

## The aenigmatite-rhönite mineral group

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**Abstract:** The aenigmatite-rhönite mineral group consists of eight minerals: Aenigmatite, rhönite, serendibite, krinovite, welshite, dorrte, wilkinsonite and høgтуavite. The general chemical formula of the minerals in this group may be written as  $\{X_2\} [Y_6] (Z_6) O_{20}$ , with  $\{X\}$  eightfold coordinated  $Na^+$ ,  $Ca^{2+}$  and  $[Y]$  sixfold coordinated  $Mg^{2+}$ ,  $Fe^{2+}$ ,  $Fe^{3+}$ ,  $Ti^{4+}$ ,  $Al^{3+}$ ,  $Mn^{2+}$ ,  $Cr^{3+}$ ,  $Ti^{3+}$ ,  $Ca^{2+}$ ,  $Sb^{5+}$ ,  $Nb^{5+}$  and  $As^{5+}$ , and  $(Z)$  fourfold coordinated  $Si^{4+}$ ,  $Al^{3+}$ ,  $Fe^{3+}$ ,  $Be^{2+}$  and  $B^{3+}$ . There are two subgroups: a sodic group, including the minerals aenigmatite, krinovite and wilkinsonite, and a calcic group with rhönite, serendibite, dorrte, welshite and høgтуavite. The general features of the crystal structure are common to all the minerals of this group. These minerals occur in a wide range of rock types, e.g. alkaline lavas, sodium-rich intrusives, granitic gneisses, skarns, limestone-basalt contacts and meteorites, but mostly as accessories. Experimental data on stability are available only for aenigmatite and rhönite. Aenigmatite was synthesized at 700°C/1000 bars and 750°C/500 bars by Thompson & Chisholm (1969) and Lindsley (1969). The oxygen fugacity is constrained to be lower than the fayalite-quartz-magnetite = FQM buffer. Rhönite is stable from 850°-1000°C/1 bar to at least 5 kbar, 900 to 1100°C (Kunzmann, 1989). There is no limit on oxygen fugacity. In alkali-basaltic rocks, the stability is restricted to pressures lower than 600 bars and temperatures from 840 to 1200°C (Kunzmann, 1989). The chemistry of this group is complex, due to the flexibility of the structure. The structural formulae of 192 available analyses can be described in terms of seven substitutions: 1:  $Si^{IV} + Na^{VIII} \rightleftharpoons Al^{IV} + Ca^{VIII}$ ; 2:  $Si^{IV} + Mg^{VI} \rightleftharpoons Al^{IV} + Al^{VI}$ ; 3:  $Ti^{VI} + Mg^{VI} \rightleftharpoons 2Al^{VI}$ ; 4:  $Mg^{VI} \rightleftharpoons Fe^{2+VI}$ ; 5:  $Al^{IV} \rightleftharpoons B^{IV}$ ; 6:  $Si^{IV} + Be^{IV} \rightleftharpoons 2Al^{IV}$ ; 7:  $Sb^{5+VI} + 2Mg^{VI} \rightleftharpoons 3Fe^{3+VI}$ . The theoretical number of end-members (and names) resulting from these seven substitutions is immense. A simplified nomenclature is proposed here based on three substitutions. I:  $2Si^{IV} + 2Na^{VIII} \rightleftharpoons 2Al^{IV} + 2Ca^{VIII}$ ; II:  $2Si^{IV} + 2(M^{2+})^{VI} \rightleftharpoons 2Al^{IV} + 2(M^{3+})^{VI}$ ; III:  $2Ti^{4+VI} + 2(M^{2+})^{VI} \rightleftharpoons 4(M^{3+})^{VI}$ . This results in a rectangular polyhedron for the aenigmatite-rhönite group, in which ten sub-volumes can be assigned to ten end-members.

**Key-words:** aenigmatite, rhönite, stability, chemistry, nomenclature

### Introduction

The aim of this paper is to present an overview of the minerals of the aenigmatite-rhönite group, based on published data as well as results obtained by the author. The present knowledge of this mineral group is summarized in terms of history, properties, structure and occurrence. Further data on

the temperature and pressure stability of rhönite, as well as the occurrence of rhönite as a low-pressure breakdown product of Ca-amphibole, are based on the author's own research. In the section on chemistry and substitutions, 192 analyses are presented which clearly demonstrate the mechanisms of substitution and the great chemical variability within this mineral group.

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In addition, 93 new microprobe analyses were performed by the author on samples of different aenigmatite-rhönite species from worldwide occurrences. The proposed substitution mechanisms provide a new perspective for the classification of this mineral group. Finally, an attempt is made to give clear and unambiguous criteria for the classification for all the known minerals in this group as well as those which may be found in the future.

## History

Mineralogists have been investigating the minerals of the aenigmatite-rhönite group for over 130 years. Breithaupt (1865) described aenigmatite,  $\text{Na}_2\text{Fe}^{2+}_5\text{TiSi}_6\text{O}_{20}$ , for the first time in a nepheline syenite from Tunugdliarfik Fjord (Greenland). The mineral cossyrite (Förstner, 1881) from a pantelleritic lava (Pantelleria, Italy) was later found to be identical with aenigmatite, so this synonym is no longer used. Rhönite,  $\text{Ca}_2(\text{Mg}, \text{Fe}^{2+})_4\text{Fe}^{3+}\text{Ti}(\text{Si}_3\text{Al}_3)\text{O}_{20}$ , was first described in 1890 by Vogelsang as a "dark hornblende" in the volcanic rocks of the Hocheifel area (Germany). The name "rhönite" was created in 1907 by Soellner, who found the mineral in a nepheline basanite from Platz, Rhön Mountains, Germany. Over the next 90 years, a great number of investigations of this mineral group were published. New members of the group are described in the following publications: boron rhönite as serendibite by Prior & Coomaraswamy (1903), chromium, magnesium aenigmatite as krinovite by Olsen & Fuchs (1968),

beryllium, antimony rhönite as welshite by Moore (1978), titanium-free rhönite as dorrite by Cosca *et al.* (1988), titanium-free aenigmatite as wilkinsonite by Duggan (1990), beryllium, iron rhönite as høgtuavite by Grauch *et al.* (1994).

## Physical and optical properties

The habit of the triclinic rhönite crystals is tabular and most of them are twinned, while the aenigmatite crystals are columnar or needlelike. The specific gravity varies between 3.43 and 3.86, depending on the chemical composition (Table 1). On the Mohs scale of hardness, these minerals have values of between 5 and 6. The colour of rhönite, wilkinsonite, aenigmatite, dorrite, welshite and høgtuavite is brown to black. Krinovite is emerald green and serendibite is dark blue. The size of the crystals ranges from 1 to 1000  $\mu\text{m}$ . The prevailing size is 1 to 100  $\mu\text{m}$ , crystals of 1000  $\mu\text{m}$  are rarely found. Determination of the optical constants is difficult due to the high absorption and dispersion. In normal thin sections (30  $\mu\text{m}$ ) these minerals seem to be opaque and look like ilmenite, rutile, pseudobrookite or hematite. Ultra-thin sections (10  $\mu\text{m}$ ) were used for optical determinations (Grauch *et al.*, 1994). The pleochroism of these minerals is very strong, with the colour depending on the mineral chemistry (Table 2). An exception is welshite, which has no pleochroism. Indices of refraction range

Table 1. Unit cell parameters for the members of the aenigmatite-rhönite group.

	rhönite	wilkinsonite	aenigmatite	dorrite	krinovite	serendibite	welshite	høgtuavite
references	1,2	3	1,4	5	6,7	8	9	10
<i>a</i> (Å)	10.415	10.355	10.416(2)	10.505(3)	10.22	10.019	10.167(8)	10.317(3)
<i>b</i> (Å)	10.800	10.812(2)	10.839(1)	10.897(3)	10.67	10.393	10.65(1)	10.724(1)
<i>c</i> (Å)	8.919	8.906(2)	8.930(1)	9.019(1)	8.80	8.630	8.787(2)	8.855(1)
$\alpha$ (°)	105.97	105.05(1)	104.86(1)	106.26(2)	105.13	106.36	106.5(8)	105.77(1)
$\beta$ (°)	96.17	96.63(1)	96.77(1)	95.16(2)	96.60	96.06	96.1(8)	96.21(1)
$\gamma$ (°)	124.82	125.20(1)	125.53(1)	124.75(2)	125.02	124.36	124.0(3)	124.77(1)
<i>V</i> (Å <sup>3</sup> )	745.9	741.07(2)	746.0(1)	772.5(4)	714.8	670.96	711(5)	730.4(1)
<i>Z</i>	2	2	2	2	2	2	2	2
specific gravity	3.4-3.65	3.89	3.74-3.86	3.959	3.38	3.42-3.51	3.77	3.85
space gr.	P1	P1	P1	P1 or P $\bar{1}$	P1 or P $\bar{1}$	P1	P1	P1

References: 1 = Deer *et al.* (1978); 2 = Bonnacorsi *et al.* (1990); 3 = Duggan (1990); 4 = Canillo *et al.* (1971); 5 = Cosca *et al.* (1988); 6 = Olsen & Fuchs (1968); 7 = Merlino (1972); 8 = Machin & Süsse (1974); 9 = Moore (1978); 10 = Grauch *et al.* (1994).

Table 2. Optical properties of the members of the aenigmatite-rhönite group.

mineral color	rhönite brown, black	wilkinsonite black	aenigmatite black, brown	dorrite red brown	krinovite emerald green	serendibite dark blue	welshite reddish black	høgtuavite black
reference	1,2,3	4	1	5	6,7	8	9	10
$n_\alpha$	brownish green reddish brown 1.790-1.808	olive green 1.79	light yellow brown, reddish brown 1.790-1.810	reddish orange 1.800	yellowish green 1.712	greenish blue yellowish green 1.700-1.738	n.a.	green 1.78
$n_\beta$	greenish brown reddish brown 1.800-1.815	greyish brown 1.79	reddish brown dark brown 1.805-1.826	yellowish brown 1.84	bluish green 1.725	blue-green pale yellow 1.703-1.741	n.a.	n.a.
$n_\gamma$	dark red brown, black opaque 1.830-1.845	dark brown 1.90	dark red brown, opaque 1.870-1.900	greenish brown 1.86	greenish black 1.760	indigo blue greenish yellow 1.706-1.743	n.a.	bronze 1.82
$2V_\alpha$	47-66	< 10	40-45	90 ?	61	78-90		large

References: 1 = Deer *et al.* (1978); 2 = Grünhagen & Seck (1972); 3 = Grandclement (1980); 4 = Duggan (1990); 5 = Cosca *et al.* (1988); 6 = Olsen & Fuchs (1968); 7 = Merlino (1972); 8 = Machin & Süsse (1974); 9 = Moore (1978); 10 = Grauch *et al.* (1994).

from 1.7 to 1.9; available values are given for all minerals of the group in Table 2.

### Structure

The general features of crystal structure are common to all minerals of this group. The aenigmatite structure was determined by Kelsey & MacKie (1964) and Merlino (1972). Rhönite was found to be isostructural with aenigmatite by Bonnacorsi *et al.* (1990). The structure consists of octahedral strips connected *via* tetrahedral chains with appendices and additional insular octahedra. The octahedral strips are three to four octahedra wide, and run parallel to the *a* axis or the  $c_m$  axis (the suffix *m* denotes axes referred to the pseudomonoclinic cell, which is used for simplicity in the structural description and oriented parallel to the (011) plane (or (100)<sub>m</sub>). The tetrahedral chains are pyroxene-like and also run parallel to the *a* (or  $c_m$ ) axis. There are six different tetrahedral positions T(1) - T(6), seven octahedral M(1) - M(7) and two eightfold coordinated positions M(8) - M(9) (Fig. 1). The M(8) and M(9) sites are occu-

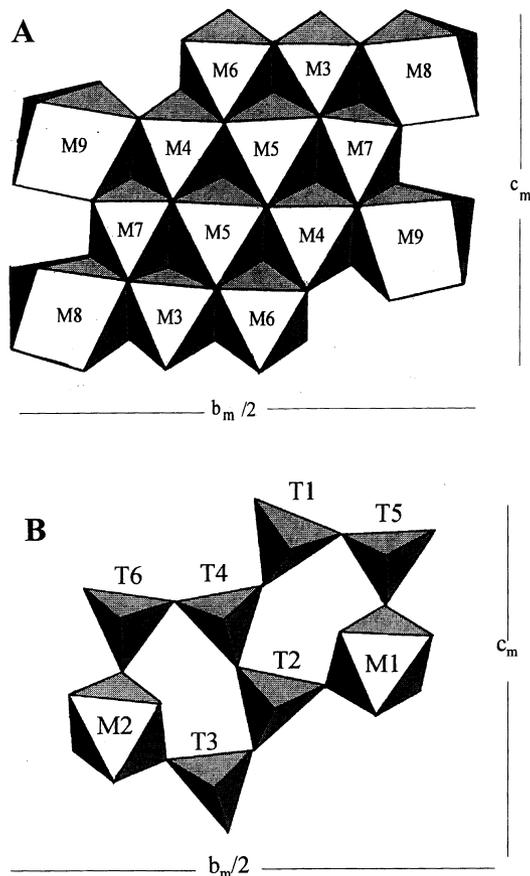


Fig. 1. The rhönite structure according to Bonnacorsi *et al.* (1990) seen along  $a_m$ ; (a) octahedral strips M(3) - M(7) with eightfold M(8) and M(9) polyhedra. (b) tetrahedral chain T(1)-T(6) with appendices and additional insular octahedra M(1)-M(2).

pied by sodium in aenigmatite, wilkinsonite and krinovite and by calcium in rhönite, dorrte, serendibite, welshite and høgtuavite. Titanium and ferrous iron prefer M(7) sites. Ferric iron and magnesium are concentrated in M(5) to M(6) sites. M(1) to M(4) are occupied with magnesium, ferrous iron and aluminium. The tetrahedral sites show a statistical distribution of silicon, aluminium and beryllium in welshite and høgtuavite, but contain boron in serendibite. Table 1 gives the unit cell parameters for all known minerals of the group.

### Occurrence and paragenesis

The minerals of the aenigmatite-rhönite group occur in a wide range of rock types, mostly as accessories. Aenigmatites have been found all over the world in sodium-rich plutonic rocks such as nepheline syenites and foyaites, but rarely in alkali granites. In alkalic lavas (phonolites, trachytes, comendites, peralkaline rhyolites) phenocrysts of aenigmatite crystallize in the groundmass. Aenigmatites occur in parageneses with aegirine-augite, hedenbergite, fayalite, as well as alkali feldspar, nepheline, ilmenite and titanite-ilmenite. Wilkinsonite occurs in the trachyte from Warrumbungle volcano, NSW, Australia, and is associated with anorthoclase, clinopyroxene, sodalite and analcite (Duggan, 1990). Rhönite crystallizes under magmatic, pneumatolytic and metamorphic conditions as well as in meteorites (Allende meteorite; Fuchs, 1971). The occurrence of rhönite in magmatic rocks is restricted to two possibilities:

- 1: As a phenocryst in the groundmass in undersaturated alkali basalts. Paragenesis: Ti-augite, olivine, nepheline, plagioclase, titanomagnetite and Ti-Ca-amphibole
- 2: As product from the breakdown of titanium-rich Ca-amphibole. Paragenesis: Ti-augite, olivine, plagioclase, titanomagnetite  $\pm$  nepheline.

The occurrence of rhönite in alkali basalt is often overlooked in thin sections. Rhönite appears opaque in normal thin sections (30  $\mu$ m) and resembles ilmenite, rutile, pseudobrookite or hematite. Nearly half of the 450 basalt samples in the Hoheifel area (West-Germany), for example, have rhönite either as phenocrysts or as a breakdown product of amphibole.

Rhönites crystallized under pneumatolytic conditions (e.g. Nickenicher Sattel, Eifel, Germany) occur with pyroxene, amphibole, biotite, nepheline, hematite, pseudobrookite and

spinel. The rhönite in an oxidized alkali gabbro (Johnston & Stout, 1984) coexists with ferrosalite, oligoclase, keneddyite, magesioferrite and kaersutite. Rhönites in a limestone-basalt contact (Réunion Island, Havette *et al.*, 1982) occur with fassaite, melilite and magnetite. In the Allende meteorite, rhönite occurs in a paragenesis with wollastonite, andradite, grossular, perovskite, spinel and gehlenite. Dorrte has only been found in a para-lava from River Basin, Wyoming by Cosca *et al.* (1988), in assemblages with magnetite, clinopyroxene, plagioclase, wollastonite, nepheline and melilites. Krinovite was found by Olsen & Fuchs (1968) within graphite nodules in octahedrite iron meteorites from Cañon Diablo, Wichita County (USA). Welshite is found in manganese iron mines in Långban, Värmland, Sweden, in an antimony-bearing skarn associated with other antimony minerals. Serendibite was found at Gangapitiya, Ceylon, in a contact zone between limestone and granulite, associated with diopside, scapolite, apatite, spinel and plagioclase (Machin & Süsse, 1974). Høgtuavite was discovered in granitic gneisses of metamorphic origin in Nordland County, Norway, by Grauch *et al.* (1994). This mineral coexists with quartz, feldspar, biotite, phenakite, zircon, fluorite, calcite, chlorite and magnetite.

### Stability

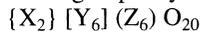
Experimental data for stability are available only for aenigmatite and rhönite. Ernst (1962) synthesized a titanium-free "aenigmatite" (now dorrte) during his experimental studies of the stability of riebeckite and riebeckite-arfvedsonite solid solutions. The titanium-free aenigmatite had a rather limited stability field in terms of temperature (650–800°C), pressure (< 900 bars) and oxygen fugacity (lower than that produced by a fayalite-quartz-magnetite = FQM buffer). Thompson & Chisholm (1969) successfully synthesized hydrothermal aenigmatite  $\text{Na}_2\text{Fe}^{2+}_5\text{TiSi}_6\text{O}_{20}$  at 700°C and 1000 bars. The oxygen fugacity was controlled by means of an iron-wüstite = IW buffer. Lindsley (1969) confirmed the results of Thompson & Chisholm and synthesized aenigmatite at 750°C/500 bars/FQM buffer. In an experiment using 750°C/500 bars/NNO (nickel/nickel oxide) buffer, however, aenigmatite broke down completely to the more oxidized assemblage acmite + Ti-magnetite + quartz. These results suggested that the stability of aenigmatite is restricted to low oxygen fugacities.

Boivin (1980) crystallized rhönite at 1 bar under NNO and IW buffer from basanite and kaersutite compositions at 1170°C. Grandclement (1980) synthesized rhönite at 1, 500 and 1000 bars, 950-1280°C with no oxygen fugacity control. Beckett (1986) synthesized Ti<sup>3+</sup>-bearing rhönite at very low oxygen fugacities (log  $f_{O_2} = 10^{-18}$ - $10^{-19}$ ) at 1233-1319°C. These rhönites have a composition similar to rhönites in the Allende meteorite. A complete discussion of the stability of synthetic and natural rhönite is given in Kunzmann (1989). A detailed discussion of the stability of rhönites in undersaturated alkali basalts is in preparation by the author. The main results are as follows: rhönite is stable from 850 - 1000°C/1 bar up to at least 5 kbar, 900 to 1100°C. There is no limit on the oxygen fugacity. Kunzmann (1989, unpublished data) synthesized rhönite on the hematite/magnetite HM, NNO, FQM, IQF buffer and under atmospheric conditions. In alkali basaltic rocks the crystallization of rhönite was experimentally determined by Kunzmann (1989). The stability is restricted to pressures below 600 bars, and temperatures from 840 to 1200°C. The normative  $ne/(ne+ab+or+lc)$  in the alkali basalts must be above 0.18 and the  $Mg/(Mg+Fe)$  ratio greater than 0.46. Due to these conditions, the occurrence of rhönite is restricted to primary undersaturated alkali basalts like nepheline basanites, olivine nephelinites or nephelinites.

Rhönite also occurs by the breakdown of titanium-rich Ca-amphiboles below 500 bars and 1060°C. The breakdown assemblage is rhönite+ ol+cpx+sp+plag+mt (Kunzmann *et al.*, 1986).

## Chemistry and substitutions

The general chemical formula of the minerals of the group may be written as:



X = Na<sup>+</sup>, Ca<sup>2+</sup> in eightfold coordination

Y = Mg<sup>2+</sup>, Fe<sup>2+</sup>, Fe<sup>3+</sup>, Ti<sup>4+</sup>, Al<sup>3+</sup>, Mn<sup>2+</sup>, Cr<sup>3+</sup>, Ti<sup>3+</sup>, Ca<sup>2+</sup>, Sb<sup>5+</sup>, Nb<sup>5+</sup>, As<sup>5+</sup> in sixfold coordination

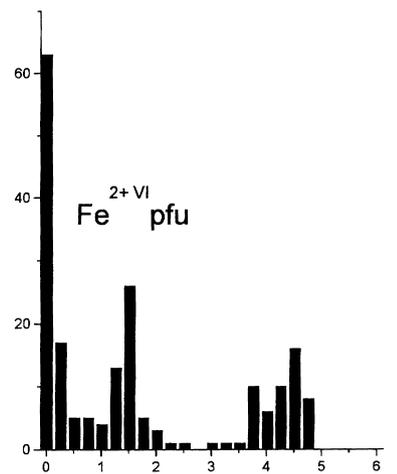
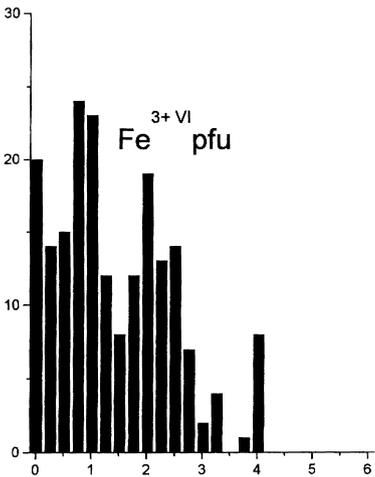
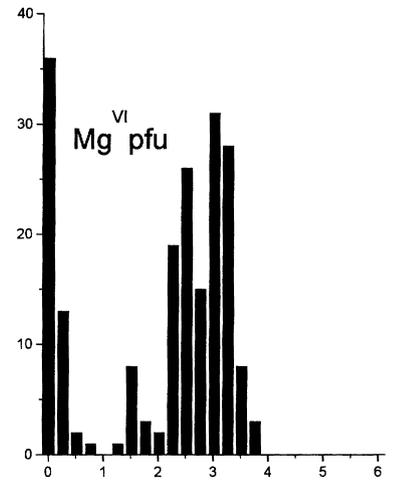
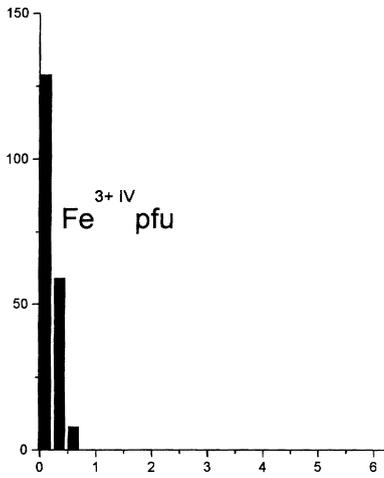
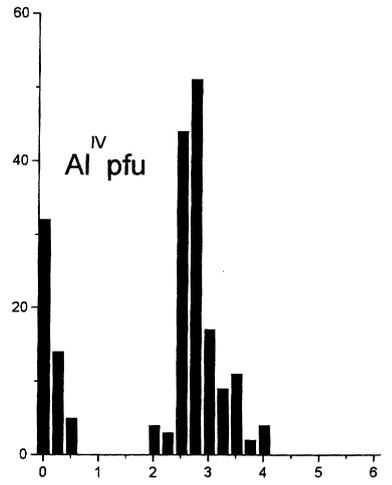
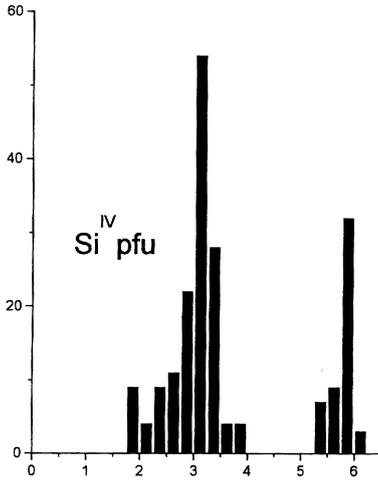
Z = Si<sup>4+</sup>, Al<sup>3+</sup>, Fe<sup>3+</sup>, Be<sup>2+</sup>, B<sup>3+</sup> in fourfold coordination

In Table 3, all members of the aenigmatite-rhönite group are listed with their ideal chemical formula. The determination of the real end-members for a classification of this group is difficult, because of their great chemical variability. For a better understanding, the cation distribution for 192 analyses (analyses available in the literature and 93 new analyses from the author) is calculated on the basis of 14 cations and 20 oxygens with the computer program RHOCALC, (Kunzmann, unpublished, available from the author by request on a floppy disk, including the 192 analyses). The structural formula is calculated according to the following rules. The six cations in the tetrahedrally coordinated position Z are filled up in order of preference Si > (Be, B) > Al > Fe<sup>3+</sup>. Surplus Al and Fe<sup>3+</sup> plus Ti<sup>4+</sup>, Mg, Fe<sup>2+</sup>, Mn, Nb, As, Sb, Cr, Ti<sup>3+</sup> and Ca are placed in the six octahedral Y sites. The two eightfold X positions are filled with Na and Ca, and if necessary, surplus Fe<sup>2+</sup>. The ferric/ferrous ratio is determined by charge balance on the basis of 14 cations. The distribution and preference of the elements in this formula are well substantiated by the structural analysis of rhönite (Bonnacorsi *et al.*, 1990) and aenigmatite (Canillo *et al.*, 1971).

Table 3. Structural formulae for all known members of the aenigmatite-rhönite group.

	{X}	[Y]	(Z)	
aenigmatite	Na <sub>2</sub>	Fe <sup>2+</sup> <sub>6</sub> Ti <sup>4+</sup>	Si <sub>6</sub>	O <sub>20</sub>
wilkinsonite	Na <sub>2</sub>	Fe <sup>2+</sup> <sub>4</sub> Fe <sup>3+</sup> <sub>2</sub>	Si <sub>6</sub>	O <sub>20</sub>
krinovite	Na <sub>2</sub>	Mg <sub>4</sub> Cr <sub>2</sub>	Si <sub>6</sub>	O <sub>20</sub>
rhönite	Ca <sub>2</sub>	(Mg, Fe <sup>2+</sup> ) <sub>4</sub> Fe <sup>3+</sup> Ti <sup>4+</sup>	Si <sub>3</sub> Al <sub>3</sub>	O <sub>20</sub>
dorrite	Ca <sub>2</sub>	Mg <sub>2</sub> Fe <sup>3+</sup> <sub>4</sub>	Si <sub>2</sub> Al <sub>4</sub>	O <sub>20</sub>
serendibite	Ca <sub>2</sub>	Mg <sub>3</sub> Al <sub>3</sub>	Si <sub>3</sub> Al <sub>1.5</sub> B <sub>1.5</sub>	O <sub>20</sub>
welshite	Ca <sub>2</sub>	Mg <sub>4</sub> Fe <sup>3+</sup> Sb <sup>5+</sup>	Si <sub>4</sub> Be <sub>2</sub>	O <sub>20</sub>
høgtuavite	(Ca, Na) <sub>2</sub>	(Fe <sup>2+</sup> , Fe <sup>3+</sup> , Ti, Mg, Sn, Mn) <sub>6</sub>	(Si, Be, Al) <sub>6</sub>	O <sub>20</sub>
synthetic baikovite *	Ca <sub>2</sub>	Mg <sub>3</sub> Ti <sup>4+</sup> Ti <sup>3+</sup> <sub>2</sub>	Si <sub>2</sub> Al <sub>4</sub>	O <sub>20</sub>

\* name not recommended by IMA.



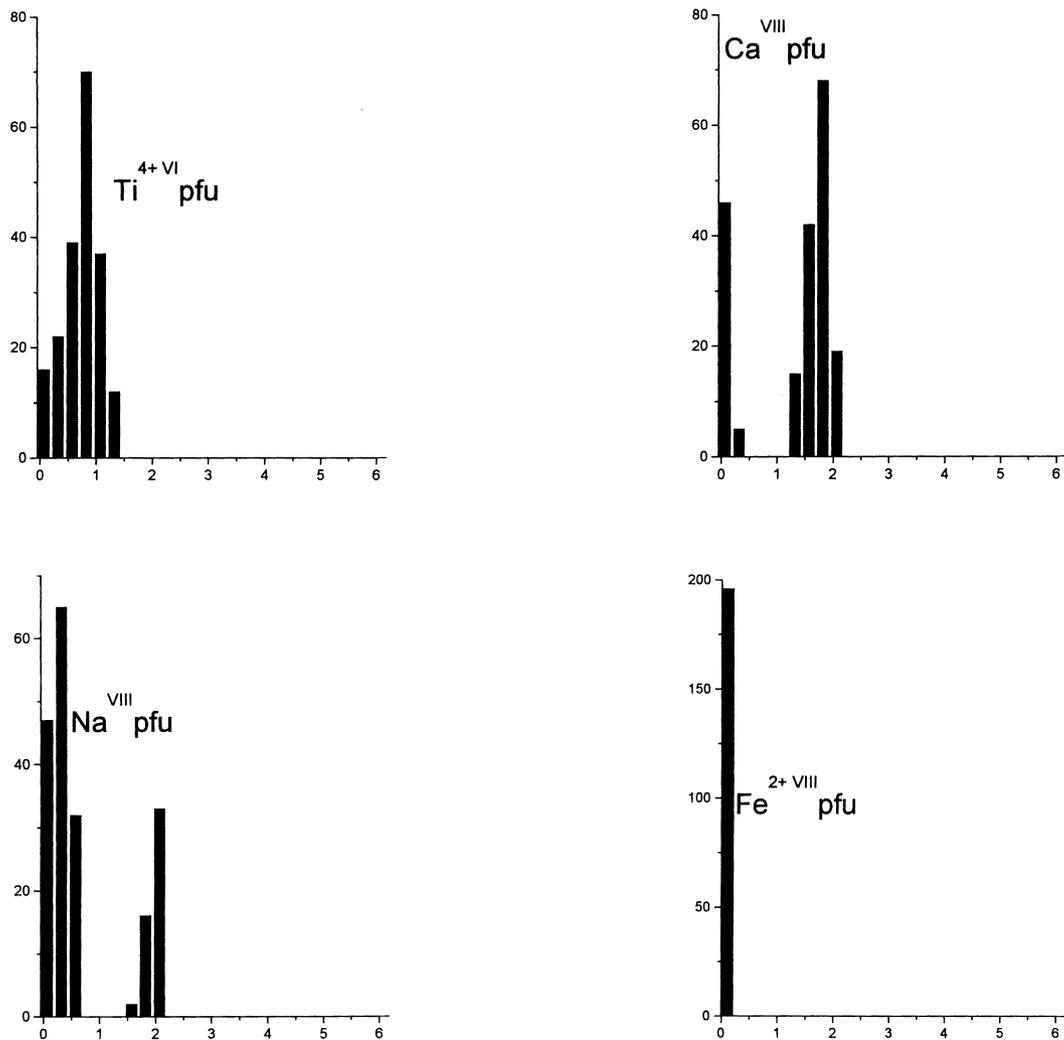


Fig. 2. Distribution of the major elements in histograms referring to the structural formula  $\{X_2\}^{VIII} [Y_6]^{VI} (Z_6)^{IV} O_{20}$  for  $Z = Si, Al, Fe^{3+}$ ;  $Y = Mg, Fe^{3+}, Fe^{2+}, Ti^{4+}$  and  $X = Ca, Na, Fe^{2+}$ .

Fig. 2 shows the distribution of the major elements in histograms referring to the structural formula. Fourfold coordinated cations: silicon ranges from 1.85-6.08 cations per formula unit (pfu), with a gap between 4 and 5 pfu. The behaviour of aluminium is similar, from 0-4.09 pfu with a hiatus near 0.5-2 pfu. This gap may be a solvus related to the substitution  $2Na + 2Si \approx 2Ca + 2Al$ . Therefore there is a gap for the eightfold coordinated cations sodium (0.5-1.5 pfu) and calcium (0.5-1.5 pfu). Only a few analyses show more than 0.5  $Fe^{3+}$  in tetrahedral coordination, while 4-8 %  $B_2O_3$  was

found in the serendibite analyses (Machin & Süssé, 1974). Welshite (Moore, 1978) has a  $BeO$  content of 4.0 % and høgтуавite contains 2.65 %  $BeO$ .

The distribution of the six cations in octahedral positions is complex in this mineral group. There are magnesium-free minerals (e.g. aenigmatite) and a maximum of up to 3.78 Mg pfu in rhönite. Ferrous iron ranges from 0 to 4.8 pfu and ferric iron from 0 to 4.06 pfu. Titanium (4+) varies from 0 to 1.38 pfu. Titanium (3+) was only found in the Allende meteorite rhönite, in the synthesized

rhönite of Beckett (1986) and in "baikovite" (Rudneva & Malysheva, 1961). Bonnacorsi *et al.* (1990) show that  $Ti^{4+}$  and  $Ti^{3+}$  are restricted to octahedral coordination. Manganese is rare (0–0.53 pfu). Chromium as a major element is only found in krinovite from the iron meteorite from Cañon Diablo, USA. Vanadium contents range up to 1 %  $V_2O_5$ . Niobium (max. 3.7 %  $Nb_2O_5$ ) and zirconium (max. 0.57 %  $ZrO_2$ ) were found in wilkinsonites by Duggan (1990). Welshite analyses (Moore, 1978) show a content of 4.0 % BeO with 3.6 %  $As_2O_5$  and 24.8 %  $Sb_2O_5$ . In the mineral høgтуавитe, 0.53 %  $SnO_2$  was found by Grauch *et al.* (1994). Only a few samples were analysed for  $H_2O$ , with a maximum content of 0.61 OH<sup>-</sup> pfu (Grünhagen & Seck, 1972). The  $K_2O$  content is not greater than 0.2 wt% in all reliable analyses.

For a classification of this group, it is necessary to elucidate the substitution mechanisms. Using aenigmatite  $\{Na_2\} [Fe^{2+}_5Ti_1] (Si_6) O_{20}$  as a starting point, we need seven substitutions to describe quantitatively the composition of the 192 mineral analyses of the group (Kunzmann *et al.*, 1986; Burt, 1994).

- 1:  $2 Si^{IV} + 2 Na^{VIII} \rightleftharpoons 2 (Al, Fe^{3+})^{IV} + 2 Ca^{VIII}$
- 2:  $2 Si^{IV} + 2 (Mg, Fe^{2+})^{VI} \rightleftharpoons 2 (Al, Fe^{3+})^{IV} + 2 (Fe^{3+}, Al)^{VI}$
- 3:  $2 Ti^{VI} + 2 (Mg, Fe^{2+})^{VI} \rightleftharpoons 4 (Fe^{3+}, Al, Cr)^{VI}$  (Cr in krinovite)
- 4:  $4 Mg^{VI} \rightleftharpoons 4 (Fe^{2+}, \pm Mn)^{VI}$
- 5:  $1.5 Al^{IV} \rightleftharpoons 1.5 B^{IV}$  (serendibite)
- 6:  $2 Si^{IV} + 2 Be^{IV} \rightleftharpoons 4 Al^{IV}$  (høgтуавитe, welshite)
- 7:  $Sb^{5+VI} + 2 Mg^{VI} \rightleftharpoons 3 Fe^{3+VI}$  (welshite)

with minor substitutions of  $As^{5+}$ ,  $Sb^{5+}$ ,  $Nb^{5+}$ ,  $Sn^{4+}$ ,  $Zr^{4+}$  and  $Ti^{3+}$  in the octahedral site. The first substitution describes the exchange between the sodium-rich minerals (*e.g.* aenigmatite) and the calcium-rich minerals (*e.g.* rhönites). Substitutions 3 and 4 only interact with octahedrally coordinated cations. The substitution 2 is basically identical to substitution 3,  $Z^{4+} + Z^{2+} \rightleftharpoons Z^{3+} + Z^{3+}$ , but the former involves exchanges of tetrahedral and octahedrally coordinated cations, whereas, in the latter, there is only an exchange between octahedrally coordinated cations. Substitutions 5, 6 and 7 are needed for the very rare minerals serendibite, høgтуавитe and welshite. For the explanation of the OH<sup>-</sup> content in some analyses (max. 0.61 pfu, Grünhagen & Seck, 1972) there may be an eighth substitution  $Fe^{2+} + (OH)^- \rightleftharpoons Fe^{3+} + O^{2-} + 1/2 H_2$ .

## Considerations for classification

The aenigmatite-rhönite group currently consists of eight minerals: rhönite, aenigmatite, wilkinsonite, krinovite, dorrite, serendibite, welshite and høgтуавитe. Three of them are new minerals discovered in the last nine years: dorrite (1988), wilkinsonite (1990) and høgтуавитe (1994). The theoretical number of end-members with the seven substitutions (including  $As^{5+}$ ,  $Sb^{5+}$ ,  $Nb^{5+}$ ,  $Sn^{4+}$ ,  $Zr^{4+}$  and  $Ti^{3+}$ ) is immense. To reduce the number of potential new mineral names, we propose a classification based on the tetrahedral sites containing just Si and Al (aenigmatite, rhönite, dorrite and wilkinsonite).

The first step is the calculation of the structural formula from chemical analysis on the basis of 14 cations and 20 oxygens (*e.g.* computer program RHOCALC). For a three-dimensional classification of the aenigmatite-rhönite group, we have to reduce the seven substitutions to three, with the following simplifications in the fourfold, sixfold and eightfold coordinations.

**eightfold coordinated cations {X}**:  $Na = Na$ ;  $Ca = Ca$  (plus  $Fe^{2+}$  if necessary from calculation).

**sixfold (octahedral) cations {Y}**:  $M^{2+} = Fe^{2+} + Mg + Mn$ ;  $M^{3+} = Fe^{3+} + Cr^{3+} + Ti^{3+}$  (plus Al if necessary from calculation);  $Ti = Ti^{4+}$  (plus traces of  $Sn^{4+}$  and  $Zr^{4+}$ ). If pentavalent cations exist in the octahedral sites (*e.g.*  $Sb^{5+}$ ,  $Nb^{5+}$ ,  $As^{5+}$ ), they should be "replaced" by substitution number seven:  $Sb^{5+VI} + 2 Mg^{VI} \rightleftharpoons 3 Fe^{3+VI}$  now  $M^{5+VI} + 2 M^{2+VI} \rightleftharpoons 3 M^{3+VI}$ .

**fourfold (tetrahedral) cations {Z}**:  $Si = Si$ ;  $Al = Al + B^{3+}$  (plus  $Fe^{3+}$  if necessary from calculation). If beryllium is found, it should be "replaced" by substitution number 6:  $2 Si^{IV} + 2 Be^{IV} \rightleftharpoons 4 Al^{IV}$ .

Using these simplifications, we obtain three substitutions instead of seven, as substitutions number 4 to 7 can be omitted.

- I:  $2 Si^{IV} + 2 Na^{VIII} \rightleftharpoons 2 Al^{IV} + 2 Ca^{VIII}$
- II:  $2 Si^{IV} + 2 (M^{2+})^{VI} \rightleftharpoons 2 Al^{IV} + 2 (M^{3+})^{VI}$
- III:  $2 Ti^{4+VI} + 2 (M^{2+})^{VI} \rightleftharpoons 4 (M^{3+})^{VI}$

If we apply these three substitutions to the ideal end-members aenigmatite  $\{Na_2\} [M^{2+}_5Ti] (Si_6) O_{20}$ , we obtain a rectangular polyhedron (Fig.3) with ten end-members. In this polyhedron, the three axes x, y, z correspond to the three substitutions I, II, III and we obtain ten end-members instead of eight, because the substitution  $Ti^{4+} + M^{2+} \rightleftharpoons 2 M^{3+}$  is found only once in rhönite  $\{Ca_2\} [M^{2+}_5Ti] (Si_4Al_2) O_{20}$ , but twice in dorrite  $\{Ca_2\} [M^{2+}_2M^{3+}_4] (Si_2Al_4) O_{20}$ . In Table 4, the ten theoretical end-members are shown along with their names (see below) as well as their occurrences in nature or in experimental syntheses.

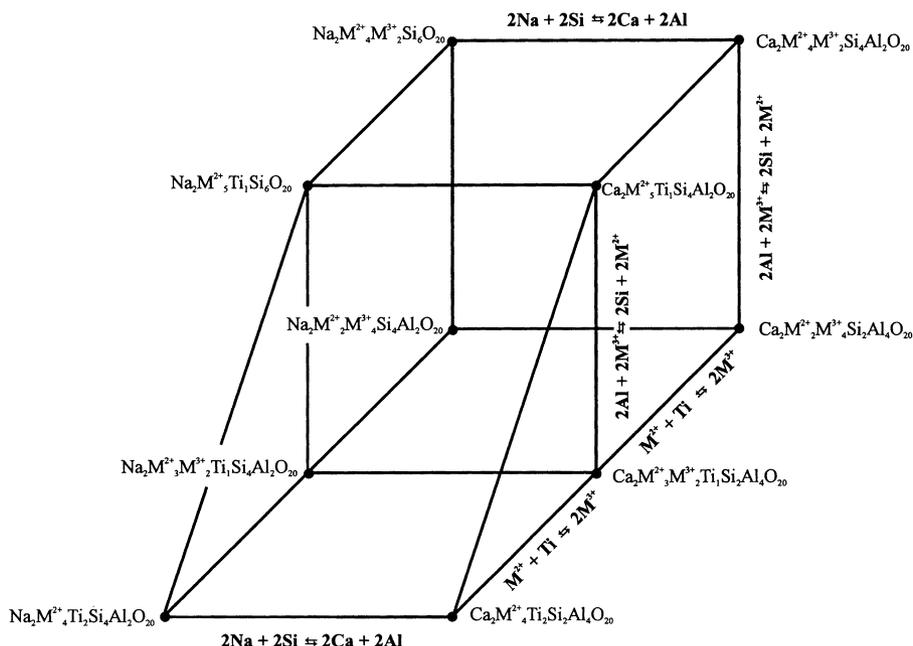


Fig. 3. The aenigmatite-rhönite group polyhedron with the three substitutions I:  $2 \text{Si}^{\text{IV}} + 2 \text{Na}^{\text{VII}} \rightleftharpoons 2 \text{Al}^{\text{IV}} + 2 \text{Ca}^{\text{VIII}}$ ; II:  $2 \text{Si}^{\text{IV}} + 2 (\text{M}^{2+})^{\text{VI}} \rightleftharpoons 2 \text{Al}^{\text{IV}} + 2 (\text{M}^{3+})^{\text{VI}}$ ; III:  $2 \text{Ti}^{4+\text{VI}} + 2 (\text{M}^{2+})^{\text{VI}} \rightleftharpoons 4 (\text{M}^{3+})^{\text{VI}}$  and the ten resulting end-members.

For classification, the polyhedron (Fig. 3) can be divided into ten sub-volumes corresponding to the ten theoretical end-members. The boundaries are set, whenever possible, to the 50 % rule (IMA) for solid solution boundaries between compositional volumes defined by end-members. First, we can divide the polyhedron into two subgroups depending on the Na or the Ca content pfu (see Fig. 4).

- 1: The aenigmatite subgroup with  $1 < \text{Na} \leq 2$  pfu
- 2: The rhönite subgroup with  $0 \leq \text{Na} \leq 1$  pfu

This boundary (50 % rule) corresponds to the substitution number I  $1 \text{Si} + 1 \text{Na} \rightleftharpoons 1 \text{Al} + 1 \text{Ca}$ . Both of the subgroups can be divided into five sub-volumes, depending on the Ti and Si content pfu. Two boundaries at Ti 0.5 pfu and Ti 1.5 pfu corresponding substitution number III ( $\text{M}^{2+} + \text{Ti} \rightleftharpoons 2\text{M}^{3+}$ )

Table 4. The proposed ten theoretical end-members of the aenigmatite-rhönite group.

End-members	Names	Occurrences
$\{\text{Na}_2\}[\text{M}^{2+}_5\text{Ti}](\text{Si}_6)_2\text{O}_{20}$	aenigmatite	in nature, synthetic <sup>1</sup>
$\{\text{Na}_2\}[\text{M}^{2+}_3\text{M}^{3+}_2\text{Ti}](\text{Si}_4\text{Al}_2)\text{O}_{20}$		not yet found
$\{\text{Na}_2\}[\text{M}^{2+}_4\text{M}^{3+}_2](\text{Si}_6)_2\text{O}_{20}$	wilkinsonite, krinovite	in nature, synthetic <sup>2</sup>
$\{\text{Na}_2\}[\text{M}^{2+}_2\text{M}^{3+}_4](\text{Si}_4\text{Al}_2)\text{O}_{20}$		not yet found
$\{\text{Na}_2\}[\text{M}^{2+}_4\text{Ti}_2](\text{Si}_4\text{Al}_2)\text{O}_{20}$		not yet found
$\{\text{Ca}_2\}[\text{M}^{2+}_5\text{Ti}](\text{Si}_4\text{Al}_2)\text{O}_{20}$	rhönite	in nature, synthetic <sup>3</sup>
$\{\text{Ca}_2\}[\text{M}^{2+}_3\text{M}^{3+}_2\text{Ti}](\text{Si}_2\text{Al}_4)\text{O}_{20}$	no name, (baikovite)	in nature, synthetic <sup>3</sup>
$\{\text{Ca}_2\}[\text{M}^{2+}_4\text{M}^{3+}_2](\text{Si}_4\text{Al}_2)\text{O}_{20}$	høgtuavite; serendibite	in nature
$\{\text{Ca}_2\}[\text{M}^{2+}_2\text{M}^{3+}_4](\text{Si}_2\text{Al}_4)\text{O}_{20}$	dorrite, welshite	in nature
$\{\text{Ca}_2\}[\text{M}^{2+}_4\text{Ti}_2](\text{Si}_2\text{Al}_4)\text{O}_{20}$		synthetic <sup>3</sup>
References: 1: Thompson & Chisholm (1969); 2: Ernst (1962); 3: Kunzmann (1989); Kunzmann & Huckenholz (1990b).		

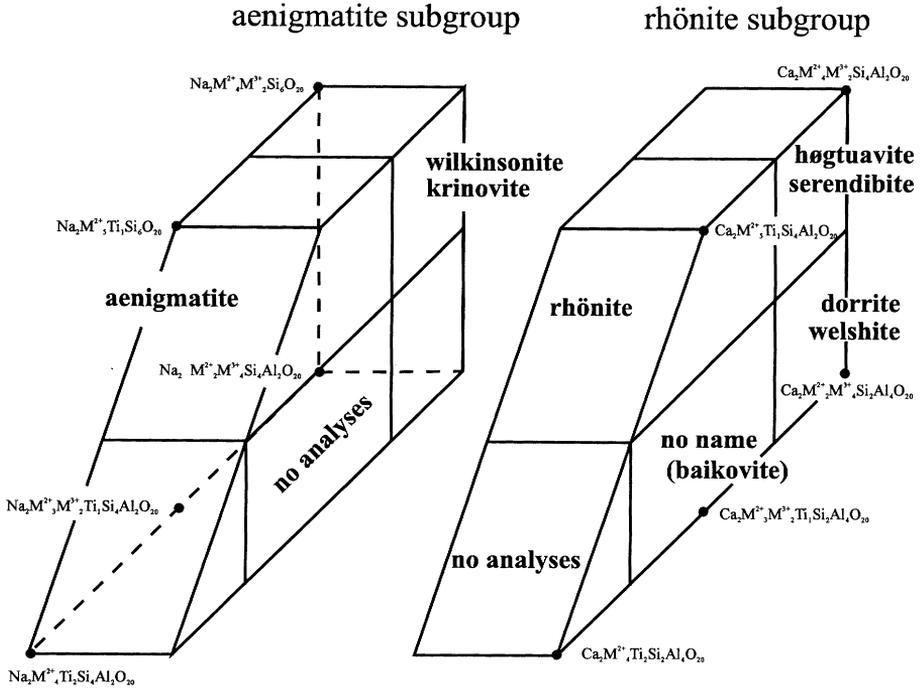


Fig. 4. The aenigmatite- and rhönite-subgroup polyhedra, including the positions of the eight minerals aenigmatite, wilkinsonite, krinovite, rhönite, dorrite, serendibite, welshite and høgтуavite. Both subgroup polyhedra can be divided into five sub-volumes, corresponding to the ten end-members.

and one boundary at 3 M<sup>3+</sup> pfu (50 % rule IMA) corresponding to substitution number II (Si + M<sup>2+</sup> ≤ Al + M<sup>3+</sup>). Each of the ten sub-volumes includes one of the ten end-members in Fig. 3. The limits of the sub-volumes correspond to existing minerals, e.g. at the locality where rhönite was first found (Platzer Kuppe, Rhön, Germany; Soellner, 1907) the mineral can still be called rhönite. These restrictions are applied to all the limits of the sub-volumes.

The three-dimensional position of all analyses in the polyhedron (Fig. 3) can be definitively fixed with two projections.

- 1: A projection on to the base of the polyhedron: Na pfu - Ti<sup>4+</sup> pfu (Differentiation aenigmatite-rhönite subgroup). In Fig. 5, all mineral analyses are plotted in this way. The x-axis corresponds to 0 ≤ Ti ≤ 2 pfu and the y-axis to 0 ≤ Na ≤ 2 pfu. All samples with Na > 1 pfu belong to the aenigmatite subgroup and those with Na ≤ 1 pfu to the rhönite subgroup. The mineral analyses of the aenigmatite subgroup are restricted to a small field whereas in the rhönite subgroup they are widely scattered.
- 2: Two projections to the sides of the polyhedron:

Si minus Na pfu - Ti<sup>4+</sup> pfu. One projection for the aenigmatite subgroup (Fig. 6) and one for the rhönite subgroup (Fig. 7).

- The x-axis corresponds to the Ti pfu in the mineral: 0 ≤ Ti ≤ 2. The y-axis is in this projection corresponds to the Si pfu minus Na pfu (2 ≤ Si minus Na ≤ 4 pfu). The compositions of all available analyses (192) are plotted in both projections. The five aenigmatite subgroup areas: **Na > 1** and
- I: 0 ≤ Ti < 0.5  
and 2 ≤ (Si - Na) < 3 not yet found
  - II: 0 ≤ Ti < 0.5  
and 3 ≤ (Si - Na) ≤ 4 wilkinsonite, krinovite
  - III: 0.5 ≤ Ti < 1.5  
and 2 ≤ (Si - Na) < 3 not yet found
  - IV: 0.5 ≤ Ti < 1.5  
and 3 ≤ (Si - Na) ≤ 4 aenigmatite
  - V: 1.5 ≤ Ti ≤ 2  
and 2 ≤ (Si - Na) < 3 not yet found

In the aenigmatite subgroup, all mineral analyses are located in the upper part of the diagram, the aenigmatite and the wilkinsonite field. Krinovite and wilkinsonite analyses are situated in the same field. In krinovite (found in the iron meteorite

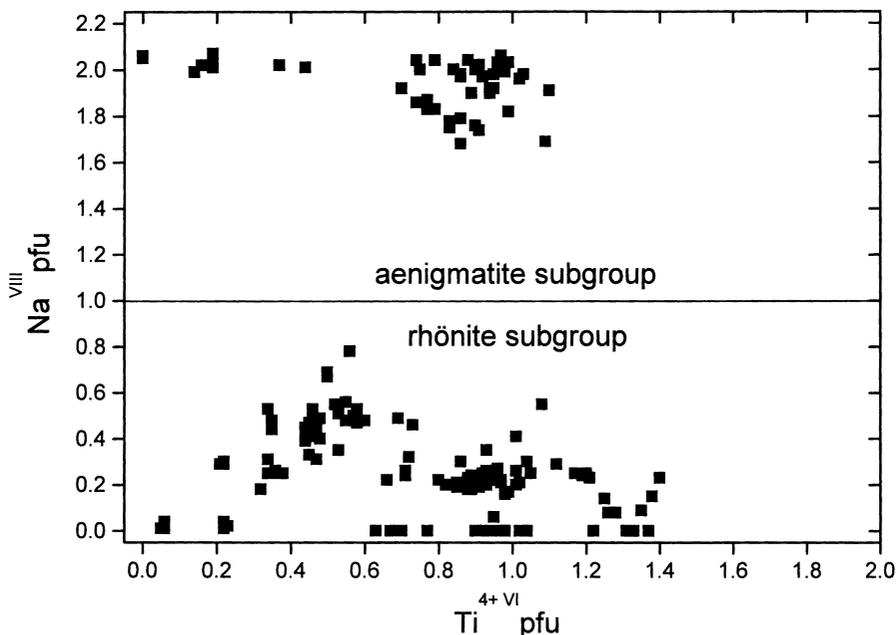


Fig. 5. A projection to the base of the polyhedron of Fig. 3: Na (pfu) - Ti<sup>4+</sup> pfu (To differentiate the aenigmatite and rhönite subgroups). The compositions of 192 mineral analyses are plotted.

from Cañon Diablo, USA) chromium predominates at M<sup>3+</sup> and magnesium at M<sup>2+</sup>, whereas in wilkinsonite Fe<sup>3+</sup> predominates at M<sup>3+</sup> and Fe<sup>2+</sup> at M<sup>2+</sup>. I recommend to name all analyses in this sub-volume wilkinsonite and name new minerals found in this subgroup wilkinsonite with addition of a relevant chemical prefix if the chemical deviation at the M<sup>2+</sup> or M<sup>3+</sup> position is more than 1 formula unit. In this case we have to rename krinovite as chromio-magnesio-wilkinsonite. The analyses in the aenigmatite sub-volume show solid solution toward wilkinsonite. At the time of writing, there are no natural samples for the other three fields.

The five rhönite subgroup 5 areas: **Na ≤ 1 and**

- I: 0 ≤ Ti < 0.5  
and 2 ≤ (Si - Na) < 3 dorrite, welshite
- II: 0 ≤ Ti < 0.5  
and 3 ≤ (Si - Na) ≤ 4 høgтуavite, serendibite
- III: 0.5 ≤ Ti < 1.5  
and 2 ≤ (Si - Na) < 3 no name
- IV: 0.5 ≤ Ti < 1.5  
and 3 ≤ (Si - Na) ≤ 4 rhönite
- V: 1.5 ≤ Ti ≤ 2  
and 2 ≤ (Si - Na) < 3 no name, only synthetic

The original dorrite (Cosca *et al.*, 1988) and welshite (Moore, 1978) compositions plot in the same field with the postulated end-member {Ca<sub>2</sub>}

[M<sup>2+</sup><sub>2</sub>M<sup>3+</sup><sub>4</sub>] (Si<sub>2</sub>Al<sub>4</sub>) O<sub>20</sub>. Dorrite is rich in magnesium at M<sup>2+</sup> and Fe<sup>3+</sup> at M<sup>3+</sup>, whereas welshite is rich in magnesium at M<sup>2+</sup>, Fe<sup>3+</sup> at M<sup>3+</sup>, antimony at M<sup>5+</sup> and Be<sup>2+</sup> on T. Most analyses in this sub-volume (see Fig. 7) are from “rhönites” crystallized under pneumatolytic conditions in alkalic lavas (*e.g.* Nickenicher Sattel and Bellerberg, Eifel, Germany). I recommend to name all analyses in this sub-volume dorrite and rename welshite as beryllio-antimono-dorrite, because there are one antimony per formula unit in sixfold coordination and two Be<sup>2+</sup> in fourfold coordination. New minerals found in this subgroup should be named dorrite with addition of a relevant chemical prefix if the chemical deviation at the M<sup>2+</sup>, M<sup>3+</sup> or T position is more than 1 formula unit. The høgтуavite-serendibite field needs more explanation. The original analysis of høgтуavite with its structural formula {Ca<sub>1.63</sub>Na<sub>0.43</sub>} [Fe<sup>2+</sup><sub>3.42</sub>Fe<sup>3+</sup><sub>2.08</sub>Ti<sub>0.30</sub>Mg<sub>0.09</sub>Sr<sub>0.03</sub>Mn<sub>0.03</sub>] (Si<sub>4.60</sub>Be<sub>0.92</sub>Al<sub>0.45</sub>) O<sub>20</sub> is given by Grauch *et al.* (1994) and has been reanalysed (original sample) in the present study with consent. Burt (1994) reduces this composition to a confusing ideal structural formula {Ca<sub>2</sub>} [Fe<sup>2+</sup><sub>5</sub>Ti<sub>1</sub>] (Si<sub>5</sub>Be<sub>1</sub>) O<sub>20</sub> for høgтуavite. In this ideal formula all M<sup>3+</sup> [Fe<sup>3+</sup><sub>2.08</sub>] is neglected and the titanium increases from 0.3 pfu to 1.0 pfu. The fol-

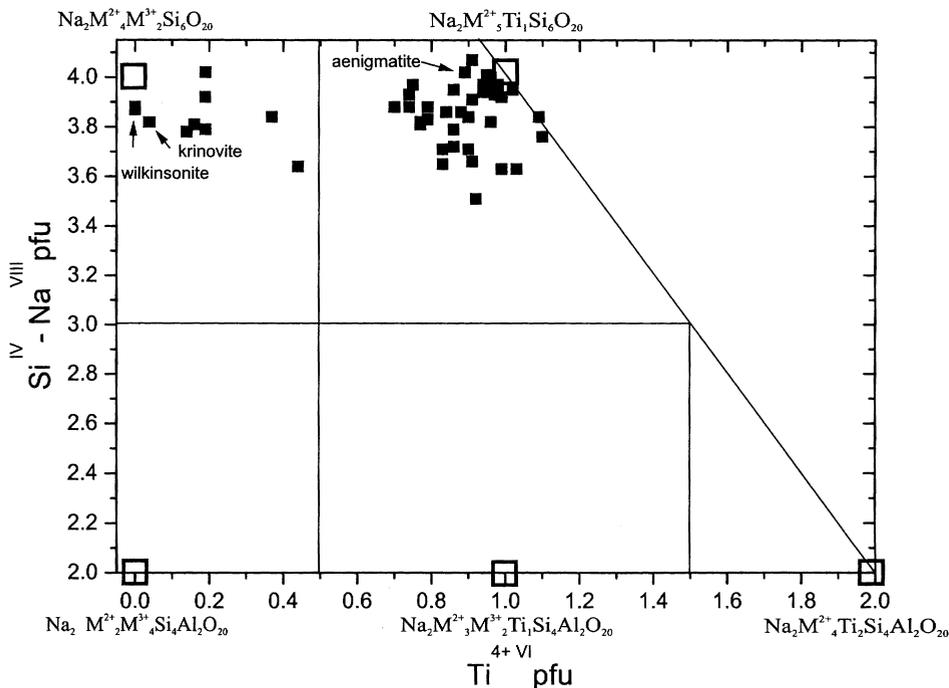


Fig. 6. The five sub-volumes of the aenigmatite subgroup in projections onto the sides of the polyhedron of Fig. 3: (Si minus Na) pfu -  $Ti^{4+}$  pfu. The x-axis corresponds to the Ti pfu in the mineral:  $0 \leq Ti \leq 2$ . The y-axis in this projection corresponds to the Si pfu minus Na pfu ( $2 \leq (\text{Si minus Na}) \leq 4$  pfu). The compositions of all 192 analyses are plotted. The original analysis of each mineral of the group is shown. The open squares represent the ideal formula suggested for each sub-volume.

lowing procedure is proposed here for høgtuavite: first, simplification to  $\{Ca_{1.63}Na_{0.43}\} [M^{2+}_{3.54}M^{3+}_{2.08}Ti_{0.30}] (Si_{4.60}Be_{0.92}Al_{0.45}) O_{20}$  and then replacement of beryllium with substitution 6 to  $\{Ca_{1.63}Na_{0.43}\} [M^{2+}_{3.54}M^{3+}_{2.08}Ti_{0.30}] (Si_{3.68}Al_{2.29}) O_{20}$ . If we now use substitutions 1, 2 and 3 (as shown above) we obtain the ideal formula  $\{Ca_{2.06}\} [M^{2+}_{3.96}M^{3+}_{1.96}] (Si_{3.97}Al_{2.00}) O_{20}$ . The projection of the original formula (Grauch *et al.*, 1994) in the aenigmatite-rhönite polyhedron is shown in Fig. 7. The nearest end-member in this figure for høgtuavite is  $\{Ca_2\} [M^{2+}_4M^{3+}_2] (Si_4Al_2) O_{20}$ . The ideal formula of serendibite is given by Burt (1994) as  $\{Ca_2\} [Mg_3Al_3] (Si_3Al_{1.5}B_{1.5}) O_{20}$ . The simplifications proposed here result in the formula  $\{Ca_2\} [Mg_3Al_3] (Si_3Al_3) O_{20}$  which is exactly on the boundary between two sub-volumes. The original composition of serendibite from Prior & Coomaraswamy (1903) plots slightly above this boundary (see Fig. 7). Therefore the analyses of høgtuavite and serendibite appear in the same sub-volume. I recommend the name høgtuavite for this sub-volume and to use the name serendibite for all

boron-minerals in this group if more than one boron pfu is replaced at the fourfold position. The mineral name makarochkinite (Yakubovich *et al.*, 1990) is not recommended by IMA, the chemical composition being very similar to høgtuavite.

The ideal formula for rhönite  $\{Ca_2\} [M^{2+}_5Ti] (Si_4Al_2) O_{20}$  reproduces the original analysis of rhönite from the type locality at Platz, Rhön Mountains, Germany by Soellner (1907). All analyses (worldwide) in this sub-volume are from phenocryst rhönites in basalts (see Fig. 7). For this sub-volume I recommend the name rhönite. The ideal formula  $\{Ca_2\} [M^{2+}_3M^{3+}_2Ti] (Si_2Al_4) O_{20}$  has no name, but there are many analyses plotting in this sub-volume (the name "baikovite" for this sub-volume is not recommended by IMA). These analyses are from "rhönites" in basalts worldwide (Kunzmann, 1989), from basalt-limestone contact (Havette *et al.*, 1982), from an oxidized alkali gabbro (Johnston & Stout, 1984) and as breakdown products of titanium-rich calcium-amphiboles (Kunzmann, 1989; Kunzmann & Huckenholz, 1990a). I recommend a new name for this unnamed

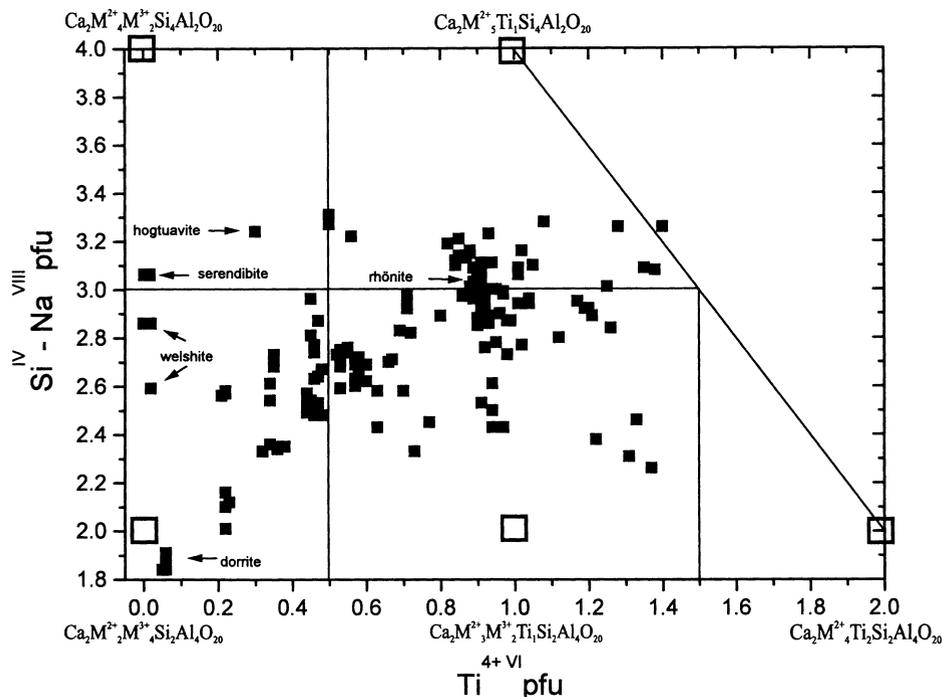


Fig. 7. The five sub-volumes of the rhönite subgroup in projections onto the sides of the polyhedron of Fig. 3: (Si minus Na) pfu -  $Ti^{4+}$  pfu. The x-axis corresponds to the Ti pfu in the mineral:  $0 \leq Ti \leq 2$ . The y-axis in this projection corresponds to the Si pfu minus Na pfu ( $2 \leq (\text{Si minus Na}) \leq 4$  pfu). The compositions of all 192 analyses are plotted. The original analysis.

sub-volume. For the sub-volume with the ideal formula  $\{Ca_2\} [M^{2+}_4Ti_2] (Si_2Al_4) O_{20}$ , no analysis is found in the literature, but this composition has been synthesized by Kunzmann (1989). For new minerals found in this group I recommend a classification in one of the ten associated sub-volumes. If more than one cation pfu (at the six- or fourfold coordination positions) is replaced by another cation, I recommend the addition of a relevant chemical prefix such as chromio-magnesio-wilkinsonite.

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