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Solid solution among members of the aenigmatite group

B. B. Jensen

Mineralogical-Geological Museum,
Oslo University,
Sars Gate 1,
N-0562 Oslo 5,
Norway

SEVERAL minerals exist which are very closely related to aenigmatite in terms of chemistry, structure and mode of occurrence. This contribution offers a new explanation for the lack of solid solution between aenigmatite and other members of the group.

Aenigmatite has the end member formula $Na_2TiFe^{2+}_5Si_6O_{20}$. It is considered to be isostructural with the following minerals which have the same stoichiometry ($M_{14}O_{20}$) and together constitute the aenigmatite group:-

Krinovite	$Na_2Cr_2Mg_4Si_6O_{20}$
Wilkinsonite	$Na_2Fe^{3+}_2Fe^{2+}_4Si_6O_{20}$
Høgtuvaite	$(Ca,Na)_2(Fe^{2+},Fe^{3+},Ti,Mg,Mn,Sn)_6(Si,Be,Al)_6O_{20}$
Welshite	$Ca_2SbFe^{3+}Mg_4Be_2Si_4O_{20}$
Rhönite	$Ca_2(Ti,Fe^{3+},Fe^{2+},Mg)_6Al_3Si_3O_{20}$
Serendibite	$Ca_2Al_3Mg_3B_{1.5}Al_{1.5}Si_3O_{20}$
Dorrite	$Ca_2Fe^{3+}_4Mg_2Al_6O_{20}$

(The synthetic material baikovite $Ca_2Ti^{4+}Ti^{3+}_2Mg_3Al_4Si_2O_{20}$ can be added to this list.)

The structure of the chain silicate aenigmatite is well studied and complex. The co-ordination is $A^{VIII}_2B^{VI}_6X^{IV}_6O_{20}$ with two structurally different *A* positions, seven *B* positions and six *X* positions (Cannillo *et al.*, 1971). Structural studies indicate the same co-ordinations for krinovite (Bonaccorsi *et al.*, 1989) and rhönite (Bonaccorsi *et al.*, 1990) although the latter has a more distorted *A* site co-ordination polyhedron, serendibite (Van Derveer *et al.*, 1993) is only seven co-ordinated at *A*. A closely related structure is sapphirine where the stoichiometry is the same but both *A* and *B* cations are six co-ordinated (Merlino, 1980). A number of synthetic phases have been prepared which have the aenigmatite structure-type: SFCA (SiFeCaAl) described by Hamilton *et al.* (1989); CSVA (CaSiVAl) described by Arakcheeva and Ivanov (1993); CaAl-ferrite (Arakcheeva, 1994); and NaMgFe-germanate (Barbier, 1995). No detailed structural data are available for the minerals wilkinsonite, høgtuvaite, welshite or dorrite.

The main chemical differences between members of the group are: (*a*) The predominance of either Na or Ca in the *A* position; (*b*) Very different cations in the six co-ordinated position. (All contain both small high valency cations and larger divalent cations in the *B* sites, but in different proportions.)

Three of these minerals occur in magmatic environments and might be expected to form solid solution series; they are aenigmatite, rhönite and wilkinsonite. However, the large number of analyses available for aenigmatite show only small departures from the ideal formula. (Larsen, 1977; Mahood and Stimac, 1990; Bonaccorsi *et al.*, 1990).

There is general agreement that a miscibility gap occurs between aenigmatite and rhönite (Yagi, 1953; Grünhagen and Seck, 1972; Johnston and Stout, 1985) and an intergrowth of rhönite/aenigmatite has been reported (Yagi, 1953). Mumme (1988) was the first to suggest that it was the substitution of Ca for

Na at *A* that gave rhönite a different structure. This structural difference apparently also affects coupled substitution on *B* sites.

The only chemical difference between aenigmatite and wilkinsonite lies in the content of the *B* sites. Duggan (1990) reported full miscibility between aenigmatite and wilkinsonite, while Gaete and Mottana (1991) found co-existing aenigmatite and wilkinsonite, although they did not consider this to be an equilibrium pair. Data on wilkinsonite are limited.

Various coupled substitutions, primarily affecting the *B* sites, can be proposed to express the chemical relationships between the members of the group (Larsen,1977; Johnston and Stout, 1985). What might hinder free substitution on octahedral sites? The cations capable of entering octahedral positions in this group show an unusually wide range of sizes and valency states. Analyses of aenigmatite indicate a maximum size difference for octahedral cations of 0.365 Å (Al-Y) and a valency range from univalent to pentavalent. Can these all be accommodated by ordering within equivalent sites, or do some of the seven structurally distinct octahedral sites in fact have different optimal sizes?

In aenigmatite ($B = \mathrm{Ti_1Fe_5^{2+}}$) the smaller Ti ions are confined almost entirely to one site (*M*7). In krinovite the two Cr ions ($B = \mathrm{Cr_2Mg_4}$) occupy *M*1, *M*2 and *M*7. In serendibite the three Al ions ($B = \mathrm{Al_3Mg_3}$) apparently occupy *M*1, *M*2, *M*3, *M*4 and *M*7. M_1 - M_4 thus accommodate ions ranging in size from Al to $\mathrm{Fe^{2+}}$ very readily, showing considerable elasticity if the octahedral sites are the same in all three minerals.

However, one can get *additional* information on cation sites from PC-IR plots. Such plots require data for a mineral and the magma from which it crystallized (Onuma *et al.*, 1968; Jensen, 1973). Points are joined for all elements of the same valence, not with straight lines, but on the assumption that all the various valency curves are parallel or sub-parallel (Philpotts, 1977). A large number of such plots have been made and the result is, in each case, a series of peaks, each peak marking a cation position in the structure and indicating the optimal size for cations entering that site. Data for such plots are available for aenigmatite from the lavas of Pantelleria, where the minerals are apparently in equilibrium with a glassy matrix. Two plots have been made, one (Fig.1) combining the major element data of Carmichael (1962) with the trace element data of Kovalenko *et al.* (1988) and the other (Fig.2) using the data of Mahood and Stimac (1990).

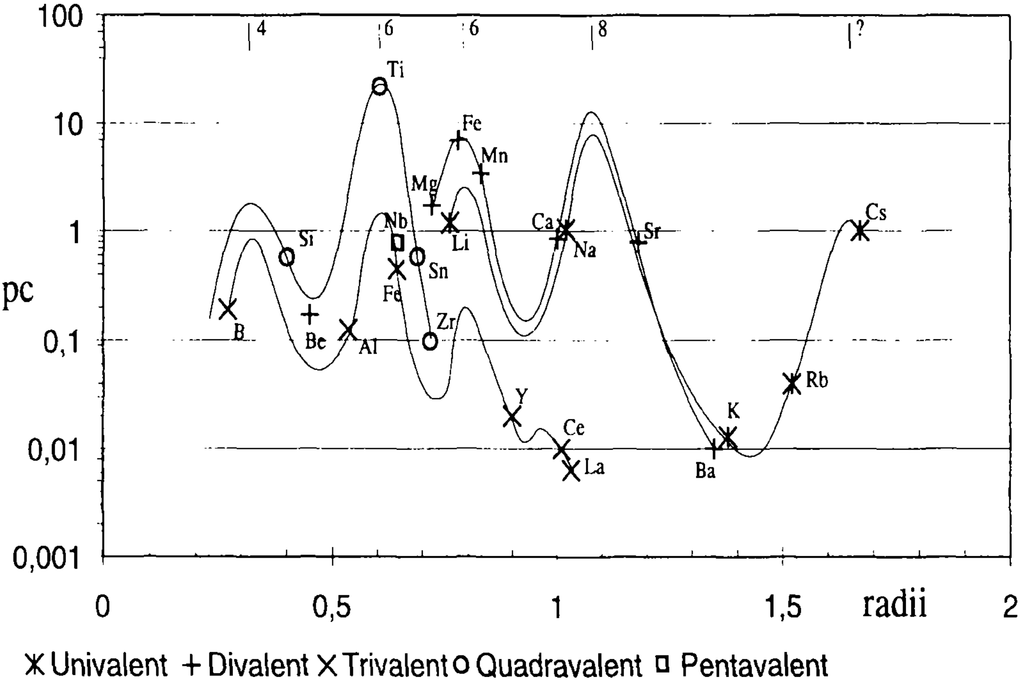

FIG. 1. PC-IR diagram for aenigmatite from Pantelleria based on the data of Carmichael (1962) and Kovalenko *et al.* (1988). Effective ionic radii (IR) of Shannon and Prewitt (1969).

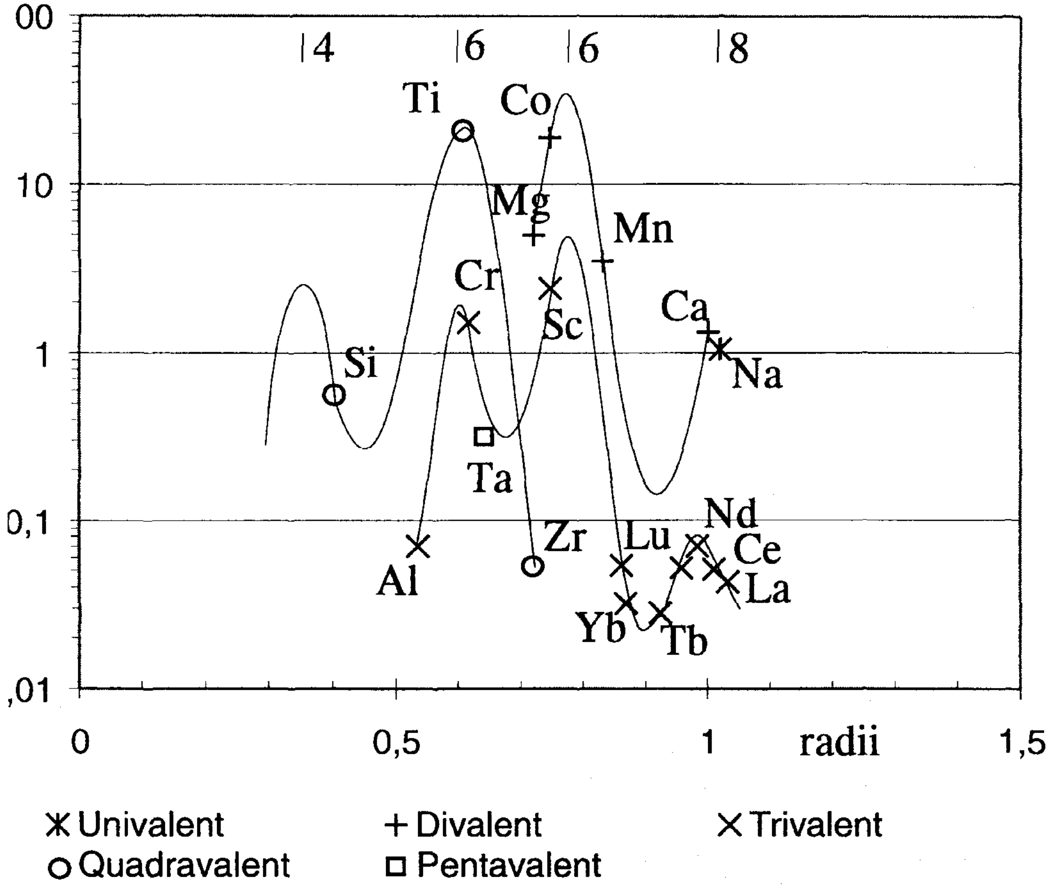

FIG. 2. PC-IR diagram of aenigmatite from Pantelleria based on the data of Mahood and Stimac (1990).

As always, one could wish for more points, but the two plots, using a somewhat different selections of elements, are very similar and indicate clearly not *one* octahedral site, but *two* with optimal ion sizes of about 0.61 Å and 0.78 Å. These peaks lie on either side of the 'usual' peak position for six coordinated ions in silicate minerals at about 0,72 Å, (as seen in pyroxene, amphibole, etc.; Jensen, 1973). The *M7* site in aenigmatite is thus not just small because it has been assigned all the Ti, but is an intrinsically smaller site incapable of accommodating ions of the size of Fe^{2+} or Mn. The six other sites accommodate the larger ions and are filled mainly with divalent iron. Substitution in aenigmatite is thus limited by a *structurally determined* 1:5 ratio of small to large cations. The general formula should, therefore, be written $A_2B_1C_5X_6O_{20}$.

There are no equivalent trace element data available to make PC-IR diagrams for rhönite or wilkinsonite or any of the other minerals of the group. However, when a formula contains small, high valence ions in the octahedral position appreciably in excess of one (e.g. Al in serendibite or Cr in krinovite) the excess must be accommodated on *M*1–6 and this is only possible if one or more of these sites is smaller in these minerals than it is in aenigmatite,(or shows a higher and very unusual degree of flexibility). The case for Fe^{3+} is slightly different since this ion is somewhat larger than Al or Cr. Trivalent ions *can* enter the larger site of aenigmatite fairly readily (Sc in Fig.2) and so it is possible to accommodate some Fe^{3+} there, when this is favourable to charge balance. However, it is most unlikely that an ion that is 0.135 Å smaller than the optimal site size could ever constitute a major component of the site, which means that also the wilkinsonite structure must involve minor differences on the *B* site, relative to aenigmatite.

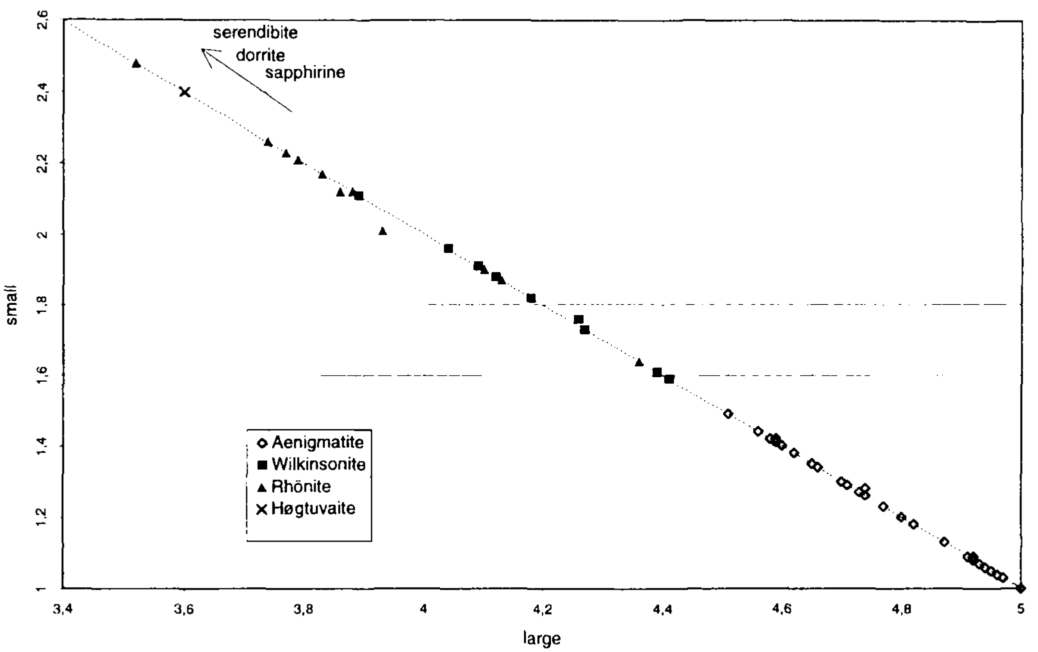

FIG. 3. Plot of 'small' against 'large' octahedrally coordinated cations for aenigmatite, rhönite, wilkinsonite and høgtuvaite. 'small' = sum of cations <0.7 Å - 6, 'large' = sum of cations >0.7 Å - 2. Most points lie exactly on the curve because data for divalent/trivalent iron is not available and has been calculated on the assumption of stoichiometry $M_{14}O_{20}$. (Analyses giving poor sums or poor stoichiometry are omitted.)

If one divides octahedral cations into 'large' (larger than Fe^{3+}) and 'small' ions and plots one against the other for rhönite, wilkinsonite and aenigmatite (Fig.3) the results will be linear[1]. Aenigmatite plots in the ratio range 1:5 to 1.5:4.5 with no extension into the field of wilkinsonite and rhönite. Aenigmatites that contain significant amounts of Fe^{3+} and Al^{3+} plot at the top of this range confirming that *limited* substitution of the type $Si^{4+}Fe^{2+}-Al^{3+}Fe^{3+}$ is operating (with possibly some $Ti^{4+}Fe^{2+}-2Fe^{3+}$).

Wilkinsonite and rhönite plots show mutual overlap, suggesting structural equivalence [høgtuvaite (Grauch *et al.*, 1994) plots in the same field]. Considerable spread on either side of the theoretical 2:4 ratio indicates greater freedom to achieve charge balance by coupled substitution for these minerals. (A closer equivalence of the six co-ordinated peaks?)

The structurally controlled 1:5 ratio is apparently specific to aenigmatite and provides sufficient limitation to inhibit severely solid solution with all other members of the group. Partition co-efficients and PC-IR plots for rhönite and wilkinsonite, if and when available, are needed to confirm these deductions. PC-IR diagrams are particularly useful here, since they are indicating a structural difference which is not readily deduced from detailed structural studies. The *optimal* size of a site, as opposed to the average bond length, is a factor which is seldom considered. The former is a property of the lattice, while the latter is primarily determined by the elements in occupation.

Octahedral sites in different minerals commonly have very similar peak positions. Small differences in optimal size of two octahedral sites *in the same mineral* have been noted previously for orthopyroxene (Onuma *et al.*, 1968; Jensen, 1973), but a difference as large as that found in aenigmatite is new.

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[1] Additional references from which data for Fig. 3 are taken are available from the author on request.

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Fractal analysis of calcsilicate bands from Mérida (Spain) contact-metamorphic aureole: implications for fluid flow

J. C. Fernández-Caliani

Dpto. de Geología,
Universidad de Huelva,
Spain

E. Galán

Dpto. de Cristalografía y Mineralogía,
Universidad de Sevilla,
Spain

MANDELBROT'S (1982) considerations about the fractal geometry of nature are being increasingly applied to the Earth Sciences for quantitative description of extremely complex or chaotic structures from a geometric standpoint. Thus, in recent years it has been demonstrated that many natural fracture patterns show fractal geometries (e.g. Korvin, 1992; Turcotte, 1992; and references therein). Accordingly, some geological aspects related to fracturing of rocks are also characterized by their fractal behaviour, such as: epicentre distributions in seismically active fault zones; geomorphology resulting from an intensely fractured massif; ore grade and tonnage of mineralized fracture systems; and spatial and temporal evolution of fluids into fracture-controlled flow zones.

Relating to the last problem, Manning (1994) has shown the fractal clustering of fracture-controlled veins from different metamorphic settings, and consequently he claims that fractal analysis techniques can contribute to the understanding of fluid flow, fluid–rock interaction and mineral reaction during metamorphism.