THE COMPOSITION OF SAPPHIRINE FROM SALVADOR, BAHIA, AND CONDITIONS OF ITS FORMATION

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RESUMO Safirina é um mineral raro de rochas metamórficas de alto grau. Duas amostras de Salvador, Bahia, foram analisadas por meio de microsonda eletrônica juntamente com os minerais associados. Essas amostras são semelhantes a outras descritas na literatura, mas possuem um teor em Fe muito alto. Quase metade desse Fe deve substituir o Al. Evidências químicas, petrográficas e de campo indicam que a safirina formou-se pela reação de sílica metassomática com espinélio num corpo de bronzitito (rocha formada principalmente de ortopiroxênio). Maior silicificação transformou a safirina em cordierita, em algumas partes. A temperatura indicada pelo teor em Al_2O_3 dos ortopiroxênios é de aproximadamente 1 000°C, e a pressão é estimada entre 5 e 8 kb.

ABSTRACT Analyses of two sapphirine specimens from Salvador, Bahia, Brazil along with partial analyses of some associated minerals were made by electron microprobe. These sapphirines are similar to other analysed specimens, but are among the most iron rich (9.2 and 9.8 wt % total iron as FeO). Nearly half of this iron must be present as Fe^{+3} substituting for Al. Field petrographic and chemical evidence suggests that the sapphirine developed by addition of silica to a spinel bearing bronzitite body. Further introduction of silica apparently produced reaction of sapphirine to cordierite in parts of the body. The temperature of formation given by Al_2O_3 content of the orthopyroxene was near 1 000°C; the pressure is estimated to be in the range 5 to 8 kilobars.

INTRODUCTION Sapphirine is an unusual mineral of high grade metamorphic rocks (granulite facies). It characteristically occurs in assemblages poor in silica but rich in both aluminum and magnesium. Sapphirine is generally considered to be a rare mineral but several new occurrences have been discovered in recent years among them the occurrence at Salvador, Bahia (Allard and Fujimori, 1966). It is probably more common than previously thought, and should be expected in rocks of favorable composition in any granulite terrain.

The simplest formula unit can be written $\text{Mg}_2\text{Al}_4\text{SiO}_{10}$. The silicon and two aluminum ions in this unit would be found in tetrahedral sites, and the remaining two aluminum and magnesium ions in octahedral sites according to the structure analysis made by Moore (1969). The sample analysed by Moore and most other natural samples have a greater number of Al ions substituting for Mg and Si, than this simple formula, (Deer, *et al.*, 1963, Schreyer and Seifert, 1969) and more complex formula units have been proposed to reflect this common substitution.

The sapphirine described by Allard and Fujimori (1966) occurs in a roughly spherical mass of phlogopite and spinel bearing bronzitite. This mass, about 5 m in diameter, is found in an outcrop of hypersthene granulite near the shore, 150 m east of the Bacia das Moças, Salvador, Brazil. Similar masses of bronzitite enclosed in hypersthene granulite occur throughout the Salvador area and are believed to be of sedimentary origin. Quartz-feldspathic granulite, granite and associated aplite and pegmatite dikes also occur in the immediate area.

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Sample description The different samples were selected for analysis, each seemed to be representative of the two most distinctive sapphirine assemblages. Number 100, from near the center of the mass, consists predominantly of coarse-grained bronzite and phlogopite with minor amount of spinel. The grains of spinel have rims of sapphirine surrounding them.

Number 101 is from nearer the outside of the mass. Here spinel is completely absent, orthopyroxene and phlogopite still predominate but sapphirine and cordierite occur as symplectitic intergrowths within large grains of hypersthene. The intergrowths have the appearance of fine bands of cordierite or sapphirine 10-50 μ in width in generally linear or plumose patterns. In places the proportions of sapphirine, (or cordierite) in these intergrowths reaches 50%. Although the appearance suggests some structural control, solution or reaction along cleavage planes is not obvious. The composition of the symplectite varies systematically across the section (2 cm) the hypersthene host crystals remain the same but on one side the intergrowth is composed entirely of sapphirine; on the other side the intergrowth is composed of cordierite; while in the intermediate area cordierite appears to be replacing sapphirine. Some of the bands or stringers of sapphirine are completely replaced by cordierite, some still contain isolated sections or islands of sapphirine.

Although no attempt was made in this study to accurately determine the optical properties, the two samples of sapphirine were apparently identical and within the range of commonly reported properties (Deer *et al.*, 1963). The only apparent differences between the two sapphirine samples were the textures and the associated minerals. A paper describing the field relationships and microscopic observations in more detail is being prepared by Dr. G. O. Allard and myself.

Mineral compositions Sapphirine, orthopyroxene, spinel and cordierite were analysed for the elements listed in Tab. I, using a *Material Analyses Co.* Model 400S electron microprobe. Although these are partial analyses, the totals, being near 100%, indicate that any other elements may be present only in very minor amounts. Analysis conditions were: accelerating voltage 15 kV; sample current 0.05 μ A on brass; RAP, PET, and Lif crystal spectrometers; sealed and thin window flow proportional counters as appropriate to detect K_{α} radiation; counting time 20 sec. using beam current stabilizer. Various analysed silicate minerals were used as standards. All analyses were corrected for background and drift using a computer program written by myself. The empirical correction factors of Albes and Ray (1970) were applied for the sapphirine and spinel where absorption and other effects were significant. In other cases standards were sufficiently close in composition to the analysed material. All calculations were carried out to four significant figures and subsequently rounded in Tab. I to values approximating the estimated accuracy.

SAPPHIRINE Although there are slight differences all three analyses of sapphirine from these samples are essentially the same. In general the analyses are very similar to those of other natural sapphirines. The iron content, however, is near the highest previously reported values. The analyses in Tab. I show a deficiency of silica as compared to the simple formula $(\text{MgFe})_2\text{Al}_4\text{SiO}_{10}$. This deficiency is also common in other analysed natural sapphirines (Deer *et al.*, 1963; Wilson and Hudson, 1967). Substitution of Al for Si in tetrahedral sites and concurrent substitution of Al and other trivalent cations for Mg and Fe^{+2} on other sites has been considered to account for most of the compositional variation of both natural and synthetic sapphirine (Deer *et al.*, 1963., Schreyer and Seyfert, 1969). If the deficiency of silica in these analyses is made up by Al in tetrahedral sites as shown in Tab. I, then a considerable portion of the iron must be present as Fe^{+3} to maintain

Table I - Mineral analyses

Sample 100				Sample 101			
Sapphirine	Bronzite	Spinel		Sapph. w/hyp.*	Sapph. w/cord.**	Hypersthene	Cordierite
SiO ₂	13.1	51.0	L.05	12.4	12.4	50.2	49.3
Al ₂ O ₃	60.2	6.9	61.5	60.7	61.8	7.6	33.9
ΣFeO***	9.2	14.3	23.7	9.8	10.0	20.9	3.3
MgO	18.7	26.6	15.8	17.5	16.8	22.3	12.3
CaO	L.02	.05	<.05	<.02	<.02	<.05	<.02
TiO ₂	.05	.1	<.05	<.05	<.05	.06	—
Total	101.2	98.9	100.0	100.4	101.0	101.0	98.8
numbers of ions on the basis of:							
Oxygen = 10	6	—		10	10	6	18
<i>mole percent</i>							
.78-Si } 1.0	.92-Si } 1.0	MgAl ₂ O ₄ = .61	.74-Si } 1.0	.74-Si } 1.0	.92-Si } 1.0	4.94-Si	
.22-Al } 4.0	.08-Al } 1.0	Fe ⁺ Al ₂ O ₄ = .33	.26-Al } 4.0	.26-N } 4.0	.08-A } 1.0	.08-Al	4.00-Al
.46-Fe } 2.11	.07-Al } 1.0	Fe ²⁺ Fe ³⁺ O ₄ = .06	4.00-Al } 2.10	.09-Al } 2.08	.08-Al } 1.01	.28-Fe	
1.65-Mg } 7.4 mol %	.22-Fe } 1.0		.05-Al } 1.56-Mg	.50-Fe } 1.50-Mg	.32-Fe } 7.8 mol %	1.83-Mg	
	.72-Mg } Al ₂ O ₃				.61-Mg } Al ₂ O ₃		
*Sapphirine associated with hypersthene				<.05 = not found at the limit of detection 0.05%			
**Sapphirine associated with cordierite				<.05 = not found at the limit of detection 0.03%			
***Total iron content reported as FeO				— = not analysed			

the charge balance (nearly 50% in sample 100). Unfortunately Fe²⁺ and Fe³⁺ cannot be determined separately by electron microprobe techniques, but other reported analysis commonly show significant Fe₂O₃ contents. In several cases Fe³⁺ accounts for about 50% of the total iron content (compare Meng and Moore, 1972 Tab. III).

HYPERSTHENE The Mg-Fe ratios of the orthopyroxene from the two samples is quite different. This is especially striking since the sapphirine is essentially of constant composition. This can easily be seen in the lower portion of Fig. 1. The orthopyroxene composition appears to change as the assemblage changes its mineralogical composition. There was no noticeable zoning or compositional gradients within grains of orthopyroxene but there was some variability between grains and the averages in Tab. I and Fig. 1 represent a spread of values in Mg and Fe. The ranges of values from the two samples, however, do not overlap and an overwhelming majority of points lie close to the average value. Another interesting feature of these analyses is the high alumina content, which remains nearly the same in both samples.

SPINEL The mole proportions of cations in the spinel analysis were recalculated to the spinel and hercynite molecules. The small amount of Fe remaining was calculated as magnetite. The results of this procedure show that the spinel phase in sample 100 is predominantly a spinel-hercynite solid solution with an almost negligible amount of magnetite.

CORDIERITE The total of the analyses in Tab. I would permit a small amount of water in the composition of this cordierite. 1.5-2.5% H₂O is common in natural cordierites

Figure 1 — Compositions of the analysed minerals. Ideal mineral compositions indicated by small triangle. Assumed initial composition is shown by a star with path of silica metasomatism indicated by an arrow. *cd*, cordierite; *hy*, hypersthene (bronzite); *sa*, sapphirine; *sp*, spinel

The occurrence of sapphirine in Bahia appears to be a result of silica metasomatism of an originally silica poor assemblage of bronzite-phlogopite-spinel. All the minerals of this assemblage, and the metasomatic products (except phlogopite), correspond to phases in the system $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ (allowing for FeO in the natural equivalents). There is a considerable amount of experimental data available on this system, some of which may be used to obtain some indication of the pressures and temperatures which produced these rocks.

A very good estimate of temperature can be made using the data of Anastasiou and Seifert (1972) on the solubility of Al_2O_3 in orthopyroxene. The two analyses of orthopyroxene in Tab. I show approximately 7 wt% Al_2O_3 . If this value is compared with the experimental results diagramed in Figs. 4, 6, and 8 of Anastasiou and Seifert it indicates a temperature about 1000°C. The temperature indicated by Anastasiou and Seifert data and its variation with pressure are shown in Fig. 2. Because their experiments were done under condition where $P(\text{H}_2\text{O}) = P(\text{total})$, their sapphirine reacted to cordierite + spinel below 3.5 kb and the upper limit of their data is 5 kb. But, since the water pressure should not directly affect the orthopyroxene or the sapphirine, this temperature curve can probably be extrapolated for pressures between 1 and 10 kb, so long as the coexisting aluminous phase is sapphirine. The effect of pressure in any case is very small. (We would, however, expect the Al_2O_3 contents of orthopyroxene to be different with different coexisting aluminous assemblages). The most serious problem in applying this geothermometer to natural assemblages is the effect of the iron content of the pyroxene on the solubility of alumina. Anastasiou and Seifert discuss the problem but give no quantitative solution. There is no firm theoretical or empirical evidence to suggest just what the effect would be for the assemblages and pressure ranges with which we are concerned. If we assume that the difference in alumina content of the two analysed pyroxenes is due *only* to enhancement of the Al_2O_3 solubility by Fe for Mg substitution, the Al_2O_3 content can then be linearly extrapolated back to pure enstatite. There it has a value of 5.1 wt% which is equivalent to a temperature of about 950°C. It is probably safe to estimate a temperature of $1000 \pm 50^\circ\text{C}$ for this sapphirine bearing bronzite.

Estimates of pressure for this assemblage can be made by considering the conditions under which cordierite and sapphirine can coexist. At 900 to 1000°C cordierite breaks down at pressures of 8 to 11 kb to assemblages of sapphirine enstatite + quartz or enstatite + sillimanite + quartz (Newton, 1972) and sapphirine will break down to cordierite and spinel at low pressures. The problem with this approach is that cordierite stability is greatly affected by the amount of water which enters its structure (much like the water in zeolites). For instance anhydrous cordierite breaks down to sapphirine and quartz (reaction 2 in reverse) at pressures of about 8.5 kb at 1000°C whereas hydrous cordierite is apparently stable up to 10 or 11 kb (Newton, 1972). Under conditions of $P(\text{H}_2\text{O}) = P(\text{total})$ sapphirine breaks down to spinel + hydrous cordierite at pressures near 3.5 kb (Fawcett and Yoder, 1966). However, it is apparently stable down to atmospheric pressure under dry conditions (relative to an anhydrous cordierite).

Using the free energy data of Bird and Anderson (1972) for hydrous cordierite, and a sorbtion energy of about 2.5 kcal per mole of water, a very rough free energy value for sapphirine can be obtained from Newton's (1972) curve for reaction (1). Further calculation then shows that the reaction:

Figure 2 — Stability relationships of sapphirine, cordierite and associated minerals. *cd·h*, hydrous cordierite; *cd*, anhydrous cordierite; *ph*, phlogopite; *en*, enstatite; *sa*, sapphirine; *sp*, spinel; *qz*, quartz. (After Newton, 1972; Fawcett and Yoder, 1966; Yoder, and Eugster, 1954; Anastasiou and Seifert, 1972)

should have a strongly positive free energy, *i.e.*, sapphirine should be stable at 1 000°C and atmospheric pressure. This is also confirmed by the fact that sapphirine can be synthesized at 1 atm. from dry mixtures of the oxides (Deer, *et al.*, 1963).

The problem of determining the stability field of a natural cordierite is compounded by the fact that cordierites can apparently take on or discharge water relatively rapidly (Schreyer and Yoder, 1964). The water in the analysis of a natural cordierite probably does not represent the amount present at the high temperature equilibrium. But, in the assemblage we are considering here, there is some evidence to suggest that the environment was not entirely dry, although $P(H_2O)$ did not necessarily equal total pressure. The primary evidence is the presence of abundant phlogopite without any evidence of its breaking down. The P-T curve for phlogopite break down [$P(H_2O) = P(\text{total})$] is shown in Fig. 2 (Yoder and Eugster, 1954). The presence of iron, as in these samples, would tend to lower the temperatures somewhat, depending upon the oxygen fugacity (Wones and Eugster, 1965). Estimates based on this work suggest that the water pressure would have to be well over 2 kb at 1 000°C. The granite, pegmatite and aplite dikes, as well as amphibole and biotite in surrounding rocks, also suggest that some water was present. Hydrous cordierite can apparently retain its water even under conditions where $P(H_2O)$ does not equal total pressure (Newton, 1972, p. 412). It seems reasonable, then, to assume that stability fields based on hydrous cordierite are applicable to the sapphirine-bearing assemblage discussed here. This would place the minimum pressure near 4 kb and the maximum near 10 kb. The beginning of melting would also place a constraint on temperature and pressure as shown in Fig. 2. At 1 000°C, we should expect to see some melting in hydrous cordierite-sapphirine assemblages at pressures above 7 kb. The absence of any melting suggests that pressures were not much, if any, higher.

CONCLUSIONS The sapphirine bearing assemblage from Salvador, Bahia apparently formed at temperatures near 1 000°C and pressures between 5 and 8 kb (depths of 15 to 24 km). The formation of sapphirine from spinel and the subsequent reaction of sapphirine to cordierite were due to the addition of silica from surrounding quartzfeldspathic rocks to an aluminum-rich ultrabasic rock, a type of paragenesis which is common for sapphirine. Many new occurrences should be found if regions of granulitic rocks (such as those of Brazil) are examined for locations where Mg and Al rich rocks could have been affected by silica metasomatism. Such sapphirine-bearing rocks can be useful in establishing temperatures of metamorphism, using the aluminum content of the orthopyroxene coexisting with the sapphirine as a geothermometer.

Acknowledgements I am very much indebted to Dr. Gilles Allard, who suggested this problem, provided the samples, and gave all the information on the field relationship. This work was prepared while I enjoyed the position of visiting professor in the Institute of Geociências, University of São Paulo and used the facilities of their microprobe laboratory. Financial support was also provided by the National Science Foundation (U.S.) through a grant to the University of Georgia.

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