

Al-Cr substitution in peraluminous sapphirines from the Bjørnesund area, Fiskenaeset region, southern West Greenland

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ABSTRACT. Cr-rich Mg-sapphirines, which are more aluminous in composition than $R^{2+}:R^{3+}:Si$ of 7:9:3 and are therefore considered to be peraluminous, are shown to have an inverse linear relationship between octahedrally co-ordinated Cr and Al. This balanced substitution, which has not previously been described, may be used to explain the major chemical variations exhibited in the described minerals. Since the peraluminous Cr-rich sapphirines are idioblastic it is suggested that they are stable members of the assemblages within which they occur. Peraluminous sapphirine is usually considered to be metastable but in this instance it is possible that chromium may assist in stabilizing its development.

THE composition and structure of sapphirine has been the subject of long debate (Deer *et al.*, 1978). The variable chemistry has been mainly explained by coupled substitution of $MgSi \rightleftharpoons 2Al$ with $Mg \rightleftharpoons Fe^{2+}$ and other possibilities such as $Si \rightleftharpoons Al + Mg$ may perhaps contribute to the observed complexities (Schreyer and Abraham, 1975). This contribution is concerned with the $Al \rightleftharpoons Cr$ substitution in some peraluminous sapphirines.

The type locality for sapphirine, at Fiskenaeset harbour, southern West Greenland, was first investigated by Giesecke in 1809 (Giesecke, 1910). Subsequently, sapphirine has been found in other localities (e.g. Herd, 1972). The mineral has also been the subject of many mineralogical studies, the earlier ones having been summarized by Bøggliid (1953). Deer *et al.* (1978) summarize most of the modern studies, whilst more recent work has been reported by Higgins *et al.* (1979) and Friend and Hughes (1981). In West Greenland the development of sapphirine-bearing assemblages is very restricted (Ramberg, 1948) and in the Fiskenaeset region sapphirine only occurs at the upper contact of the Fiskenaeset anorthosite complex (Herd, 1972) where the anorthosite is intrusive into amphibolitic supracrustal rocks which contain aluminous ultra-

mafic bodies (Friend and Hughes, 1977). More details of the Archaean geology of the Fiskenaeset region may be found in Bridgwater *et al.* (1976).

The nature of the sapphirine-bearing assemblages in the vicinity of Fiskenaeset have been described in detail by Herd (1972, 1973). In his re-examination of the known localities and investigation of new occurrences that he discovered whilst remapping, Herd (1972) came to the conclusion that sapphirine-bearing assemblages had developed by reactions in rocks with very high Mg and Al contents in two quite different situations. First, there were those localities, such as the type locality, where a reaction involving ultramafic material had occurred. Secondly, there were those occurrences which, on the grounds of bulk chemistry, were considered to have involved aluminous, Mg-rich sedimentary material in the production of the mineral assemblages (Herd, 1973).

The locality from which the material for this study was collected, some 10 km north of Bjørnesund, was first discovered by Walton (1973) and was remapped in detail by the author in 1974 (fig. 1). Here it was established that the development of the sapphirine-bearing assemblages (which include other highly aluminous phases such as kornepine, corundum, and spinels of various composition) was due to the reaction of anorthosite with aluminous ultramafic rocks into which it was intruded (Friend and Hughes, 1977, 1981). Metasedimentary material, which is rare in the general vicinity, and which does not occur at the Bjørnesund reaction site, is considered not to be involved. The ultramafic rocks are progressively less altered away from the contact zone with the anorthosite and this affords an ideal opportunity to examine the progressive development of these minerals and their assemblages.

Mineral chemistry and petrography. Analyses of sapphirine which contain a detectable amount of

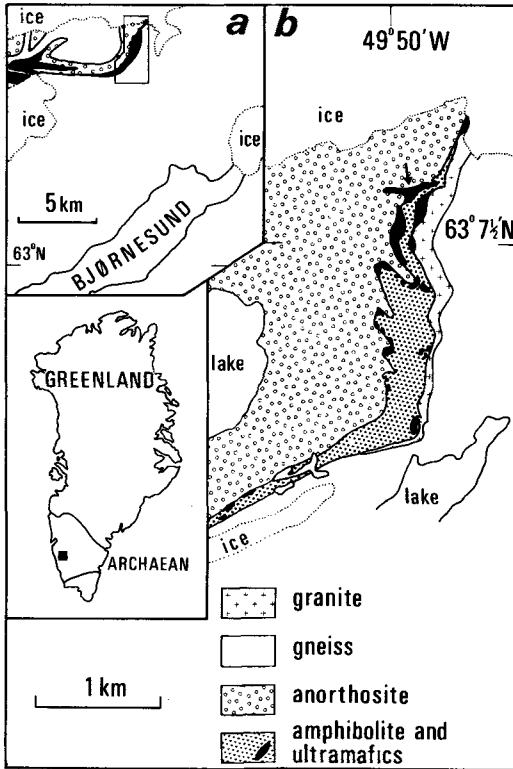


FIG. 1. Location of the reaction zone at the upper intrusive contact of the Fiskenaeset anorthosite complex north of Bjørnesund. (a) Sketch map of the area showing the generalized geology. Black = amphibolite and included ultramafics; dots = anorthosite; white = gneisses and undifferentiated rocks. (b) Sketch map of the detailed geology of the reaction zone showing the positions of the ultramafic rocks. The locality of GGU 149434 and GGU 183544 is arrowed.

Cr_2O_3 have occasionally appeared in the literature (e.g. Herd, 1973; Higgins *et al.*, 1979). During the present work on the Bjørnesund reaction zone material it was discovered that in one sample (149434) an unusual maroon-coloured sapphire occurred which contained the highest amounts of Cr_2O_3 (7.40%) then reported (Friend and Hughes, 1981). Sample 149434 consists of laths of apple-green magnesio-cummingtonite and optically zoned, idiomorphic maroon sapphire which contains embayed inclusions of both red spinel and ruby corundum. Phlogopite and some scattered opaque grains complete the assemblage. Since the lowest Cr_2O_3 value found in the sapphirines from 149434 was 4.20% an attempt was made to find a sample which gave a range of lower values. This was accomplished during studies of 183544 in which sapphirines with contrasting lower Cr_2O_3

values were found. The sample 183544 is a very inhomogeneous complex association containing several distinct mineral assemblages. The rock contains a number of different sapphirines ranging from a pale greyish-red through to a pale maroon colour; buff and yellowish-green orthorhombic amphibole; bright apple-green monoclinic amphibole; phlogopite; plagioclase; red spinel; rare ruby corundum, and accessories such as rutile and opaque iron oxide. A microprobe section was taken from this complex association (183544/1) containing buff magnesio-gedrite (using the nomenclature of Leake, 1978); idiomorphic greyish red to pale maroon, colour-zoned sapphire containing occasional inclusions of ruby spinel; rare crystals of embayed, pale greyish-red, inclusion-free sapphire; phlogopite and rutile. The sapphirines in this section show a range of Cr_2O_3 values from 5.53% down to 0.23% (see Table I), thus overlapping the bottom portion of and extending to lower values the range (7.52% to 4.20%) found in 149434.

The analysed sapphirines in 149434 and 183544 have several significant properties. They are all highly magnesian with $\text{Mg}/(\text{Mg} + \text{Fe})$ ratios about 0.97 and a range of Cr_2O_3 values from unusually high (7.52%) down to the very low values (0.23%) more typically encountered in other sapphirines (see data in Deer *et al.*, 1978; Higgins *et al.*, 1979). The range of the chemistry can be related to the optical zoning observed in the minerals which is often particularly marked around the aluminous inclusions. The structural formulae (Table I) have been recalculated according to the method of Higgins *et al.* (1979) to obtain a value for Fe^{3+} after allocating Al^{3+} to fill the Si deficiency in the tetrahedral sites. In all cases the amount of Fe^{3+} required to balance the formula, is small or zero. The structural formulae obtained agree well with the theoretical general formula given by Moore (1969) with cation totals being very close to 14 per 20 oxygens.

The general variation of the Cr-rich sapphire chemistry, plotted in the appropriate portion of the system SiO_2 -(Mg,Fe)O-(Al,Cr) $_2\text{O}_3$ - H_2O is shown in fig. 2a and b. The compositions of the analysed sapphirines lie very close to the tie-line $\text{R}^{2+} + \text{Si} = 2\text{R}^{3+}$ which connects the theoretical end members $(\text{Mg}_8\text{Si}_6\text{O}_{20}-\text{Mg}_2\text{Al}_6\text{O}_{20})$. As Fe^{3+} has not been determined analytically it has not been taken into account in this diagram. Therefore, most of the analyses tend to plot slightly below the line. Since the majority of the analyses plot to the right of the accepted end-member $\text{R}^{2+} : \text{R}^{3+} : \text{Si} = 7:9:3$, the sapphirines may be considered to be peraluminous. In this respect these sapphirines are comparable with those reported by Schreyer and Abraham (1975) in whiteschists from

Afghanistan. Generally the analysed sapphirines reported here (Table I) are poor in silica which also tends to cause the analyses to plot to the lower right hand side of the diagram. The silica-poor nature of these Cr-rich sapphirines is further emphasized in fig. 3a in which the data are plotted to show the variation of $\text{Si}:\Sigma\text{R}^{3+}$. It is clear from

this diagram that the analyses extend the range of substitution above that reported by Schreyer and Abraham (1975, 1976) and Ellis *et al.* (1980). The range of the number of Si atoms (1.240–1.507) in the structural formula is relatively restricted as would be expected since the $\text{R}^{2+} + \text{Si} \rightleftharpoons 2\text{R}^{3+}$ substitution works against high Si content.

TABLE I. Microprobe analyses of the sapphirines

	4	6	12	17	25	34	39	46
SiO ₂	11.2	11.3	12.1	11.6	11.2	12.2	11.4	12.3
Al ₂ O ₃	63.0	63.8	63.3	60.6	61.8	60.7	63.5	61.7
Cr ₂ O ₃	5.42	4.20	4.73	7.52	7.36	6.38	4.89	6.09
FeO*	0.62	0.52	0.57	0.61	0.80	0.54	0.86	0.52
MnO	n.d.	0.12	0.15	n.d.	n.d.	n.d.	n.d.	n.d.
MgO	18.9	19.1	19.2	18.5	18.6	19.3	18.8	19.1
Total	99.14	99.04	100.05	98.83	99.76	99.12	99.45	99.71
Cations per 20 oxygens								
Si	1.372	1.333	1.417	1.382	1.330	1.447	1.338	1.445
Al	4.673	4.667	4.583	4.678	4.670	4.553	4.662	4.555
Al	4.119	4.218	4.154	3.865	3.959	3.943	4.173	4.015
Cr	0.507	0.392	0.438	0.711	0.690	0.599	0.455	0.567
Fe ³⁺	0.047	0.052	0.003	0.061	0.029	0.011	0.024	—
Mg	3.334	3.355	3.348	3.293	3.281	3.410	3.303	3.353
Fe ²⁺	0.025	—	0.052	—	0.050	0.043	0.061	0.052
Mn	—	0.012	0.015	—	—	—	—	—
	3	5	10	13	14	15	20	21
SiO ₂	11.8	12.4	12.1	11.3	12.7	12.6	13.0	12.1
Al ₂ O ₃	63.3	63.8	63.6	63.2	65.3	66.0	64.6	64.5
Cr ₂ O ₃	4.38	1.95	3.12	5.18	0.40	0.23	1.20	2.41
FeO*	1.43	0.99	0.85	1.05	0.97	0.99	0.96	1.08
MnO	n.d.	n.d.	n.d.	n.d.	n.d.	0.12	n.d.	n.d.
MgO	18.8	19.9	19.4	18.9	19.8	19.7	20.0	19.8
Total	99.71	99.14	99.07	99.63	99.17	99.64	99.76	99.89
Cations per 20 oxygens								
Si	1.391	1.465	1.419	1.334	1.481	1.460	1.507	1.412
Al	4.609	4.535	4.581	4.666	4.519	4.540	4.493	4.588
Al	4.171	4.282	4.243	4.121	4.448	4.486	4.350	4.276
Cr	0.408	0.181	0.297	0.483	0.036	0.021	0.110	0.222
Fe ³⁺	0.047	—	0.041	0.062	0.035	0.033	0.033	0.090
Mg	3.295	3.476	3.395	3.323	3.439	3.401	3.463	3.442
Fe ²⁺	0.111	0.098	0.043	0.042	0.059	0.063	0.060	0.015
Mn	—	—	—	—	—	0.011	—	—

Analyses 4–46: sample GGU 149434; 3–21: sample GGU 183544/1.

n.d. = not detected. In all, thirteen elements were sought (Na, Mg, Al, Si, K, Ca, Cr, V, Ti, Fe, Mn, Zn).

* All Fe analysed as FeO. Fe³⁺ has been allocated to the structural formula to balance the stoichiometry as per the method of Higgins *et al.* (1979).

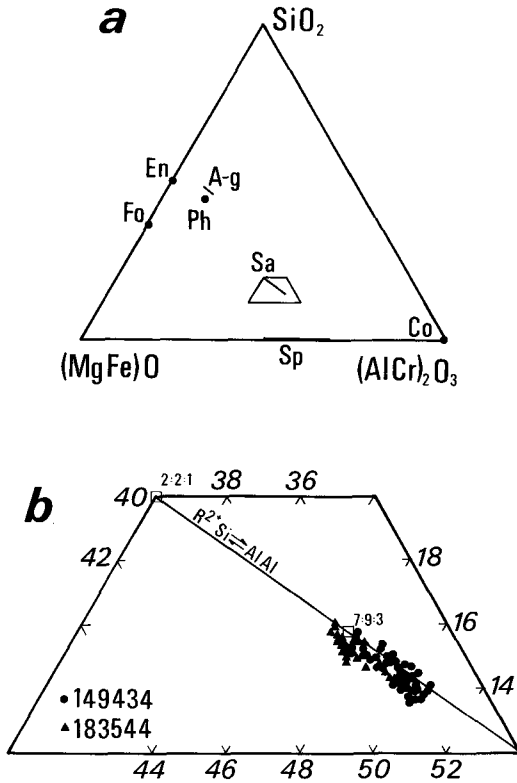


FIG. 2. (a) The system SiO_2 -(Mg,Fe)O-(Al,Cr) $_2$ O $_3$ -H $_2$ O (mol. %) showing the index for the enlarged portion. The positions of the accompanying minerals in the assemblage are also shown. Fo = forsterite, En = enstatite, Ph = phlogopite, A-g = aluminous gedrite, Sa = sapphire, Sp = spinel, Co = corundum. (b) The position of the analysed sapphirines along the tie-line connecting the theoretical end-members.

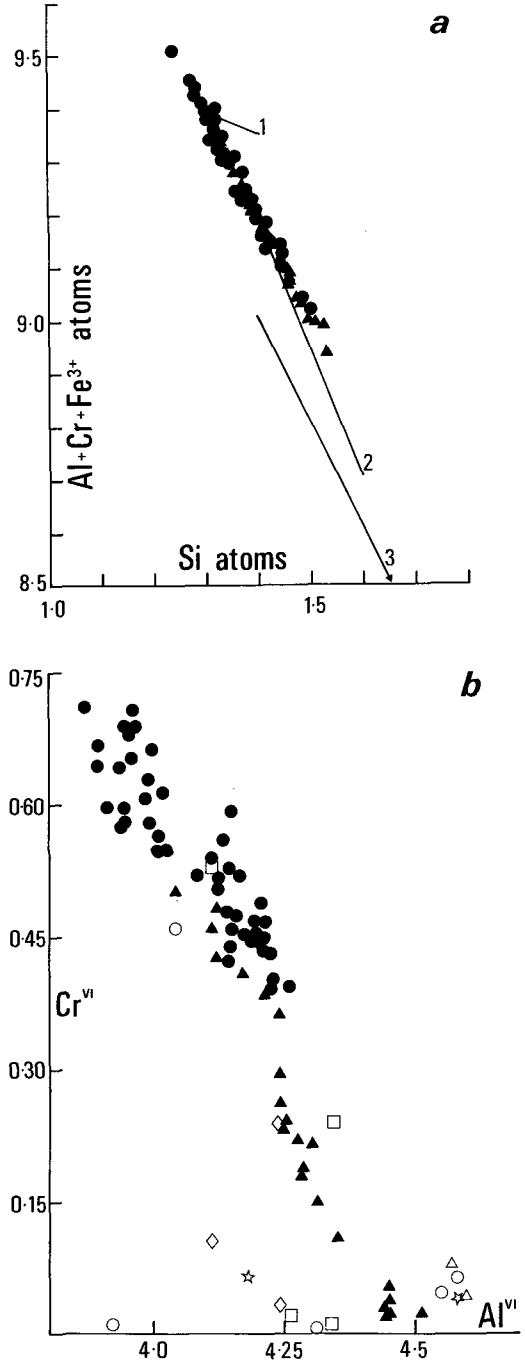
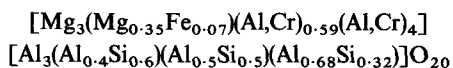


FIG. 3. (a) Variation of the composition of the sapphirines showing the linear relationship between Si and Al+Cr+Fe $^{3+}$. The relevant portions of the range of other peraluminous and silica-poor sapphirines are included. 1 = Schreyer and Abraham (1975); 2 = Schreyer and Abraham (1976); 3 = Ellis *et al.* (1980). Dots = 149434; triangles = 183544/1. (b) Plot of octahedrally coordinated Al vs. Cr demonstrating the inverse, linear relationship between the two elements. Dots = 149434; solid triangles = 183544/1. Open symbols represent other sapphirine data

from the literature. Triangles = Cameron (1976); stars = Meyer and Brookins (1976); circles = Deer *et al.* (1978); squares = Higgins *et al.* (1979); and diamonds = Ellis *et al.* (1980).

Herd (1972, 1973), Cameron (1976), Higgins *et al.* (1979) and Ellis *et al.* (1980) report other Cr-bearing sapphirines, as do Deer *et al.* (1978) who consider that most naturally occurring sapphirines probably contain some Cr_2O_3 . To date, because of the lack of any coherent trend in the data, $\text{Cr} \rightleftharpoons \text{Al}$ substitution in sapphire has only been assumed to take place (e.g. Ellis *et al.*, 1980), but has never been conclusively demonstrated. However, the range of Cr_2O_3 (0.23–7.52 wt. %) in the samples allows the nature of the relationships between Cr and Al to be clearly shown. Fig. 3 shows a plot of octahedrally coordinated Al *vs.* Cr. It is evident that there is a well-defined inverse linear relationship between the two elements and this clearly implies that they are in a balanced substitutional relationship. Including data on other Cr-bearing sapphirines reported in the literature shows that there are two groups of sapphirines—those whose analyses plot on or very close to the observed $\text{Al} \rightleftharpoons \text{Cr}$ substitution line and those which show an irrational relationship to the proposed substitution line. All of these latter examples have less than 0.066 Cr in their structural formula. It is therefore suggested that in the cases showing a correlation with the defined trend actual $\text{Cr} \rightleftharpoons \text{Al}$ substitution is operating. In those data points which deviate from the trend it is presumed that as Cr is present only as a trace constituent and the substitution may not be related to Al. It is concluded that all of the reported sapphire analyses depart from the theoretical end-member 7:9:3 composition because of the substitution $\text{R}^{2+} + \text{Si} \rightleftharpoons 2(\text{Al}, \text{Cr})$ and hence fall to the right of that point on fig. 2b. An example of a possible composition would be (149434, analysis 12):



with some uncertainty over the precise nature of the Al-Si distribution in the tetrahedral sites (Moore, 1969; Schreyer and Abraham, 1975). Since the analyses do not deviate significantly from the $\text{R}^{2+} + \text{Si} \rightleftharpoons 2(\text{Al}, \text{Cr})$ substitution line it is probable that other substitutions, for example $\text{Si} \rightleftharpoons \text{Al}^{\ddagger}\text{Mg}$ (Schreyer and Abraham, 1975), have not taken place.

Discussion. It has been shown that the Cr-rich sapphirines reported here (Table I) are peraluminous in terms of the definition of Schreyer and Abraham (1975, 1976). They regard peraluminous sapphire as a metastable, intermediate reaction product prior to the formation of stable corundum + cordierite. In both 149434 and 183544 relict ruby corundum may be found within idiomorphic Cr-rich sapphire. This strongly suggests that the sapphire is the stable phase and

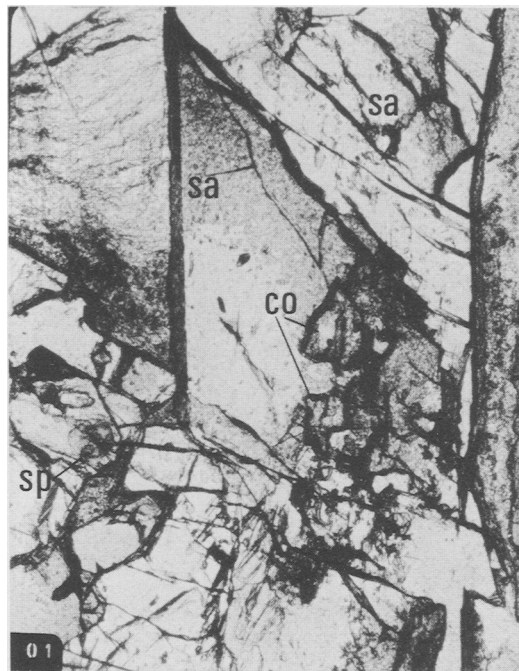
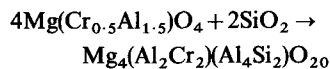


FIG. 4. Photomicrograph of a portion of an idiomorphic sapphire (sa) containing embayed ruby corundum (co). Red spinel (sp) inclusions are present in an adjacent sapphire crystal, GGU 149434. Height of photograph 2.5 mm.

not the corundum (fig. 4) as cordierite is absent from the observed assemblages. From these and other samples taken from the Bjørnesund area it is known that sapphire has progressively developed from chrome-bearing ruby spinel. In both the samples discussed here embayed inclusions of spinel occur in the sapphire. Whilst in other samples, containing spinel-phlogopite layers, thin rims of idiomorphic sapphire can be seen to have developed over the spinel. The simple reaction of spinel and silica can explain the observed reaction:



Corundum and ruby spinel are present in this example as intermediate phases which pre-date the development of sapphire. This must imply that there is some earlier or intermediate assemblage which has developed from the original ultramafic rocks prior to the development of the present sapphire-bearing assemblages. It is expected that work in progress will be able to order the sequential development of the mineral assemblages.

Acknowledgements. I thank Dr D. J. Hughes and other colleagues who have worked in the Fiskenaasset region, together with the Director of the Geological Survey of Greenland with whose permission this paper is published. I especially thank Erik Olsen for his expert seamanship, J. V. P. Long and P. J. Treloar for the use of the microprobe at Cambridge University, D. J. Allen and C. Jones for technical assistance, and C. G. Topley for helpful comments.

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[Manuscript received 2 July 1981]