Peraluminous sapphirine as a metastable reaction product in kyanite–gedrite–talc schist from Sar e Sang, Afghanistan

WERNER SCHREYER AND KURT ABRAHAM

Institut für Mineralogie, Ruhr-Universität Bochum, Germany

SUMMARY. Minute crystals of pure Mg-sapphirine approximating $(Mg_{3.23}Al_{4.74})^{vi}(Al_{4.69}Si_{1.31})^{iv}O_{20}$, and thus having more aluminous compositions than the hitherto accepted 7:9:3 end member, were formed together with Mg-cordierite and corundum along narrow zones of the schist through reaction of the pre-existing high-pressure assemblages kyanite–gedrite and kyanite–talc. These sapphirines are considered to be metastable intermediate products growing under the influence of the structurally similar host mineral kyanite. Under equilibrium conditions they continued to react with kyanite to form the stable assemblage cordierite–corundum. Peraluminous sapphirines including those most recently synthesized may be metastable phases under all conditions of crystallization.

THE problem of the chemical compositions of natural and synthetic sapphirines has been a matter of debate for many years. Gossner and Mussgnug (1928) studying natural crystals proposed the formula $Mg_2Al_4SiO_{10}$ ($= 2MgO.2Al_2O_3.SiO_2$) with a limited solid solution due to substitution of MgSi by AlAl. Later Foster (1950), who first synthesized sapphirine in the system $MgO–Al_2O_3–SiO_2$ at atmospheric pressure, found that the composition $4MgO.5Al_2O_3.2SiO_2$ (4:5:2) was most appropriate for his synthetic materials. However, Kuzel (1961) refuted this latter formula as not being in agreement with the crystallographic data even on synthetic crystals, and he proposed a composition $Mg_7Al_{18}Si_3O_{40} = 7MgO.9Al_2O_3.3SiO_2$ (7:9:3) for synthetic Al-rich sapphirines. This composition lies on the line of MgSi $\rightleftharpoons$ AlAl substitution as proposed by Gossner and Mussgnug (1928) and as shown in figs. 1 and 2. Using higher confining pressures, between 6 and 10 kb, Schreyer and Seifert (1969a) as well as Seifert (1974) synthesized sapphirines with compositions close to or identical with $2MgO.2Al_2O_3.SiO_2$ (2:2:1), which are clearly unstable at low pressures. This indicates that the compositions of sapphirines may be severely influenced by the pressures of formation. Temperature must also be an important variable, because Seifert (1974) obtained sapphirines slightly less aluminous than 7:9:3 at similar high pressures but at higher temperatures. Yet Taylor (1973) reported microprobe analyses of synthetic sapphirines made at 15 kb and temperatures near 1400 °C yielding compositions close to 2:2:1. Thus the extent of sapphirine solid solution along the MgSi $\rightleftharpoons$ AlAl substitution line as a function of pressure and temperature is by no means clear as yet.

Under these circumstances it was found of particular interest that natural sapphirines were discovered with compositions even more aluminous than the 7:9:3

composition. In addition, sapphirines of similar compositions have recently been synthesized by Bishop and Newton (ms. 1974).

In the present paper analytical data and petrographic observations on the new peraluminous natural sapphirines will be presented together with a discussion on their mode of origin. A comparison will also be made with the analyses of other natural sapphirines as plotted in fig. 2. Finally the problem of stability of peraluminous sapphirines will be discussed in the light of most recent experimental work.
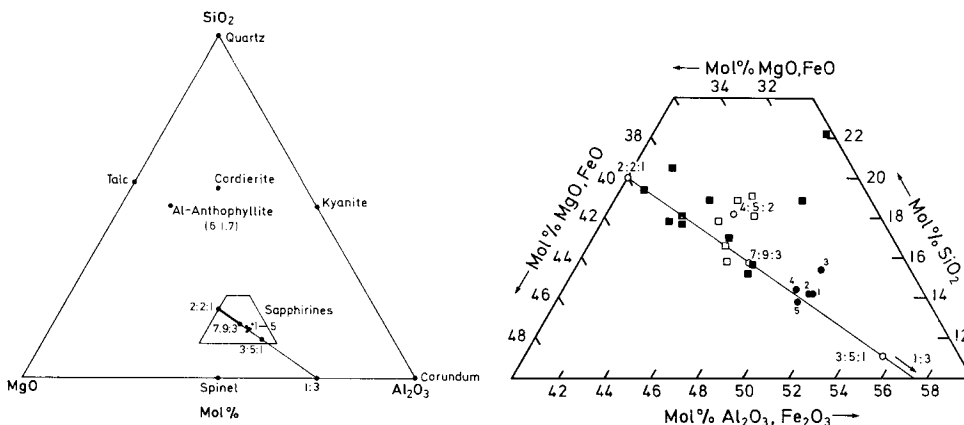

FIGS. 1 and 2: FIG. 1 (left). Triangular plot of the system MgO–Al₂O₃–SiO₂–H₂O on to the water-free base plane showing only phases of relevance for the petrology of the Sar e Sang whiteschist. Instead of the sodian varieties actually occurring in the schist (Schreyer *et al.*, manuscript 1974), pure talc and an Al-anthophyllite, substituting for gedrite, are plotted. The ratios accompanying some compositions are in the order MgO:Al₂O₃:SiO₂. The small dots marked 1 to 5 represent the analyses of peraluminous sapphirines. The compositional range framed by solid lines is shown, at an enlarged scale, in fig. 2, which includes the additional Fe oxides. The line interconnecting the compositions 2:2:1 to 1:3 is the locus of continuous substitution AlAl for MgSi in 2:2:1 sapphirine. FIG. 2 (right). Enlarged portion of a projection of the system MgO–FeO–Al₂O₃–Fe₂O₃–SiO₂ as indicated in fig. 1, showing the substitution line $R^{2+}Si \rightleftarrows R^{3+}R^{3+}$ (arrow) believed to be valid for sapphirine solid solutions. Some existing and hypothetical sapphirine compositions (open circles) are marked by their oxide ratios MgO:Al₂O₃:SiO₂. Solid dots accompanied by the numbers 1 to 5 are the plotted analyses of peraluminous sapphirines as given in Table I. The squares represent sapphirine analyses taken from the literature (see text): solid squares = complete analyses, open squares = analyses giving only FeO values.

Geological and petrological background. The host rock of the new peraluminous sapphirine is a kyanite–gedrite–talc schist occurring within a characteristic talc-rich horizon of the well-known lapis lazuli deposit Sar e Sang, Afghanistan. A brief account of the discovery of this rock and its petrological significance was given by Kulke and Schreyer (1973). On the basis of experimental data the assemblages talc–kyanite and gedrite–kyanite are stable at high water pressures (Schreyer and Seifert, 1969b). For schists consisting mainly of talc and kyanite, Schreyer (1973, 1974) has, therefore, proposed the name *whiteschist* in order to draw attention to their special conditions of formation. As pointed out by Kulke and Schreyer (1973) the Sar e Sang whiteschists also contain, in addition to their high-pressure assemblages, mineral

phases like cordierite and corundum, which are interpreted as products of late-stage, lower-pressure reactions at the partial expense of the high-pressure phases. One such reaction relating mineral pairs through crossing tie lines that can easily be seen in fig. 1 is

$$\text{talc} + \text{kyanite} \rightleftharpoons \text{cordierite} + \text{corundum}. \tag{1}$$
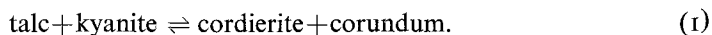
In other cases the high-pressure pair gedrite-talc shows similar reactions. A more detailed account on the chemistry of all the phases present in the Sar e Sang white-schists will be given elsewhere (Schreyer *et al.*, manuscript 1974). The new sapphirine, on which emphasis is placed in the present paper, appears also as a product of late-stage reaction, preferably at the expense of gedrite-bearing assemblages.
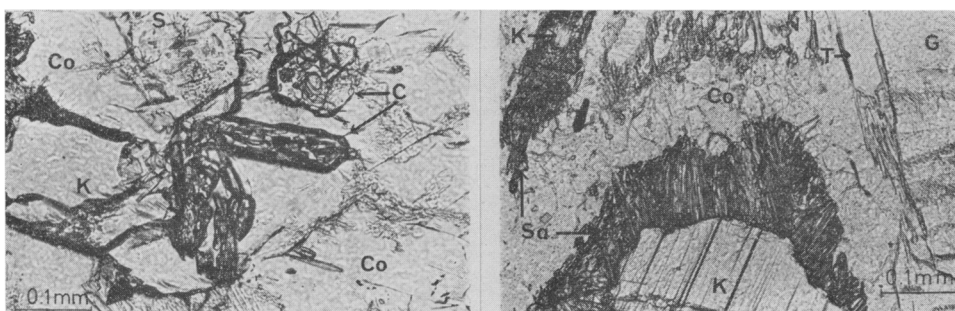
FIGS. 3 and 4: FIG. 3 (left). Microphotograph showing relatively large, partly euhedral crystals of corundum (C) containing numerous minute inclusions. Corundum formed, together with cordierite (Co), around relic-grains of kyanite (K) and sillimanite (S). Kyanite–talc schist, Sar e Sang, Afghanistan. FIG. 4 (right). Microphotograph showing zone of late-stage mineral growth between kyanite (K) and gedrite (G) or talc (T) or both. Kyanites are surrounded by a dense felt of sapphirine (Sa) needles embedded in cordierite (Co). Gedrite–kyanite–talc schist, Sar e Sang, Afghanistan.

Petrography. The products of late-stage reactions occur in the Sar e Sang white-schist exclusively within thin skins or, referring to thin section studies, along narrow channels between the earlier high-pressure minerals (Kulke and Schreyer, 1973, fig. 2). Cordierite predominates in these channels, but in many instances dense felts composed of very fine-grained crystals with higher refractive indices were recognized, always located on the corroded surfaces of kyanite bordering against the cordierite channels. Whereas some portions of these felts showing coarser size and even euhedral hexagonal crystal faces could be identified optically with good confidence as corundum (fig. 3), there are others containing pronounced needle-like crystals of apparent non-hexagonal character that left the microscopist in considerable doubts about their true character. Fig. 4 shows one of these problematic aggregates forming along a former grain boundary between kyanite and gedrite. Since some of the needles appeared to exhibit a slightly bluish tint, it was first assumed that they would be small crystals of yoderite. However, very careful microprobe work proved them to be sapphirines (see next section). In rare cases, composite felts were observed consisting of both corundum and sapphirine, and it seems that corundum is the later mineral enclosing parts or even bundles of the sapphirine. The abundant minute inclusions in the larger corundum

grains (fig. 3) may, in addition to cordierite, be sapphirines too. It should be stressed that the similarity in their optical properties precludes a clear microscopic distinction between minute grains of sapphirine and corundum. The problem is aggravated by the probability that needle-like skeletal crystals of corundum that do not show hexagonal forms are, in fact, pseudomorphs after sapphirine.

Microprobe analysis. The results of initial qualitative microprobe investigations of the fine-grained felts of needle-like materials are shown in fig. 5. Whereas the picture of back-scattered electrons (fig. 5, A) shows the microstructure of the aggregate
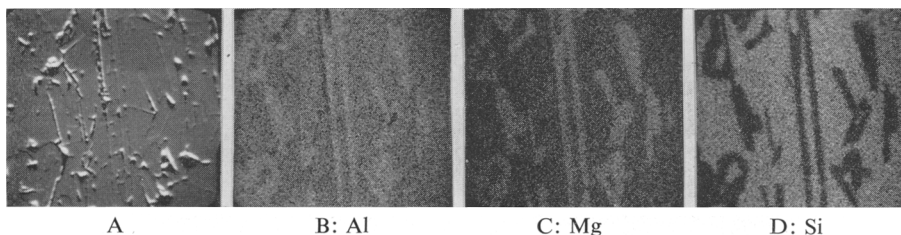

| A | B: Al | C: Mg | D: Si |

FIG. 5. Pictures of backscattered electrons (A) and Al-, Mg-, and Si-radiation (B–D as indicated) of hollow sapphirine needles lying within cordierite and sectioned at different angles. Specimen as in fig. 4.

particularly clearly, the element distribution is obvious from the pictures using Al-, Mg-, and Si-radiation (fig. 5, B–D). The sapphirine needles are best characterized by their low contents of Si (fig. 5, D). Thus it is seen that the needles often enclose narrow and long channels of cordierite, which also forms the matrix. One gets the impression that perhaps sapphirine grew initially in the form of whiskers.

The results of five quantitative microprobe analyses on sapphirine needles are compiled in Table I. Although the analytical totals are all somewhat below 100 %, no cations other than Mg, Al, and Si have been detected. Thus these sapphirines fall into the pure system $MgO–Al_2O_3–SiO_2$ in which all the experimental work on the sapphirines has been done. In particular they apparently represent the first iron-free sapphirines detected in a natural environment.

Following the crystallochemical formula of sapphirine $M_7(M)O_2[T_6O_{18}]$ as recently given by Moore (1969) the microprobe analyses were recalculated on the basis of 20 oxygens. Table I shows that the agreement with the general formula regarding site occupancy is very good except for crystal 3 which has a slight deficiency in octahedral occupancy.

The five analyses were also recalculated in terms of mole % MgO, Al_2O_3, and SiO_2 (Table I) and are plotted as solid dots in the ternary system of figs. 1 and 2. It is easily recognized that all the analyses plot towards considerably more aluminous compositions than 7:9:3. Except for analysis no. 3 the compositions of the sapphirines lie very close to the extended MgSi $\rightleftharpoons$ AlAl substitution line connecting 2:2:1 and 7:9:3 (fig. 2). Analytical error or the proximity of kyanite or cordierite to the analysed area of crystal no. 3 might be reasons for this deviation, which is also expressed in the low site occupancy.

Compositions of other natural sapphirines. In order to compare the compositions of the Sar e Sang sapphirines with those of other natural occurrences, complete analyses of natural sapphirines published thus far have been plotted as squares in fig. 2. In addition to the compilation by Deer *et al.* (1962) the analyses reported by Warren (1912), Lacroix and de Gramont (1921), McKie (1963), Barker (1964), Wilson and Hudson (1967), Lutts and Kopaneva (1968), Forestier and Lasnier (1969), Haapala *et al.* (1971), and Monchoux (1972) were used. Analyses giving only Fe_2O_3

TABLE I. *Microprobe analysis of sapphirines from kyanite–gedrite–talc schist, Sar e Sang, Afghanistan*

	1	2	3	4	5
SiO_2	11·1	11·3	12·2	11·5	11·1
Al_2O_3	67·9	68·6	68·2	68·2	68·4
MgO	18·4	18·7	18·1	19·1	19·1
	97·4	98·6	98·5	98·8	98·6

Number of cations on the basis of 20 oxygens

	1	2	3	4	5
T { Si	1·31	1·31	1·41	1·33	1·29
{ Al	4·69	4·69	4·59	4·67	4·71
	6·00	6·00	6·00	6·00	6·00
M { Al	4·74	4·72	4·76	4·68	4·69
{ Mg	3·23	3·25	3·15	3·31	3·32
	7·97	7·97	7·91	7·99	8·01

Mole per cent recalculated

	1	2	3	4	5
MgO	34·9	35·1	34·0	35·6	35·7
Al_2O_3	50·9	50·8	50·7	50·1	50·5
SiO_2	14·2	14·2	15·4	14·4	13·8
	100·0	100·1	100·1	100·1	100·0
n-value (Vogt, 1947)	2·72	2·72	2·32	2·64	2·88

were rejected; the same holds for the analysis reported by Mountain (1939), in which the H_2O^+ value of 4·8 % is excessively high probably due to secondary alteration (Deer *et al.*, 1962). The analytical values for CaO, Na_2O, K_2O, and BeO were neglected so that the plot in fig. 2 represents a projection of somewhat more complex sapphirine compositions into the limiting system $(Mg,Fe)O–(Al,Fe)_2O_3–SiO_2$.

It can easily be seen from fig. 2 that all previous analyses of natural sapphirines cluster around the theoretical line of substitution between the limiting oxide ratios 2:2:1 and 7:9:3. The strongest deviations from the substitution line are noted for the analyses given by Lutts and Kopaneva (1968) as well as by Monchoux (1972) both exhibiting unusually low $(Mg,Fe)O$-values. Nevertheless even their $(Al,Fe)_2O_3$-values hardly exceed that of the theoretical composition 7:9:3. Thus the plot of fig. 2

corroborates the peraluminous nature of the sapphirines from Sar e Sang described in the present paper.

On the basis of an earlier compilation of analyses Vogt (1947) had suggested a general formula for sapphirine as $Mg_{16-n}Al_{32+2n}Si_{8-n}O_{80}$ with n varying from 0 to about 2·5. This formula implies that all sapphirines should plot along the substitution line shown in fig. 2 but even beyond the 7:9:3 composition which has $n = 2·0$. Among the analyses used by Vogt (1947) there is only one yielding a n-value beyond 2·0, that is of the sapphirine from Blinkwater, Transvaal (Mountain, 1939) with $n = 2·23$, which was, however, rejected for fig. 2 because of its high H_2O^+ value. On the basis of the analyses of the Sar e Sang sapphirines (Table I) it is now clear that even higher n-values are possible in Vogt's formula: neglecting the problematic analysis no. 3 of Table I the n-values of the peraluminous sapphirines range from 2·64 to 2·72.

The reasons for the more or less pronounced deviations of the compositions of natural sapphirines in fig. 2 from the ideal substitution line $R^{2+}Si \rightleftharpoons R^{3+}R^{3+}$ are, of course, hard to evaluate. They may be partly analytical errors, as assumed for analysis no. 3 of Table I, and partly due to additional unknown lattice substitutions through which less common cations such as Ca^{2+}, Na^+, K^+, and Be^{2+} are incorporated within the sapphirine structure. It is somewhat unlikely, however, that these are the only reasons, because the contents of such additional cations are generally very low and also because there is a clear tendency for deviations towards more SiO_2-rich compositions, i.e. into the upper portion of fig. 2. Thus it might be worth considering whether or not in addition to the accepted $MgSi \rightleftharpoons AlAl$ substitution in natural sapphirines a second substitution $Si \rightarrow Al + \frac{1}{2}Mg$ may become operative, which would leave part of their Mg positions vacant. Such linking of the two types of substitutions leading to a ternary range of solid solutions has been found at high temperatures in the MgAl-silicate cordierite (Schreyer, 1964).

Crystal chemical considerations. The complicated crystal structure of sapphirine has recently been solved by Moore (1969). As in spinel, the structure is based on a cubic close oxygen packing, in which cations fill part of the tetrahedrally and octahedrally co-ordinated interstices. Unlike that in spinel, however, the cation occupancy of these interstices is very complicated, as eight different octahedral sites $M(1)$–$M(8)$, and six tetrahedral sites $T(1)$–$T(6)$ have to be distinguished. According to Moore (1969) one of the octahedral sites, $M(3)$, is occupied by both Mg and Al, whereas the rest contain solely either Mg or Al. Similarly, three of the tetrahedral sites $T(2)$–$T(4)$, contain both Al and Si, whereas the others are only occupied by either Al or Si. Thus, for the 7:9:3 sapphirine he studied Moore (1969) determined the structural formula: $[Mg_{3·0}(Mg_{0·5}Al_{0·5})Al_{4·0}]^{vi}[Al_{3·0}(Al_{0·25}Si_{0·75})(Al_{0·5}Si_{0·5})(Al_{0·75}Si_{0·25})]^{iv}O_{20}$.

It must be conceded at this point that the use of oxide ratios in crystallochemical discussions on sapphirine compositions has the disadvantage that they cannot be directly related to the unit cell contents, nor are they directly comparable among themselves. Nevertheless oxide ratios are used as the basis here, because all previous and current discussions (Bishop and Newton, ms. 1974) are centred around them, and also because they are of direct interest to the experimentalists who have contributed vastly to this problem.

No structure determination is available on a $2:2:1$ sapphirine. But after translation into the formalism of crystal chemistry its structural formula must approximate to $[Mg_{3.0}(Mg)Al_{4.0}]^{vi}[Al_{3.0}(Si)(Al_{0.25}Si_{0.75})(Al_{0.75}Si_{0.25})]^{iv}O_{20}$, with the main uncertainty lying in the Al/Si order–disorder relations on tetrahedral sites. Applying the opposite substitution $(Al_{1.0}$ for $Mg_{0.5}Si_{0.5})$ to a $7:9:3$ sapphirine a theoretical member $Mg_3Al_{10}SiO_{20}$ $(= 3:5:1)$ is obtained for which a hypothetical structural formula might be derived: $[Mg_{3.0}(Al)Al_{4.0}]^{vi}[Al_{3.0}(Al_{0.5}Si_{0.5})(Al_{0.75}Si_{0.25})(Al_{0.75}Si_{0.25})]^{iv}O_{20}$.

Fig. 2 shows that the compositions of the Sar e Sang peraluminous natural sapphirines lie about midway between $7:9:3$ and $3:5:1$. It is probable that the $M(3)$ position occupied by equal amounts of Mg and Al in $7:9:3$ sapphirine, and free from Al in $2:2:1$ types, contains an excess of Al over Mg in the peraluminous sapphirines, the site occupancy approximating $(Mg_{0.25}Al_{0.75})$. Thus the complete structural formula of the peraluminous sapphirines, using analysis No. 1 of Table I as an example, might be near $[Mg_{3.0}(Mg_{0.23}Al_{0.74})Al_{4.00}]^{vi}[Al_{3.00}(Al_{0.40}Si_{0.60})(Al_{0.50}Si_{0.50})$ $(Al_{0.79}Si_{0.21})]^{iv}O_{20}$. Again the main uncertainty lies in the tetrahedral Al/Si distribution.

However, it should be clear that these deductions can only apply to sapphirines showing the same scheme and also degree of cation ordering as that studied by Moore (1969). Other sapphirines may indeed show either less or more ordering. Thus the sapphirine described by McKie (1963) has a doubled b-axis. Additional complications arise after the recent discovery of a triclinic polymorph of sapphirine by Merlino (1973). Under these circumstances an unambiguous substitution scheme and also an explanation why the particular peraluminous compositions of the Sar e Sang sapphirines are preferred over other possible ones can only be expected from structure determinations on these materials.

Regarding a further extension of sapphirine solubility along the MgSi $\rightleftharpoons$ AlAl substitution line towards still more aluminous members it is interesting to note that Saalfeld and Jagodzinski (1957) have synthesized a monoclinic, metastable, silica-free Mg-aluminate, which according to Moore (1969) seems to have a sapphirine-related structure with a composition $Mg_2Al_{12}O_{20}$ $(1:3)$. This composition would represent an absolute end member of the sapphirine solid solution series (see fig. 1). Jagodzinski (1957) has found that the metastable Mg-aluminate has a structure that can be regarded as a distorted cubic close oxygen packing, which further corroborates the similarity with sapphirine.

Petrologic considerations. The sapphirine found among the mineral constituents of the Sar e Sang whiteschist is particularly interesting for two reasons: Peraluminous sapphirine developed in a rock that is not excessively rich in Al_2O_3 (Kulke and Schreyer, 1973); and the development of sapphirine from the assemblage kyanite–gedrite (or kyanite–talc) is inconsistent with phase relations outlined by Schreyer and Seifert (1969*b*), which would imply the formation of corundum+cordierite, or yoderite+cordierite.

Furthermore, considering the components available in the whiteschist (Schreyer *et al.*, ms. 1974) only one of the two phases sapphirine and corundum may coexist stably with Mg-cordierite without violating the phase rule. In this regard the

petrographic relationship between sapphirine and corundum previously described is most logically interpreted as indicating that the peraluminous sapphirine is a metastable intermediate reaction product prior to stable corundum formation. This interpretation is consistent with the experimental findings at elevated pressures that the stable sapphirine composition does not become more aluminous than $7:9:3$ even when coexisting with excess corundum (Seifert, 1974), and that the silica-free sapphirine-like phase of Saalfeld and Jagodzinski (1957) is itself metastable (see above). It is further supported through the instability of the assemblage Al-silicate–sapphirine at temperatures low enough to retain the hydrous phases talc and gedrite. Seifert (1974) found experimentally that the assemblage sapphirine+mullite is only stable at temperatures above some $1170\,°–1270\,°C$ in the pressure range up to 5 kb, and it is replaced by the cordierite–corundum pair at lower temperatures (see also Seifert, 1973). The stability of a tie-line sapphirine–kyanite, or during the late whiteschist stage sapphirine–sillimanite (see fig. 3 and Kulke and Schreyer, 1973), would, however, be the necessary prerequisite for *stable* formation of *any* sapphirine from the high-pressure talc–gedrite–kyanite assemblages.

Thus there are good arguments for the metastable formation of the peraluminous sapphirine. From the crystallographic point of view, the growth of a cubic close-packed structure like sapphirine at the expense and around the fringes (fig. 4) of cubic close-packed kyanite may even seem a logical intermediate step before the formation of the hexagonal close oxygen packing of corundum. Yet no clear indications of an oriented intergrowth of kyanite and sapphirine, which one might expect from a topotactic reaction, were encountered. It is interesting, however, that the metastable silica-free sapphirine-like phase of Saalfeld and Jagodzinski (1957) was also obtained through low-temperature reaction of a cubic close-packed starting material, namely an excess-Al spinel solid solution.

The apparent preference of the felts made up of sapphirine (fig. 4) to grow along late-stage channels between kyanite and gedrite rather than talc may be due to the fact that compared with talc the orthoamphibole can release only a smaller amount of H_2O available for fluxing the reaction. Using the Na-free orthoamphibole of the system $MgO–Al_2O_3–SiO_2–H_2O$ called aluminous anthophyllite (Yoder, 1971) as substitute for gedrite (fig. 1) the metastable reaction would thus be

$$\text{aluminous anthophyllite} + \text{kyanite} \rightarrow \text{cordierite} + \text{peraluminous sapphirine.} \quad (2)$$
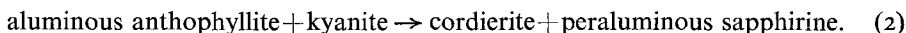
The final, stable disappearance of the metastable sapphirine within the bulk composition of the whiteschist will probably be effected through continuous reaction with its host mineral kyanite according to the equation

$$\text{kyanite} + \text{peraluminous sapphirine} \rightarrow \text{cordierite} + \text{corundum} \quad (3)$$

which is also a crossing-tie-line relationship according to fig. 1. Simple addition of reactions (2) and (3) finally yields aluminous anthophyllite+kyanite → cordierite+ corundum (4) which is considered the stable reaction comparable to reaction (1) involving talc. The reaction sequence thus outlined may also elegantly explain the abundant minute cordierite inclusions found within the larger corundum grains (fig. 3).

The small amount of sodium present in the gedrite of the whiteschist (Schreyer *et al.*, ms. 1974) does not seem to affect the phase relations discussed here as Na is incorporated in additional plagioclase present in small amounts.

The problem of stability of peraluminous sapphirines. The phase petrological conclusion that the peraluminous Sar e Sang sapphirines formed as metastable reaction products within the bulk composition of the schist under the conditions of a late-stage, low-pressure event does not, of course, necessarily imply that peraluminous sapphirines are metastable phases under all conditions of pressure, temperature, and bulk chemistry. This statement is particularly relevant in view of the fact that Bishop and Newton (ms. 1974) have just synthesized peraluminous sapphirines in the system $MgO-Al_2O_3-SiO_2$ with compositions intermediate between 7:9:3 and the Sar e Sang material. Their conditions of synthesis were identical to those applied already by Foster (1950), i.e. sintering of oxide mixes at high temperatures and one atmosphere. On the basis of their results Bishop and Newton (ms. 1974) suggest that the Al-content of sapphirine may be useful as a geobarometer with tetrahedral Al progressively decreasing with the crystallization pressure.

It is already clear from the compositions of the Sar e Sang peraluminous sapphirines that a simple pressure dependence of the Al-contents of sapphirines cannot exist, because the Sar e Sang materials, which had certainly formed at higher pressures than the synthetic crystals of Bishop and Newton, have higher Al-contents than the latter. Moreover the question arises whether or not the sapphirines synthesized by Bishop and Newton do themselves exhibit stable equilibrium compositions. Reactions could, of course, not be reversed and the sintering process finally resulting in sapphirine growth initially led to extensive formation of spinel, which clearly represents a metastable intermediate reaction product. Therefore, the crystallization history of these first synthetic peraluminous sapphirines seems to be similar to that deduced for the Sar e Sang sapphirines and, even more so, to that of the metastable Mg-aluminate phase of Saalfeld and Jagodzinski (1957). Given still longer durations of crystallization these synthetic peraluminous sapphirines might have gradually approached the 7:9:3 sapphirine composition previously established as the end member of the sapphirine series at elevated pressures (Seifert, 1974). Such a compositional tendency towards 7:9:3 might actually be reflected in the wide spread of analyses shown by Bishop and Newton (ms. 1974). If this mechanism of gradual change with time of metastable sapphirine compositions towards the stable 7:9:3 end member holds, it is clear that the conflicting one-atmosphere liquidus relationships of sapphirine in the system $MgO-Al_2O_3-SiO_2$ as determined by Foster (1950) on one side and by Keith and Schairer (1952) on the other both represent different degrees of metastability. In this case the stable extent of the sapphirine liquidus field both in temperature and composition has yet to be determined.

Considering all the evidence from the analytical and experimental work on natural and synthetic sapphirines available thus far it appears most likely to the present authors that peraluminous sapphirines are indeed altogether metastable phases.

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