Recommended nomenclature for the
sapphirine and surinamite groups (sapphirine supergroup)

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ABSTRACT

Minerals isostructural with sapphirine-$1A$, sapphirine-$2M$, and surinamite are closely related chain silicates that pose nomenclature problems because of the large number of sites and potential constituents, including several (Be, B, As, Sb) that are rare or absent in other chain silicates. Our recommended nomenclature for the sapphirine group (formerly aenigmatite group) makes extensive use of precedent, but applies the rules to all known natural compositions, with flexibility to allow for yet undiscovered compositions such as those reported in synthetic materials. These minerals are part of a polysomatic series composed of pyroxene or pyroxene-like and spinel modules, and thus we recommend that the sapphirine supergroup should encompass the polysomatic series. The first level in the classification is based on polysome, i.e. each group within the supergroup corresponds to a single polysome. At the second level, the sapphirine group is divided into subgroups according to the occupancy of the two largest M sites, namely, sapphirine (Mg), aenigmatite (Na), and rhönite (Ca). Classification at the third level is based on the occupancy of the smallest M site with most shared edges, $M7$, at which the dominant cation is most often Ti (aenigmatite, rhönite, makarochkinite), Fe^{3+} (wilkinsonite, dorrite, høgtuvaite) or Al (sapphirine, khmaralite); much less common is Cr (krinovite) and Sb (welshite). At the fourth level, the two most polymerized T sites are considered together, e.g. ordering of Be at these sites distinguishes høgtuvaite, makarochkinite and khmaralite. Classification at the fifth level is based on $X_{Mg} = Mg/(Mg + Fe^{2+})$ at the M sites (excluding the two largest and $M7$). In principle, this criterion could be expanded to include other divalent cations at these sites, e.g. Mn. To date, most minerals have been found to be either Mg-dominant ($X_{Mg} > 0.5$), or Fe^{2+}-dominant ($X_{Mg} < 0.5$), at these M sites. However, X_{Mg} ranges from 1.00 to 0.03 in material described as rhönite, i.e. there are two species present, one Mg-dominant, the other Fe^{2+}-dominant. Three other potentially new species are a Mg-dominant analogue of wilkinsonite, rhönite in the Allende meteorite, which is distinguished from rhönite and dorrite in that Mg rather than Ti or Fe^{3+} is dominant at $M7$, and an Al-dominant analogue of sapphirine, in which Al > Si at the two most polymerized T sites *vs*. Al < Si in sapphirine. Further splitting of the supergroup based on occupancies other than those specified above is not recommended.

Statement of the problem

The sapphirine group and related mineral surinamite are chain silicates that pose nomenclature problems because of the large number of sites and potential constituents, including several (Be, B, As, Sb) that are rare or absent in related

chain silicates, together with extensive cation disorder at these sites and the difficulty of deriving Fe valence ratios from electron microprobe analyses; the question of Ti valence arises in rhönite from the Allende meteorite. We have chosen sapphirine rather than aenigmatite to name the supergroup and larger group therein because sapphirine was the first of these minerals to be discovered, chemically analysed and to have its crystal structure refined. There are 15 independent cationic sites in the centrosymmetric triclinic members of the sapphirine group, 12 in the related monoclinic mineral surinamite and over 20 in members lacking a centre of symmetry (welshite) or having a superstructure (khmaralite). Applying the standard CNMNC guidelines (Nickel and Grice, 1998) to each site individually would result in a plethora of species that would be difficult to distinguish on a routine basis and have little geological or petrological significance. However, failing to take into account cation distribution and order could result in overly broad species definitions. Complicating the situation in the sapphirine group are superstructures, polysomatism and polytypism and changes in symmetry dictated by cation order. Because most sapphirine-group minerals have triclinic symmetry, it took some time to agree on a unit cell, namely the Delaunay cell, which was first proposed by Kelsey and McKie (1964) for aenigmatite and generally adopted afterwards.

To date, criteria applied to distinguish one species from another have been applied *ad hoc*, making use of site occupancies when available, but relying on stoichiometry in the absence of a crystal structure refinement. In many cases recognizing a new species seemed relatively easy because its composition differed so much from existing species, e.g. Ca *vs.* Na, presence of Be, Sb, As or B. However, other species proved more difficult, most recently makarochkinite, where detailed crystallographic study was needed to demonstrate ordering of Ti at a single *M* site.

Kunzmann (1999) proposed a classification for the sapphirine group that was not reviewed by the CNMMN. His classification included only the Na- and Ca-bearing members, aenigmatite and rhönite subgroups, respectively, and was based largely on composition with much less reliance on crystal structure. Consequently, as models to follow in developing a classification, we have sought examples from other mineral groups that have been reviewed recently and approved by the CNMMN (now CNMNC) or in the process of being considered by the CNMNC. Our approach follows more the direction taken by Hawthorne and Oberti (2006) for amphiboles, for which cation sites were grouped for classification (Hatert and Burke, 2008), rather than treated individually as in the unique-name system adopted by Johnsen *et al.* (2003) for eudialyte. Our criteria distinguish species in a systematic fashion, that is, we have identified critical individual sites or several sites taken together that can be used as criteria. These criteria include a mixture of chemical and crystallographical properties. Nonetheless, it appears that full application of our nomenclature will require crystal structure refinements.

Our recommended nomenclature has been approved by the Commission on New Minerals, Nomenclature and Classification, International Mineralogical Association.

Definition of the sapphirine and surinamite groups

Strunz and Nickel (2001) broadened the traditional aenigmatite or aenigmatite-rhönite group (e.g. Kunzmann, 1999) to include the closely related minerals sapphirine and surinamite. Minerals in this group are monoclinic and triclinic chain silicates containing kinked, winged chains of tetrahedra and walls of octahedra. Strunz and Nickel (2001) also suggested that jonesite might be a related mineral, but a subsequent crystal structure refinement of jonesite did not bear this out (Krivovichev and Armbruster, 2004). Gaines *et al.* (1997) suggested that magbasite, $KBa(Mg,Fe^{2+})_6(Al,Sc)Si_6O_{20}F_2$, which was described by Semenov *et al.* (1965), could be in the sapphirine group, but there is no evidence for such a relationship. Only a powder diffraction pattern was reported in the original description (single crystal data could not be obtained) and it differs substantially from that of aenigmatite reported by Kelsey and McKie (1964). The chemical composition recalculated on a 28 cation basis (cf. 15 cations in the given formula) gave 4.9 F, 1.6 Ba and 1.8 K, none of which are reported in comparable quantities, if at all, in sapphirine-group minerals and compounds (cf. 4OH in a synthetic isostructural with aenigmatite, Yang and Konzett, 2000).

We agree with Strunz and Nickel (2001) that sapphirine and aenigmatite should be included in the same group, but we disagree that surinamite also belongs there. Instead, classification of

sapphirine and related minerals are better understood in terms of a polysomatic series involving one clinopyroxene-like module (or a close-packed isotype of clinopyroxene like $CoGeO_3$, which was refined by Peacor, 1968) and one spinel module (Dornberger-Schiff and Merlino, 1974; Christy and Putnis, 1988; Barbier and Hyde, 1988; Bonaccorsi et al., 1990, Arakcheeva and Ivanov, 1993; Merlino and Pasero, 1997; Gasparik et al., 1999; Zvyagin and Merlino, 2003), which more specifically defines the relationship of surinamite to sapphirine and aenigmatite and leaves open the possibility of other polysomes being included in the future. Thus, we are introducing the concept of a sapphirine supergroup that would encompass all the polysomes. The sapphirine group includes only the polysome consisting of one clino-pyroxene or pyroxene-like module and one spinel module. The sapphirine group can be divided into three subgroups on the basis of the dominant cations in the polyhedra outside the octahedral walls; a fourth subgroup needs more study (Table 1). In the aenigmatite and rhönite subgroups, the octahedral walls are cross-linked into continuous sheets by $7-8$ coordinated polyhedra containing Na and Ca, respectively. The corresponding sites in the sapphirine subgroup are 6 coordinated, and the octahedral walls are not cross-linked.

The surinamite group would include the polysome consisting of two pyroxene modules and one spinel module. To date, there is only one known natural compound in this group occurring as an independent phase, surinamite itself, and thus designating a surinamite group anticipates the recognition of more species. The surinamite structure differs from those of the sapphirine group in the proportion of wing to chain tetrahedra: 20% vs. 33%, and in the position of the wings, which are all on one side of the chains in surinamite, but on both sides in the sapphirine group.

Historical synopsis

Sapphirine, khmaralite

Sapphirine is the first sapphirine-group mineral to be discovered, chemically analyzed and to have its crystal structure refined. Giesecke found sapphirine in 1809 at Fiskenæsset, West Greenland, and called it 'blauer Diamantspath (saphirine)' in his catalogues (Bøggild, 1953). The first description of Giesecke's mineral, including a density measurement and full chemical analysis, was reported by Stromeyer (1819, 1821), who retained Giesecke's name 'saphirine', later changed to the present spelling with double p. Over a century of study (e.g. Ussing, 1889; Lorenzen, 1893), including single-crystal X-ray diffraction (XRD) (Goßner and Mußgnug, 1928; Kuzel, 1961; McKie, 1963; Fleet, 1967), gave a range of compositions from $Mg_2Al_4Si_2O_{10}$ to somewhat richer in Al than $Mg_7Al_{18}Si_3O_{40}$, the formula given in Table 1; these formulae are related by the Tschermak's substitution $Mg + Si \rightleftharpoons 2Al$ (e.g. Vogt, 1947). However, a fuller understanding of its crystal chemistry was not possible until Moore's (1968; 1969) successful refinement of the structure of monoclinic sapphirine from Fiskenæsset. Merlino (1970, 1972) recognized that the crystal structures of sapphirine, aenigmatite, krinovite and rhönite, were all closely related, and thereby provided the conceptual basis for the sapphirine group. Merlino (1980) refined the crystal of the triclinic polytype, further linking the sapphirine subgroup with the other two subgroups. In addition to the $1A$ and $2M$ polytypes, which dominate natural sapphirine (e.g. Christy, 1989), Merlino and Pasero (1987) and Christy and Putnis (1988) found $3A$, $4M$ and $5A$ polytypes as domains ranging from less than 100 Å to several thousand ångströms thick.

Grew (1981) described a 'beryllian sapphirine' containing 1.4 Be per formula unit of 28 cations from Zircon Point, a small exposure in Khmara Bay, Enderby Land, East Antarctica. Christy (1988), using transmission electron microscopy (TEM), recognized this mineral as having a superstructure with doubled a axis ($P2_1/c$ setting). Refinement of the structure using XRD became possible only when the very weak superstructure reflections could be measured, which Barbier et al. (1999) succeeded in doing with a Siemens diffractometer and a SMART area detector, and thus were able to demonstrate ordering of Be at alternating $T2$ and $T3$ sites in doubled tetrahedral chains. The refinement served to distinguish khmaralite from sapphirine-$2M$ both by the presence of the $2 \times a$ superstructure and the predominance of Be at one tetrahedral site. The name 'beryllosapphirine' was not applied by Barbier et al. (1999) because they reasoned that a mineral of this name should have the same space group as sapphirine-$2M$ and similar cell parameters, and thus they named the mineral for the locality. Grew et al. (2000) reported a weak $2 \times a$ superstructure in a sample from a second locality in Khmara Bay that

TABLE 1. Minerals of the sapphirine supergroup, including possible species not yet approved by IMA CNMNC (*in italics*)

Mineral symmetry	End-member formula*	First report; structure refinement[†]
Sapphirine group: <PS>Polysome		
Sapphirine subgroup: Mg-dominant		
Sapphirine-2M Monoclinic $P2_1/a$	$Mg_4(Mg_3Al_9)O_4[Si_3Al_9O_{36}]$	Giesecke in Stromeyer (1819); [†]Moore (1969); [†]Higgins and Ribbe (1979);
Sapphirine-1A Triclinic $P\bar{1}$	$Mg_4(Mg_3Al_9)O_4[Si_3Al_9O_{36}]$	[†]Merlino (1980)
Khmaralite Monoclinic $P2_1/c$	$Mg_4(Mg_3Al_9)O_4[Si_5Be_2Al_5O_{36}]$	[†]Barbier et al. (1999)
Unnamed Al analogue of sapphirine	$Mg_4(Mg_{1.5}Fe_{0.3}^{2+}Fe_{1.6}^{3+}Al_{8.5})O_4[Si_{1.7}Al_{10.3}O_{36}]*$	Sabau et al. (2002)
Aenigmatite subgroup: Na-dominant		
Aenigmatite Triclinic $P\bar{1}$	$Na_4(Fe_{10}^{2+}Ti_2)O_4[Si_{12}O_{36}]$	Breithaupt (1865); [†]Cannillo et al. (1971); [†]Grew et al. (2008)
Wilkinsonite Triclinic $P\bar{1}$	$Na_4(Fe_8^{2+}Fe_4^{3+})O_4[Si_{12}O_{36}]$	Duggan (1990); [†]Burt et al. (2007)
Unnamed Mg-analogue of wilkinsonite	$Na_4(Mg_5Fe_7^{3+})O_4[Si_9Fe_3^{3+}O_{36}]$	Gaeta and Mottana (1991)
Krinovite Triclinic $P\bar{1}$	$Na_4(Mg_8Cr_4^{3+})O_4[Si_{12}O_{36}]$	Olsen and Fuchs (1968); [†]Bonaccorsi et al. (1989)
Rhönite subgroup: Ca-dominant		
Rhönite	$Ca_4(Mg_8Fe_2^{3+}Ti_2)O_4[Si_6Al_6O_{36}]$	Soellner (1907); [†]Bonaccorsi et al. (1990)
Unnamed Fe^{2+}-analogue of rhönite	$Ca_4(Fe_{10}^{2+}Ti_2)O_4[Si_8Al_4O_{36}]$	Grünhagen and Seck (1972); Havette et al. (1982); Olsson (1983); Gamble and Kyle (1987); Kuehner and Irving (2007); Treiman (2008)
Unnamed Ti^{3+}-bearing Mg-analogue of rhönite (Allende meteorite) Triclinic $P\bar{1}$	$Ca_4(Mg_7AlTi_2^{3+}Ti_2^{4+})O_4[Si_5Al_7O_{36}]$	Fuchs (1971); [†]Bonaccorsi et al. (1990)
Dorrite Triclinic $P\bar{1}$ or $P1$	$Ca_4(Mg_3Fe_9^{3+})O_4[Si_3Al_8Fe^{3+}O_{36}]$	Cosca et al. (1988)
Serendibite Triclinic $P\bar{1}$	$Ca_4(Mg_6Al_6)O_4[Si_6B_3Al_3O_{36}]$	Prior and Coomaraswamy (1903); [†]Van Derveer et al. (1993)
Hogtuvaite Triclinic $P\bar{1}$	$Ca_4(Fe_6^{2+}Fe_6^{3+})O_4[Si_8Be_2Al_2O_{36}]$	Grauch et al. (1994); [†]Grew et al. (2005)
Makarochkinite Triclinic $P\bar{1}$	$Ca_4(Fe_8^{2+}Fe_2^{3+}Ti_2)O_4[Si_8Be_2Al_2O_{36}]$	Polyakov et al. (1986); [†]Yakubovich et al. (1990); [†]Grew et al. (2005)
Welshite Triclinic $P\bar{1}$	$Ca_4(Mg_9Sb_3^{5+})O_4[Si_6Be_3AlFe_2^{3+}O_{36}]$	Moore (1978); [†]Grew et al. (2007)
Fe-Ga subgroup		
Unnamed Fe-Sn-Ga-Ge mineral	$(Fe,Ga,Sn,Zn)_{16}O_4[(Ga,Ge)_{12}O_{36}]$	Johan and Oudin (1986)
Surinamite group <PPS> Polysome		
Surinamite Monoclinic $P2/n$	$Mg_3Al_3O[Si_3BeAlO_{15}]$	de Roever et al. (1976); [†]Moore and Araki (1983); [†]Barbier et al. (2002)
Unnamed Be-free analogue of surinamite	$Mg_4Al_2O[Si_3Al_2O_{15}]$	Christy and Putnis (1988)

* Except for unnamed Al analogue of sapphirine, for which the formula was calculated from electron microprobe data. [†] Only complete refinements listed.

contained $0.87-1.05$ Be per 28 cations, i.e. the appearance of the superstructure defining khmaralite coincides with Be occupancy approaching 50% at the $T2$ and $T3$ sites considered together.

Aenigmatite, wilkinsonite, krinovite

Breithaupt (1865) simultaneously introduced two new monoclinic minerals 'kölbingite' and 'ainigmatite', which he discovered in samples of peralkaline plutonic rocks from the Ilímaussaq complex, Kangerdluarssuk, Greenland (Bøggild, 1953). He named the first for his late friend Kölbing and the second from the Greek *ainigma* for its enigmatic nature by comparison with 'kölbingite'; indeed, aenigmatite has proven to be a most appropriate name. Breithaupt (1865) reported both minerals as being greenish to velvet-black in colour and having the identical prismatic habit, but differing in streak, density and hardness, and suggested that 'ainigmatite' was pseudomorphous after 'kölbingite'. No quantitative analysis was given for either mineral; preliminary analyses gave Ca, Fe and Si, with Fe largely ferrous in 'kölbingite' and ferric in aenigmatite. Lorenzen (1882) doubted the pseudomorphous nature of aenigmatite because the aenigmatite crystals available to him were all very fresh and unaltered (he did not have any crystals of 'kölbingite' to compare). Forsberg (in Brögger, 1887, 1890) was the first to obtain a complete analysis of the major constituents in aenigmatite including Ti, which he found was major. Brögger (1887, 1890) also gave some optical properties of aenigmatite, and thus was able to finally confirm its validity as a mineral species. Brögger (1887, 1890) also suggested that 'kölbingite' was an intergrowth of arfvedsonite and aenigmatite by noting that the density and streak color of 'kölbingite' are intermediate between those of arfvedsonite and aenigmatite. Ussing (1898) was able to examine a 'kölbingite' crystal from the material studied by Breithaupt, and showed that similar specimens in the Mineralogical Museum in Copenhagen consisted of aenigmatite coated with aegirine, leading him to conclude that Breithaupt's (1865) 'kölbingite' was but a mixture of aenigmatite and aegirine.

Foerstner (1881) described the new triclinic mineral 'cossyrite' in volcanic rocks of the island Pantelleria, southern Italy (Cossyra in ancient times), and reported a chemical analysis, but not including Ti. Groth (1883) noted that 'cossyrite' and aenigmatite could be related, which Brögger

(1887, 1890) confirmed by detailed comparison of the chemical composition and crystal morphology. Thus, Brögger (1887, 1890) gave aenigmatite priority, and considered the name 'cossyrite' to be only a synonym. Discredition of 'cossyrite' was complete when powder X-ray data by A.S. Anisimova confirmed its identity as aenigmatite (Fleischer, 1964).

Brögger (1887, 1890) suggested that aenigmatite could be a triclinic member of the amphibole group despite the nearly 10º difference in the angle between the cleavages (66º *vs.* 56º for arfvedsonite) and a significant difference in axial ratio, both of which he attributed to substitution of Si by Ti. In contrast, Soellner (1909) placed 'cossyrite' and aenigmatite in a separate group that was on a par with pyroxenes and amphiboles. X-ray studies by Goßner and Mußgnug (1929) showed that aenigmatite is not related to amphibole, and this conclusion was confirmed by morphological crystallography (Palache, 1933) and chemical analyses (Fleischer, 1936). On the basis of literature data and new analyses, Kelsey and McKie (1964) settled on the now accepted crystallographic orientation (Delaunay cell), unit cell content and formula (Table 1). Thompson and Chisholm (1969) synthesized aenigmatite with the composition deduced by Kelsey and McKie (1964).

Three groups simultaneously solved the crystal structure of aenigmatite: Merlino (1970); Cannillo and Mazzi; and Fang, Robinson and Ohya; the latter two groups reported their results in a joint publication (Cannillo *et al.* 1971). Choi (1983) and Choi and Burns (1983) reported Mössbauer spectroscopic evidence for the presence of Fe^{3+} on tetrahedral sites. A new refinement and Mössbauer spectrum (Grew *et al.*, 2008) confirm the essential features reported earlier, but bring greater precision to cation ordering in aenigmatite.

Hodges and Barker (1973) reported extensive solid solution by the substitution of Fe^{2+} + Ti by $2Fe^{3+}$ between 'ideal aenigmatite' and the titanium-free aenigmatite which had been synthesized by Ernst (1962) in the Na-Fe-Si-H-O system. Duggan (1990) described the latter as the new mineral wilkinsonite from peralkaline, silica-undersaturated trachyte of Warrumbungle volcano, New South Wales, Australia, which he named to honor J.F.G. Wilkinson for his work on volcanic rocks where the mineral was found. In demonstrating the solid solution between the two minerals, Hodges and Barker (1973) and Duggan (1990) did not measure Fe^{3+} directly, but

calculated it from stoichiometry. The structure of wilkinsonite is the most recent of sapphirine-group minerals to be refined (Burt *et al.*, 2007).

Olsen and Fuchs (1968) described krinovite as a monoclinic Na-Mg-Cr silicate from three octahedrite meteorites. The mineral was named to honor E.L. Krinov for his work on meteorites. Its relationship to aenigmatite was not demonstrated until Merlino (1972) carried out a crystallographic study establishing its triclinic symmetry, and selected a triclinic cell to conform to the Delaunay cell used by Kelsey and McKie (1964) for aenigmatite. Bonaccorsi *et al.* (1989) solved the structure.

Rhönite, dorrite, høgtuvaite, makarochkinite, welshite, serendibite

Soellner (1907) first recognized rhönite, which he named for the Rhön Mountains of central Germany, as a distinct triclinic mineral and realized it was isomorphic with aenigmatite and 'cossyrite'. Soellner found rhönite in alkaline basaltic rocks not only in the Rhön Mountains, but also at several localities elsewhere in Germany and in Bohemia plus one in Sweden. Walenta (1969) confirmed triclinic symmetry using single-crystal methods, and Merlino (1972) fixed the triclinic cell to conform to the Delaunay cell used by Kelsey and McKie (1964) for aenigmatite. Bonaccorsi *et al.* (1990) first refined the structure. Although rhönite had a simpler history than aenigmatite, settling on a formula was complicated by the greater compositional variation in rhönite. Fleischer (1936) suggested that aenigmatite and rhönite were related by the substitution Ca + Al $\rightleftharpoons$ Na + Si by analogy with feldspar, but Cameron *et al.* (1970) found that other substitutions were involved and noted the substantial compositional gap between the two minerals.

Fuchs (1971, 1978), Mason and Taylor (1982) and Simon *et al.* (1999) described rhönite containing about twice as much Ti as in other rhönite from calcium and aluminum rich inclusions in the Allende meteorite. Stoichiometry requires that a substantial portion of the Ti be trivalent. The presence of Ti^{3+} in a synthetic analogue 'baykovite' is indicated by its distinctive absorption (Rudneva and Malysheva, 1960). Structures of Allende rhönite and 'baykovite' were refined by Bonaccorsi *et al.* (1990) and Arakcheeva (1995), respectively.

Cosca *et al.* (1988) described a Ti-poor, Fe^{3+}-rich analogue of rhönite from pyrometamorphic melt-rock (paralava) in the Powder River Basin, Wyoming, as the new mineral dorrite in honor of John A. Dorr, Jr., a professor at the University of Michigan. Negligible Ti content and dominance of Fe^{3+} at octahedral sites were cited to distinguish dorrite from rhönite. On the basis of single-crystal data and absent a structure refinement, Cosca *et al.* (1988) inferred that dorrite was isostructural with aenigmatite and rhönite, and thus calculated dorrite composition assuming aenigmatite-group stoichiometry. Calculated Fe^{3+} occupies 66−73% of the octahedral sites in type dorrite, and Al + Fe^{3+} exceeds Si at the tetrahedral sites. Refinements of SFCA (silico-ferrite of Ca and Al) and SFCAM (plus Mg) in the matrix of sinter ore show that these ferrites are isostructural with rhönite and compositionally closest to dorrite (Mumme, 1988, 2003; Hamilton *et al.*, 1989; Mumme *et al.*, 1998; Sugiyama *et al.*, 2005).

Makarochkinite is named for Boris A. Makarochkin, Russian chemist and mineralogist, who studied the rare minerals from the Il'men Mountains, southern Urals, near Miass, Russia where the mineral was found in a pegmatite (Polyakov *et al.*, 1986). These authors reported that a proposal for makarochkinite was submitted to the CNMMN, but apparently there is no record of a vote; Shcherbakova *et al.* (2004) were skeptical that the materials ever reached the Commission. Høgtuvaite was first introduced as a new species with an end-member formula $Ca_4(Fe_{10}^{2+}Ti_2)O_4[Si_{10}Be_2]O_{36}$ from Be-rich orthogneiss at Høgtuva, a window of Proterozoic rocks in the Caledonides, Nordland County, Norway (Grauch *et al.* 1994; Burt 1994). The mineral was distinguished from rhönite because it contained sufficient Be to fill one tetrahedral site. In the absence of a structure refinement, Burt (1994) applied the vector method to define høgtuvaite. Grauch *et al.* (1994) equated makarochkinite with høgtuvaite, but learned too late of the crystal structure refinement of makarochkinite, which gave 50% Be occupancy at two sites (Yakubovich *et al.*, 1990), to include it in their discussion. Makarochkinite remained a synonym for høgtuvaite until Grew *et al.* (2005) obtained CNMMN approval for its being distinct from høgtuvaite on the basis of new structural refinements showing dominance of Ti at *M*7, whereas distinction from rhönite remained based on stoichiometry, i.e. sufficient Be to occupy the equivalent of one tetrahedral site. The formulae proposed by Grew *et al.* (2005) for høgtuvaite and

makarochkinite take into account the significant amounts of Al and Fe^{3+} present in both minerals (Table 1).

Ever since its first mention as an unnamed monoclinic mineral, $Ca_2(Mg,Fe)_4SbSi_4O_{12}(OH)_8$, from the Fe-Mn skarn deposit of Långban, Sweden (Moore, 1967), welshite has been one of the most intractable of the sapphirine group. After announcing the name (for Wilfred R. Welsh, teacher and amateur mineralogist) in 1970 (Moore, 1970) and obtaining approval by the CNMMN in 1973, Moore (1978) finally published his description of welshite as a sapphirine-group mineral with the formula $Ca_4Mg_8Fe_2^{3+}Sb_2^{5+}O_4[Si_8Be_4O_{36}]$. Taking advantage of Mössbauer spectroscopy and ion microprobe analyses of Be, Grew et al. (2001) had a firmer basis for determining a formula and locating Fe in the structure. However, attempts to refine the crystal structure were foiled by polysynthetic twinning and an eclectic composition until J. Barbier successfully overcame these difficulties to solve one welshite structure, showing this mineral to be the only non-centrosymmetric sapphirine-group mineral and allowing for the development of a satisfactory end-member formula (Grew et al., 2007).

Prior and Coomaraswamy (1903) first described serendibite from a calc-silicate skarn in Sri Lanka and named it for Serendib, the old Arabic designation for this island. Ye. N. Belova (in Pertsev and Nikitina, 1959) and Süsse (1968) carried out single-crystal work on serendibite and determined that it is triclinic, but Machin and Süsse (1974) were the first to recognize its relationship to the sapphirine group and adopted the Delaunay cell used by Kelsey and McKie (1964) for aenigmatite. Buerger and Venkatakrishnan (1974) refined the structure, but only to R = 7.1%. They reported B ⇌ Al and Mg ⇌ Ca substitutions, anomalous features that prompted Van Derveer et al. (1993) to refine the structures of three serendibite samples differing in Fe content to weighted R = 2.8−3.3 wt.%, and thereby established Si ⇌ B substitution at the $T1$ and $T4$ sites and Ca ⇌ Na substitution at the $M8$ and $M9$ sites.

Surinamite

Surinamite was first described as sapphirine in a metamorphic rock from the Bakhuis Mountains, Surinam (de Roever, 1973), but chemical analyses and X-ray study showed it to be a new ferromagnesian aluminosilicate (de Roever et al., 1976; Moore, 1976). De Roever et al., (1981) and Grew (1981) discovered independently that Be is an essential constituent; the formula proposed by de Roever et al., (1981) with 1 Be per 11 cations was confirmed by crystal structure refinements (Moore and Araki, 1983; Barbier et al., 2002). Surinamite being similar in appearance to sapphirine is no accident. As mentioned above, both structure types belong to a polysomatic series consisting of pyroxene and spinel modules. The sapphirine and surinamite structure types are intergrown on a submicroscopic scale in natural ferromagnesian aluminosilicate (Christy and Putnis, 1988) and synthetic Mg-Ga germanate (Barbier, 1996).

Crystal structures

Sapphirine-1A

In the five polytypes of sapphirine that have been recognized (Merlino and Pasero, 1987; Christy and Putnis, 1988), order-disorder features are present (Merlino and Zvyagin, 1998), but only the centrosymmetric triclinic sapphirine-1A (Fig. 1) is topologically identical with minerals in the aenigmatite and rhönite subgroups (Table 2). There are six tetrahedral sites of equal rank in chains parallel to the a axis. Tetrahedral linkage is 1 for the two tetrahedral wings ($T5$, $T6$), 3 for the two chain tetrahedra ($T2$, $T3$) linked to the wings and 2 for the other chain tetrahedra ($T1$, $T4$). There are seven octahedral sites. Five ($M1−M4$, $M7$) of these constitute the walls, which lie in the (011) plane and extend parallel to the a axis, and two are outside the wall ($M8$, $M9$). $M7$ is distinctive in that it shares the most edges (7) with adjacent polyhedra. The main difference between sapphirine-1A and minerals in the aenigmatite and rhönite subgroups is that the $M5$ and $M6$ sites (corresponding to $M8$ and $M9$ in the other subgroups) in sapphirine-1A are 6-coordinated. These octahedra do not cross-link the octahedral walls, but can be considered part of these walls (Moore, 1969). The oxygen anions are cubic close-packed in sapphirine, whereas Ca and Na disrupt close packing in the other subgroups.

In general, cation ordering in the sapphirine group is primarily driven by charge ordering and should be similar given the similar topologies of the structures. However, the degree of ordering will depend on the chemical composition of a particular phase through the charges of the cations occupying the various M and T sites. In
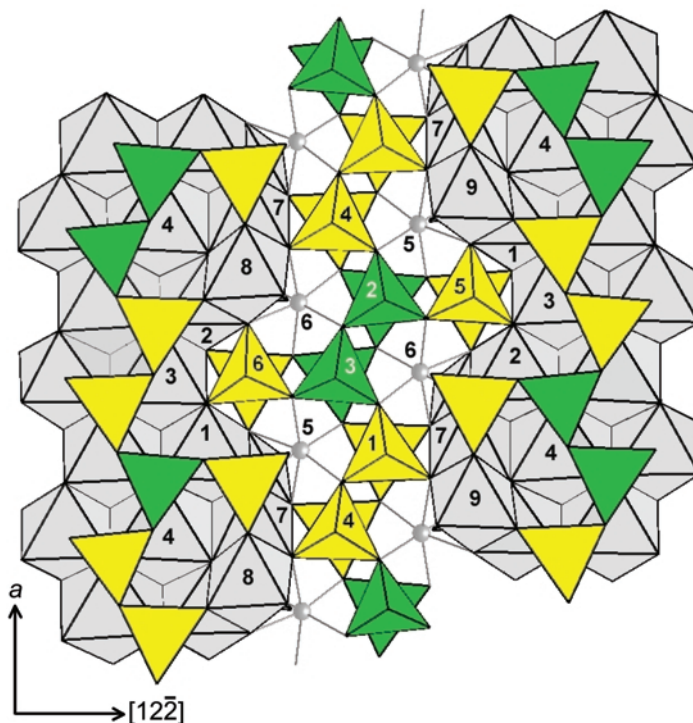
FIG. 1. Crystal structure of sapphirine-1*A*. Numbering of sites corresponds to column 1 of Table 2. Oriented to facilitate comparison of site numbering with that in the makarochkinite structure shown in Fig. 3. Green tetrahedra: Si = Al or Si > Al; yellow tetrahedra: Al or Al > Si.

sapphirine-1*A* there is a moderately high degree of cation order at both the *M* and the *T* sites.

Sapphirine-2M and khmaralite

The two monoclinic minerals in the sapphirine subgroup are not topologically identical to sapphirine-1*A*, but differ in the number of *M* sites: the two non-wall *M* sites in the triclinic structure are equivalent in sapphirine-2*M*. Khmaralite differs from sapphirine-2*M* in having a supercell due to doubling along the *a* axis; it has 12 *T* sites and 16 *M* sites (Fig. 2; Table 3). This response to Be incorporation differs from that in the rhönite subgroup, and allows a maximum of only 2 Be per 28 cations.

Aenigmatite, wilkinsonite, krinovite

The compositions of the aenigmatite subgroup minerals whose structures have been refined (Tables 2, 3) are relatively highly ordered, with all the *T* sites occupied by Si; *M*7 occupied by the more highly charged cation, e.g. Ti in aenigmatite and Cr in krinovite, and *M*3−*M*6 sites by divalent cations. Cr also occupies the *M*1 and *M*2 sites in krinovite. The new refinement of aenigmatite (Grew *et al.*, 2008) gives greater cation order at *M*1−*M*7 sites than earlier reported (Cannillo *et al.*, 1971), *viz.* 100% (*vs.* 59%) of Ti at *M*7 and subordinate Mg substitutes for Fe only at *M*3−*M*6. Fe^{3+} is dominant at the *M*1, *M*2 and *M*7 sites in wilkinsonite (Burt *et al.*, 2007).

Rhönite, rhönite (Allende), høgtuvaite, makarochkinite, welshite

Compositions of the *M*1−*M*7 and *T* sites are more complex and cation disorder greater in the five rhönite subgroup minerals for which structure refinements are known (Fig. 3; Table 2). *M*8 and *M*9 are dominantly Ca and the distinction between the seven shorter bonds and one longer bond is commonly more marked. Be and B are concentrated on the most polymerized *T* sites (*T*1, *T*4). Ti is ordered at *M*7 in høgtuvaite, makarochkinite

TABLE 2. Simplified occupancies in minerals of the aenigmatite subgroup, rhönite subgroup (except dorrite) and sapphirine-1A based on crystal structure refinements.

S.G.	Spr-1A $P\bar{1}$		Aen $P\bar{1}$	Wlk $P\bar{1}$	Krin $P\bar{1}$	Rhö $P\bar{1}$	Rhö-All $P\bar{1}$	Høg $P\bar{1}$	Mkr $P\bar{1}$	Welshite* $P1$	Srd $P\bar{1}$
$T3$**	Si = Al	$T1$**	Si	Si	Si	Si = Al	Si = Al	Si = Be	Si = Be	Si/Be	B ⩾ Si
$T4$	Al > Si	$T2$	Si	Si	Si	Si = Al	Si = Al	Si	Si	Si/Be	Si
$T1$	Al	$T3$	Si	Si	Si	Si = Al	Si = Al	Si > Al	Si = Al	Be = Al/Si	Al
$T2$**	Si > Al	$T4$**	Si	Si	Si	Si = Al	Si = Al	Si = Be	Si = Be	Be/Si	B
$T6$	Al > Si	$T5$	Si	Si	Si	Si = Al	Al	Si	Si	Al = Fe/Si	Si
$T5$	Al	$T6$	Si	Si	Si	Si = Al	Al	Si	Si	Si/Al = Fe	Si
$M8$**	Al	$M1$**	Fe	Fe	Cr	Mg	Mg = Ti	Fe	Fe	Mg	Al
$M9$**	Al	$M2$**	Fe	Fe	Cr	Mg	Mg = Ti	Fe	Fe	Mg	Al
$M1$	Al	$M3$	Fe	Fe	Mg	Mg	Mg = Ti	Fe	Fe	Mg/Sb	Al or Mg
$M2$	Al	$M4$	Fe	Fe	Mg	Mg	Mg = Ti	Fe	Fe	Mg/Sb	Al
$M4$	Mg	$M5$	Fe	Fe	Mg	Mg	Mg	Fe	Fe	Mg/Mg	Mg
$M3$	Mg	$M6$	Fe	Fe	Mg	Mg	Mg	Fe	Fe	Mg/Mg	Mg
$M7$	Al	$M7$	Ti	Fe	Cr	Ti	Mg = Ti	Fe	Ti	Sb/Mg	Al
$M5$	Mg	$M8$	Na	Na	Na	Ca	Ca	Ca	Ca	Ca/Ca	Ca
$M6$	Mg	$M9$	Na	Na	Na	Ca	Ca	Ca	Ca	Ca/Ca	Ca

Sources given in Table 1. Dorrite is not included because the structure has not been refined. S.G. − space group. The site labelling (first column) applies only to sapphirine-1A (the third column gives the correspondence for the other minerals). Equal sign (=) indicates approximately equal occupancy by the given constituents.
* For welshite, all sites are split except for non-wall octahedra $M1$ and $M2$, so occupancies for both sites are given, separated by a forward slash, with the A-labelled site second.
** Indicates the most polymerized T sites and non-wall octahedral sites.
Abbreviations: Spr-1A − sapphirine-1A, Aen − aenigmatite, Wlk − wilkinsonite, Krin − krinovite, Rhö − rhönite, Rhö-All − rhönite from the Allende meteorite, Høg − høgtuvaite, Mkr − makarochkinite, Srd − serendibite.

and rhönite, whereas Mg, Fe^{2+} and Fe^{3+} are disordered over the $M1-M6$ sites. The Allende rhönite differs in that Ti (including Ti^{3+} as well as Ti^{4+}) and Mg are disordered over the $M1-M4$ and $M7$ sites, leaving $M5$ and $M6$ dominated by Mg.

In contrast to other minerals in the aenigmatite and rhönite subgroups, rhönite has at least two polytypes. Bonaccorsi *et al*. (1990) gave HRTEM evidence for an 8-layer polytype of rhönite (rhönite-8A) that is 200 Å wide in a crystal from Scharnhausen, Germany.

Welshite is unique among minerals in the sapphirine group in being non-centrosymmetric with 12 T sites and 16 M sites, the increase resulting from the loss of the symmetry center (Fig. 4). The first successful crystal structure refinement also resulted in a new end-member formula (Table 1), which differs significantly from the one proposed by Moore (1978) and given in standard references, $Ca_4(Mg_8Sb_2Fe_2^{3+})O_4$ $[Si_8Be_4O_{36}]$ (e.g. Strunz and Nickel, 2001). Be is not restricted to the most polymerized T sites ($T1$, $T1$A, $T4$, $T4$A) sites nor is Sb restricted to the M

sites with the most shared edges ($M7$, $M7$A). Nonetheless, there is considerable cation order, which allows for incorporation of more Be than in other minerals of the group, up to 3.46 *vs*. the maximum of 2.1 Be per 28 cations (høgtuvaite) and still avoids Be−O−Be bridges.

Surinamite

Surinamite (Fig. 5) is highly ordered compared to sapphirine and khmaralite. As in sapphirine, the oxygen anions are cubic close-packed. Only one polytype (1M) has been reported for natural surinamite, which has space group $P2/n$, although a different polytype (2M) with space group $C2/c$ is realized in a synthetic Ga-Ge analogue of surinamite (Barbier, 1996, 1998).

Compositional variations

Sapphirine-1A and -2M, khmaralite

The principal compositional variations in Be- and B-free sapphirine include the homovalent Fe ⇌
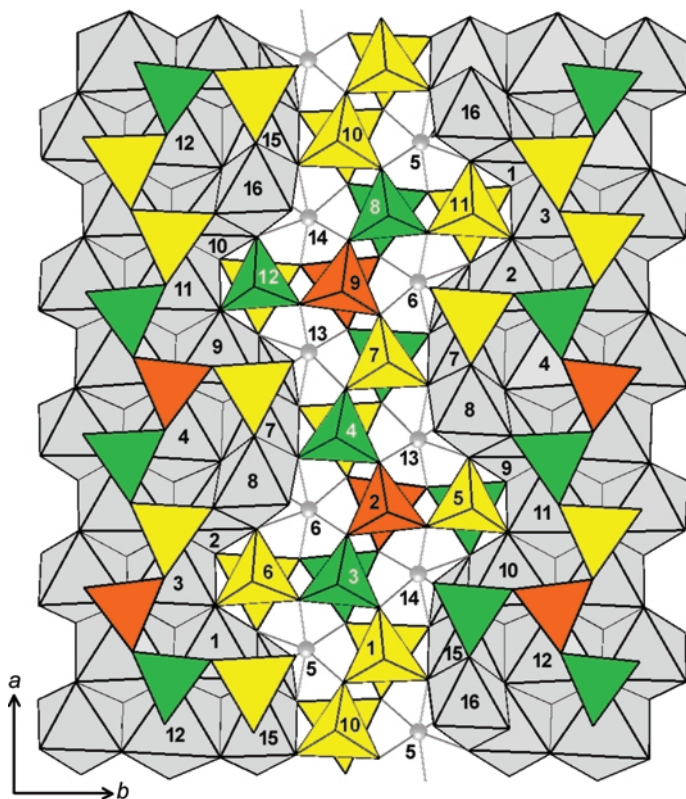
FIG. 2. Crystal structure of khmaralite. Numbering of sites corresponds to column 1 of Table 3 (cf. column 1, Table 2). Oriented to facilitate comparison of site numbering with that in the makarochkinite structure shown in Fig. 3. Green tetrahedra: Si, Si >> Be > Al or Si > Al; yellow tetrahedra: Al or Al > Si; orange tetrahedra: Be = Si + Al or Be > Al.

Mg, Fe $\rightleftharpoons$ Al, and Cr $\rightleftharpoons$ Al substitutions, and the heterovalent (Mg, Fe) + Si $\rightleftharpoons$ 2(Al, Fe, Cr) (Tschermaks) substitution (e.g. Deer *et al.*, 1978; Higgins *et al.*, 1979; Christy, 1989; Podlesskii *et al.*, 2008), but Fe- and Cr-dominant analogues have not been reported in nature, nor has a Fe-dominant analogue been synthesized. Total Fe (as FeO) is in the range 0.05−16.55 wt.% (minimum and maximum from Mangari area, Kenya and Vizianagaram, India, by Mercier *et al.*, 1999 and Kamineni and Rao, 1988, respectively), but in most cases, both Fe^{3+} and Fe^{2+} are present, and their proportions are generally calculated from stoichiometry in the absence of a direct determination, e.g. by Mössbauer spectroscopy. Up to 2.77 Fe^{2+} per 28 cations and $Fe^{2+}/(Fe^{2+} + Mg) = 0.36$ has been calculated from stoichiometry (Vizianagaram, India, Kamineni and Rao, 1988). Maximum Fe^{3+} contents directly measured by Mössbauer spectro-

scopy are 0.85 per 28 cations in Fe^{2+}-bearing sapphirine (Wilson Lake, Canada, Burns and Solberg, 1990) and 1.00 per 28 cations in a sapphirine lacking Fe^{2+} (Mautia Hill, Tanzania, McKie, 1963; Bancroft *et al.*, 1968). The highest Fe^{3+} contents obtained by other methods are 1.93 Fe^{3+} per 28 cations that Sahama *et al.* (1974) determined by wet chemistry in a sapphirine from Labwor, Uganda, and 1.89 Fe^{3+} per 28 cations that Gnos and Kurz (1994) calculated in a sapphirine from the Semail ophiolite in the United Arab Emirates. However, these contents exceed the maximum that Steffen *et al.* (1984) were able to incorporate in synthetic Mg-sapphirine: 1.4 Fe^{3+} per 28 cations. The presence of Fe^{2+} could favour incorporation of Fe^{3+}; nonetheless, Fe^{3+} contents exceeding 1.4 need confirmation.

Using Mössbauer spectroscopy, Bancroft *et al.* (1968) and Steffen *et al.* (1984) located Fe^{3+} at

TABLE 3. Simplified occupancies in the monoclinic minerals sapphirine-2M and khmaralite.

S.G.	Sapphirine-2M $P2_1$/a	Khmaralite $P2_1$/c	Equivalent site* $P\bar{1}$
T3**	Si = Al	Si >> Be > Al	T1**
T9**	—	Be > Al	T1**
T4	Al	Si > Al	T2
T10	—	Al	T2
T1	Al	Al > Si	T3
T7	—	Al > Si	T3
T2**	Si	Be = Si + Al	T4**
T8**	—	Si	T4**
T6	Al > Si	Al > Si	T5
T12	—	Si	T5
T5	Al	Al > Si	T6
T11	—	Al	T6
M8**	Al	Al	M1**, M2**
M16**	—	Al	
M1	Al	Al	M3
M9	—	Al > Mg	M3
M2	Al	Al	M4
M10	—	Al > Mg	M4
M4	Mg	Mg	M5
M12	—	Mg	M5
M3	Al = Mg	Al	M6
M11	—	Mg > Al	M6
M7	Al	Al	M7
M15	—	Al	M7
M5	Mg	Mg > Al	M8
M13	—	Mg	M8
M6	Mg	Mg	M9
M14	—	Mg	M9

Sources given in Table 1. S.G. – space group. Equal sign (=) indicates approximately equal occupancy by the given constituents.
* In the other subgroups (Table 2).
** Indicates the most polymerized T sites and non-wall octahedral sites.

tetrahedral sites, whereas Burns and Solberg (1990) concluded that Fe^{3+} occupies octahedral sites, which is consistent with Fe^{3+} occupancy determined by single-crystal refinement in sapphirine-1A from Wilson Lake, Canada (Merlino, 1980). Nonetheless, Fe^{3+} occupancy in sapphirine remains an open question.

The maximum Cr content is 1.42 per 28 cations (7.52 wt.% Cr_2O_3, Fiskenæsset region, Greenland, Friend, 1982); the corresponding $Cr^{3+}/(Cr^{3+} + {}^{vi}Al)$ ratio is 0.15, i.e. 15% of a Cr end-member if Cr occupies only octahedral sites as suggested by the large octahedral site preference energy for Cr^{3+} (Navrotsky, 1975; Burns, 1993). Brigida *et al.* (2007) synthesized at 1340ºC and 1 bar a sapphirine for which a formula with 83% of a Cr end-member, $Mg_4(Mg_{3.8}Cr_{6.7}Al_{1.4})O_4[Si_{4.1}Al_{7.9}O_{36}]$, can be written if all Cr^{3+} remains octahedrally coordinated at this temperature.

The Tschermak substitution is extensive in sapphirine. Si ranges from 1.71 to 4.49 per 28 cations in Be poor compositions; that is, a few compositions extend beyond the usual limits of Si = 2 and Si = 4 given for sapphirine, which correspond to the 2:2:1 and 3:5:1 compositions in terms of the $(Mg,Fe,Mn)O:(Al,Fe,Cr,V)_2O_3:SiO_2$ ratio (Fig. 6). The great majority of compositions are closer to the 7:9:3 composition, which is given as the end-member in Table 1. Preference for this ratio is not surprising given the considerable octahedral ordering in sapphirine, i.e. Mg at M4, M5, and M6, ^{vi}Al at M1, M2, M7, M8 and M9,
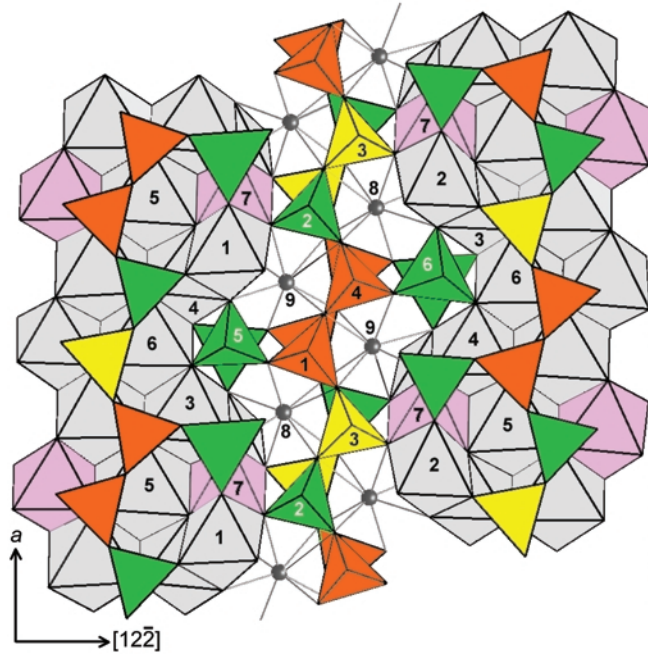
FIG. 3. Crystal structure of makarochkinite, which is representative of the structures of the centrosymmetric triclinic Na and Ca aenigmatite subgroup. Numbering of sites corresponds to column 3 of Table 2 (cf. column 4, Table 3). Green tetrahedra: Si; yellow tetrahedra: Si = Al; orange tetrahedra: Be = Si; lavender octahedra: Ti.
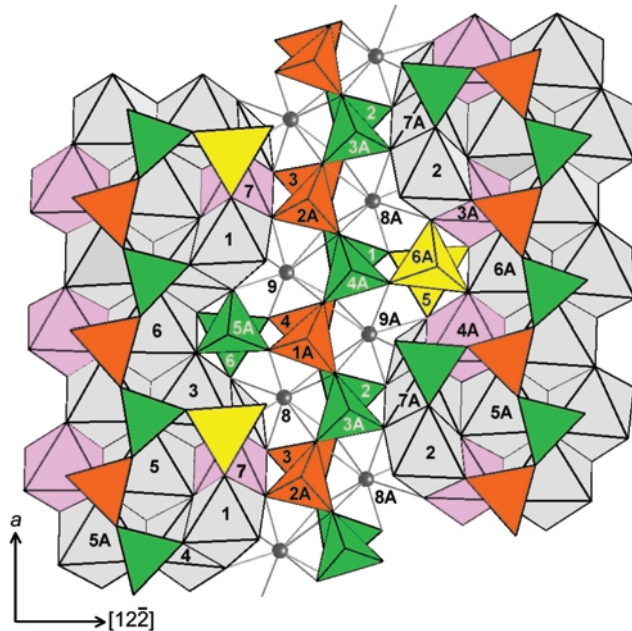

FIG. 4. Crystal structure of welshite, which is uniquely non-centrosymmetric Ca aenigmatite subgroup mineral. Numbering of sites corresponds to column 3 of Table 2, but sites are split (lettered *vs.* unlettered) due to absence of symmetry centre. Green tetrahedra: Si; yellow tetrahedra: Al = Fe; orange tetrahedra: Be or Be = Al; lavender octahedra: Sb.
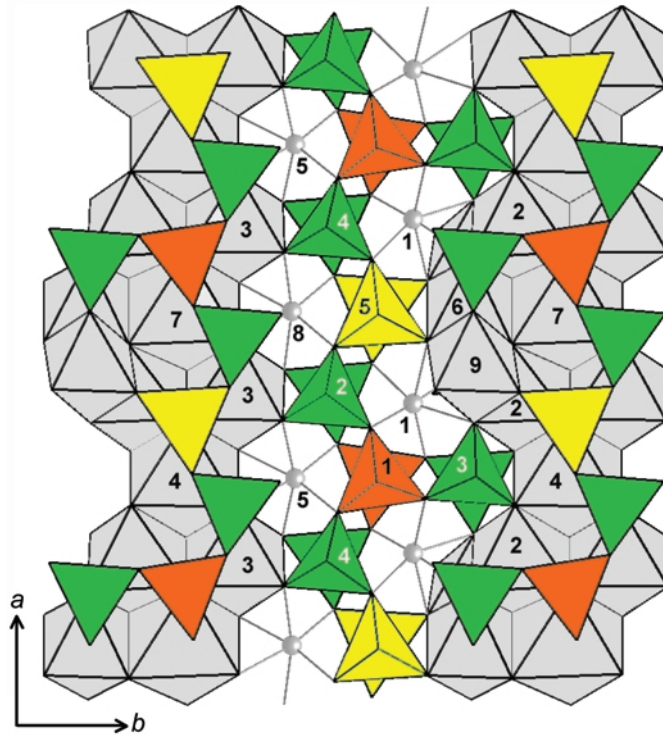
FIG. 5. Crystal structure of surinamite. Green tetrahedra: Si; yellow tetrahedra: Al; orange tetrahedra: Be.

with $M3$ generally split (Moore, 1969; Higgins and Ribbe, 1979; Merlino, 1980), summing to ~7 Mg and ~9 ^{vi}Al per 28 cations (Tables 2, 3). The tetrahedra are less well ordered (at least in the long range); the ratio of ~3 Si to ~ 9 ^{iv}Al in typical sapphirine is dictated by charge balance.

Calcium is generally a minor component of sapphirine, rarely exceeding 0.2 wt.% CaO (Christy, 1989). However, Grew *et al.* (1992) reported B-rich sapphirine containing up to 5.4 wt.% CaO, which was attributed to 35% serendibite in solid solution.

Other constituents reported in sapphirine in amounts exceeding 1 wt.% oxide are MnO (to 1.16 wt.%, Madurai Block, south India; Tateishi *et al.*, 2004) and TiO_2 (to 1.25 wt.% in terrestrial sapphirine, Vestfold Hills, Antarctica, Harley and Christy, 1995; and 1.60−2.30 wt.% in sapphirine in plagioclase-olivine inclusions in the Allende meteorite, Sheng *et al.* 1991). Stoichiometric calculation of compositions of 'fassaite' in other plagioclase-olivine inclusions gave Ti^{3+} = 60−80% of total Ti (Sheng *et al.*, 1991), suggesting that the Ti in the Allende sapphirine

could also be trivalent in part (Ti^{3+}-bearing rhönite is also from Allende, but in Ca-Al-rich inclusions). Assuming Ti is trivalent improves stoichiometry of the two compositions reported by Sheng *et al.* (1991).

Beryllium is incorporated in sapphirine through the substitution Be + Si $\rightleftharpoons$ 2Al, which relates the end-members for sapphirine and khmaralite given in Table 1 (Grew, 1981; Barbier *et al.*, 1999, 2002; Christy *et al.*, 2002; Grew *et al.*, 2006). There appears an unbroken solid solution between Be-free sapphirine and khmaralite containing 1.57 Be per 28 cations, the maximum Be in natural khmaralite (Fig. 6). The superstructure with doubled chain periodicity characteristic of khmaralite appears at about 1 Be per 28 cations (Grew *et al.*, 2000). The octahedral composition of khmaralite is roughly 7 (Mg, Fe^{2+}) and 9 (Al, Fe^{3+}) (Table 3) as a consequence of the marked ordering at octahedral sites, an ordering very similar to that of sapphirine (Barbier *et al.*, 1999). Moreover, sapphirine and khmaralite having intermediate Be contents plot close to a line joining the end-member sapphirine and khmaralite compositions
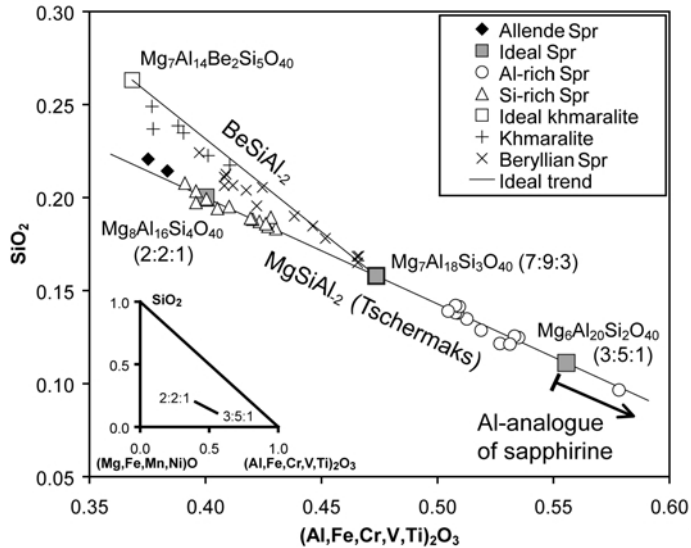
FIG. 6. Composition of sapphirine in terms of mole proportions SiO_2, (Mg, Fe, Mn, Ni)O and $(Al,Fe,Cr,V,Ti)_2O_3$. Al-analogue of sapphirine refers to a distinct species, yet unnamed, in which Si < 2 per 28 cations (Table 4). $BeSiAl_{-2}$ and $MgSiAl_{-2}$ refer to the substitutions Be + Si $\rightleftharpoons$ 2Al and Mg + Si $\rightleftharpoons$ 2Al, respectively. Analyses of sapphirine selected to show only relatively Si-rich compositions (Dawson *et al.*, 1997; Gnos and Kurz, 1994; Grew *et al.*, 1994; Harley and Christy, 1995; Owen *et al.*, 1988; Sajeev and Osanai, 2004; Sheng *et al.*, 1991; Sills *et al.*, 1983; Simon and Chopin, 2001) and Al-rich 'peraluminous' compositions (Godard and Mabit, 1998; Grew *et al.*, 1988; Harley and Christy, 1995; Liati and Seidel, 1994; Nijland *et al.*, 1998; Sabau *et al.*, 2002; Schreyer and Abraham, 1975; Warren and Hensen, 1987); most sapphirine compositions are intermediate and have not been plotted. Ti is assumed to be trivalent only in the Allende sapphirine; in all others, Ti is assumed to be tetravalent. Be = 1 atom per 28 cations serves as the distinction between khmaralite and beryllian sapphirine. The plot includes all available compositions of khmaralite and Be-rich beryllian sapphirine (BeO > 1 wt.%) (Grew, 1981; Barbier *et al.*, 1999; Grew *et al.*, 2000 and unpublished data), but only selected compositions for beryllian sapphirine with Be contents between 1 and 0.2 wt.% BeO (Grew *et al.*, 2006).

(Fig. 6). Christy *et al.* (2002) synthesizied beryllian sapphirine in the $MgO-BeO-Al_2O_3-SiO_2-H_2O$ system, but none had the superstructure characteristic of khmaralite. No more than 2 Be per 28 cations could be incorporated, and this amount only in starting compositions corresponding to the 2:2:1 composition plus 0.5 $BeSiAl_{-2}$. Two runs of this composition gave single-product sapphirine, implying its composition was $Mg_4(Mg_4Al_8)O_4$ $[Si_6Be_2Al_4O_{36}]$, but this was not confirmed by direct analysis.

Ca-poor sapphirine associated with prismatine at several localities incorporates up to 0.85 wt.% B_2O_3, corresponding to 0.35 B per 28 cations (Grew, 1986; Grew *et al.*, 1990, 1991*b*). B-bearing sapphirine compositions are somewhat richer in Si than the 7:9:3 composition; the B contents correspond to ~17% of a B analogue to the 7:9:3 composition, $Mg_4(Mg_3Al_9)O_4$ $[Si_3B_2Al_7O_{36}]$. Ca-bearing sapphirine, to date

only found at Johnsburg, New York, USA (Grew *et al.*, 1992), contains significantly more B. A formula for the averaged composition with 2.08 wt.% B_2O_3 is $Mg_{3.6}Ca_{0.4}(Mg_{2.8}Fe_{0.1}Al_9)O_4$ $[Si_{3.2}B_{0.8}Be_{0.1}Al_{7.9}O_{36}]$, but the sapphirine is very heterogeneous compositionally. Examination by TEM led Grew *et al.* (1992) to conclude that the heterogeneous material is structurally a single-phase triclinic Ca-B sapphirine; this phase appears to be a solid solution of serendibite and B-bearing sapphirine that subsequently exsolved Ca-richer material. The averaged composition (1.47 wt.% CaO, 2.08 wt.% B_2O_3) corresponds roughly to 10% serendibite and 25% $Mg_4(Mg_3Al_9)O_4[Si_3B_2Al_7O_{36}]$ in solid solution.

Aenigmatite, wilkinsonite, krinovite

Aenigmatite and wilkinsonite constitute a continuous solid solution series linked predominantly by

TABLE 4. Classification scheme for the sapphirine supergroup.

Polysome (group)	Largest M (subgroup)	Most shared edges	$Q^3\,T$	X_{Mg}	Mineral or possible mineral
Sapphirine					
	$M5$, $M6$ Sapphirine	$M7$	$T2$, $T3$		
<SP>	Mg	Al	Si > Al	>0.5	SAPPHIRINE
<SP>	Mg	Al	Al > Si	>0.5	Al analogue of sapphirine
<SP>	Mg	Al	Be = 1[1]	>0.5	KHMARALITE[2]
	$M8$, $M9$ Aenigmatite	$M7$	$T1$, $T4$		
<SP>	Na	Ti^{4+}	Si	<0.5	AENIGMATITE
<SP>	Na	Fe^{3+}	Si	<0.5	WILKINSONITE
<SP>	Na	Fe^{3+}	Si	>0.5	Mg analogue of wilkinsonite
<SP>	Na	Cr	Si	>0.5	KRINOVITE
	Rhönite				
<SP>	Ca	Ti^{4+}	Si > Al	>0.5	RHÖNITE
<SP>	Ca	Ti^{4+}	Si > Al	<0.5	Fe^{2+} analogue of rhönite
<SP>	Ca	Ti^{4+}	Be = 1[1]	<0.5	MAKAROCHKINITE
<SP>	Ca	Fe^{3+}	Si, Al	>0.5	DORRITE
<SP>	Ca	Fe^{3+}	Be = 1[1]	<0.5	HØGTUVAITE
<SP>	Ca	Mg	Si, Al	>0.5	Unnamed[3]
<SP>	Ca	Al	B = 1[1]	>0.5	SERENDIBITE
<SP>	Ca	Sb, Mg	Be = 1[4]	>0.5	WELSHITE[4]
	Unnamed				
<SP>	Fe^{2+}	?	?	<0.5	Unnamed Fe-Sn-Ga-Ge
Surinamite					
	$M1$, $M5$, $M8$	$M6$	$T1$		
<PPS>	Mg	Al	Be	>0.5	SURINAMITE
<PPS>	Mg	Al	Al or Si	>0.5	Be-free analogue of surinamite

Columns are 1 − Group name and polysome symbol; 2 − Subgroup name and occupant of two or three largest M sites, 3 − Occupants of M site with most shared edges, 4 − Occupants of most polymerized T sites. 5 − X_{Mg} = atomic Mg/(Mg + Fe^{2+}) at other M sites. Names of minerals approved by the CNMNC (CNMMN) are in capital letters.
[1] Total Be or B occupancy at the two T sites considered together for the end-member composition given in Table 1.
[2] Khmaralite contains two sapphirine sub-cells ($M1−8$, $T1−6$ and $M9−16$, $T7−12$). Be > 0.5 at each of $T2$ and $T9$.
[3] Ti^{3+}-bearing Mg-analogue of rhönite.
[4] Welshite has $P1$ symmetry so that the $T1–T6$ and $M3–M9$ sites are doubled. Be = 1 at $T1A$ and $T4$, contributing 2 Be to the end-member formula (Table 1) from these sites; Sb = 1 at $M7$ and Mg = 1 at $M7A$.
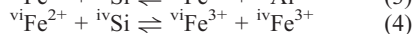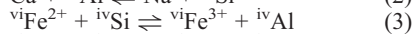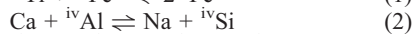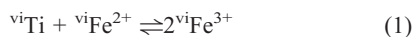
the substitution $Fe^{2+} + Ti \rightleftharpoons 2Fe^{3+}$ (Hodges and Barker, 1973; Larsen, 1977; Duggan, 1990). Homovalent substitutions, notably Mn or Mg for Fe^{2+} and Al for Fe^{3+}, are limited in extent. For example, Ridolfi *et al.* (2006) reported an aenigmatite in one sample of a silica-saturated peralkaline syenite autolith, from Kilombe volcano, Kenya, with 5.98−7.93 wt.% MnO, which corresponds to 1.428 and 1.894 Mn per 28 cations and Mn/(Mn + Fe^{2+}) = 0.15 and 0.20,

respectively, and is the richest in Mn yet reported. In most cases, Mg contents are lower, mostly <1 wt.% MgO, but with two notable exceptions. Price *et al.* (1985) and Price (pers. comm.) reported 8.88−10.61 wt.% MgO, corresponding to 3.53−4.21 Mg per 28 cations and Mg/(Mg+Fe^{2+}) = 0.43−0.48 in aenigmatite from nepheline syenite on Mount Kenya. Aenigmatite found in an albite clast in the Kaidun meteorite, a breccia, contains 3.64−6.81 wt.% MgO, corre-

sponding to 1.50−2.71 Mg per 28 cations and Mg/(Mg+Fe^{2+}) = 0.16−0.29, Ivanov *et al.*, 2003; Zolensky and Ivanov, 2003). Bischoff *et al.* (1993) reported 3.7 wt.% MgO in a phase in an alkali-granite clast in meteorite Adzhi-Bogdo; this phase is probably aenigmatite (Ivanov *et al.*, 2003). With Mg/(Mg+Fe^{2+}) = 0.06 (Ivanov *et al.* 2003; Zolensky and Ivanov, 2003), wilkinsonite associated with aenigmatite in the Kaidun meteorite is more magnesian than any terrestrial material with the exception of wilkinsonite containing 5.50 wt.% MgO, i.e. Mg/(Mg + Fe^{2+}) = 0.53, from a syenitic ejectum, Wonchi volcano, Ethiopia (Gaeta and Mottana, 1991). In contrast to the magnesian aenigmatite from Mount Kenya, in which divalent cations total 8.5−9.0 per 28 cations, close to the ideal 10, divalent cations total only 5.1 in the Wonchi wilkinsonite, significantly less than the 8 per 28 cations in ideal wilkinsonite.

Aenigmatite and wilkinsonite deviate to some degree from ideal stoichiometry. Ti exceeds 2 atoms per 28 cations in some samples, and most analyses give Fe^{3+} in excess of that expected from Fe^{2+} + Ti $\rightleftharpoons$ 2Fe^{3+} (Fig. 7*a*). Non-stoichiometry also results from incorporation of constituents other than Fe, Ti, Mg, Mn, Na and Si. The most important of these are Ca and Al, e.g. Ca content ranges from negligible to nearly 1 atom per 28 cations, i.e. ~25% substitution of Na by Ca (Fig. 8). In most analyses the sum of Na + Ca + K ranges from 4.0 to 4.2 atoms, i.e. somewhat in excess of stoichiometry with more scatter at low Ca content. This excess in electron microprobe analyses could be due to improper standardization of Na as Larsen (1977) suggested. Aluminum content ranges from 1.5 to 6 times Ca content, and is close to 1.5 in Ca-rich analyses (Fig. 8*b*). K$_2$O contents greater than 0.2 wt.% (>0.07 K per 28 cations) are rarely reported, and only in wet chemical analyses with one exception (0.75 wt.% or 0.28 K per 28 cations, Wonchi wilkinsonite, Gaeta and Mottana, 1991).

Larsen (1977) invoked the following four coupled substitutions to account for compositional variation in aenigmatite from the Ilímaussaq complex, Greenland:

$$^{vi}Ti + {}^{vi}Fe^{2+} \rightleftharpoons 2^{vi}Fe^{3+} \qquad (1)$$
$$Ca + {}^{iv}Al \rightleftharpoons Na + {}^{iv}Si \qquad (2)$$
$$^{vi}Fe^{2+} + {}^{iv}Si \rightleftharpoons {}^{vi}Fe^{3+} + {}^{iv}Al \qquad (3)$$
$$^{vi}Fe^{2+} + {}^{iv}Si \rightleftharpoons {}^{vi}Fe^{3+} + {}^{iv}Fe^{3+} \qquad (4)$$

Taking into account the refinement of wilk-insonite (Burt *et al.*, 2007), substitution 1 can be written more specifically as $^{M7}Ti + {}^{M1,M2}Fe^{2+} \rightleftharpoons$ $^{M7}Fe^{3+} + {}^{M1,M2}Fe^{3+}$, which is probably the most important substitution relating the two minerals. Substitutions 3 and 4 can explain why analyses from other areas as well as Ilímaussaq give more Fe^{3+} than predicted by substitution 1 (e.g. Vesterøya, Norway, Grew *et al.*, 2008) and why Al > Ca. Substitution 2 links end-member aenigmatite with our suggested end-member composition for the Fe^{2+} analogue of rhönite (Table 1), whereas substitutions 2 and 3 working in tandem at a 2:1 ratio, together with Mg $\rightleftharpoons$ Fe^{2+}, link end-member aenigmatite with the composition given for rhönite in Table 1. The trend at greater Ca contents (Al/Ca = 1.5, Fig. 8*b*) is consistent with the latter, i.e. over 20% solid solution of a Fe^{2+}-dominant analogue of the rhönite composition given in Table 1.

The new structure refinement and Mössbauer data (Grew *et al.*, 2008) confirm earlier suggestions based on Mössbauer spectroscopy (Choi, 1983; Choi and Burns, 1983; Burns and Solberg, 1990) that tetrahedral Fe^{3+} is present in aenigmatite. The sum Si + Al is significantly less than 12 in other aenigmatite samples (Fig. 7*b*), and this deficit at tetrahedral sites is best explained by tetrahedral Fe^{3+} in the absence of other tetrahedrally coordinated cations such as Be and B. Thus, substitution 4, which introduces tetrahedral Fe^{3+}, undoubtedly plays a role, albeit minor, in aenigmatite crystal chemistry.

Nb, Zr, Sn and Zn are reported in amounts up to 1 wt.% oxide, sometimes more (e.g. 3.72 wt.% Nb$_2$O$_5$ in wilkinsonite, corresponding to 0.49 Nb per 28 cations; Duggan, 1990). Other elements, notably Li (to 0.06 wt.% Li$_2$O, corresponding to 0.07 Li per 28 cations, Howie and Walsh, 1981; Raade and Larsen, 1980; Åsheim *et al.*, 2008), could also be significant; but relatively few papers report analyses of these minor constituents. Åsheim *et al.* (2008) reported other trace element contents in aenigmatite from the Larvik plutonic complex, Norway, including 28−31 ppm Be and 11−92 ppm B (cf. ~20 ppm Be, Lovozero, Vlasov *et al.*, 1966). Because the ferric/ferrous ratio in most samples is calculated from stoichiometry, ignoring Nb, Zr, Sn, Zn and Li can lead to errors in calculating Fe^{3+} content, above and beyond errors inherent in the calculation itself.

Only one analysis of krinovite has been reported (Olsen and Fuchs, 1968). Its composition approaches that of the end-member with 5% substitution of Mg by Fe (Bonaccorsi *et al.*,
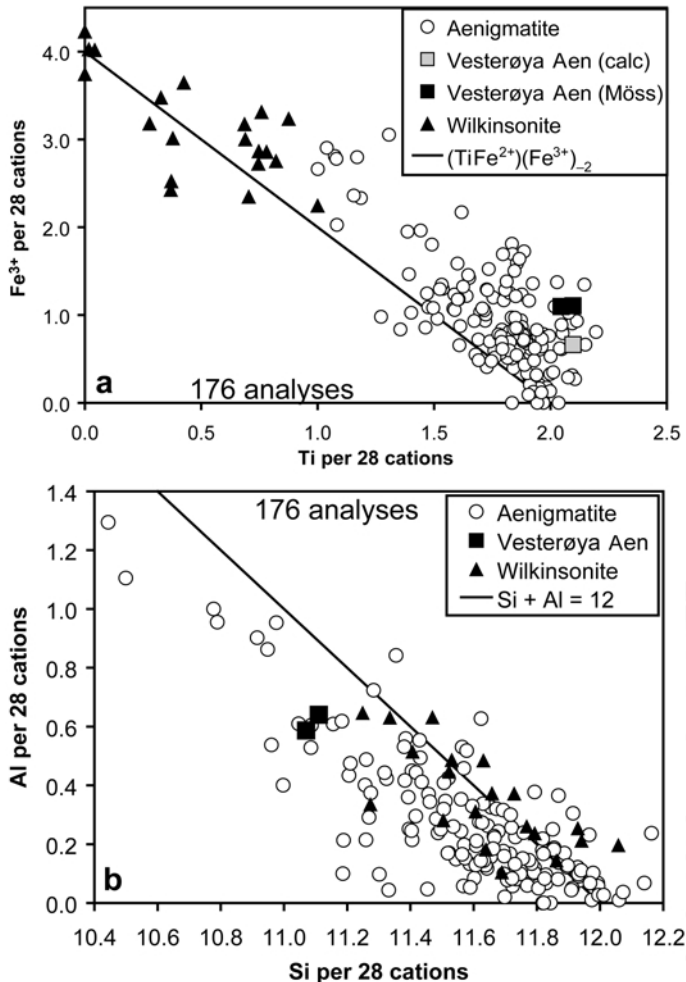
FIG. 7. Compositional variations of aenigmatite (Aen) and wilkinsonite as functions of Ti and Si. $(TiFe^{2+})(Fe^{3+})_{-2}$ in (*a*) indicates the substitution $^{vi}Ti + {}^{vi}Fe^{2+} \rightleftharpoons 2\ ^{vi}Fe^{3+}$ relating aenigmatite and wilkinsonite. Vesterøya Aen refers to electron microprobe data on a sample from Vesterøya, Norway from which a crystal was used to newly refine the structure ($Fe^{3+}/\Sigma Fe$ calculated from chemical data and measured by Mössbauer spectroscopy, Grew *et al.*, 2008). We calculated Fe^{3+}/Fe^{2+} ratio in all the other analyses by assuming 28 cations and 40 oxygens whether or not Fe^{3+} had been measured directly in wet chemical analyses or calculated by the original authors from electron microprobe analyses. Sources of other data: Abbott (1967); Avanzinelli *et al.* (2004); Barker and Hodges (1977); Barker (*unpublished data*); Birkett *et al.* (1996); Bischoff *et al.* (1993); Bohrson and Reid (1997); Borley (1976); Bryan (1969); Bryan and Stevens (1973); Bulakh (1997); Carmichael (1962); Curtis and Currie, 1981; Dawson (1997); Downs (2006); Duggan (1990); Ewart *et al.* (1968); Farges *et al.* (1994); Ferguson (1978); Gaeta and Mottana (1991); Gibb and Henderson (1996); Grapes *et al.* (1979); Henderson *et al.* (1989); Howie and Walsh (1981); Ike (1985); Ivanov *et al.* (2003); Jones (1984); Jørgensen (1987); Kelsey and McKie (1964); Krivdik and Tkachuk (1988); Larsen (1977); Lindsley and Haggerty (1970); Mahood and Stimac (1990), Marks and Markl (2003); Marsh (1975); Mitrofanov and Afanas'yeva (1966); Nash *et al.* (1969); Nicholls and Carmichael (1969); Nkoumbou *et al.* (1995); Platt and Woolley (1986); Powell (1978); Price (personal communication, 2007); Price *et al.* (1985); Ren *et al.* (2006); Stolz (1986); Velde (1978); Vlasov *et al.* (1966); White *et al.* (2005); Yagi and Souther (1974); Zies (1966).
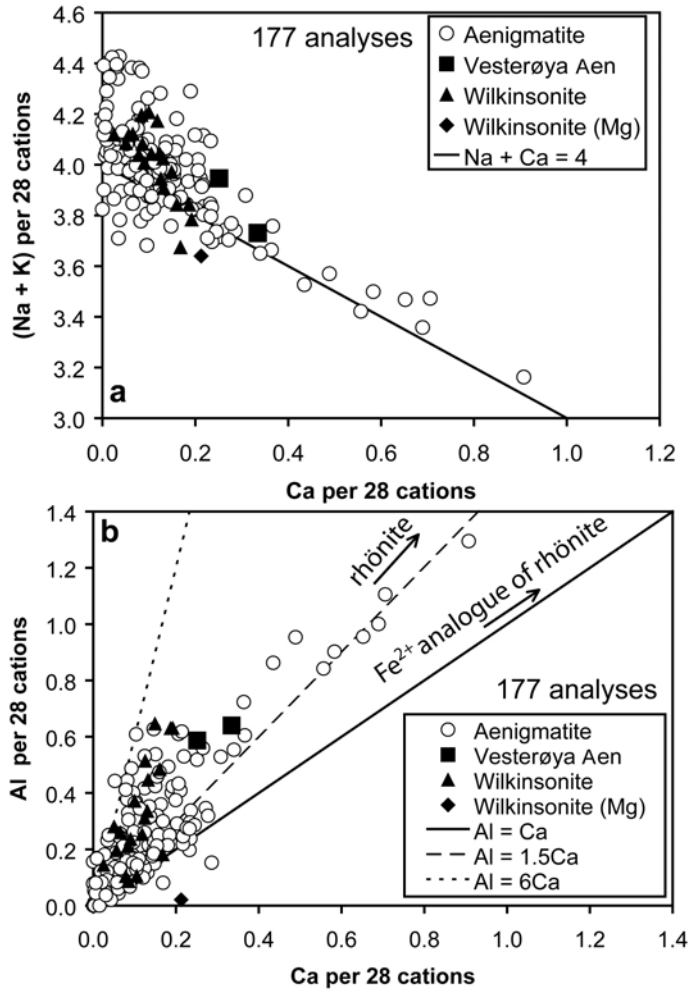
FIG. 8. Compositional variations of aenigmatite (Aen) and wilkinsonite as a function of Ca. Arrows in (*b*) point to the end-member composition of rhönite plus $Fe^{2+}Mg_{-1}$ and to the suggested end-member composition of the Fe^{2+} analogue of rhönite (Table 1). Vesterøya Aen refers to electron microprobe data on a sample from Vesterøya, Norway from which a crystal was used to newly refine the structure (Grew *et al.*, 2008). Wilkinsonite (Mg) refers to the unnamed Mg-dominant analogue reported by Gaeta and Mottana (1991). Other sources are given in the caption to Fig. 7.

1989); other minor constituents are Al_2O_3 (0.6 wt.%), TiO_2 (0.5 wt.%), CaO and MnO (0.1 wt.% each).

Rhönite, dorrite, makarochkinite, høgtuvaite

The Be-poor ferromagnesian silicates rhönite (including the Fe^{2+}-dominant analogue and rhönite in Ca-Al-rich inclusions in the Allende meteorite) and dorrite appear to constitute a complex solid solution involving several compo-

nents (e.g. Cosca *et al.*, 1988; Kunzmann, 1989, 1999). There is no evidence for a miscibility gap between dorrite and rhönite (Fig. 9) as Cosca *et al.* (1988) suggested on the basis of the many fewer compositions available to them. Total Ti ranges from nearly negligible in dorrite to over 4.5 atoms per 28 cations in Allende rhönite. However, there is a major change at Ti $\approx$ 3.1 atoms. For Ti < 3.1, with one exception (see below), formula calculation using stoichiometry and assuming all Ti is Ti^{4+} gives Fe^{3+}, whereas
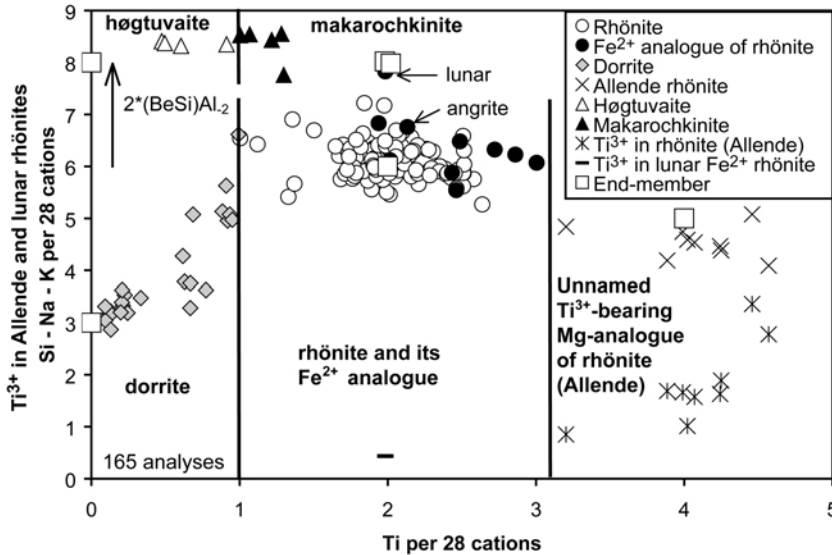
FIG. 9. Si and Ti contents of dorrite, rhönite and its Fe^{2+} analogue and its Ti^{3+}-bearing Mg analogue (Allende), høgtuvaite and makarochkinite (modelled on Kunzmann, 1999, Fig. 7 and Grew et al., 2005, Fig. 5). Except for analyses of makarochkinite and høgtuvaite for which Mössbauer data were available (Grauch et al., 1994; Grew et al., 2005), we calculated Fe^{3+}/Fe^{2+} ratio by assuming 28 cations and 40 oxygens (unless 28 cations gave all Fe as Fe^{3+}) whether or not Fe^{3+} had been measured directly in wet chemical analyses or calculated by the original authors from electron microprobe analyses. End-member compositions are given in Table 1 (compositions for makarochkinite and Fe^{2+} analogue of rhönite are superimposed, and thus the plotted squares are slightly displaced from the ideal value). Vertical arrow shows the effect of the substitution Be + Si $\rightleftharpoons$ 2Al, which relates høgtuvaite and makarochkinite to rhönite and its unnamed Fe^{2+} analogue. The vertical lines indicate species boundaries for the names in bold. Included with dorrite (diamonds) are the Fe^{3+}-rich 'melilite' of Foit et al. (1987), 'mineral X_1' of Havette et al. (1982) and several analyses given as 'rhönite' by Kunzmann (1989), Rondorf (1989) and Johnston and Stout, 1984. Two compositions approach a Fe-analogue: one from Luna 24 regolith (lunar, Treiman, 2008), and another from angrite NWA 4590, a meteorite (angrite, Kuehner and Irving, 2007). Sources of the other compositional data: Alletti et al. (2005); Boivin (1980); Bonaccorsi et al. (1990); Brooks et al. (1979); Cameron et al. (1970); Corsaro et al. (2007). Cosca et al. (1988); Downes et al. (1995); Fodor and Hanan (2000); Fuchs (1971, 1978); Gamble and Kyle (1987); Grapes et al. (2003); Grew et al. (2005); Grünhagen and Seck (1972); Hurai et al (2007); Jannot et al. (2005); Johnston and Stout (1985); Kunzmann (1989), Kyle and Price (1975); Magonthier and Velde (1976); Mao and Bell (1974); Mason and Taylor (1982); Nédli and Tóth (2003); Nishio et al. (1985); Olsson (1983); Polyakov et al. (1986); Prestvik et al. (1999); Simon et al. (1999); Soellner (1907); Timina et al. (2006); Warren et al. (2006).

for Ti > 3.1, this stoichiometric calculation gives negative Fe^{3+}. If we assume that all Fe is Fe^{2+}, then compositions with Ti > 3.1 give both Ti^{4+} and Ti^{3+}, and the latter increases with increasing total Ti. The only natural phase containing more than 3.1 Ti and calculated Ti^{3+} is rhönite from the Allende meteorite. 'Baykovite' ('baikovite'), a component of Si-Ti slag, is an isostructural phase containing 5.82−6.01 Ti, of which 3.63−3.76 is Ti^{3+} per 28 cations (Rudneva and Malysheva, 1960; Arakcheeva, 1995); an average formula from the reported data is $Ca_4(Ca_{0.3}Mg_{5.55}Al_{0.24}Ti^{3+}_{3.69}Ti^{4+}_{2.23})O_4[Si_{3.6}Al_{8.4}O_{36}]$.

Total Ca + Na + K (K is much subordinate to Na) sum close to 4 atoms per 28 cations in rhönite and dorrite (except for 5 of 8 compositions in the type dorrite sample), with up to nearly 40% substitution of Ca by Na+K (Fig. 10). Corsaro et al. (2007) reported up to 1.3 wt.% SrO (0.21 Sr per 28 cations). Al decreases in a 1:1 ratio with Ca (Fig. 11), which is not consistent with solid solution towards aenigmatite (cf. Fig. 8b). Most dorrite contains relatively little Na + K, but Ca > 4 atoms per 28 cations, implying Ca substitution at sites other than M8 and M9; up to 0.9 excess Ca per 28 cations is ordered at M5 in SFCA and
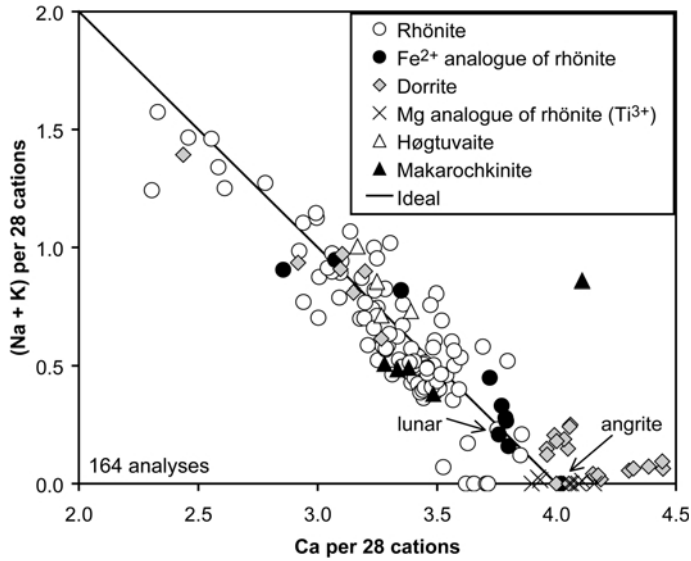
FIG. 10. Na and Ca contents of dorrite, rhönite and its Fe^{2+} analogue and its Ti^{3+}-bearing Mg analogue, høgtuvaite and makarochkinite. Allende rhönite containing 4.86 Ca (Fuchs, 1971) is not plotted. Ca content includes Sr in the 7 analyses reported by Corsaro *et al.* (2007). Other information and sources are given in the caption of Fig. 9.

SFCAM (Hamilton *et al.*, 1989, Mumme *et al.*, 1998; Sugiyama *et al.*, 2005) and 0.29 Ca at *M*5 and *M*6 in 'baykovite' (Arakcheeva, 1995). Al increases with Ca in rhönite and some dorrite (i.e. from Kauai, Hawaii, USA and Nickenicher-Sattel,

Eifel, Germany), a trend consistent with the substitution (Na, K) + Si $\rightleftharpoons$ Ca + Al (e.g. Kunzmann, 1989, 1999; this paper, Fig. 11). In dorrite from the type locality (Cosca *et al.*, 1988), Buffalo, Wyoming (Foit *et al.*, 1987) and from
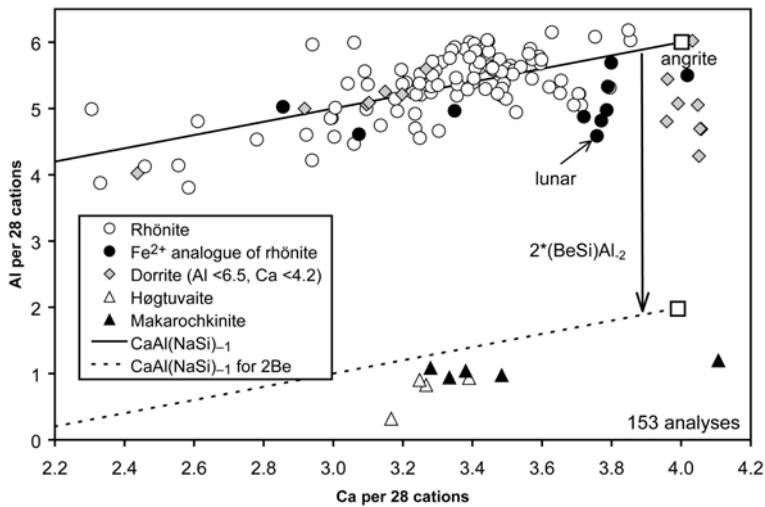

FIG. 11. Al and Ca contents of dorrite, rhönite and its Fe^{2+}-dominant analogue, høgtuvaite and makarochkinite. Unfilled squares correspond to end-members (Table 1). Arrow shows the effect of the substitution Be + Si $\rightleftharpoons$ 2Al. Ca content includes Sr in the 7 analyses reported by Corsaro *et al.* (2007). Other information and sources are given in the caption of Fig. 9.

Reunion Island (Havette *et al*., 1982), Al does not vary with Ca. In many of these compositions, Al ranges from 3 to 7 cations and Si < 4 cations per 28 cations, implying considerable Al $\rightleftharpoons$ Fe^{3+} substitution at tetrahedral sites as inferred by Cosca *et al*. (1988).

After deducting the amount equivalent to Na + K, Si increases with total Ti from 3 atoms per 28 cations in Ti-poor dorrite to an average of about 6.3 atoms (range is 5.5–7.8) at Ti = 2 atoms (ideal rhönite) and then decreases to 4.1–5.1 atoms in the Allende rhönite (Fig. 9).

Rhönite is the only sapphirine-group mineral reported to include compositions with both $Mg/(Mg + Fe^{2+}) > 0.5$ and $Mg/(Mg + Fe^{2+}) < 0.5$. Ten out of 122 rhönite compositions (excluding material in the Allende meteorite) accepted for plotting in Fig. 9 gave, after stoichiometric calculations, an excess of Fe^{2+} over Mg, e.g. $Mg/(Mg + Fe^{2+}) = 0.16$–0.42 for five samples from Saint-Leu, Reunion Island (Havette *et al*., 1982). Meteoritic (angrite) and lunar rhönite are also clearly Fe^{2+}-dominant with $Mg/(Mg + Fe^{2+}) = 0.17$ and 0.03, respectively. The latter is the only rhönite with a normal Ti content (~2 per 28 cations) to give Ti^{3+} when its formula is calculated on a 28 cation/40 oxygen basis (Fig. 9).

Manganese contents greater than 0.4 wt.% MnO have not been reported in rhönite, but up to 1.2 wt.% MnO has been found in dorrite (Nickenicher-Sattel, Eifel, Germany, Kunzmann, 1989 and pers. comm., 2007). Other constituents reported in rhönite include Cr (up to 3.27 wt.% Cr_2O_3 or 0.69 Cr per 28 cations from basanite, Tergesh Pipe, Siberia, Timina *et al*., 2006) and V (up to 3.32. wt.% V_2O_3 or 0.69 V per 28 cations, Allende meteorite, Mason and Taylor, 1982). Scandium (0.32–0.38 wt.% oxide) is also reported in rhönite from Allende (Simon *et al*., 1999). In contrast to aenigmatite, wilkinsonite, høgtuvaite and makarochkinite, high field-strength elements such as Nb and Zr have been very rarely sought in rhönite although it is likely they might substitute for Ti.

Høgtuvaite and makarochkinite are related by the substitution $Ti + Fe^{2+} \rightleftharpoons 2Fe^{3+}$ and form a solid solution series ranging from 0.5 to 1.3 Ti per 28 cations (Fig. 9). Mössbauer spectroscopy suggests that Fe^{3+} preferentially occupies the $M1$, $M2$ and $M7$ sites, and Fe^{2+}, the $M3$–$M6$ sites; only a few per cent Fe^{3+} was found at tetrahedral sites in the crystal structure refinements (Grew *et al*., 2005). Both minerals contain 9 Si (generally 8.5 Si after deduction for alkalis) and 1 Al per 28 cations,

which are related to the average Si and Al contents of rhönite by the substitution $2Be + 2Si \rightleftharpoons 4Al$ (Figs 9, 11). $X_{Mg} = 0.018$–0.19 for høgtuvaite and makarochkinite, which are significantly less magnesian than most rhönite. Phases intermediate in Be content between høgtuvaite-makarochkinite and rhönite-dorrite have not been reported. Elements reported in amounts exceeding 500 ppm in høgtuvaite and makarochkinite include Zn, Y, Sn, Nb, Ta and Th (Grauch *et al*., 1994; Grew *et al*., 2005).

Serendibite

The principal compositional variations in serendibite include the homovalent Fe $\rightleftharpoons$ Mg, Fe $\rightleftharpoons$ Al substitutions, and the heterovalent (Mg,Fe) + Si $\rightleftharpoons$ 2(Al,Fe) (Tschermaks) and Na + Si $\rightleftharpoons$ Ca + Al substitutions (Grew *et al*., 1991*a*; Van Derveer *et al*., 1993; Grew, 1996; Aleksandrov and Troneva, 2006). In terms of mole proportions (Mg,Fe,Mn)O, $(Al,Fe)_2O_3$, and SiO_2, Na-poor serendibite ranges from $SiO_2 = (Mg,Fe,Mn)O = 0.33$ (1:1:1 composition) to $SiO_2 = 0.36$ (4:3:4 composition, which was selected as the end-member, Table 1) via the Tschermaks substitution. Compositions of Na-bearing serendibite (with Na/(Na+Ca) ratio up to 0.15) are similar, but shifted to higher Si because of the substitution Na + Si $\rightleftharpoons$ Ca + Al. Boron content ranges 2.8–3.3 atoms per 28 cations in most analyses (2.91–3.26 B in three crystal-structure refinements, Van Derveer *et al*., 1993), whence our selection of 3 B in the end-member formula. Van Derveer *et al*. (1993) obtained ion microprobe B contents in two samples of 3.6 and 4.2 B atoms per 28 cations, which they attributed to analytical error. Savel'yeva *et al*. (1995) reported a serendibite from the Ozyorskiy massif near Lake Baikal, Russia that is poorer in Si than the 1:1:1 composition and having a total of 96.69 wt.%, suggesting a B_2O_3 content of 3–4 wt.%, equivalent to 1.3–1.7 B per 28 cations or about half that in the end-member formula. Composition of the Ozyorskiy serendibite in terms of the mole proportions (Mg,Fe,Mn)O, $(Al,Fe)_2O_3$ and SiO_2 is estimated to be 1:1.6:1 $(SiO_2 = 0.27)$, i.e. midway between 4:3:4 serendibite $(SiO_2 = 0.36)$ and ideal dorrite (1:3:1 composition, $SiO_2 = 0.2$). This could indicate possible miscibility between dorrite and serendibite but for the large difference between the two minerals in Fe^{3+} and Al contents calculated to occupy octahedral sites.

Possible Fe analogues constitute up to 26% of natural serendibite, whereas MnO, TiO_2 and other

potential constituents do not exceed 0.5 wt.% oxide. Total Fe as FeO ranges from 0.76 to 14.75 wt.%, the extremes being reported by Schmetzer *et al.* (2002) and Nicollet (1990), respectively. The most Fe-rich serendibite has Fe > Mg, but $X_{Fe^{2+}}$ could not be calculated from stoichiometry because there is no information on boron content. The maximum $X_{Fe^{2+}} = 0.26$ reported to date was calculated for a sample containing 13.34 wt.% Fe as FeO from the Tayozhnoye deposit, Siberia (Grew *et al.*, 1991*a*). The proportion of Fe^{3+} equals or exceeds Fe^{2+} content in most Fe-rich samples from this deposit and from the type locality (Grew *et al.*, 1991*a*, Van Derveer *et al.*, 1993). The latter authors reported no evidence for tetrahedrally coordinated Fe^{3+} in Tayozhnoye serendibite, and thus $Fe^{3+}/(Fe^{3+} + Al)$ ratio at octahedral sites can be calculated from bulk Fe^{3+}; it reaches 0.20 in these serendibite samples.

Welshite

Most welshite samples studied by Grew *et al.* (2007), which included the type specimen (Moore 1978) and one of the two samples analysed by Grew *et al.* (2001), had compositions intermediate between the end-member given in Table 1, $Ca_4(Mg_9Sb_3^{5+})O_4[Si_6Be_3AlFe_2^{3+}O_{36}]$, and an Fe-free equivalent, $Ca_4(Mg_9Sb_3^{5+})O_4[Si_6Be_3Al_3O_{36}]$, with the first being closer to the average. The 12 tetrahedral sites in these samples (type 1) can be split into two equal subsets: (1) Si + As = 6 with up to 0.6 As, and (2) Al + Fe + Be = 6 with Be ranging from 2.76 to 3.46 atoms per 28 cations and Al, from 0.99 to 2.47 atoms. Mn and Fe^{3+} are subordinate substituents at octahedral sites. However, two samples (type 2, including the second of the two samples analysed by Grew *et al.*, 2001) showed much greater variation related by the coupled substitution $^MSb^{5+} + {}^{vi}Mg^{2+} + {}^{iv}Fe^{3+} \rightleftharpoons {}^MFe^{3+} + {}^{vi}Fe^{3+} + {}^{iv}Si^{4+}$, where M refers specifically to the $M7$, $M3A$ and $M4A$ octahedral sites. This substitution relates the end-member given in Table 1, $Ca_4(Mg_9Sb_3^{5+})O_4[Si_6Be_3Al Fe_2^{3+}O_{36}]$, with a hypothetical Sb-free end-member, $Ca_4(Mg_6Fe_6^{3+})O_4[Si_9Be_3O_{36}]$ if Al and Fe^{3+} are considered together. The lowest measured Sb reported by Grew *et al.* (2007) is 1.45 atoms per 28 cations in one compositional zone of a highly heterogeneous grain of type 2 welshite, about midway between the two end-members. A partial single-crystal refinement of a fragment from this grain found 1.64 Sb that appears to be partially disordered at $M7$, $M3A$ and $M4A$, which are fully occupied by Sb in type 1 welshite (Sb = 3).

Surinamite

Surinamite compositions closely approach the ideal formula (Table 1) with 12−25% of Fe^{2+} substitution for Mg and 0−13% of Fe^{3+} substitution of ^{vi}Al (Baba *et al.*, 2000; Grew *et al.*, 2000; Barbier *et al.*, 2002). Proportions of Fe^{2+} and Fe^{3+} were calculated from stoichiometry using ideal or measured Be content, but in one case, Fe^{2+}/Fe^{3+} ratio was determined by crystal structure refinement and Mössbauer spectroscopy. MnO contents do not exceed 2 wt.%, whereas other constituents are present in amounts not exceeding a few tenths wt.%, e.g. $\leqslant 0.33$ wt.% P_2O_5 (Grew, 2002). Ion microprobe analyses of surinamite from South Harris, Scotland gave a deficiency of 0.18−0.23 Be per 11 cations relative to the ideal formula with the charge balanced by a corresponding addition of divalent cations at the octahedral sites (Baba *et al.*, 2000), i.e. by solid solution of 18−23% of a Be-free analogue of surinamite, $Mg_4Al_2O[Si_3Al_2O_{15}]$, which Christy and Putnis (1988) suggested could also be present as one-cell wide lamellae associated with stacking faults in sapphirine from Finero, Italy.

Recommended nomenclature

Introduction

To date, recognizing distinct mineral species in the sapphirine supergroup has been *ad hoc*. This approach was tolerated because most members are distinct from one another in more than one compositional variable, and their recognition as distinct species did not raise a problem. However, other members, notably rhönite-dorrite-høgtuvaite-makarochkinite solid solutions in which Mg, Fe and Ti are the dominant cations at octahedral sites, raised nomenclature problems. There is a large number of sites with extensive cation disorder, and there are ambiguities in determining the valence of Fe and Ti from electron microprobe analyses. The crystal structures of relatively few samples have been refined (Table 2), and even crystal-structure refinements provide only broad constraints on Fe and Ti valence. For example, the distinction between makarochkinite and høgtuvaite could only be established by single crystal refinement that demonstrated that Ti is ordered at the $M7$ site. Ordering of Ti at $M7$ also distinguishes rhönite

from dorrite. However, Mg and Ti are disordered in rhönite from the Allende meteorite, and Ti is not the dominant cation at $M7$ (Bonaccorsi *et al.*, 1990). Tetrahedral compositions also raise questions. For example, høgtuvaite was originally approved as a species distinct from rhönite because its Be content approached 1 atom per 20 O, i.e. Be appeared to fill one tetrahedral site. However, structure refinements show that that Be is split about equally between two T sites in both høgtuvaite and makarochkinite, that is, one of the two makarochkinite samples studied by Grew *et al.* (2005) would have been called Fe^{2+}-dominant, Be-bearing rhönite if the 50% rule (Nickel and Grice, 1998) had been strictly applied to each of the Be-bearing tetrahedral sites.

The recommended classification (Table 4) was developed to address these problems. It makes extensive use of precedent, but applies the rules to all known natural compositions (Tables 4 and 5), with flexibility to allow for yet undiscovered compositions such as those reported in synthetic materials (Table 6). Because the sapphirine supergroup is a polysomatic series, the first level of classification is based on polysome, that is, each group within the supergroup corresponds to a single polysome. This polysomatic series consists of pyroxene (or pyroxene-like, P) and spinel (S) modules. Using the notation of Zvyagin and Merlino (2003), two polysomes have been found in nature, $<(P/2)S(P/2)>$ (sapphirine group) and $<PSP>$ (surinamite), where P/2 refers to half a pyroxene module included in an order-disorder or OD layer; $<(P/2)S(P/2)>$ can be simplified to $<PS>$ with a composition $M_{28}O_{40}$.

The sapphirine group is divided into subgroups according to the occupancy of the two largest M sites ($M5$ and $M6$ in the sapphirine subgroup, $M8$ and $M9$ in the other subgroups), followed by division by occupancy of the smallest M site ($M7$

in all subgroups), then by occupancies of the most polymerized T sites, and lastly by $Mg/(Mg+Fe^{2+})$ ratio at the $M1$−$M6$ sites ($M1$−$M4$, $M8$−$M9$ in sapphirine). Further splitting of the supergroup based on occupancies other than those specified below is not recommended.

The only other polysome found in nature, $<PSP>$ (or $<PPS>$) has the formula $M_{22}O_{32}$, and is represented by the beryllosilicate surinamite. Christy and Putnis (1988) suggested that a Be-free analogue of surinamite could be present as lamellae in sapphirine, implying that subdivisions of $<PPS>$ analogous to those for $<PS>$ may eventually be needed in a surinamite group.

Two other polysomes $<SSP>$, $M_{20}O_{28}$ and $<SSPSP>$, $M_{34}O_{48}$ have been synthesized (Table 6), respectively, the Ca-Al ferrites $CaFe_3AlO_7$ and SFCA-I (Arakcheeva *et al.*, 1991; Mumme *et al.*, 1998) and SFCA-II (Mumme, 2003). Examples of the $<P>$, $<S>$, $<PS>$, $<PPS>$ and $<SSP>$ polysomes were illustrated by Merlino and Pasero (1997).

Sapphirine subgroup − a special case

Sapphirine-2*M* and khmaralite are not topologically identical to sapphirine-1*A* and minerals in the aenigmatite and rhönite subgroups. Nonetheless, we have decided to let the similarities in chemical composition, specifically, dominance of Mg at the $M5$ and $M6$ sites, override the differences in crystal structure by including both polytypes of sapphirine and khmaralite in the sapphirine subgroup.

First level: ‹PS› polysome, Sapphirine group
Second level: Two largest M sites.

Occupancy at the $M8$ and $M9$ sites is used to distinguish the three known subgroups, namely

TABLE 5. Examples of compositions in the sapphirine group containing substantial amounts of a potential new species, but not enough to qualify as new

	Sapphirine subgroup	
B analogue of sapphirine	$Mg_4(Mg_3Al_9)O_4[Si_3B_2Al_7O_{36}]$	Grew *et al.* (1990, 1991*b*, 1992) up to 25% of the B analogue
	Aenigmatite subgroup	
Mg analogue of aenigmatite	$Na_4(Mg_{10}Ti_2)O_4[Si_{12}O_{36}]$	Price *et al.* (1985 and unpublished data) reported $Mg/(Mg + Fe^{2+})$ up to 0.48

TABLE 6. Compounds related to the sapphirine supergroup, either synthetic or not strictly natural.

<table>
<tr><td colspan="3" align="center">Sapphirine group: <PS> Polysome</td></tr>
<tr><td colspan="3">Sapphirine subgroup</td></tr>
<tr><td>Cr dominant analogue
of sapphirine (synthetic)</td><td>$Mg_4(Mg_{3.8}Cr_{6.7}Al_{1.4})O_4[Si_{4.2}Al_{7.8}O_{36}]$</td><td>Brigida *et al.* (2007)</td></tr>
<tr><td>Ga, Ge analogues
of sapphirine-1*A*
(synthetic) $P\bar{1}$</td><td>$Mg_4(Mg_2Ga_{10})O_4[Ge_2Ga_{10}O_{36}]$ (3:5:1) to
$Mg_4(Mg_8Ga_4)O_4[Ge_8Ga_4O_{36}]$ (3:1:2)</td><td>Barbier (1990, 1998)</td></tr>
<tr><td colspan="3">Aenigmatite subgroup</td></tr>
<tr><td>Synthetic $P\bar{1}$</td><td>$Na_4(Mg_{8.5}Fe^{3+}_3Si_{0.5})O_4[Si_{12}O_{36}]$ to
$Na_4(Mg_9Fe^{3+}_2Si)O_4[Si_{12}O_{36}]$</td><td>Gasparik *et al.* (1999)</td></tr>
<tr><td>Synthetic $P\bar{1}$</td><td>$Na_4Mg_{12}(OH)_4[Si_{12}O_{36}]$</td><td>Yang and Konzett (2000)</td></tr>
<tr><td>Synthetic $P\bar{1}$</td><td>$Na_4Mg_{7.2}Fe^{3+}_{4.8}O_4[Ge_{11.2}Fe^{3+}_{0.8}O_{36}]$</td><td>Barbier (1995)</td></tr>
<tr><td>Synthetic $P\bar{1}$</td><td>$Na_4(Na_{1.48}Mn^{2+}_{5.54}Mn^{3+}_{4.98})O_4[Ge_{12}O_{36}]$</td><td>Redhammer *et al.* (2008)</td></tr>
<tr><td colspan="3">Rhönite subgroup:</td></tr>
<tr><td>'Baykovite'
(synthetic) $P\bar{1}$</td><td>$Ca_4(Ca_{0.3}Mg_{5.55}Al_{0.24}Ti^{3+}_{3.69}Ti^{4+}_{2.23})O_4[Si_{3.6}Al_{8.4}O_{36}]$</td><td>Rudneva and Malysheva, 1960);
Arakcheeva (1995)</td></tr>
<tr><td>'Leucorhönite'*</td><td>$Ca_4(Ca_{0.4}Mg_{6.8}Fe^{2+}_{1.1}Fe^{3+}_{2.1}Al_{1.5}Ti_{0.1})O_4[Si_{8.3}Al_{3.7}O_{36}]$</td><td>Chesnokov *et al.* (1994)</td></tr>
<tr><td>'Malakhovite'*
(cf. SFCA)</td><td>$Ca_4(Ca_{0.7}Mg_{1.3}Fe^{2+}_{0.7}Fe^{3+}_{9.2}Ti_{0.1})O_4[Si_{2.6}Al_{2.6}Fe^{3+}_{6.8}O_{36}]$</td><td>Chesnokov *et al.* (1993)</td></tr>
<tr><td>SFCA
(synthetic) $P\bar{1}$</td><td>$Ca_4(Ca_{0.6}Mg_{1.6}Fe^{3+}_{9.8})O_4[Si_{2.2}Al_{3.0}Fe^{3+}_{6.8}O_{36}]^†$</td><td>Mumme *et al.* (1988);
Hamilton *et al.* (1989)</td></tr>
<tr><td>SFCAM
(synthetic) $P\bar{1}$</td><td>$Ca_4(Ca,Fe,Mg,Al)_{12}O_4[(Fe,Al,Si)_{12}O_{36}]$</td><td>Sugiyama *et al.* (2005)</td></tr>
<tr><td>CSVA
(synthetic) $P\bar{1}$</td><td>$Ca_4(Mn_{0.024}Fe_{0.026}Mg_1Al_{5.5}Ti_{0.3}V_{5.15})O_4[Si_{2.36}Al_{9.64}O_{36}]$</td><td>Arakcheeva and Ivanov (1993)</td></tr>
<tr><td colspan="3" align="center">Surinamite group: <PPS> Polysome</td></tr>
<tr><td>Al, Ge analogue
of surinamite (synthetic)
*C*2/*c* and *P*2/*n*</td><td>$Mg_4Al_2O[Ge_3Al_2O_{15}]$</td><td>Barbier (1996)</td></tr>
<tr><td>Ga, Ge analogue
of surinamite (synthetic)
*C*2/*c*</td><td>$Mg_4Ga_2O[Ge_3Ga_2O_{15}]$</td><td>Barbier (1996, 1998)</td></tr>
<tr><td colspan="3" align="center"><SSP> Polysome</td></tr>
<tr><td>Synthetic ferrite
$P\bar{1}$</td><td>$Ca_{7.12}Fe^{2+}_{0.88}Fe^{3+}_{23.82}Al_{8.18}O_{56}$ ('$CaFe_3AlO_7$')</td><td>Arakcheeva *et al.* (1991)</td></tr>
<tr><td>SFCA-I
(synthetic) $P\bar{1}$</td><td>$Ca_{3.18}Fe^{2+}_{0.82}Fe^{3+}_{14.66}Al_{1.34}O_{28}$</td><td>Mumme *et al.* (1998)</td></tr>
<tr><td colspan="3" align="center"><SSPSP> Polysome</td></tr>
<tr><td>SFCA-II
(synthetic $P\bar{1}$)</td><td>$Ca_{5.1}Fe^{2+}_{0.9}Fe^{3+}_{18.7}Al_{9.3}O_{48}$</td><td>Mumme (2003)</td></tr>
</table>

* Combustion products found in waste dumps of coal mines in the Chelyabinsk basin. These products are considered to be substances formed by human intervention, and thus are not minerals (Nickel and Grice, 1998).
† Formula is written assuming Al is all tetrahedrally coordinated, but an undetermined amount might be octahedrally coordinated (Hamilton *et al.*, 1989).

sapphirine (Mg), aenigmatite (Na), and rhönite (Ca); the corresponding sites in sapphirine-1A are $M5$ and $M6$ (Tables 2 and 3). Na and Ca at these two sites are largely disordered, so that the two sites can be considered as a unit in distinguishing the aenigmatite and rhönite subgroups. Na content (cut off at 2 Na per 28 cations) is the most readily applied measure. Calcium could also occupy the $M5$ and $M6$ sites, which has been reported in synthetic compounds (Hamilton *et al.*, 1989; Arakcheeva, 1995; Sugiyama *et al.*, 2005). In solid solutions between serendibite and sapphirine-1A, i.e. Ca- and B-bearing sapphirine (Grew *et al.*, 1992), Ca, Na and Mg presumably occupy the $M5$ and $M6$ sites, but it is not known whether there is any ordering. The report of a Fe-Sn-Ga-Ge phase possibly isostructural with sapphirine (Johan and Oudin, 1986) suggests the possibility of a Fe^{2+}-dominant subgroup. No mineral approaches an Mn-dominant subgroup: the maximum reported is 0.2 Mn at $M8$ and $M9$ in makarochkinite, i.e. 5% occupancy at each site (Grew *et al.*, 2005).

Third level: M7 site

Occupancy at the $M7$ site is used to distinguish species within the aenigmatite subgroup and species or clusters of species within the rhönite subgroup; Al is dominant in both species of the sapphirine subgroup. In most cases, smaller, more highly charged cations, principally Al (sapphirine, serendibite), Ti^{4+} (aenigmatite, rhönite, makarochkinite), Cr^{3+} (krinovite), and Nb^{5+} are ordered at $M7$. Fe^{3+} is the dominant cation at $M7$ in høgtuvaite and wilkinsonite (Grew *et al.*, 2005; Burt *et al.*, 2007), and presumably also in dorrite by analogy with similar synthetic compounds (Hamilton *et al*, 1989; Mumme *et al.*, 1998; Sugiyama *et al.*, 2005). Figure 7a illustrates the substitution $^{vi}Ti + {}^{vi}Fe^{2+} \rightleftharpoons 2^{vi}Fe^{3+}$ relating aenigmatite and wilkinsonite. Rhönite-like minerals but with Ti < 1 per 28 cations are dorrite (Fig. 9), e.g. 'rhönite' from Kauai, Hawaii, USA (Johnston and Stout, 1984) and Nickenicher-Sattel (alternative name, Eicher Sattel), Eifel, Germany (Kunzmann, 1989 and pers. comm., 2007; Rondorf, 1989). In addition, Cosca *et al.* (1988) recognized an unknown (X_1, Havette *et al.*, 1982) and Fe^{3+}-rich melilite (Foit *et al.*, 1987) as dorrite.

Welshite and Allende rhönite are distinct from the others in that Mg and Sb^{5+} or Ti are present in roughly equal amounts at $M7$, but the ordering in these two phases differs. Welshite lacks a centre of symmetry and the $M7$ site is split into two sites. In the sample for which a refinement is available, $M7$ and $M7A$ are fully occupied by Sb and Mg, respectively, i.e. ordering of Sb and Mg is complete within the error of the refinement. The presence of welshite containing only 1.45 Sb per 28 cations (*vs.* 3 in the ideal formula) and 3.44 Fe^{3+} at octahedral sites suggests the possibility of a Fe^{3+}-dominant analogue of welshite with Fe^{3+} > (Sb + Mg) at $M7$ and $M7A$, but this could not be demonstrated by single-crystal refinement (Grew *et al.*, 2007). In contrast, Ti is not ordered at $M7$ in rhönite from the Allende meteorite. Bonaccorsi *et al.* (1990) refined the occupancy at $M7$ in a crystal from Allende to be 44% Ti, 56% Mg and gave a formula for the analysed crystal as $^{M8,M9}(Ca_4)^{M5,M6}(Mg_{3.4}Fe^{2+}_{0.6})^{M1-M4,M7}(Mg_{2.4}Al V_{0.6}Ti^{3+}_{1.6}Ti^{4+}_{2.4})O_4[Si_4Al_8O_{36}]$. Thus, the Allende rhönite does not qualify either as rhönite (Ti^{4+}-dominant at $M7$) or dorrite (Fe^{3+}-dominant at $M7$). We suggest that Allende rhönite be considered a distinct species with Mg dominant at $M7$.

Although $^{vi}Fe^{3+}/(^{vi}Fe^{3+} + {}^{vi}Al)$ ratio reaches 0.20 in a serendibite from the Tayozhnoye deposit (see above), $Fe^{3+}/(Fe^{3+} + Al) = 0.091$ at $M7$ in this sample (5152, Van Derveer *et al.*, 1993), i.e. this sample contains only 9% of the Fe^{3+} analogue of serendibite.

Gasparik *et al.* (1999) synthesized Mg-analogues of wilkinsonite with Si > 12 atoms per 28 cations at 13−14 GPa and 1450−1700ºC, i.e. Si occupies octahedral sites. One refinement gave 0.806 (Mg, Si) + 0.194 Fe^{3+} at $M7$ and a relatively short <$M7-O$> of 1.981 Å, which suggests that Si could a major constituent at this site, but leaves open the question whether it is the most abundant.

Fourth level: Most polymerized T sites

Occupancy at the $T2$ and $T3$ sites in the sapphirine subgroup ($T1$ and $T4$ in the other subgroups), which are the most polymerized in the sapphirine group (Q^3 in the terminology of Christy *et al.*, 1992), is used to distinguish species within clusters defined by $M7$ occupancy. Following Grew *et al.* (2005), we recommend considering the two Q^3 sites together. These two sites are occupied by Si or by Si and Al in roughly equal amounts in the aenigmatite subgroup and rhönite. Si dominance at the two sites was inferred for the relatively Mg- and Si-rich dorrite-like synthetic ferrite, SFCAM (Sugiyama *et al.*, 2005), whereas in SFCA containing less Si and little or no Mg, Si is dominant at $T4$ but absent at $T1$ (Hamilton *et al.*, 1989; Mumme *et*

al., 1998). Only Al is reported at the two Q^3 sites in Si-free ferrite (Mumme, 2003). In the three sapphirines for which crystal structures are available (Moore, 1969; Higgins and Ribbe, 1979; Merlino, 1980), Si is the dominant cation at these two sites (Tables 2 and 3), an occupancy that Christy *et al.* (1992) attributed to preference for Si−O−Al bridges. Al would be the dominant cation at these two T sites in sapphirine containing less than 2 Si per 28 cations (Fig. 6), i.e. less Si than the composition $Mg_6Al_{10}O_4[Si_2Al_{10}O_{36}]$. Such sapphirine would be a distinct species, the Al-dominant analogue. Sabau *et al.* (2002) reported a sapphirine with 1.709 Si per 28 cations, which is the only composition we found that would qualify as an Al-dominant analogue of sapphirine. According to Christy *et al.* (1992), sapphirine compositions with Si < 2 appear to be unstable relative to spinel-bearing assemblages, and thus this species is expected to be rare.

In høgtuvaite, makarochkinite, serendibite and khmaralite, Be and B are markedly ordered at both sites relative to the other T sites. Linkage between T1 and T4 (rhönite subgroup) precludes the presence of significantly more than 50% Be at both sites simultaneously in relatively disordered structures, e.g. respectively, 44−48% and 46−52% in makarochkinite and, respectively, 50% and 51% in høgtuvaite as Be−O−Be bridges would result in underbonding of the bridging O (Christy *et al.*, 2002; Grew *et al.*, 2005). If the two sites are considered together, the Be content in end-member formulae is 2 per 28 cations, equivalent to filling one tetrahedral site. In more ordered structures, occupancy reaches 100% Be (welshite) and 70% Be (khmaralite), so the 50% rule could be applied to one site. Nonetheless, we would prefer to have a criterion based on bulk chemistry that would be applicable to all sapphirine-group minerals. Khmaralite was distinguished from sapphirine by both the presence of a superstructure (doubled chain periodicity) and Be ordering (Barbier *et al.* 1999), but in the present nomenclature, the critical distinction is Be > 1 atom per 28 cations in khmaralite, which is roughly coincident with appearance of the superstructure (Grew *et al.*, 2000). Christy *et al.* (2002) described a synthetic beryllian sapphirine containing up to 2 Be per 28 cations, e.g. $Mg_4(Mg_4Al_8)O_4[Al_4Be_2Si_6O_{36}]$, but lacking the superstructure characteristic of khmaralite. The synthetic sapphirine is dominantly the 1A polytype with lamellae of the 2M polytype. In

principle, if such a sapphirine were found naturally, it would be a species distinct from khmaralite because it would lack the superstructure characteristic of khmaralite.

By analogy with Be, we group the sites for B, although B−O−B bridges are tolerated in serendibite, and B occupancy at T1 and T4 can simultaneously exceed 50% by a significant amount, reaching 65% and 98%, respectively, in serendibite (Van Derveer *et al.*, 1993). The possibility of a B-dominant analogue of sapphirine is suggested by the average composition reported by Grew *et al.* (1992) from Johnsburg, New York. The B content of the average (0.84 B per 28 cations) corresponds to 10% serendibite and 25% of a B-analogue of sapphirine, $Mg_4(Mg_3Al_9)O_4[Si_3B_2Al_7O_{36}]$ (Table 1). Although 25% is not sufficient to define a new species, study of the Johnsburg sample at higher resolution than was possible by Grew *et al.* (1992) might reveal patches containing more of the $Mg_4(Mg_3Al_9)O_4$ $[Si_3B_2Al_7O_{36}]$ end-member than of either of the serendibite or B-free sapphirine end-members, and thereby qualify as a new B-dominant analogue of sapphirine distinct from serendibite. TEM study indicates that the sapphirine grains are uniformly sapphirine-1A despite their chemical heterogeneity (Grew *et al.*, 1992).

Ge and Ga are potential substituents at the T2(T4) and T3(T1) sites. There is a Fe-Sn-Ga-Ge mineral possibly isostructural with sapphirine (Johan and Oudin, 1986) and several synthetic compounds (Table 6), i.e. a Mg- and Ge-analogue of wilkinsonite (Barbier, 1995) and Ga- and Ge analogues of sapphirine-1A with $MgO:Ga_2O_3:GeO_2$ ratios ranging from 3:5:1 almost to 3:1:2 (Barbier, 1990; 1998). A Na-Mn^{2+}-Mn^{3+} germanate isostructural with aenigmatite has been synthesized without any Ga (Redhammer *et al.*, 2008).

Fifth level: Mg/(Mg + Fe²⁺) ratio

A final criterion is Mg/(Mg + Fe^{2+}) = X_{Mg} ratio at M1−M6 sites (M1−M4, M8−M9 in sapphirine). With rare exception, each mineral listed in Table 1 has been found to be either Mg-dominant, i.e. X_{Mg} > 0.5, or Fe^{2+}-dominant, i.e. X_{Mg} < 0.5, at these M sites. However, X_{Mg} ranges from 1.00 to 0.03 in material described as rhönite. In this case, the 10 analyses giving X_{Mg} < 0.5 correspond to the Fe^{2+}-dominant analogue, which is a distinct species (Table 4). The most magnesian wilkinsonite (X_{Mg} = 0.53) is poten-

tially a distinct species, and the most magnesian aenigmatite reported to date, $X_{Mg} = 0.48$ (Table 5), suggests the possibility of finding the Mg-dominant analogue of aenigmatite, which would also be a distinct species.

According to Hatert and Burke (2008), this criterion could be expanded to include other divalent cations at the $M1-M6$ sites ($M1-M4$, $M8-M9$ in sapphirine) resulting in ternary and higher order solid solutions, e.g. Mn, which is a significant, albeit subordinate, constituent at these sites in welshite, but is minor in other sapphirine-group minerals.

Other criteria

Further breakdown is possible because larger octahedral cations tend to be ordered at the $M5$ and $M6$ sites and larger tetrahedral cations at the $T5$ and $T6$ sites. However, in many cases occupancies at these sites are correlated with occupancies at the sites used to distinguish the different species, e.g. Fe ordering at M sites is correlated with presence of Be in khmaralite (Barbier *et al.*, 1999). Grew *et al.* (2007) suggested the possibility of splitting out species in welshite based on the dominance of Fe^{3+} and Al at $T5$ and $T6A$. However, in one sample, tetrahedral Fe^{3+} content is correlated with Sb content. Tetrahedral Fe^{3+} content in dorrite from the type locality is calculated to range from 0.4 to 5.5 atoms per 28 cations (Cosca *et al.*, 1988), suggesting the possibility of Fe^{3+} dominance at $T5$ and $T6$ in some samples but Al dominance in others, i.e. two species could be split out on the basis of $T5$ and $T6$ occupancy. However, further splitting would result in a needless proliferation of species, and is not consistent with earlier decisions by the CNMNC on sapphirine-group minerals.

A special case is OH. Minerals of the sapphirine group are presumed to be anhydrous, and crystal structure refinements show no evidence for the presence of OH in natural material. However, an OH-bearing, Ti-free Mg analogue of aenigmatite has been synthesized at 10 GPa and 1250ºC (Yang and Konzett, 2000), suggesting the possibility of OH incorporation at high pressure.

First level: ‹PPS› polysome, surinamite group

This group contains only one natural member that is found as an independent phase, surinamite, and the designation of group anticipates discovery of other members. Christy and Putnis (1988)

suggested that lamellae associated with stacking faults in sapphirine from Finero, Italy could be a Be-free analogue of surinamite. By analogy with the sapphirine group, the criterion for distinguishing the Be-free analogue would be occupancy of Al or Si instead of Be at the $T1$ site. Barbier (1996, 1998) synthesized Ge- and Ga-analogues of Be-free surinamite in one of which Ga and Ge occupy the $T1$ site (Table 6).

Possible new names and species

The new nomenclature does not result in new names for existing species. Names in current usage (Tables 1, 4) remain unchanged. However, new names would be required for the compositions that we suggest are sufficiently distinct to be recognized as new species in the above section outlining our nomenclature. It would be premature for us to propose specific names here, but only to summarize the compositional features indicating that the minerals in question are distinct from recognized species.

Unnamed Al-analogue of sapphirine

Sabau *et al.* (2002) reported a peraluminous sapphirine from the South Carpathians, Romania, for which the calculated formula contained only 1.71 Si per 28 cations, i.e. less Si than the composition $Mg_6Al_{10}O_4[Si_2Al_{10}O_{36}]$ (Fig. 6). In such a sapphirine, Al would be the dominant cation at the $T2$ and $T3$ sites, i.e. the Al-dominant analogue of sapphirine.

Unnamed Mg-analogue of wilkinsonite

Recalculation of the analysis of wilkinsonite in a syenitic ejectum from the inner caldera of the Wonchi volcano, Ethiopia (Gaeta and Mottana, 1991) gave X_{Mg} (as Mg/(Mg + Fe^{2+} Mn + Ni) = 0.47, $X_{Fe^{2+}} = 0.42$, $X_{Mn} = 0.10$ and $X_{Ni} = 0.01$, i.e. Mg is the dominant divalent cation presumed to occupy the $M1-M6$ sites. In principle the mineral would be a new species because of the rule of the dominant constituent for homovalent ternary solid solutions (Hatert and Burke, 2008). However, given the relatively small excess of Mg over Fe^{2+} and the large error in calculating Fe^{3+}/Fe^{2+} ratio from stoichiometry, its species status is less certain than that for nearly end-member Fe^{2+}- analogue of rhönite (see below). The formula calculated for the Wonchi wilkinsonite implies that not only is there significantly more octahedral Fe^{3+} and less total

divalent cations than in other wilkinsonite, but also significant Fe^{3+} is substituting for Si at tetrahedral sites (the composition cannot be plotted in Fig. 7), whence the different formula given for a possible Mg analogue in Table 1.

Unnamed Fe²⁺-analogue of rhönite

Recalculation of analyses of rhönite from (1) phonolitic differentiate, Puy de Saint-Sandoux, Auvergne, France (Grünhagen and Seck, 1972), (2) coral penetrated by basalt at Saint-Leu, Reunion Island (Havette *et al.*, 1982), (3) basanite, Scania, Sweden (Olsson, 1983) and (4) a spinel-wehrlite xenolith from Foster Crater, McMurdo Volcanic Group, Antarctica (Gamble and Kyle, 1987) gave $Mg/(Mg + Fe^{2+}) = 0.156-0.499$. In addition, $Mg/(Mg + Fe^{2+}) = 0.17$ and 0.03 in rhönite from angrite Northwest Africa 4590 (Kuehner and Irving, 2007) and the Luna 24 regolith (Treiman, 2008), respectively, and identity of the analysed grain in Luna 24 as rhönite was confirmed by Raman spectroscopy. Even allowing for the large uncertainty in the calculation based on stoichiometry, we conclude that most of these rhönite samples are clearly Fe^{2+}-dominant and distinct from other rhönite, i.e. they are the Fe^{2+}-dominant analogue. Many of the compositions are also distinct in other ways, e.g. the Reunion Island rhönite contains more Ti than most (2.43−3.00 Ti per 28 cations, Fig. 9). Trivalent cations at the *M* sites in this and the angrite rhönite are calculated to total 0−1.5 per 28 cations, less than in the end-member formula for rhönite. Our proposed end-formula for the unnamed Fe-analogue of rhönite (Table 1) approximates Treiman's (2008) formula of the lunar rhönite, although its composition differs in its high Si and low Al contents from other rhönite (Figs 9, 11)

Unnamed Ti³⁺-bearing Mg-analogue of rhönite

Rhönite that is associated with melilite, 'fassaite', spinel and perovskite in inclusions in the Allende meteorite contains 3.20 to 4.57 Ti per 28 cations (Fuchs, 1971, 1978; Mao and Bell, 1974; Mason and Taylor, 1982; Simon *et al.*, 1999) and the calculated proportion of Ti^{3+} increases with total Ti (Fig. 9). Ti is not ordered at *M*7; instead, Mg is dominant at this site (Bonaccorsi *et al.*, 1990), an *M*7 occupancy that distinguishes the Allende mineral from both rhönite (Ti^{4+}-dominant) and dorrite (Fe^{3+}-dominant). A salient feature of the

Allende mineral is the identity of the most abundant octahedrally coordinated trivalent cation: Ti^{3+} *vs.* Fe^{3+} in rhönite and its Fe^{2+} analogue (except one), whence the rationale for calling the Allende mineral an unnamed Ti^{3+}-bearing Mg-analogue of rhönite.

Unnamed Fe-Sn-Ga-Ge mineral

Johan and Oudin (1986) reported a Fe-Sn-Ga-Ge mineral in grains about 15 μm across in sphalerite from Montauban, Haute Garonne, France. The grains have pseudohexagonal outlines. In calculating formulae from electron microprobe analyses, Johan and Oudin (1986) reported that assuming 7 cations and 10 oxygens gave a better stoichiometry (e.g. Table 7) than assuming 3 cations and 4 oxygens (spinel stoichiometry); our attempt to calculate a formula assuming 3 cations and 4 oxygens from the six published analyses gave negative Fe^{3+} contents (from 10 to 12 wt.% Fe_2O_3). It is thus unlikely the mineral is a spinel, and we concur with the conclusion

TABLE 7. Selected compositions of unnamed Fe-Sn-Ga-Ge mineral (from Johan and Oudin, 1986)

Analysis	3	6
	Wt.%	
GeO_2	8.68	5.07
SnO_2	14.63	13.12
Fe_2O_3	5.97	4.34
Ga_2O_3	45.94	55.33
MnO	0.74	0.85
FeO	19.79	15.90
ZnO	3.93	4.46
Sum	99.68	99.07
	Formulae	
Ge	2.153	1.270
^{iv}Ga	9.847	10.730
Sum *T*	12.000	12.000
Sn	2.518	2.281
^{vi}Ga	2.869	4.741
Fe^{3+}	1.941	1.426
Zn	1.253	1.436
Mn	0.271	0.314
Fe^{2+}	7.148	5.801
Sum *M*	16.000	15.999

Electron microprobe analyses. Formula and Fe^{3+}/Fe^{2+} ratio calculated assuming 28 cations and 40 oxygens.

reached by Johan and Oudin (1986) that the mineral could be related to sapphirine. Nonetheless, XRD data will be needed to confirm the relationship. The analysed grains range in Ga_2O_3 content from 45.9 to 55.3 wt.% (e.g. Table 7) and the most important substitution appears to be $^{iv}Ge + {}^{vi}Fe^{2+} \rightleftharpoons {}^{iv}Ga + {}^{vi}Ga$, but substitutions such as $^{vi}Sn + {}^{vi}Fe^{2+} \rightleftharpoons 2^{vi}Ga$ and $Fe^{3+} \rightleftharpoons Ga$ (at either M or T sites) probably also play a role.

Unnamed Be-free analogue of surinamite

Christy and Putnis (1988) reported one-cell wide layers having the surinamite structure in TEM images of sapphirine from Finero, Italy, in which the 1A, 2M and 4M polytypes are present. The surinamite-like lamellae are attributed to $\mathbf{b}$/5 stacking faults on (010), along which every fourth spinel-like layer is missing, i.e. <PSPSPSPS> (4 sapphirine layers) becomes <PPSPSPS> (1 surinamite and 2 sapphirine layers). Christy and Putnis (1988) suggested $Mg_4Al_2O[Si_3Al_2O_{15}]$ as a structural formula for the surinamite layer; this formula is derived from the surinamite formula by replacing ^{iv}Be with ^{iv}Al and one ^{vi}Al with one ^{vi}Mg.

Acknowledgements

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