Magnesian högbomite in a sapphirine-bearing rock from the Fiskenaesset region, W. Greenland

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ABSTRACT. Högbomite occurs in a 20 × 80 cm gedrite-rich lens between meta-volcanic amphibolite and anorthosite at the top of the Fiskenaesset Complex in the Angnertussoq area 13 km SE of Fiskenaesset. Between coarse prismatic gedrites there are clusters with chlorite, spinel, sapphirine, rutile, högbomite and corundum. Högbomite forms 200 μm grains often associated with rutile, surrounded by spinel and sapphirine but never in contact with gedrite. Usually sapphirine forms rims on spinel and contains relict gedrite. Corundum is intergrown with spinel and sapphirine. Reactions suggested by the textures are: 1. Gedrite + spinel + rutile → sapphirine + högbomite + chlorite. 2. Sapphirine → chlorite + corundum + spinel. 3. Högbomite → rutile + corundum + spinel. In some areas without rutile or högbomite the reaction gedrite + spinel + ? → sapphirine + chlorite took place.

Mg/(Mg + Fe + Mn) ratios are in the following order: sapphirine (0.95–0.92) > chlorite (0.94) > hornblende (~ 0.91) > anthophyllite (~ 0.86) > gedrite (~ 0.86) > spinel (0.77–0.74) > högbomite (0.75–0.71). Högbomite usually has an anhydrous total of c. 98 %; on the basis of 31 oxygens and with total Fe as FeO one representative analysis has Mg 4.59, Fe 1.73, Zn 0.02, Ni 0.05, Al 14.78, Cr 0.02, Ti 1.2 atoms per formula unit.

HÖGBOMITE occurs in a sapphirine-bearing rock (GGU No. 97037) 13 km SE of Fiskenaesset village within the Archaean craton of W. Greenland. The host material of the högbomite belongs to a 20 × 80 cm lens of gedrite-type sapphirine rock which is located at the contact between a thin layer of the Fiskenaesset Complex and a metavolcanic amphibolite (Windley et al., 1973). Several other sapphirine-bearing lenses are situated along this top contact of the Fiskenaesset Complex (fig. 1) (Herd,
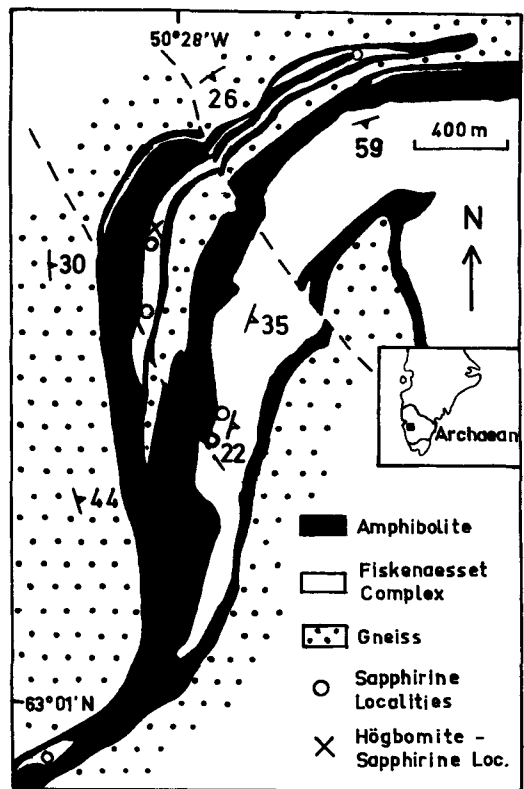

FIG. 1. Simplified geological map of the NW Angnertussoq area, Fiskenaesset region showing the högbomite–sapphirine locality.

1973). These rocks belong to an overturned isoclinal syncline on the west side of the main Angnertussoq layer of the Fiskenaesset Complex (Windley, 1976). All the rocks in the syncline have been extremely thinned tectonically; they now dip shallowly to the east. Boudinaged lenses of chromitite up to 60 cm thick occur nearby within anorthosites which form the topmost stratigraphic zone of the Fiskenaesset Complex (Windley *et al.*, 1973; Myers, 1981). This is the first occurrence of högbomite in Greenland.

Petrography

In thin section the samples consist, in decreasing order of abundance, of gedrite (pale brown), chlorite (colourless), spinel (blue-violet), sapphirine (very pale greenish-blue), anthophyllite, rutile (red-brown), högbomite (yellow-brown), corundum, hornblende and phlogopite (pale reddish brown). Gedrites in prismatic blades up to 1.5 cm long with a decussate texture make up about 80% of the rocks. In the rims of several large gedrites, anthophyllite occurs as lamellar intergrowths with lamellae parallel to (120) or as patchy intergrowths. Except for anthophyllite and hornblende all the remaining phases largely occur together in clusters among the
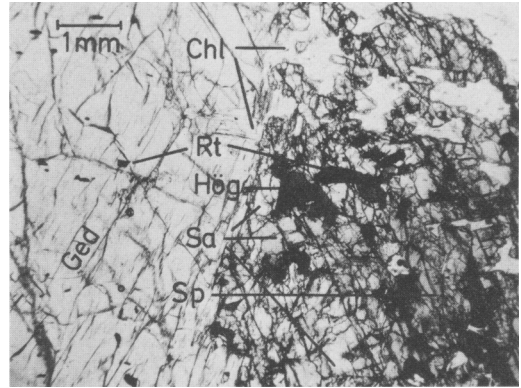

FIG. 2. Photomicrograph showing a part of a large 1.5 cm long gedrite and one cluster with högbomite, sapphirine, spinel, corundum, chlorite, and rutile.

gedrites (fig. 2). In the clusters spinel and sapphirine are the main phases and sapphirines occur typically as rims on the spinel. Rutile occurs equally within gedrite as in the clusters. Corundum occurs as subidioblastic grains intergrown with spinel and sapphirine and rarely it rims sapphirine. Högbomite
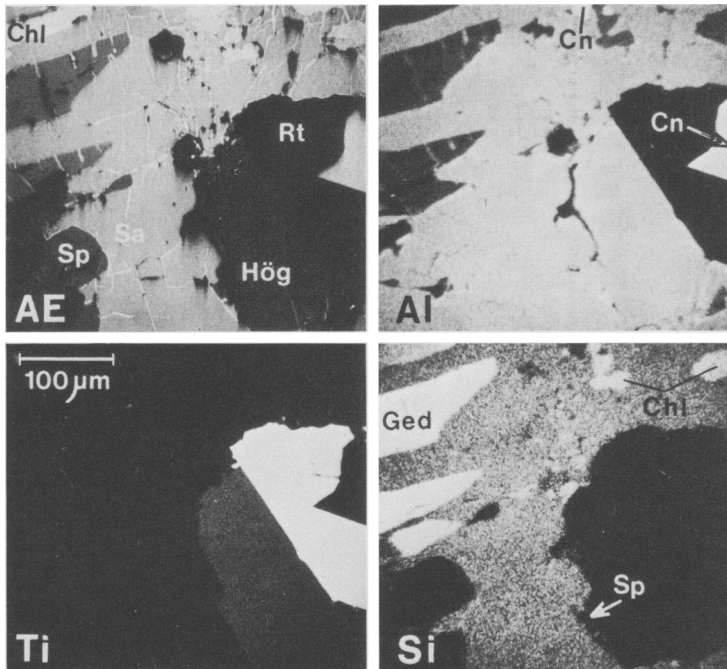

FIG. 3. Photoset showing absorption electron patterns (AE) and X-ray element distribution of Al, Ti and Si for the cluster phases. Gedrites are inclusions in sapphirine and are in optical continuity with large matrix gedrite. Phase abbreviations see fig. 5.

forms subidioblastic to xenoblastic grains up to 200 μm often adjacent to rutile within spinel and sapphirine, and it is never in contact with gedrite and hardly ever with chlorite. Sapphirine contains relict grains of gedrite (fig. 3) in optical continuity with bordering major gedrite. Chlorite flakes (fig. 2) typically rim the clusters along sapphirine–gedrite and spinel–gedrite boundaries and small chlorite grains (fig. 3) occur with corundum and spinel within some sapphirines. Anthophyllite forms patches along the margins of gedrite and hornblende and subidioblastic grains in the chlorite matrix.

Two main reactions took place in these rocks. The starting material that we observe is gedrite + spinel + rutile, the spinel and rutile forming minor grains within and among the larger gedrites. The reaction between these three phases gave rise to sapphirine, högbomite and chlorite. Thus the högbomite is within both the reactant spinel and the product sapphirine and often close to rutile. Breakdown of sapphirine without involving another phase gave rise in the second reaction to chlorite, corundum and spinel, the main effect of which was to produce corundum intergrown with all other phases in the clusters. We have also noted the local breakdown of högbomite to produce rutile and corundum and possibly spinel. Finally, in some areas where gedrite was in contact with spinel, but without rutile (or högbomite), there is now a reaction rim of sapphirine and chlorite. We have tried to explain this by the reaction: gedrite + spinel = sapphirine + chlorite, but X_{Mg} [Mg/(Mg + Fe + Mn)] constraints prevent this explanation (see below).

Mineral chemistry

The microprobe analyses were made by the wavelength dispersive method (at Kiel and Leicester) using 18 kV, 50 or 100 nA, 1 μm beam diameter and mineral standards. ZAF correction programmes were used. For zoned grains analyses were made not closer than 10–20 μm from the grain boundary.

Silica-free phases. Högbomite is characteristically zoned and the composition changes from grain to grain (Table I). The zoning shows a composition change from the core to the rim, for example, TiO_2 (8.1–5.7 wt. %), Al_2O_3 (63.5–64.8), total FeO (10.5–10.0) and MgO (15.6–16.8). The analyses do not show a linear distribution in $(Mg,Fe)O–Al_2O_3–TiO_2$ space (fig. 4). The important feature of the Fiskenaesset högbomite is that its X_{Mg} ratio is higher (0.708–0.750) than that of other högbomites in the literature, apart from the possible exception of that from Mautia Hill, Tanzania, determined with an X-ray microanalyser by McKie (1963). The X_{Mg} of the Fiskenaesset högbomite is noticeably close to that of spinel (see also Teale, 1980; Coolen,

TABLE I. *Representative analyses of högbomite and spinel*

Section no.	Högbomite						Spinel						
	5		2	4		3	5		4			5/1	
Anal. ref. no.	1 core	2 rim	3 (a)	4 core	5 rim	6 (a)	1 core	2 rim	3 core	4 rim	5 rim	6 (a)	7 (a)
TiO_2	8.1	5.7	7.8	7.9	5.6	6.5	—	—	—	—	—	—	—
Al_2O_3	63.5	64.8	64.3	64.6	64.9	63.6	67.5	66.9	66.8	66.3	66.9	66.7	66.1
Cr_2O_3	0.11	0.11	0.09	0.04	0.05	0.13	0.08	0.09	0.06	0.05	0.05	0.09	0.09
FeO	10.5	10.0	10.3	10.6	9.8	11.6	11.8	11.7	12.4	12.1	11.3	12.1	12.0
MnO	—	—	0.02	0.02	—	—	0.01	0.01	—	—	0.05	0.01	0.01
MgO	15.6	16.8	15.8	15.1	16.7	15.8	20.2	20.3	19.8	19.5	21.3	19.5	19.8
ZnO	0.15	0.12	0.13	0.09	0.16	0.09	—	—	—	—	—	0.5	0.6
NiO	0.28	0.31	0.33	0.33	0.30	0.28	—	—	—	—	—	0.5	0.6
Anhydrous total	98.2	97.8	98.8	98.7	97.5	98.0	99.6	99.0	99.1	98.0	99.6	99.4	99.2
O basis	31						4						
Ti	1.203	0.846	1.150	1.166	0.833	0.972	—	—	—	—	—	—	—
Al	14.785	15.081	14.865	14.954	15.137	14.906	1.996	1.991	1.993	1.998	1.977	1.989	1.981
Cr	0.017	0.017	0.014	0.006	0.008	0.020	0.002	0.002	0.001	0.001	0.001	0.001	0.001
Fe	1.734	1.651	1.689	1.740	1.622	1.928	0.248	0.247	0.262	0.259	0.237	0.255	0.255
Mn	—	—	0.003	0.003	—	—	0.001	0.001	—	—	0.001	0.001	0.001
Mg	4.592	4.943	4.618	4.419	4.924	4.681	0.755	0.764	0.747	0.743	0.796	0.736	0.749
Zn	0.022	0.018	0.019	0.013	0.023	0.013	—	—	—	—	—	0.009	0.011
Ni	0.045	0.049	0.052	0.052	0.048	0.045	—	—	—	—	—	0.009	0.012
Mg/(Mg + Fe)	0.726	0.750	0.732	0.717	0.748	0.708	0.751	0.756	0.740	0.742	0.770	0.743	0.746

35 point analyses of högbomite, 19 of spinel; total Fe as FeO; (a) average analyses (> 4) of grains without zoning; Section no. 5/1 not in contact with rutile and högbomite.
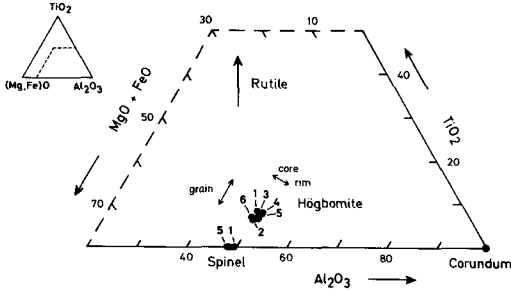
FIG. 4. Part of the $(Mg,Fe)O-Al_2O_3-TiO_2$ triangle showing distribution of högbomite and spinel analyses. Nos. are ref. nos. in Table I.

1981). From grain to grain there is a simple substitution of $(Mg+Fe)$ for Ti, whilst the Al content is nearly constant. In contrast, cores of zoned grains have low Al and Mg and rims have low Ti and Fe. Therefore element substitutions are not linear in the $(Mg,Fe)O-Al_2O_3-TiO_2$ triangle in fig. 4. NiO ranges from 0.26 to 0.33 wt. % and ZnO from 0.9 to 0.16 wt. %. Cobalt was checked, but not detected.

There are Al spinels with minor Fe_2O_3 as

indicated by the low totals (Table I) and by the fact that the analyses plot on the $(Mg,Fe)O$ side of the $1:1$ ratio with Al_2O_3 in fig. 4. The TiO_2 content is less than 0.05 wt. %. The X_{Mg} range is 0.740–0.770. Some spinels distant from höbomite but in the same cluster have NiO and ZnO about 0.4 wt. %; we consider these belong to the first generation of spinels from which högbomite was derived (NiO : 0.26–0.33 wt. %; ZnO : 0.09–0.16 wt. %, see Table I, anal. 6 and 7). Spinels close to högbomite bear no detectable Ni and Zn; these belong to the second generation derived from sapphirine and högbomite reactions 2 and 3 (see below). Corundum is nearly pure Al_2O_3 with small amounts of Cr_2O_3 (< 0.01 wt. %) and Fe_2O_3 (< 0.1 wt. %) and with no TiO_2. Rutile contains *c.* 0.06 wt. % Cr_2O_3.

Silicates. All silicates (see Table II), and spinel are plotted in $(Mg,Fe,Mn)O-Al_2O_3-SiO_2$ and $FeO-MgO-SiO_2$ space (fig. 5). The latter illustrates the very small X_{Mg} range of the relevant silicates. Sapphirines show a distinct range in SiO_2 and Al_2O_3 from rim to core and from grain to grain. There are two types of rims—those in contact with högbomite are lower in Al_2O_3 (Table II, rim 1) than those in contact with other minerals (Table II, rim 2). Point analyses plot close to the line from $2:2:1$
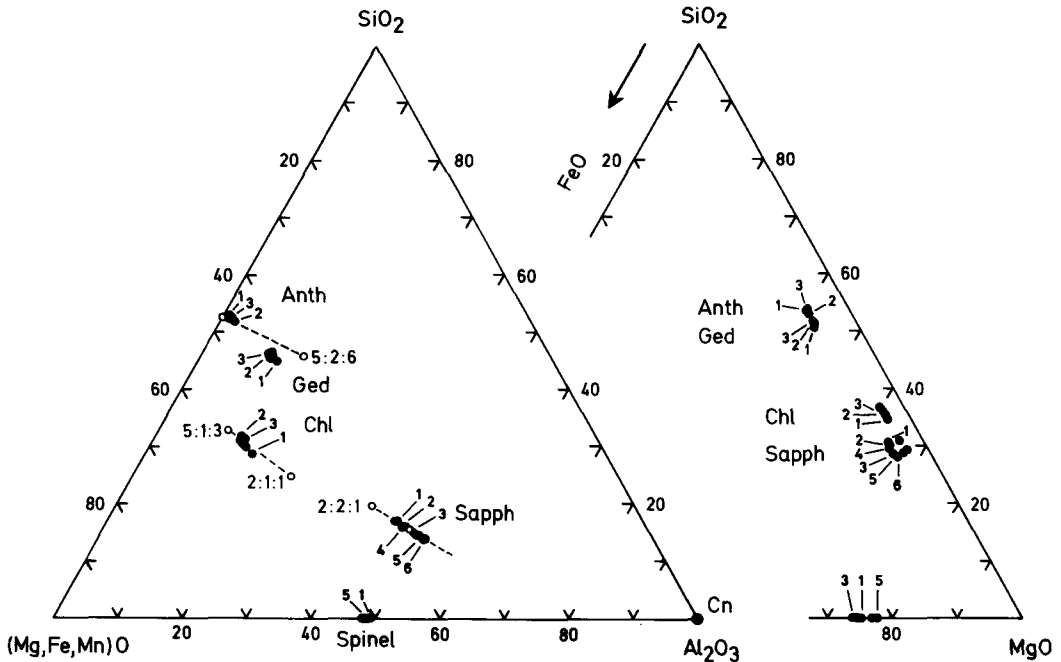

FIG. 5. $(Mg,Fe,Mn)O-Al_2O_3-SiO_2$ and $FeO-MgO-SiO_2$ triangles showing the compositions of anthophyllite, gedrite, chlorite, sapphirine, spinel, and corundum. Sapphirine is calculated on the basis of 14 cations (Moore, 1969); all other minerals on the basis of oxygens. Phase abbreviations: Anth anthophyllite, Chl chlorite, Cn corundum, Ged gedrite, Sapph sapphirine.

TABLE II. *Representative analyses of silicates*

Mineral	Sapphirine [31]						Chlorite [19]			Gedrites [24] and anthophyllites [15]						Hornblende [5]	
Section no.	5	5	5	2	5	3	5	5/1	3/1	5	5/1			4/1		5/1	
Ref. no.	1 (core)	2 rim 1	3 rim 2	4	4	6	1	2	3	Ged 1 (b)	Ged 2 core	Ged 3 rim	Anth 1	Ged 4 rim	Anth 2	1	2
SiO_2	14.2	13.6	12.3	13.2	11.4	11.1	25.5	28.9	27.6	44.1	44.8	46.4	56.9	44.9	56.9	49.9	50.1
TiO_2	0.04	0.05	0.02	0.03	0.05	0.09	—	0.08	0.06	0.16	0.36	0.21	0.07	0.24	0.06	0.41	0.45
Al_2O_3	63.1	63.6	65.8	64.4	67.3	68.0	25.1	20.8	21.3	19.0	17.4	16.2	3.1	17.7	2.4	9.5	10.1
FeO	3.2	3.1	3.1	3.2	2.9	2.6	3.7	3.5	3.5	6.9	6.6	6.9	9.0	7.4	7.7	3.5	3.4
MnO	—	—	0.02	—	—	0.03	—	—	0.03	0.03	0.02	0.08	0.05	0.03	0.05	—	—
MgO	19.7	19.7	18.9	19.1	17.7	17.6	30.0	31.8	31.0	22.9	24.6	24.2	27.8	23.8	28.5	20.0	19.7
CaO	—	—	—	—	—	—	—	—	—	0.4	0.6	0.6	0.4	0.6	0.4	12.5	12.3
Na_2O	—	—	—	—	—	—	—	—	—	1.9	2.3	1.9	0.27	2.2	0.14	1.2	0.9
Anhydrous total	100.1	100.1	100.1	99.9	99.4	99.4	84.3	85.1	83.5	95.4	96.7	96.6	96.6	96.6	96.1	97.0	97.0
On the basis of 14 cations (Moore 1969)																	
FeO	2.6	2.0	1.6	2.3	2.6	2.5											
Fe_2O_3	0.7	1.2	1.6	1.0	0.4	0.2											
Basis	14 cations						28 (O)			23 (O)						23 (O)	
Si	1.645	1.603	1.427	1.537	1.335	1.298	4.987	5.580	5.439	6.191	6.208	6.351	7.739	6.241	7.806	6.977	6.984
Al	4.355	4.597	4.573	4.463	4.665	4.702	5.786	4.734	4.947	3.108	2.842	2.683	0.492	2.877	0.385	1.566	1.660
Al	4.287	4.403	4.427	4.374	4.624	4.671	—	—	—	—	—	—	—	—	—	—	—
Ti	0.004	0.004	0.002	0.003	0.004	0.008	—	0.012	0.009	0.018	0.038	0.031	0.003	0.025	0.006	0.043	0.047
Fe^{3+}	0.062	0.103	0.141	0.085	0.033	0.015	—	—	—	—	—	—	—	—	—	—	—
Fe^{2+}	0.248	0.198	0.160	0.226	0.251	0.239	0.605	0.565	0.577	0.811	0.765	0.799	1.024	0.865	0.879	0.409	0.396
Mn	—	—	0.002	—	—	—	—	—	0.005	0.003	0.002	0.004	0.004	0.004	0.006	—	—
Mg	3.400	3.410	3.268	3.313	3.088	3.067	8.742	9.150	9.102	4.783	5.080	5.030	5.637	4.925	5.830	4.167	4.092
Ca	—	—	—	—	—	—	—	—	—	0.059	0.998	0.089	0.061	0.067	0.060	1.872	1.837
Na	—	—	—	—	—	—	—	—	—	0.534	0.618	0.564	0.071	0.576	0.037	0.325	0.243
Mg/(Mg+Fe+Mn)	0.932	0.945	0.953	0.936	0.925	0.928	0.935	0.942	0.940	0.855	0.869	0.862	0.846	0.850	0.868	0.911	0.912

[ ] number of point analyses; total Fe as FeO; (b) inclusion in sapphirine; Section nos. 3/1, 4/1, and 5/1 no cluster phases; Anal. ref. no: Ged 3 coexists with Anth 1 and 4 with 2; Hornblende: K_2O 0.07 wt. %, Cr_2O_3 0.003 wt. %

towards and beyond 7:9:3 on fig. 5. Chlorites (sheridanite) lie between 5:1:3 and 2:1:1 on fig. 5 and are characterized by a low FeO content. Small chlorite grains adjacent to högbomite (analysis 1, Table II) have higher Al_2O_3 values than chlorite flakes in the gedrite–anthophyllite matrix distant from högbomite (analyses 2 and 3).

Orthoamphiboles. Gedrite (high Al and Na) shows small ranges in composition from core to rim and from grain to grain, while anthophyllite (low Al and Na) has no zoning but a small compositional range from grain to grain. Both phases are rich in MgO and they have very similar X_{Mg} ratios, but coexisting anthophyllite–gedrite (rim analyses 20 μm from anthopyllite) pairs have contrary X_{Mg} relations (fig. 6A and B). Consequently the distribution of X_{Mg} versus Al^{IV} and Al^{VI} gives rise to

a horizontal line and a crossing of the tie lines which connect the coexisting phases. These relations contrast with the negative slope of all coexisting phases plotted by Spear (1980). Fig. 6C is a plot of A site occupancy (Robinson et al., 1971) versus the Al^{IV} and the connecting tie lines of coexisting pairs are mutually parallel and have a positive slope, indicating a spatial difference in the A site occupancy. The Al^{IV} contents and A site occupancy values are close to the two theoretical orthoamphibole formulae and this has relevance for the spacing of the solvus for the coexisting phases (Robinson et al., 1982). The CaO and TiO_2 contents of gedrite are slightly and markedly higher respectively than those of anthophyllite (see later).

Clinoamphibole. The pale yellow hornblende has no zoning and no variations from grain to grain. The X_{Mg} is much higher than that of the orthoamphiboles (Table II).

Reaction chemistry

The X_{Mg} [Mg/(Mg + Fe + Mn)] ratios for the relevant phases have the following order: sapphirine (0.95–0.92) > chlorite ($\sim$ 0.94) > hornblende ($\sim$ 0.91) > anthophyllite ($\sim$ 0.86) > gedrite ($\sim$ 0.86) > spinel (0.77–0.74) > högbomite (0.75–0.71). In view of these values and of the textural relationships, we predict the following reactions

$$\text{spinel} + \text{gedrite} + \text{rutile} \rightarrow \\ \text{högbomite} + \text{sapphirine} + \text{chlorite} \quad (1)$$
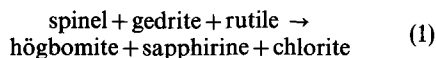
The högbomite obtained its cations from spinel, rutile, and gedrite by reaction 1, but the lack of equilibrium conditions did not allow these three phases to remain in significant proportions in the present rocks. The sapphirine breakdown reaction was

$$\text{sapphirine} \rightarrow \text{chlorite} + \text{corundum} + \text{spinel} \quad (2)$$
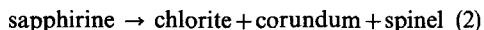
The three product phases occur together within sapphirine aggregates. This reaction took place in the presence of an introduced fluid phase, expressed in part by veinlets in sapphirine filled with chlorite and an Al-rich phase which is too fine-grained to confirm as corundum. This reaction should have taken place under conditions of $P_{H_2O} = P_{total}$. The reaction

$$\text{högbomite} \rightarrow \text{spinel} + \text{corundum} + \text{rutile} \quad (3)$$

involved the breakdown of högbomite by the production of new idiomorphic rutile sometimes in 1–3 μm needles in corundum. Also, large spinel grains with corundum inclusions are inferred to belong to this reaction in order to balance it. In some areas away from the main clusters where there is no högbomite and rarely rutile, gedrite and
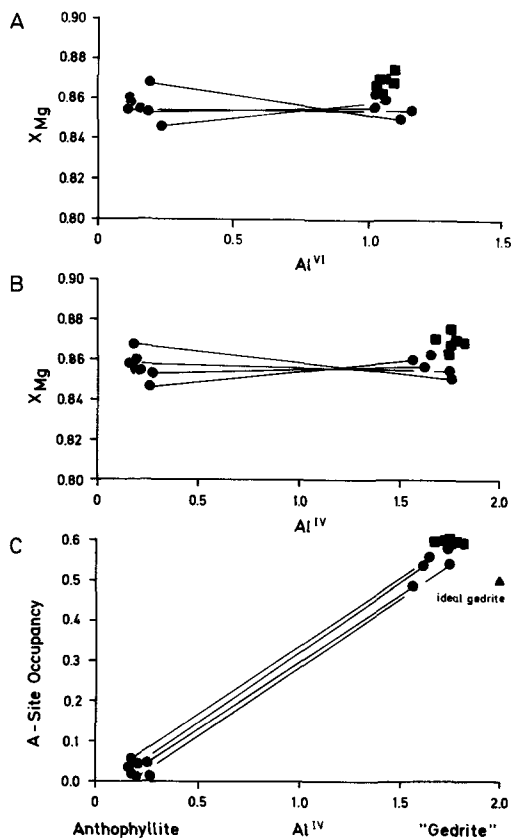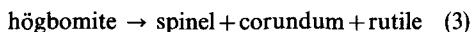
FIG. 6. Coexisting gedrite–anthophyllite pairs. Rim composition of gedrite (filled circle) has been connected with the coexisting anthophyllite (filled circle). Core composition of gedrite is represented by a filled square and the 'ideal gedrite' (Robinson et al., 1971) by a filled triangle. A. X_{Mg} [Mg/(Mg + Fe + Mn)] vs. Al^{VI}. B. X_{Mg} vs. Al^{IV}. C. A site occupancy (Spear, 1980) vs. Al^{IV}.

spinel are separated by zoned rims of sapphirine (next to spinel) and chlorite, and thus we are tempted to consider the reaction:

$$\text{gedrite} + \text{spinel} + ? \rightarrow \text{sapphirine} + \text{chlorite} \quad (4)$$
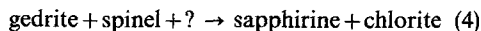
However, from the X_{Mg} balance between these four phases the reactant side is more Fe-rich than the product side and therefore an additional unknown Fe-enriched phase should have taken part in the reaction.

Discussion

The coexistence of high Al–Na gedrite and low Al–Na anthophyllite in patchy intergrowths enables us to discuss the generation of these orthoamphibole pairs in terms of temperature-dependent exsolution. Spear (1980) defined the orthoamphibole solvus for an X_{Mg} value of 0.6. Although the X_{Mg} values in this paper are higher (0.85–0.87), a correlation of our tetrahedral and octahedral Al and A site occupancy of Na with his solvus (his fig. 4) indicates an average temperature of $c.$ 500 °C for our exsolution. We do not correlate this temperature with that relevant to the högbomite-producing reaction.

The TiO_2 content of our anthopyllites is consistently less than that of gedrites, in agreement with Spear (1980, fig. 10) for pairs coexisting with rutile, but our gedrites have higher TiO_2 values, up to 0.43 wt. %. Spear (1980) showed that the orthoamphibole pairs that coexist with ilmenite have lower X_{Mg} than those with rutile. This is consistent with the fact that the majority of högbomites reported in the literature coexist with ilmenite and have low X_{Mg} values, in contrast to our högbomite that coexists with rutile and is a highly magnesian species.

The development of högbomite in these rocks is clearly dependent on the prior existence of rutile. Although the TiO_2 of the gedrite reaches 0.43 wt. % it would not be sufficient to enable högbomite to form in the absence of rutile. It could be that the Ni and Zn content of spinel were important enough in the spinel–rutile–gedrite reaction to produce högbomite with the present content of NiO and ZnO. If rutile and högbomite did not take part in this reaction, then gedrite plus spinel would have reacted to produce sapphirine and chlorite plus another phase.

Reaction 2 (Sa → Chl + Cn + Sp) can be compared with the experimental data of Seifert (1974) within the pure MASH system. The reaction takes place at $c.$ 700 °C over a wide pressure range. The fact that we are dealing with an X_{Mg} of 0.94 (sapphirine and chlorite) would decrease the temperature by not more than 100 °C.

The following are possible constraints on högbomite formation. It required a prior bulk compositional assemblage of gedrite, spinel and rutile with a NiO and ZnO content of $c.$ 0.3% and 0.2% respectively in the spinel. In the absence of rutile we see that reaction 1 did not take place, but rather gedrite is separated from spinel by sapphirine and chlorite.

Because our högbomite is so fine-grained and intergrown with spinel, we have not attempted to separate it for crystallographic X-ray study (Gatehouse and Grey, 1982). Our work suggests that magnesian högbomite from Fiskenaesset is a complex solid solution with perhaps more than two substitutions of all participating elements.

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