

## VECTOR REPRESENTATION OF SOME MINERAL COMPOSITIONS IN THE AENIGMATITE GROUP, WITH SPECIAL REFERENCE TO HØGTUVAITE

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### ABSTRACT

Aenigmatite-group compositions conform to the general formula  $A_2B_6T_6O_{20}$ , where  $^{18}A$  cations are Na and Ca,  $^{16}B$  are  $Fe^{2+}$ ,  $Fe^{3+}$ , Mg, Al, Cr, Ti, and  $Sb^{5+}$ , and  $^{14}T$  are Si, Al, B, and Be in named end-members. These include the sodic minerals aenigmatite, krinovite, and wilkinsonite, and the calcic minerals rhönite, serendibite, dorrite, welshite, and høgтуvaite (a new Be-bearing end-member: Grauch *et al.* 1994). Graphical representation of the compositional relations among these phases is made possible by the vector method, which has recently been applied to a number of other mineral groups. The fundamental principle is that a chemical displacement such as  $CaAl(NaSi)_{-1}$ , having both direction and magnitude, can be thought of as a vector of unit length and arbitrary orientation. Compositional relations are simplified by condensing on vectors of isovalent substitution, such as  $Fe^{3+}Al_{-1}$  and  $Fe^{2+}Mg_{-1}$ . In vector diagrams, *bound vectors* are attached to a point and show the relations among basis and derived vectors. The corresponding *free vectors* generate the accessible compositional range (e.g., triangle, quadrilateral, or pentagon), starting from an initial formula or composition (additive component of J.B. Thompson, Jr.). When this approach is used on the aenigmatite group, the compositions of the main minerals are derived from that of aenigmatite by application of the basis vectors  $CaAl(NaSi)_{-1}$ ,  $Al_2(MgTi)_{-1}$ , and  $Al_2(MgSi)_{-1}$ . Høgтуvaite is derived by  $BeSiAl_{-2}$  acting on rhönite, and welshite by  $AlSbBe(MgTiSi)_{-1}$  acting on høgтуvaite. Other theoretical end-members can be generated by the vector method; in the aenigmatite group, many are probably unstable with regard to a mixture of clinopyroxene plus olivine or spinel, especially if they lack Ti or excess Al.

*Keywords:* exchange vectors, aenigmatite group, høgтуvaite, beryllium.

### SOMMAIRE

La composition des minéraux du groupe de l'aenigmatite répond à la formule générale  $A_2B_6T_6O_{20}$ , dans laquelle Na et Ca occupent la position  $^{18}A$ ,  $Fe^{2+}$ ,  $Fe^{3+}$ , Mg, Al, Cr, Ti et  $Sb^{5+}$ , la position  $^{16}B$ , et Si, Al, B et Be, la position  $^{14}T$  dans le cas des pôles qui sont déjà homologués. Parmi ceux-ci se trouvent les minéraux sodiques aenigmatite, krinovite et wilkinsonite, et les minéraux calciques rhönite, serendibite, dorrite, welshite et høgтуvaite, cette dernière étant le pôle à Be: (Grauch *et al.* 1994). Une représentation graphique des relations compositionnelles parmi ces phases est rendue possible grâce à la méthode des vecteurs, qui a récemment été appliquée avec succès à d'autres groupes de minéraux. Le principe fondamental veut qu'un déplacement compositionnel, par exemple  $CaAl(NaSi)_{-1}$ , possédant à la fois une direction et une amplitude, s'exprime sous forme de vecteur d'une longueur unitaire et d'orientation quelconque. Les relations parmi les compositions sont simplifiables en termes de vecteurs de substitution isovalente, par exemple  $Fe^{3+}Al_{-1}$  et  $Fe^{2+}Mg_{-1}$ . Dans les diagrammes vectoriels, les vecteurs rattachés à un point démontrent les relations parmi le vecteur de base et les vecteurs dérivés. Le vecteur libre correspondant définit l'étendue accessible dans l'espace compositionnel (c'est-à-dire, un triangle, un quadrilatère ou un pentagone), à partir d'une formule ou d'une composition initiale (composant additif de J.B. Thompson, Jr.). Dans le contexte du groupe de l'aenigmatite, la composition des minéraux principaux est dérivée à partir de celle de l'aenigmatite par l'application des vecteurs opérationnels  $CaAl(NaSi)_{-1}$ ,  $Al_2(MgTi)_{-1}$  et  $Al_2(MgSi)_{-1}$ . La høgтуvaite découle de l'application du vecteur  $BeSiAl_{-2}$  agissant sur le pôle rhönite, et la welshite résulte de l'application du vecteur  $AlSbBe(MgTiSi)_{-1}$  agissant sur le pôle høgтуvaite. On peut prédire la composition de pôles nouveaux par la méthode des vecteurs; dans le cas du groupe de l'aenigmatite, plusieurs seraient instables par rapport à un mélange de clinopyroxène + olivine ou spinelle, surtout s'ils sont dépourvus de titane ou contiennent un excès d'aluminium.

(Traduit par la Rédaction)

*Mots-clés:* vecteurs d'échange, groupe de l'aenigmatite, høgтуvaite, béryllium.

## INTRODUCTION

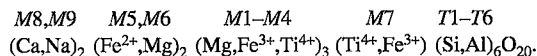
Vectors, by definition, have both a direction and magnitude. An example of a vector quantity is the physical displacement represented by walking five meters north. Ionic substitutions in minerals likewise have both a direction (or "sense") and a magnitude (or "extent"); therefore, although it is not yet conventional to do so, these chemical displacements (Burt 1991) also can be treated as vectors, a concept, if not a terminology, that originated with W.L. Bragg (Thompson 1981; *cf.* Smith 1959).

Aenigmatite-group minerals, although relatively rare, occur in a variety of high-temperature environments, ranging from volcanic and plutonic to metamorphic and metasomatic; they also occur in meteorites (*e.g.*, Deer *et al.* 1978). The purpose of this paper is to apply vector methods to the graphical representation of complex coupled substitutions in the aenigmatite group; algebraic vector representations of mineral compositions in the aenigmatite group were given by Johnston & Stout (1985). Emphasis will be placed on coupled substitutions involving Be and Sb<sup>5+</sup> (which were not considered by Johnston & Stout) and on derivation of the new Be end-member høgтуvaite described in the accompanying article (Grauch *et al.* 1994). To the best of the author's knowledge, this is the first new mineral whose initial description is based on the vector method.

Structural and crystal-chemical features in this group have recently been reviewed by Deer *et al.* (1978) and Bonaccorsi *et al.* (1990). The idealized compositions of mineral end-members recognized to date are listed in Table 1. The formula of this group is generally given as <sup>[8]A</sup><sub>2</sub><sup>[6]B</sup><sub>6</sub><sup>[4]T</sup><sub>6</sub>O<sub>20</sub>, with A = Na or Ca, B = Fe<sup>2+</sup>, Mg, Fe<sup>3+</sup>, Al, Cr<sup>3+</sup>, Ti<sup>3+</sup>, Ti<sup>4+</sup>, or Sb<sup>5+</sup>, and T = Si, Al, Fe<sup>3+</sup>, B, or Be. Structural refinements by Bonaccorsi *et al.* (1990) reveal that a more accurate representation for rhönite, a common member of the group, is

TABLE 1. MINERALS IN THE AENIGMATITE GROUP

General: <sup>[8]A</sup> <sub>2</sub> <sup>[6]B</sup> <sub>6</sub> <sup>[4]T</sup> <sub>6</sub> O <sub>20</sub>	
Mineral Name	Idealized Composition
Aenigmatite	Na <sub>2</sub> (Fe <sup>2+</sup> <sub>5</sub> Ti)Si <sub>6</sub> O <sub>20</sub>
Dorrite	Ca <sub>2</sub> (Mg <sub>2</sub> Fe <sup>3+</sup> <sub>4</sub> )(Al <sub>4</sub> Si <sub>2</sub> )O <sub>20</sub>
Høgтуvaite	Ca <sub>2</sub> (Fe <sup>2+</sup> <sub>5</sub> Ti)(BeSi <sub>5</sub> )O <sub>20</sub>
Krinovite	Na <sub>2</sub> (Mg <sub>4</sub> Cr <sup>3+</sup> <sub>2</sub> )Si <sub>6</sub> O <sub>20</sub>
Rhönite	Ca <sub>2</sub> (Fe <sup>2+</sup> <sub>5</sub> Ti)(Al <sub>2</sub> Si <sub>4</sub> )O <sub>20</sub>
Serendibite	Ca <sub>2</sub> (Mg <sub>3</sub> Al <sub>3</sub> )(B <sub>1.5</sub> Al <sub>1.5</sub> Si <sub>3</sub> )O <sub>20</sub>
Welshite	Ca <sub>2</sub> (Mg <sub>4</sub> Fe <sup>3+</sup> <sub>2</sub> Sb <sup>5+</sup> )(Be <sub>2</sub> Si <sub>4</sub> )O <sub>20</sub>
Wilkinsonite	Na <sub>2</sub> (Fe <sup>2+</sup> <sub>4</sub> Fe <sup>3+</sup> <sub>2</sub> )Si <sub>6</sub> O <sub>20</sub>



The large irregular M8 and M9 polyhedra, in addition to being crystallographically distinct from each other, are quite different in shape in rhönite (calcic) and aenigmatite (sodic: Bonaccorsi *et al.* 1990). This feature explains the lack of complete solid-solution between the two and presumably why natural phases tend to be either Na-dominant (aenigmatite, krinovite, and wilkinsonite: Duggan 1990) or Ca-dominant (rhönite, serendibite, welshite, dorrite, and høgтуvaite). The six octahedrally coordinated sites can be subdivided among the larger M5 and M6 sites, typically with divalent cations, the smaller M1-M4 sites, and the still smaller M7 site, typically with a high-valence cation such as Ti or Sb<sup>5+</sup>. A variety of tetrahedrally coordinated cations occupy the T1-T6 sites; this helps explain why coupled substitutions in this group can be quite complex (*cf.* Johnston & Stout 1985). Significant vacancies at cation sites or heterovalent substitutions involving anions have not been described, however, which at least makes the aenigmatite group simpler than the tourmaline group, for example (Burt 1989).

A further complication is that many potential end-member aenigmatite-group compositions, especially those lacking Ti or Al, are unstable with respect to a mixture of clinopyroxene plus spinel or olivine (or both). Table 2b shows this relation for some simple Ti-free compositions. This complication can be

TABLE 2. STABILITY AND INSTABILITY IN THE AENIGMATITE GROUP

General: A <sub>2</sub> B <sub>6</sub> T <sub>6</sub> O <sub>20</sub> = 2ABT <sub>2</sub> O <sub>6</sub> + 2B <sub>2</sub> TO <sub>4</sub>		
a) Examples of Stability:		
2NaFe <sup>3+</sup> Si <sub>2</sub> O <sub>6</sub> + 2Fe <sub>2</sub> SiO <sub>4</sub> = Na <sub>2</sub> (Fe <sup>2+</sup> <sub>4</sub> Fe <sup>3+</sup> <sub>2</sub> )Si <sub>6</sub> O <sub>20</sub>		
Aegirine	Fayalite	Wilkinsonite
2NaCr <sup>3+</sup> Si <sub>2</sub> O <sub>6</sub> + 2Mg <sub>2</sub> SiO <sub>4</sub> = Na <sub>2</sub> (Mg <sub>4</sub> Cr <sup>3+</sup> <sub>2</sub> )Si <sub>6</sub> O <sub>20</sub>		
Kosmochlor	Forsterite	Krinovite
2CaAl <sub>2</sub> SiO <sub>6</sub> + 2MgFe <sup>3+</sup> <sub>2</sub> O <sub>4</sub> = Ca <sub>2</sub> (Mg <sub>2</sub> Fe <sup>3+</sup> <sub>4</sub> )(Al <sub>4</sub> Si <sub>2</sub> )O <sub>20</sub>		
"CATS"	Magnesioferrite	Dorrite
b) Examples of Instability:		
Ca <sub>2</sub> (Mg <sub>4</sub> Al <sub>2</sub> )(Al <sub>2</sub> Si <sub>4</sub> )O <sub>20</sub> = 2CaMgSi <sub>2</sub> O <sub>6</sub> + 2MgAl <sub>2</sub> O <sub>4</sub>		
	Diopside	Spinel
Ca <sub>2</sub> (Fe <sup>2+</sup> <sub>4</sub> Fe <sup>3+</sup> <sub>2</sub> )(Fe <sup>3+</sup> <sub>2</sub> Si <sub>4</sub> )O <sub>20</sub> = 2CaFeSi <sub>2</sub> O <sub>6</sub> + 2Fe <sub>3</sub> O <sub>4</sub>		
	Hedenbergite	Magnetite
Ca <sub>2</sub> (Mg <sub>6</sub> )Si <sub>6</sub> O <sub>20</sub> = 2CaMgSi <sub>2</sub> O <sub>6</sub> + 2Mg <sub>2</sub> SiO <sub>4</sub>		
	Diopside	Forsterite
Na <sub>2</sub> (Al <sub>6</sub> )(Al <sub>4</sub> Si <sub>2</sub> )O <sub>20</sub> = 2NaAlSiO <sub>4</sub> + 4Al <sub>2</sub> O <sub>3</sub>		
	Nepheline	Corundum

explained by the observation that the rhönite structure has a regular alternation of pyroxene-like and spinel-like structural elements (Bonaccorsi *et al.* 1990). The implication is that one cannot simply substitute cations into the general aenigmatite-group formula above and expect to get a single stable phase. Insofar as possible, therefore, the following discussion will be restricted to compositions known to crystallize as stable aenigmatite-group minerals.

APPLICATION TO COMMON SUBSTITUTIONS

For purposes of graphical simplification, all compositions depicted will be "condensed on" or projected down vectors of isovalent substitution (such as  $Fe^{2+}Mg_{-1}$  and  $Fe^{3+}Al_{-1}$ ). This is done to allow complex coupled substitutions to be emphasized and is not meant to imply that the Na-Ca-Mg-Ti-Sb-Be-Al-Si end-members derived are representative of Fe-rich natural compositions, or even are stable.

On the planar vector diagrams derived below, an inset shows various *bound vectors* (*e.g.*, Hoffmann 1975) that are attached to a fixed point; it depicts the relations among the two basis vectors and various other vectors derived by taking linear combinations. For example, in Figure 1, the two basis vectors, arbitrarily drawn orthogonal and of the same length for ease of plotting, are  $CaAl(NaSi)_{-1}$  and  $Al_2(MgTi)_{-1}$ .

Taking twice the first and subtracting the second leads to  $Ca_2MgTi(NaSi)_{-2}$ , a vector of zero Al (labeled  $Al_T$ ). Lines of constant total Al (slope  $-1/2$ ) are parallel to this vector on the composition diagram below. The horizontal basis vector is a vector of constant Mg, Ti, and octahedrally coordinated Al; the vertical one is one of constant Na, Ca, Si, and tetrahedrally coordinated Al.

The corresponding *free vectors*, that operate freely on the plane (Hoffmann 1975), if allowed to do so on a single arbitrary initial formula [additive composition of Thompson (1981, 1982), here chosen as "Mg-analog of aenigmatite"], generate the accessible planar *composition diagram* (triangle, quadrilateral, or pentagon in the examples below), which is bound by lines of zero content of various elements (Burt 1991). These *chemical limits* are generally more extensive than *crystal-chemical limits* provided by consideration of typical coordination numbers in crystals (Burt 1991). For example, in Figure 1, the chemical limits define a quadrilateral bounded by lines of zero Na, Ca, Al, and Ti, but the lowermost composition has tetrahedrally coordinated Mg and Ti and is therefore presumably unstable. More reasonable and restrictive crystal-chemical limits are provided by the solid rectangle. The remaining figures are drawn in a similar fashion and have similar properties.

Actually, the composition to the upper right is

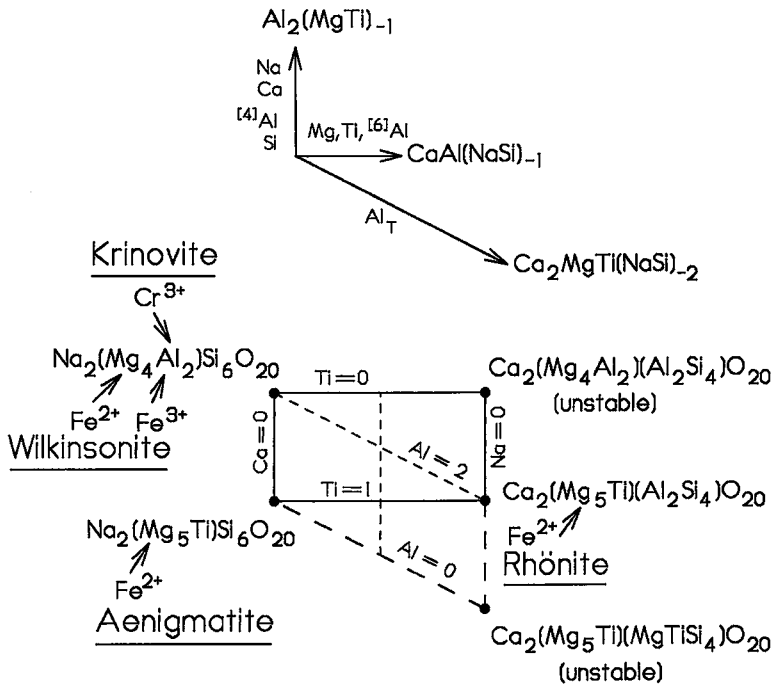


FIG. 1. Condensed aenigmatite-group composition plane.

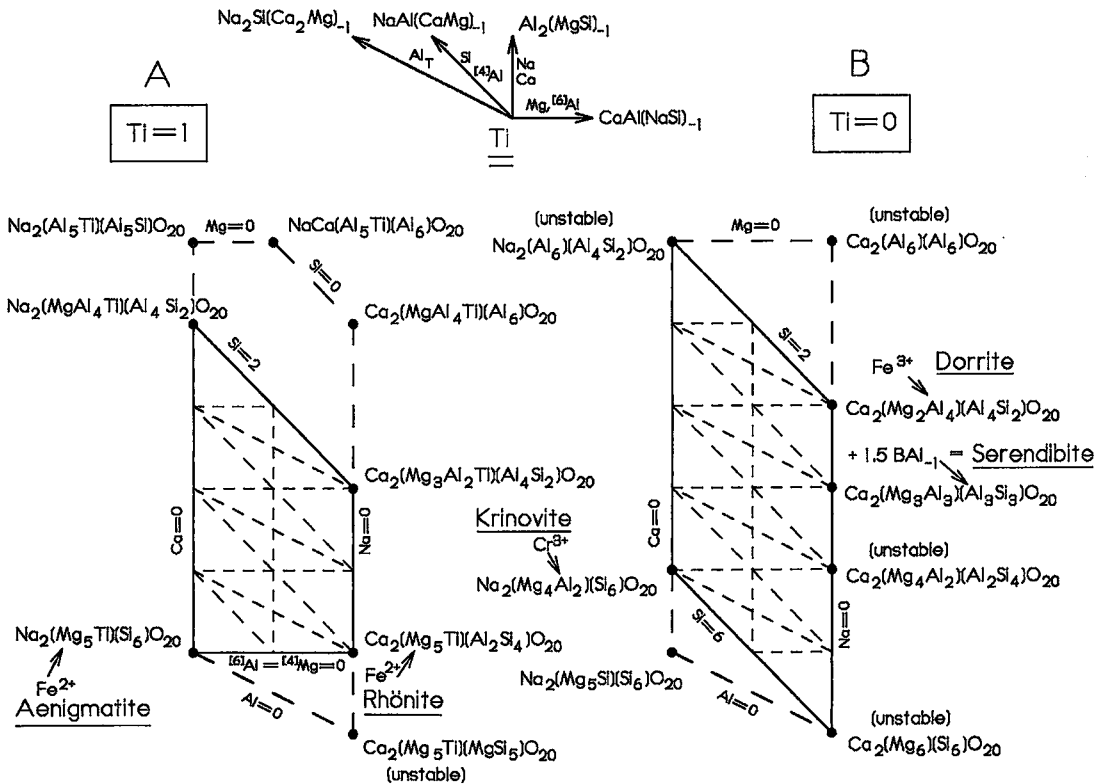


FIG. 2. Tschermak substitution planes at  $Ti = 1$  (A) and  $Ti = 0$  (B). The doubly underlined "Ti" beneath the bound vector inset indicates that these vectors are drawn for constant Ti.

probably unstable also (in the absence of the Tschermak substitution; see Fig. 2), because, as shown in Table 2b, this theoretical end-member is equivalent to a stable mixture of diopside plus spinel (or hedenbergite plus magnetite in the Fe-analog system). In any case, the natural minerals aenigmatite, rhönite, wilkinsonite, and krinovite plot on this condensed diagram at the points shown.

Figures 2A, 2B, 3A and 3B depict the four planar faces of a three-dimensional figure generated by adding a vertical Tschermak vector  $Al_2(MgSi)_{-1}$  to the planar rectangle of Figure 1. Figure 2 extends upward from the bottom (A) and top (B) of this rectangle, whereas Figure 3 extends upward from the left (A) and right (B). The chemical limits define for Figure 2A a pentagon bounded by lines of zero Na, Ca, Mg, Al, and Si (or one for each of the five elements involved in the exchanges), and for Figure 2B a quadrilateral. The more restricted crystal-chemical limits exclude significant tetrahedrally coordinated Mg and Si less than 2 in Figure 2A and exclude octahedrally coordinated Si (except at high P) and Si less than 2 in Figure 2B. Note also on the Ti-free

Figure 2B that the Tschermak substitution stabilizes dorrite and, with half B substitution for  $^{14}Al$ , serendibite.

In Figure 3, the chemical limits define a quadrilateral in 3A and a triangle in 3B; these are not completely drawn owing to the improbability of significant tetrahedral Ti. The arguments for the other crystal-chemical limits are similar to those used for Figure 2. The rectangle boldly outlined on the right was depicted by Cosca *et al.* (1988) in their description of dorrite. The point B' represents the approximate composition of "baikovite", a phase found in metallurgical slag (Rudneva & Malysheva 1961); the approximate composition of "SFCA", another synthetic phase (Mumme 1988), also is shown.

Figures 1–3 together perhaps demand a 3-D figure, but its depiction would add little practical value to the planes presented and is left as an exercise for the reader. Another possible exercise (for those nostalgic for Gibbs triangles) would be to place the three exchange operators  $CaAl(NaSi)_{-1}$ ,  $Al_2(MgTi)_{-1}$ , and  $Al_2(MgSi)_{-1}$  at the corners of a small equilateral triangle (left, right, top) that is surrounded by lots of blank

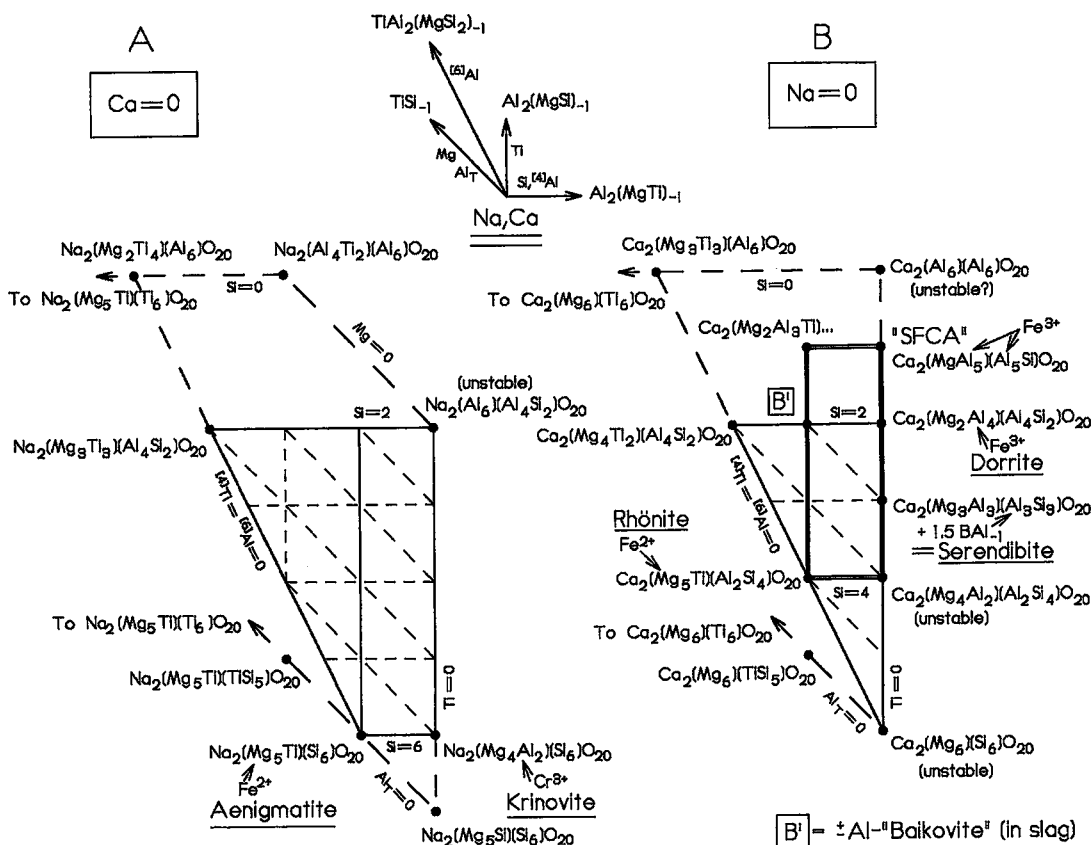


FIG. 3. Tschermak substitution planes at Na,Ca = 2,0 (A) and Na,Ca = 0,2 (B). The doubly underlined "Na,Ca" beneath the bound vector inset indicates that these vectors are drawn for constant Na,Ca.

paper, and then to plot the compositions of all of the other exchange operators (or vectors) in barycentric fashion. ( $\text{TiSi}_{-1}$  will plot at infinite distance to the upper left and  $\text{NaAl}(\text{CaMg})_{-1}$  at infinite distance to the upper right.) Various parallel and intersecting lines would correspond to the planar faces of the undrawn 3-D figure, and various points at their intersections would correspond to the exchange vectors (also, to edges of the 3-D figure).

BERYLLIUM SUBSTITUTION AND HØGTUVAITE

Substitution of Be in rhönite is possible via  $\text{BeSiAl}_{-2}$ , and in aenigmatite via  $\text{Ca}_2\text{Be}(\text{Na}_2\text{Si})_{-1}$ . In either case, a new Be end-member, ideal høgtuvaite,  $\text{Ca}_2(\text{Mg}_5\text{Ti})(\text{BeSi}_5)\text{O}_{20}$ , is generated, as is shown in Figure 4. The vectors are drawn at constant Mg (or Fe), and the chemical limits define a triangle. Had vector  $\text{BeSiAl}_{-2}$  been drawn twice as long and at  $120^\circ$  from  $\text{CaAl}(\text{NaSi})_{-1}$ , the chemical limits would have

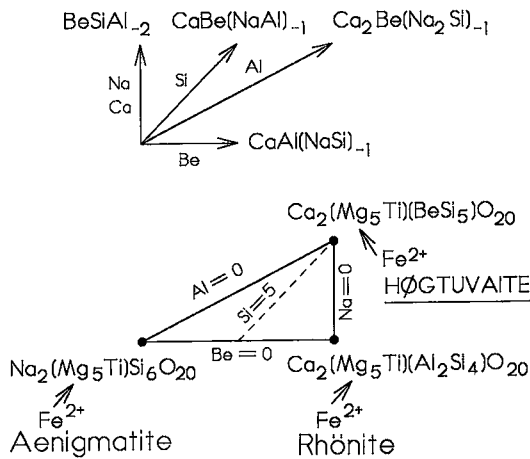


FIG. 4. Vector generation of an ideal Be end-member (høgtuvaite) from either aenigmatite or rhönite.

defined a Gibbs triangle, making this the only diagram in this paper where such a triangle could have been used conveniently (*i.e.*, there can be a one-to-one correspondence between Gibbs triangles and vector diagrams). However, it should be noted that the same bound vector inset on Figure 4 can be used for depicting Be-substitutions in other mineral series, such as albite-anorthite or paragonite-margarite. This fact would be missed in the purely triangular representation.

Natural høgтуvaite (Grauch *et al.* 1994) contains Al, partly introduced *via* the Tschermak substitution. Figure 5 shows that the chemical limits for Tschermak-substituted rhönite and høgтуvaite define a quadrilateral; the crystal-chemical limits (Si greater than 2, no significant tetrahedral Mg, no octahedral Be) define a much more restricted pentagon. *Via* the vector  $\text{Al}_2\text{Be}(\text{Mg}_2\text{Si})_{-1}$ , the tetrahedral Be content of Tschermak-substituted høgтуvaite can exceed 1, even where tetrahedral Al is 0, and for Al-rich compositions Be could theoretically climb as high as 3.5.

Figure 5B shows suggested nomenclature for the mineral names rhönite and høgтуvaite. Phases toward the left side of the pentagon (with considerable tetrahedral Al) would be called rhönite; those toward the

right (with no tetrahedral Al), høgтуvaite. The dividing point would be the midpoint along the horizontal.

The composition of natural høgтуvaite from Norway (Grauch *et al.* 1994) can be approximated in condensed form as the ideal end-member  $\text{Ca}_2(\text{Mg}_5\text{Ti})(\text{BeSi}_5)\text{O}_{20}$  plus 1.0  $\text{Al}_2(\text{MgSi})_{-1}$  (decreases Si), plus 0.5  $\text{NaSi}(\text{CaAl})_{-1}$  (adds Na), plus 0.4  $\text{Al}_2(\text{MgTi})_{-1}$  (decreases Ti), or  $(\text{Ca}_{1.5}\text{Na}_{0.5})(\text{Mg}_{3.6}\text{Ti}_{0.6}\text{Al}_{1.8})(\text{Be}_{1.0}\text{Al}_{0.5}\text{Si}_{4.5})\text{O}_{20}$ . These are all vectors depicted in earlier figures. The ideal Be end-member for this composition (obtained by applying the substitution  $\text{BeSiAl}_{-2}$  to completion) would have tetrahedral  $(\text{Be}_{1.25}\text{Si}_{4.75})$ . In other words, the natural phase is 1.00/1.25 or 80% toward the Be end-member, and constitutes a valid new mineral species.

#### SUBSTITUTION INVOLVING PENTAVALENT ANTIMONY AND WELSHITE

Beryllium occurs in another aenigmatite-group mineral, welshite (Moore 1978), which is unique in its group by having  $\text{Sb}^{5+}$  in place of Ti. Figure 6 shows condensed høgтуvaite-welshite compositional relations, starting from aenigmatite. The chemical and

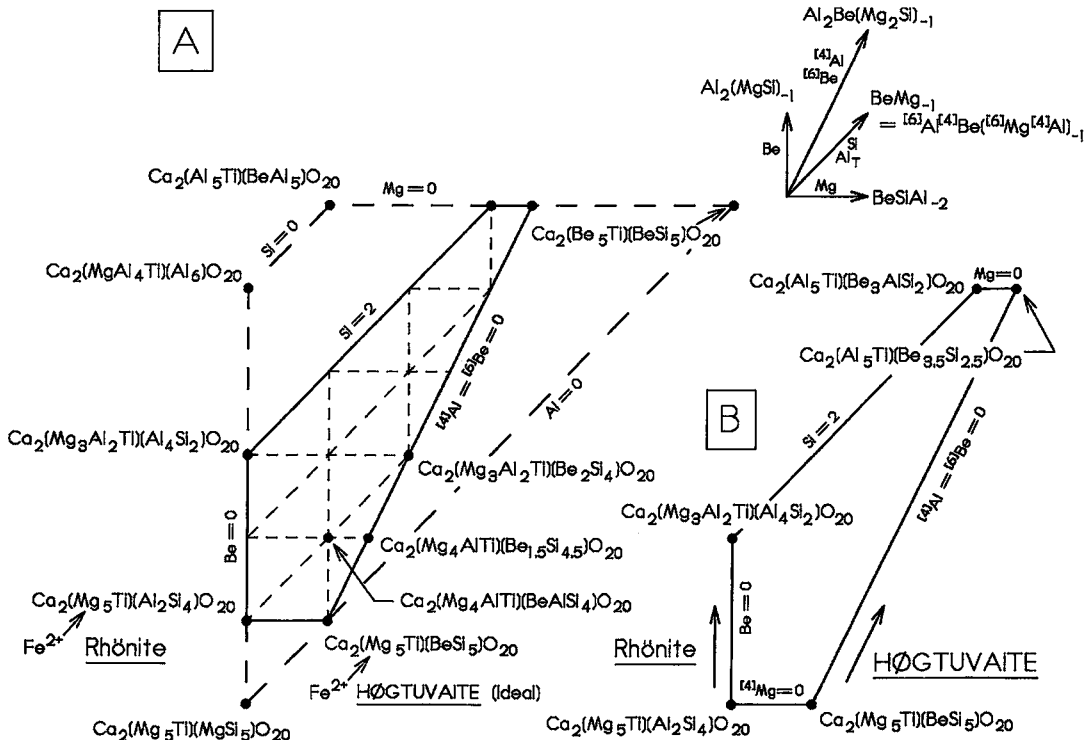


FIG. 5. Effect of Tschermak substitution on Be contents in ideal høgтуvaite. (A) Composition plane. (B) Suggested nomenclature.

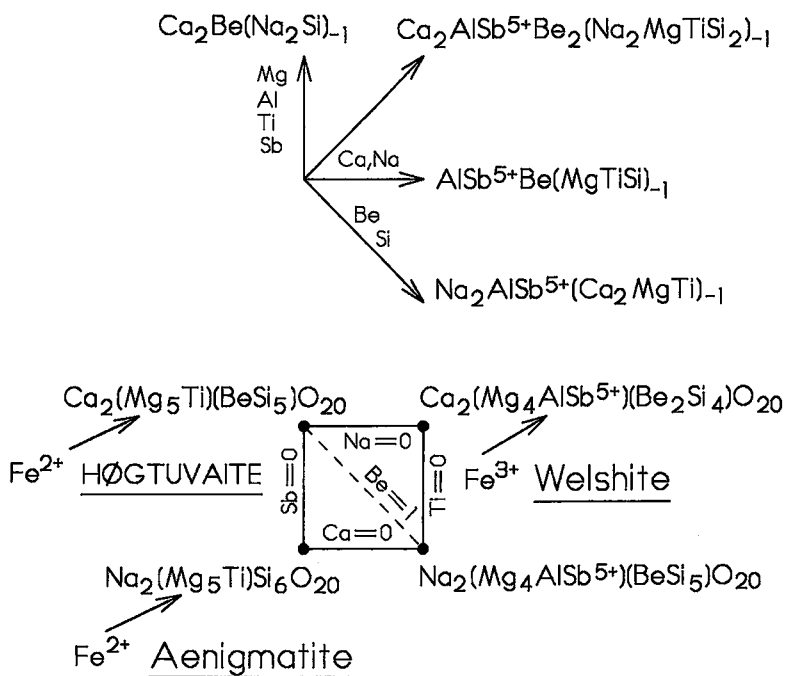


FIG. 6. Condensed høgтуvaite-welshite compositional relations with aenigmatite.

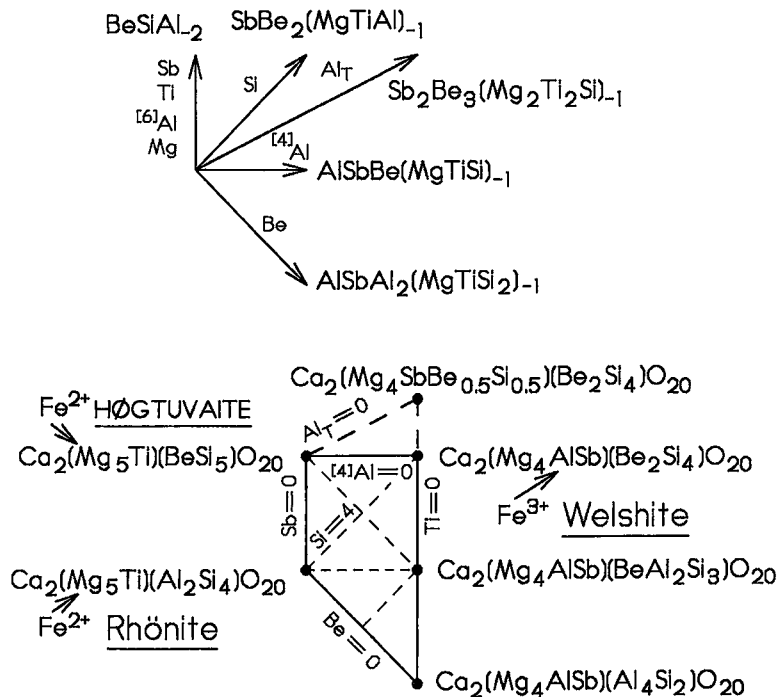


FIG. 7. Condensed høgтуvaite-welshite compositional relations with rhönite.

crystal-chemical limits both define a rectangle. Note the existence of a new possible end-member, to the lower right. It would have Be and  $\text{Sb}^{5+}$ , like welshite, but would be Na-dominant, like aenigmatite.

Welshite and høgтуvaite are both Ca-dominant, however, so that their condensed derivation from rhönite seems more appropriate (Fig. 7). The chemical limits define a quadrilateral that is truncated at the top by the improbability of octahedrally coordinated Si. Note the existence of a new possible Ca-Sb end-member, free of Be and Ti, to the lower right. Furthermore, aenigmatite-group phases with other pentavalent cations, such as  $\text{Nb}^{5+}$ , can be considered to be depicted on Figures 6 and 7 (inasmuch as these figures are "condensed").

Numerous other vector diagrams could be drawn for the aenigmatite group (and have been by the author), but those presented seem to cover the majority of compositions described to date as minerals (and therefore presumed to be stable). Even with this restriction, at least two (or four, if  $\text{Nb}^{5+}$  is considered) possible new end-members have been derived.

#### SUMMARY AND CONCLUSIONS

For minerals with complex coupled substitutions, such as those in the aenigmatite group, vector depictions provide the only practical method to represent mineral compositions or to derive possible new end-members. Gibbs triangles are not convenient for generation of compositional limits bounded by quadrilaterals and even pentagons. In vector diagrams, *bound vectors* are attached to a point, and show the relations among various vectors (basis and derived) in a plane. Linear combinations of the vectors generate new vectors with zero content of various elements; these vectors parallel lines of constant concentration of those elements on planar composition diagrams. The composition diagram is generated by allowing the corresponding *free vectors* to act on an arbitrary initial composition, the additive component of Thompson (1982), until the closed *chemical limits* (triangle, quadrilateral, or pentagon) are defined by lines of zero content of various elements. More restrictive *crystal-chemical limits* are derived by consideration of typical coordination numbers of ions and other factors such as the minimum content of Si in stable silicates.

Many reasonable-appearing theoretical end-members in the aenigmatite group are unstable with respect to a mixture of clinopyroxene plus olivine or spinel (or both), particularly for compositions relatively poor in Al or lacking Ti (or Sb or presumably Nb).

In condensed aenigmatite space, the compositions of most igneous and metamorphic end-members can be shown starting from the Mg-analog of aenigmatite and applying the three exchange vectors  $\text{CaAl}(\text{NaSi})_{-1}$ ,  $\text{Al}_2(\text{MgTi})_{-1}$ , and  $\text{Al}_2(\text{MgSi})_{-1}$  (with  $1.5\text{BAI}_{-1}$  added for serendibite). The new end-member

høgтуvaite is generated by  $\text{BeSiAl}_{-2}$  acting on rhönite. Welshite can be derived from høgтуvaite by  $\text{AlSbBe}(\text{MgTiSi})_{-1}$ , or from rhönite by  $\text{AlSbBe}_2(\text{MgTiAl})_{-1}$ .

#### ACKNOWLEDGEMENTS

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