rudashevskyite.

A different approach to nomenclature has to be considered if the known compositions in a binary partial solid-solution series cluster around the 50% mark, but do not appear to extend to either end-member (Fig. 4c). In principle, only one name should be given to such a limited compositional range because the situation also applies to small deviations from the fixed 1:1 ratio in valency-imposed double site-occupancies (see above). The distinction in these cluster ranges made by Nickel (1992), now between "small" and "large", for the eventual use of separate names might have to be used if the range is shown to extend beyond the cluster conception.

Example: In pentlandite, $Fe(Fe,Ni)_8S_8$, Fe and Ni substitute for each other to a limited extent, with compositions centered around Fe:Ni = 1:1; compositions near the Fe and Ni end members are not known. It has not been found necessary to divide pentlandite into two species.

Ternary partial solid-solution series

Similar considerations should be applied to ternary or higher-order partial solid-solution series (Figs. 5a, b). It is evident that analysis of new mineral specimens may enlarge the compositional range within a partial solid-solution series, thus bringing a mineral from the left side to the right side of Figure 5 (or from the upper to lower level in Fig. 4c), and eventually necessitating a change in nomenclature.

SOLID SOLUTIONS WITH STRUCTURAL ORDER

If there is structural order involving the ions that define the end members within an otherwise disordered solid-solution series, the ordered phase is to be given a mineral name different from those of the end members. Where structural ordering occurs, at least one crystallographic site is split in two distinct positions, thus leading to a change of symmetry and also commonly to a doubling of some unit-cell parameters. A somewhat artificial ordering of cations, without a specific table of site occupancies, but with a concurrent artificial lowering of symmetry, should be avoided as the key point in new-mineral proposals.

Example 1: Ordering of Ca and Mg ions in dolomite, $CaMg(CO_3)_2$, results in a crystal structure distinct from those of the end members calcite, $CaCO_3$, and magnesite, $MgCO_3$ of the $(Ca,Mg)CO_3$ series.

Example 2: At temperatures below 700°C, Mg and Al atoms are disordered in the diopside, $CaMgSi_2O_6$, and jadeite, $NaAlSi_2O_6$, end members with $C2/c$ space

BINARY PARTIAL SOLID SOLUTIONS

« 50 % mark »

a

Mineral 1   Mineral 2

« 50 % mark »

b

Mineral 1   Mineral 2
Mineral 3

« 50 % mark not applicable »

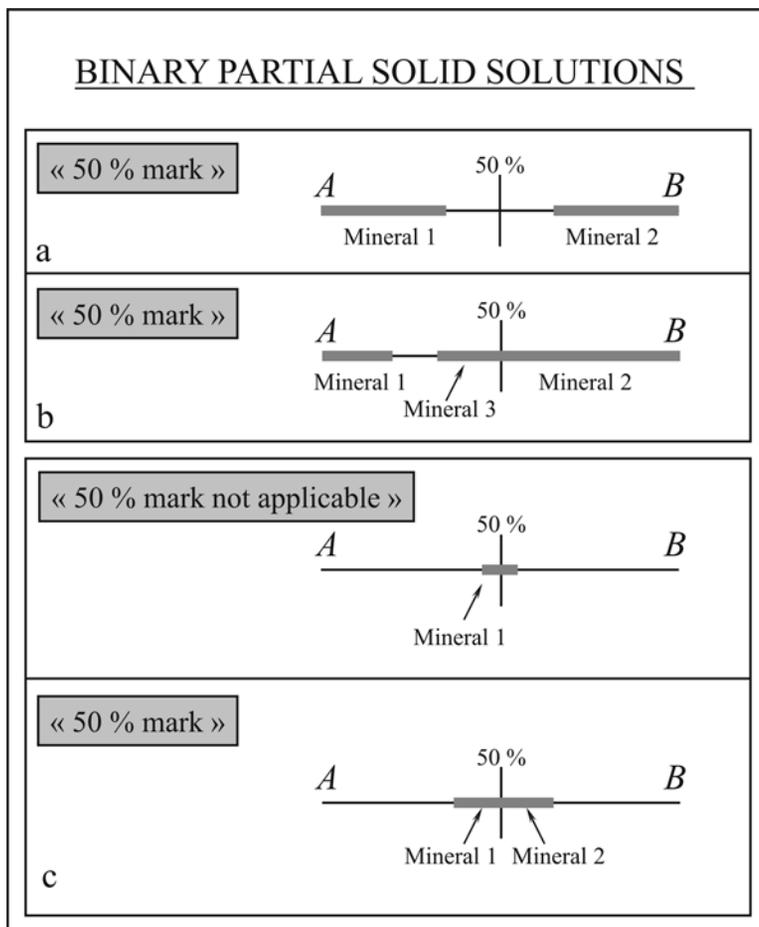Mineral 1

« 50 % mark »

c

Mineral 1   Mineral 2

FIG. 4.   Diagrammatic representations of partial binary solid-solution series. a. Series with
a miscibility gap. b. Series with a miscibility gap, but with one member encompassing
the midpoint. c. Series with members limited around the midpoint.

group, but ordered in the intermediate member ompha-cite, ideally $(Ca_{0.5}Na_{0.5})(Mg_{0.5}Al_{0.5})Si_2O_6$, with $P2/n$ space group.

Both are examples of so-called "non-convergent order" in thermodynamics.

CONCLUSIONS

The nomenclature of members in complete solid-solution series remains in principle determined by the application of the dominant-constituent rule, but the rule has been extended with the dominant-valency rule by considering a group of atoms with the same valency state as a single constituent. The old dominant-constituent rule (with only atoms, molecular groups or vacancies as constituents) can only be applied without problems or errors to solid-solution series involving homovalent substitutions or singular coupled heterovalent substitutions. The extension with the dominant-valency rule is imposed by all cases of coupled heterovalent–homovalent substitutions. The application of the old dominant-constituent rule in such systems is a possible source of problems or errors, as illustrated by examples given in this paper. The extension with the dominant-valency rule is necessary to establish charge-balanced end-member formulae for solid-solution series with complex mechanisms of substitution.

Although these general guidelines are recommended, a certain degree of flexibility might be necessary in the cases of conflicting dominant-constituent and dominant-valency rules, and in partial solid-solution series. Proposals for mineral names in this category will be judged by the CNMNC on the merits of each particular case.
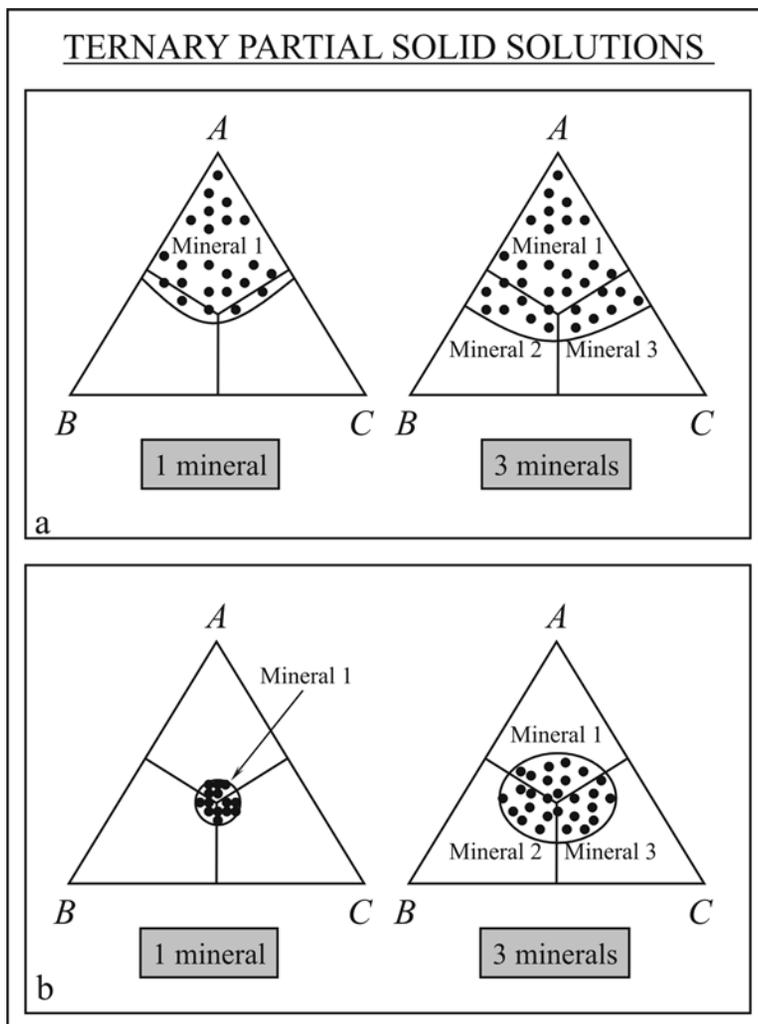
FIG. 5.   Diagrammatic representations of partial ternary solid-solution series. a. Series with members encompassing geometrical boundaries. b. Series with members having compositions about the geometric midpoint.

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