

Compositional variation in h gbomites from north Connemara, Ireland

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ABSTRACT. H gbomite occurs in two contrasting mineral assemblages within the Currywongaun-Doughruagh intrusion of north Connemara: a cordierite-rich pelitic xenolith and an orthopyroxenite. In the latter, h gbomite and green spinel form blebs within magnetite-ilmenite grains. The h gbomite displays significant compositional variation from grain to grain: TiO₂ (3.0-6.3%), FeO (21.6-21.3%), MgO (10.0-7.5%), ZnO (3.6-2.4%). This chemical heterogeneity appears to represent variable degrees of partial substitution of Mg and Zn by Ti, in the replacement of spinel by h gbomite. By contrast, in the cordierite-hornfels, the h gbomite compositions are more notably enriched in iron: TiO₂ (4.7-7.0%), FeO (29.6-24.3%), MgO (4.2-6.2%), ZnO (2.7-2.1%). This iron-rich h gbomite appears to have formed primarily by interaction between opaque ore and adjacent cordierite, rather than by replacement of spinel.

Two high-grade metamorphic episodes appear to be necessary for h gbomite growth, one determining chemical composition and the other appropriate physical parameters. In the Connemara occurrences thermal metamorphism and partial melting, coupled with contamination of the surrounding magma, controlled the formation of mineral assemblages rich in Fe, Mg, Al, Ti, and Zn. Emplacement of the intrusion was accompanied by amphibolite facies regional metamorphism and it is to this metamorphic event that the growth of h gbomite may be attributed.

KEYWORDS: h gbomite, orthopyroxenite, cordierite-hornfels, Connemara, Ireland.

H GBOMITE in accessory amounts is of common occurrence in many desilicated pelitic xenoliths in the ultrabasic and basic intrusions of central Connemara (Leake and Skirrow, 1960; Evans, 1964). In these corundum-, spinel-, and magnetite-bearing assemblages, h gbomite frequently rims the iron ore, intervening between magnetite and corundum or magnetite and spinel, as well as occurring within the magnetite itself.

Within the Currywongaun-Doughruagh intrusion of north Connemara (Kanaris-Sotiriou and Angus, 1976), h gbomite has been found in two quite distinctive and contrasting assemblages. The first is a cordierite-rich, hornfelsed pelitic xenolith recorded by one of us (N.S.A.) and subsequently

described by Leake (1965), and the second is essentially an orthopyroxenite of magmatic origin. They occur in adjacent exposures in the NE corner of the Currywongaun body, about 750 m NE of the summit of Currywongaun, but their interrelationships with one another and with the surrounding norite are indeterminate due to poor exposure. They occur some 30 m from the inferred edge of the intrusion which is emplaced into a series of semi-pelitic and psammitic schists.

Broadly similar developments of h gbomite are well documented (Friedman, 1952; McKie, 1963), but, as in the Connemara examples, chemical data on these occurrences of accessory h gbomite is understandably meagre. In more recent years, microprobe analyses of h gbomite, principally from high-grade regional metamorphic rocks (Woodford and Wilson, 1976; Wilson, 1977; Teale, 1980; Coolen, 1981; Mancktelow, 1981; Spry, 1982; Ackermund *et al.*, 1983) and less commonly from titano-magnetite rich rocks ( ech *et al.*, 1976; Zakrzewski, 1977; Devaraju *et al.*, 1981) have been published. These reveal a variety of compositions and illustrate that h gbomite may contain large amounts of Co ( ech *et al.*, 1976) or Zn (Wilson, 1977; Spry, 1982), while Mancktelow (1981) has extended the range of known iron compositions to considerably higher values in the Reedy Creek h gbomite of South Australia.

Mineral assemblages and chemistry

Orthopyroxenite. This consists of subhedral grains of hypersthene (75 vol. %), partly replaced by prismatic anthophyllite, and enveloped by irregular opaque ore grains (25 vol. %). The ores are mainly magnetite with lesser amounts of ilmenite of variable composition (Table I), and together they may form conspicuous segregations up to 10 mm long. H gbomite and green spinel occur as small inclusions or exsolution blebs and diffuse lamellae in the magnetite-ilmenite grains. A single ore grain may contain discrete blebs of green spinel and

TABLE I. Analyses of minerals associated with hōgbomite in the orthopyroxenite

No. of analyses	Hypersthene (1)	Anthophyllite (4)	Magnetite (8)	Ilmenite (composition range)
SiO ₂	51.29	53.30	0.19	0.21–0.29
Al ₂ O ₃	3.29	4.00	0.54	—
TiO ₂	0.11	0.07	0.22	47.48–19.22
FeO	21.58	16.27	91.12	50.42–72.27
MgO	22.17	22.13	0.08	1.22–0.32
MnO	0.55	0.53	—	0.51–0.00
CaO	0.20	0.43	—	—
Na ₂ O	—	0.44	—	—
ZnO	0.04	—	—	—
Anhydrous total	99.23	97.17	92.15	99.84–92.10
$X_{Fe} = Fe/(Fe + Mg)$	0.35	0.29		

Hypersthene was analysed by X-ray fluorescence and atomic absorption techniques. Other analyses are means of the indicated number of electron microprobe point analyses.

hōgbomite, as well as 'intergrowths' of the two minerals, and, although it is usually anhedral, rare well-formed hōgbomite crystals with rectangular or hexagonal outlines are sometimes evident. Little if any hōgbomite or spinel is developed along hypersthene–ore boundaries, but grains frequently occur at magnetite–ilmenite junctions.

Analyses of the cores of three individual hōgbomite grains, illustrating the compositional variation in TiO₂, MgO, and ZnO, are presented in Table II. The associated green spinel displays little variation in composition and is represented by the mean of ten point analyses. The spinel and hōgbomite compositions have been recalculated to Zakrzewski's (1977) proposed formula, $R_2^{2+}Ti_xR_4^{3+}O_8$, and, although it has not been conclusively verified, the analyses fit this structural formula reasonably well (Table II). The role of Si⁴⁺ in the structure of hōgbomite has not been explained, although published data frequently demonstrate its presence in small quantities. In the data presented here, silica occurs in amounts at or near the detection limit of the electron microprobe. For the purpose of formula recalculations, Si⁴⁺ has been assumed to be present as a solid solution of (Mg,Fe)₂SiO₄ with hōgbomite, and any inaccuracies introduced by this assumption are expected to be small. Although there is a reluctance to propose solid solution of silicon in an oxide structure, recent studies of silicon in magnetite (Newberry *et al.*, 1982) have revealed silicon in solid solution with an average value of 1.2 wt. % Si, equivalent to solid solution of 9 mole % Fe₂SiO₄.

The green spinel contains almost equal amounts of Fe²⁺ and Mg in the structure, indicating a

composition on the hercynite–pleonaste boundary, while the presence of about 4% ZnO points to a solid solution with about 7% gahnite. The Zn is

TABLE II. Electron-microprobe (EDS) analyses of hōgbomite and spinel from the orthopyroxenite

No. of analyses	Hōgbomite			Spinel
	(1)	(1)	(1)	(10)
SiO ₂	—	—	0.23	0.31
Al ₂ O ₃	61.22	61.33	61.18	61.66
TiO ₂	3.00	4.50	6.31	0.70
FeO	21.59	21.57	21.32	21.97
MgO	10.04	9.47	7.49	10.92
ZnO	3.56	2.66	2.42	3.97
Anhydrous total	99.41	99.53	98.95	99.53
	Number of cations on the basis of 8 oxygens*			
Si	—	—	0.012	0.017
Al	3.854	3.832	3.842	3.906
Fe ³⁺	0.146	0.168	0.134	0.068
Ti	0.121	0.179	0.253	0.028
Fe ²⁺	0.819	0.789	0.817	0.920
Mg	0.799	0.748	0.595	0.875
Zn	0.140	0.104	0.095	0.158
$X_{Fe} = Fe/(Fe + Mg)$	0.55	0.56	0.62	0.53

Each analysis is the mean of the indicated number of point analyses.

* Formula calculated on the basis of Zakrzewski (1977).

presumably leached and concentrated from the opaque ore which typically reveals several hundred ppm Zn when analysed by AAS. Usually significant levels of TiO_2 (0.5 to 1.0%) are also present which may indicate some limited solid solution with hōgbomite.

The hōgbomite, in contrast to the green spinel, is not consistent in composition (Table II). Notably, TiO_2 ranges from 3.0 to 6.3%, with MgO (10.0 to 7.5%) and ZnO (3.6 to 2.4%) displaying sympathetic variation. This compositional variation of hōgbomite and its relationship to the spinel is shown in fig. 1. Mg and, to some extent, Zn show inverse correlations with Ti (fig. 1a and b), and although Fe^{2+} is lower in hōgbomite than in spinel (fig. 1c), it lacks the strong correlation shown by Mg. This lower Fe^{2+} in hōgbomite is balanced to some extent by higher Fe^{3+} , as the plot of Ti v. $\text{Fe}^{2+} + \text{Fe}^{3+}$ (fig. 1d) shows broadly comparable total iron levels in the two minerals.

The heterogeneity displayed by the hōgbomite compositions appears to represent varying degrees

of partial substitution of Mg and Zn by Ti in the replacement of spinel by hōgbomite. This was initially put forward as a mechanism of hōgbomite formation by Friedman (1952) and subsequently substantiated by Zakrzewski (1977), who also suggested that the loss of Al in hōgbomite is compensated by oxidation of Fe. Similar substitutions of the type $\text{Ti} \rightleftharpoons 2\text{R}^{2+}$ and $\text{Ti} \rightleftharpoons 2\text{Al}$ were put forward by Coolen (1981), with the charge balance in the latter type maintained by coupling the Ti substitution with an iron-oxidation reaction and a Fe-Al substitution to give the net equation: $\text{Ti} + 2\text{Fe}^{3+} \rightleftharpoons 2\text{Fe}^{2+} + 2\text{Al}$.

Cordierite-rich hornfels. Leake (1965) has previously described this hornfels and his account needs only minor qualification. Partially pinitized cordierite (90% by vol.) and opaque ore (9%) constitute the bulk of the rock, with hōgbomite comprising about 0.5%, and biotite and anthophyllite the remainder. The opaque ore has developed along the cordierite grain boundaries and comprises both magnetite and ilmenite (Table III).

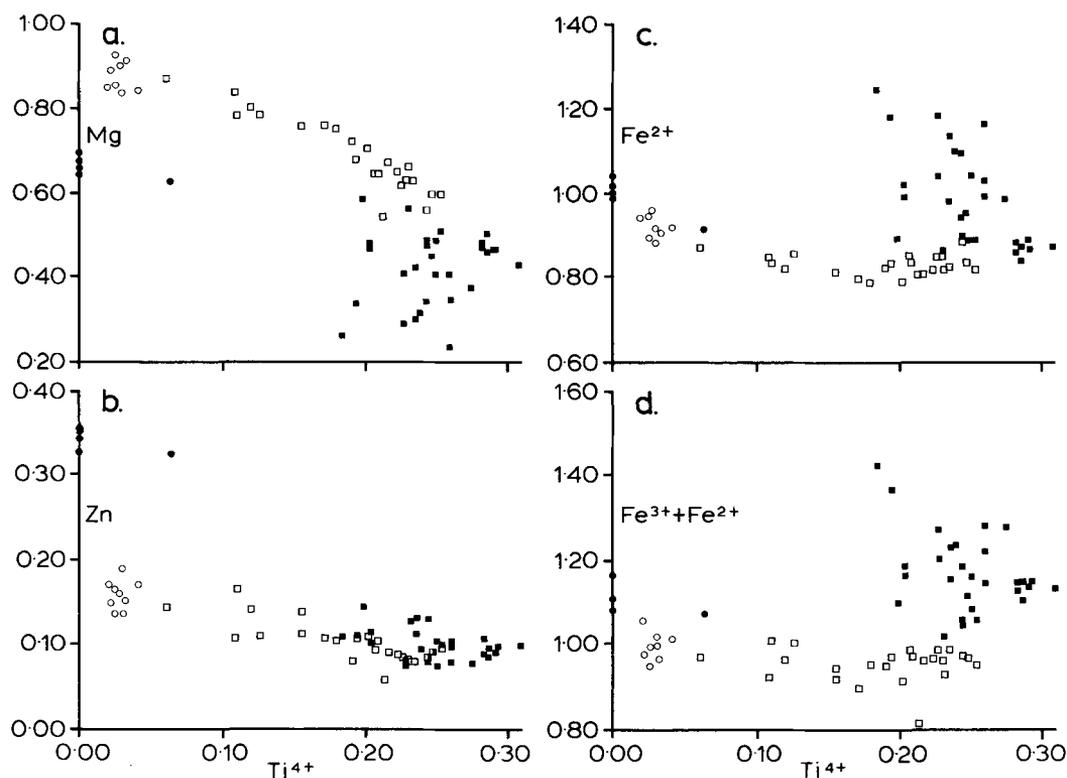


FIG. 1. Individual analyses of hōgbomite and spinel. (a) Mg v. Ti^{4+} ; (b) Zn v. Ti^{4+} ; (c) Fe^{2+} v. Ti^{4+} ; (d) $\text{Fe}^{3+} + \text{Fe}^{2+}$ v. Ti^{4+} . Cations calculated on basis of Zakrzewski's formula (1977). Open squares hōgbomite and open circles spinel in orthopyroxenite. Solid squares hōgbomite and solid circles spinel in cordierite hornfels.

TABLE III. *Analyses of minerals associated with h ogbomite in the cordierite-hornfels*

No. of analyses	Cordierite (1)	Anthophyllite (7)	Magnetite (7)	Ilmenite (7)
SiO ₂	48.17	51.81	0.13	0.07
Al ₂ O ₃	33.56	5.24	0.42	0.09
TiO ₂	0.01	0.25	0.17	46.96
FeO	4.87	16.83	92.68	51.05
MgO	10.57	20.58	—	—
MnO	0.09	0.51	—	1.35
CaO	0.06	0.53	—	—
Na ₂ O	0.34	0.51	—	—
K ₂ O	0.02	—	—	—
ZnO	0.01	—	—	—
Anhydrous total	97.70	96.26	93.40	99.52
$X_{Fe} = Fe/(Fe + Mg)$	0.21	0.31		

Cordierite was analysed by X-ray fluorescence. Each of the other analyses is representative of seven energy-dispersive electron microprobe analyses.

TABLE IV. *Electron microprobe analyses of spinel and h ogbomite from the cordierite-hornfels*

No. of analyses	(29)	H�ogbomite (composition range)		Spinel (6)	
SiO ₂	0.19	0.23	0.00	0.10	
Al ₂ O ₃	57.77	58.43	58.21	59.70	
TiO ₂	5.98	4.69	6.97	0.26	
FeO	25.36	29.61	24.31	24.21	
MgO	5.15	4.15	6.23	8.03	
MnO	0.18	—	—	—	
ZnO	2.44	2.72	2.13	8.34	
Anhydrous total	97.07	99.86	97.85	100.64	
		Number of cations on the basis of 8 oxygens			
Si	0.009	0.013	0.00	0.006	
Al	3.776	3.786	3.733	3.865	
Fe ³⁺	0.204	0.189	0.267	0.124	
Ti	0.250	0.194	0.285	0.011	
Fe ²⁺	0.976	1.174	0.839	0.988	
Mg	0.426	0.340	0.505	0.658	
Zn	0.100	0.110	0.086	0.338	
Mn	0.009	—	—	—	
$X_{Fe} = Fe/(Fe + Mg)$	0.73	0.80	0.69	0.63	

Each analysis is the mean of the indicated number of microprobe point analyses.

* Formula calculated on the basis of Zakrzewski (1977).

As in the orthopyroxenite, the högbomite is invariably associated with the ores, but the grains are larger and more irregular, and tend to have developed along cordierite-ore grain junctions and to have extended along intergranular boundaries within the ore. Green spinel is extremely rare, occurring as minute relicts within högbomite crystals, accompanied by tiny granules of (?)corundum.

The mean of 29 högbomite analyses, together with two specific analyses to illustrate the extremes of compositional variation, are presented in Table IV. Also included is the mean of six analyses made on two grains of green spinel, and all analyses have again been recalculated to Zakrzewski's (1977) proposed formula.

The green spinel is richer in Fe and Zn and poorer in Mg and Ti than its counterpart in the orthopyroxenite, and on the basis of the limited analytical data appears to be fairly consistent in composition. An even greater contrast is evident in the composition of the högbomite: TiO₂ contents are notably higher (fig. 1), with values approaching 7.0%, while the mean value of 6.0% is close to the upper limit recorded in the orthopyroxenite högbomite. More pronounced, however, are the degree of iron enrichment and Mg depletion (fig. 1a and c). FeO (total) has a mean value of 25.4%, and with some values approaching 30.0%, putting these among the most iron-rich högbomites yet recorded (Mancktelow, 1981). There is a clear inverse relationship between Fe²⁺ and Mg which is not evident in the högbomite from the orthopyroxenite (fig. 2), and although there appears to be no overall pattern to the Fe³⁺ variation (fig. 1d), generally the högbomite in the cordierite-hornfels is more highly oxidized. Zn displays little variation and the mean of 2.4% ZnO is similar to that of the högbomite in the orthopyroxenite. The presence of Zn in högbomite (and associated spinels) has been noted by most authors and it would appear to be a ubiquitous though usually minor constituent of the mineral.

In contrast to the apparent gradation in chemical composition from the green spinel into the more Ti-rich högbomite in the orthopyroxenite, no such relationship is apparent between these minerals in the cordierite-hornfels (fig. 1). Also in terms of Ti, Fe, and Mg there is a clear compositional distinction between the högbomites in the two assemblages. These compositional contrasts could possibly arise if the Fe-rich högbomite of the cordierite hornfels formed primarily by interaction between opaque ore (magnetite and ilmenite) and adjacent cordierite, rather than by replacement of spinel which would seem to have played only a minor contributory role. The wide range of Fe²⁺/Mg ratios (fig. 2) may indicate a lack of

equilibrium between individual grains (no compositional zoning was detected) due to most of the component elements being drawn from the immediate vicinity of each grain, coupled with arrested development of the mineral before subsequent recrystallization and homogenization.

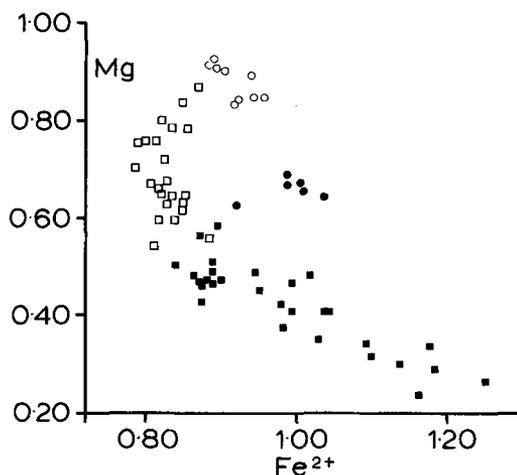


Fig. 2. Mg v. Fe²⁺ for högbomite and spinel. Symbols as in fig. 1.

Discussion

The requisite conditions for högbomite formation have been referred to recently by several authors.

In the Strangways Range of central Australia, Wilson (1977) recorded högbomite, developed from green spinel, in highly aluminous magnesian granulite-facies rocks that appear to have formed during a high amphibolite-facies retrogression of the granulites. Teale (1980) proposed a broadly similar origin for högbomite in a spinel-phlogopite schist from Mount Painter Province of South Australia. The original assemblage formed during an initial upper amphibolite-facies metamorphism, while a second similar metamorphic event, under conditions of high oxygen fugacity, led to partial replacement of spinel by högbomite and corundum. Chemically this spinel and derivative högbomite are more magnesian, with correspondingly less Fe and Zn, than their equivalents in the orthopyroxenite of Currywongaun.

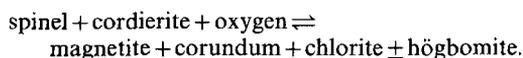
Högbomite comparable in composition to that of the cordierite-rich hornfels has been described from aluminous segregations within laminated meta-arkoses at Reedy Creek, in South Australia (Mancktelow, 1981). The högbomite is enclosed

within cordierite aggregates, both as separate inclusions and intergrown with magnetite, ilmenite-hematite, and green hercynite, but no clear replacement relationship is evident between the hercynite and hōgbomite. Mancktelow states that the hōgbomite 'appears to be a stable member of this upper amphibolite-facies mineral assemblage, with no evidence of breakdown or alteration'. Like the Reedy Creek hōgbomites with a mean FeO (total) of 26.3%, those in the cordierite-hornfels are equally rich in FeO (25.4%), but also have significantly higher Zn and Ti contents.

In these varied Australian examples, hōgbomite appears to be a stable component of an upper amphibolite-facies metamorphic event subsequent to an earlier high-grade amphibolite or granulite facies metamorphism. Similarly, Zn-rich hōgbomite in phlogopite-staurolite-cordierite schists within the Geco base-metal deposit of Ontario (Spry, 1982) appears to have formed during an upper amphibolite to lower granulite-facies metamorphism. In the Furua granulites in southern Tanzania, and in the granulite facies metaperidotites of Galicia in Spain, hōgbomite growth can also be correlated with similar retrogressive metamorphic events (Coolen, 1981).

Two high-grade metamorphic episodes, therefore appear to be necessary for hōgbomite growth. The first determines the essential chemical composition, that is a mineral assemblage rich in Fe, Mg, and Al, accompanied by Ti and Zn. The second metamorphism is instrumental in producing the appropriate physical parameters and presumably high oxygen fugacity necessary for hōgbomite development. In attempting to equate these requirements with the Connemara occurrences, a direct analogy is not immediately obvious. However, Evans (1964) has shown that relative increases in Mg, Fe, and Ti in the pelitic hornfels of the Cashel-Lough Wheelaun intrusion in south Connemara arise by removal of K, Na, Ca, Si, and Al in the form of a fractional granitic melt. The origin of the cordierite-rich hornfels in Currywongaun can similarly be linked to thermal metamorphism and partial melting of the original pelitic xenolith, and the adjacent orthopyroxenite, with its abnormally Fe-rich orthopyroxene (Fe_{35}), probably crystallized from the surrounding contaminated basic magma. The syntectonic nature of the Connemara basic intrusions is well established (Leake, 1970; Kanaris-Satiriou and Angus, 1976) particularly their complex magmatic and structural

evolution during the regional D_2 and D_3 deformations. Of specific interest in the present context is the emplacement of the Currywongaun-Doughruagh intrusion into Middle Dalradian sediments undergoing amphibolite-facies regional metamorphism and it is to this regional metamorphic event that the growth of hōgbomite in the cordierite-rich xenolith and orthopyroxenite may be attributed. This equates well with the formation of hōgbomite in the Cashel hornfels in which the high oxidation ratios [$Fe^{3+}/(Fe^{2+} + Fe^{3+})$] were attributed by Evans (1964) to an amphibolite facies metamorphism which produced a reaction in the xenoliths along the lines:



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