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Högbomite from the Vumba schist belt, Botswana

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Abstract

Högbomite and zincian högbomite are reported for the first time from a Mg-Fe-Al–rich layer within the serpentinite unit of the Vumba schist belt, Botswana. The zincian högbomite in one sample is a secondary product of a Zn-bearing hercynite. The FeO content ranges from 28 to 30 wt%, making it among one of the most Fe-rich zincian högbomites reported in the literature. Apart from the usual mineral assemblage spinel + corundum + chlorite + ilmenite ± rutile, a rare Na-mica (preiswerkite) is also found interfingered with chlorite and in contact with zincian högbomite and zincian hercynite.

In a second sample, a small grain of green spinel, found enclosed in a larger brown högbomite grain, is discontinuously zoned in Zn (1.23 wt% ZnO in core and about 24 wt% ZnO at the rim). The högbomite, which makes up about 50 vol% of the rock, contains a maximum of 0.70 wt% ZnO. Representative electron-microprobe analyses of högbomites give the following structural formulae, based on 8 oxygens:

$$\text{D-136:}\quad (\mathrm{Mg_{0.39}Fe^{2+}_{1.07}Mn_{0.01}Zn_{0.08}})\mathrm{Ti_{0.23}}(\mathrm{Fe^{3+}_{0.22}Al_{3.78}})\mathrm{O_8}$$
$$\text{D-225:}\quad (\mathrm{Mg_{0.92}Fe^{2+}_{0.57}Mn_{0.01}Zn_{0.02}})\mathrm{Ti_{0.24}}(\mathrm{Fe^{3+}_{0.29}Al_{3.71}})\mathrm{O_8}.$$

Based on field relations, textural features, and the composition of the minerals, the högbomites are considered to have been formed during the retrograde stage of the granulite- to amphibolite-facies metamorphism.

Introduction

Högbomite was discovered by Gavelin (1916) in Lapland (Sweden). Since then, it has been reported from different localities and rock types. Most of the högbomite occurrences are reported from high-grade metamorphic rocks (Woodford and Wilson, 1976; Teale, 1980; Coolen, 1981; Mancktelow, 1981; Spry, 1982; Essene et al., 1982; Ackermand et al., 1983; Angus and Middleton, 1985; Grew et al.; 1987). Some are reported from titanomagnetite rich rocks (Zakrzweski, 1977; Devaraju et al., 1981) and from marble skarns (Gieré, 1986).

The published analyses reveal a variation in composition and document the occurrence of Co-rich (Cech et al., 1976) and Zn-rich (Wilson, 1977) varieties of this mineral. The $\mathrm{Fe_{tot}}/(\mathrm{Fe_{tot}} + \mathrm{Mg})$ ratio ranges from 0.02 to 0.62 for most of the högbomites reported. The only analyses that extend the $\mathrm{Fe_{tot}}/(\mathrm{Fe_{tot}} + \mathrm{Mg})$ ratio to a higher value of 0.69–0.80 are those reported by Mancktelow (1981) and Angus and Middleton (1985).

Högbomite and zincian högbomite have been found in an Al-Fe-Mg–rich layer within the main serpentinite unit of the Vumba schist belt, Botswana. The samples containing högbomite (D-225) and zincian högbomite (D-136) occur 20 km apart (Fig. 1).

As has been reported by Nel (1949), the högbomite from the corundum fields of the eastern Transvaal, South Africa is found in coarse-grained rocks, which occur as isolated blebs and lenses, a few inches thick, aligned parallel to the pseudostratification of the surrounding serpentine-rich rocks of the complex. This geologic setting seems to be similar to that of the högbomite occurrences of Botswana. In this study we discuss the textural features, chemical compositions, and conditions of formation.

Geologic setting

The Vumba schist belt is an Archean granite-greenstone terrane in the northeast district of Botswana. The belt consists of polymetamorphosed sequences of ultrabasic rocks of komatiitic affinity, basalts, calc-alkaline rock types ranging from andesite to rhyolite in composition, a minor amount of sedimentary rocks, and banded iron formation. Intercalated in the ultrabasic rocks (main serpentinite hill chain) are diverse rock types, which display unusual chemical patterns. They form thin layers consistently less than 0.5 m along strike. The chemical and petrographic data suggest that they represent the intercalation of felsic or sedimentary material and mark the top of the individual ultrabasic (komatiitic) flows.

The belt has been subjected to five metamorphic phases (M1–M5, Rammlmair et al., in prep). The intensity of each metamorphic event varied within the belt. The M1 event was of low intensity and metamorphic grade. M2 reached the granulite facies in the west but only amphibo-

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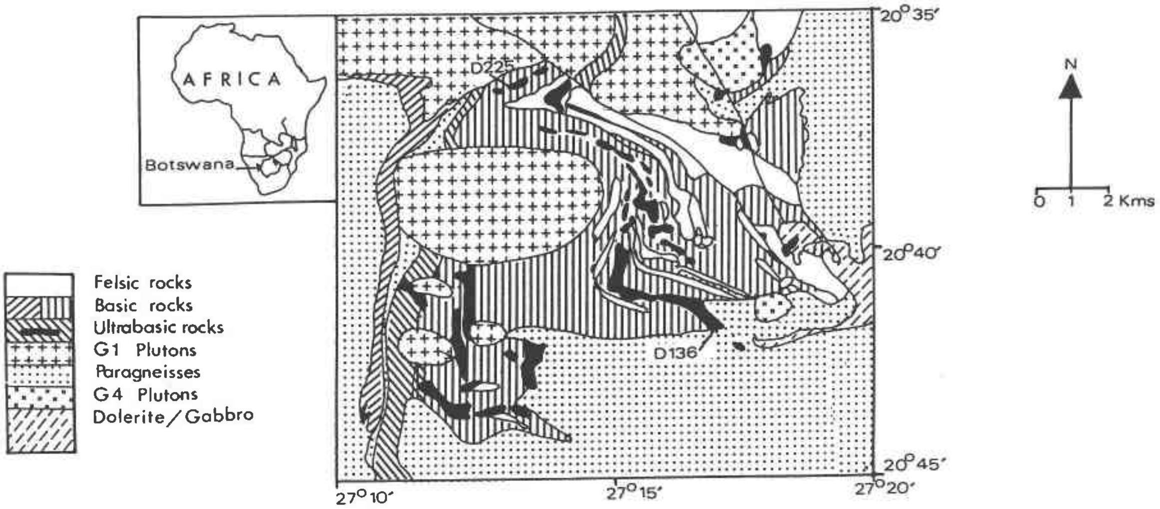

Fig. 1. A simplified geologic map of the Vumba schist belt, Botswana (Litherland, 1975), showing the locations of högbomite-bearing samples D-136 and D-225. G1 plutons are deformed tonalites and monzonites; G4 plutons are, generally, adamellitic granites.

lite facies in the east. The M3 amphibolite-grade metamorphism was most intense in the east. M4, the retrograde stage of M3, reached greenschist facies in the west but amphibolite facies in the east. The M5 event had negligible effect in the west and did not exceed the greenschist facies in the east (Fig. 1).

PETROGRAPHY

Two textural occurrences of högbomite are distinguished microscopically. Fine högbomite crystals form at the rim of large green spinels (sample D-136, type 1), or single, idiomorphic, twinned crystals are found within a chlorite-phlogopite-diaspore matrix (sample D-225, type 2, Fig. 2).

As documented by many authors (Gavelin, 1916; Nel, 1949; Friedman, 1952; Zakrzweski, 1977), högbomite is commonly associated with spinel (type 1, sample D-136). The modal abundance of zincian högbomite associated with green spinel is very low (about 0.5 vol%), and the grain size is generally less than 0.2 mm. Small aggregates of these grains are always found at the rims of large spinel grains, implying their secondary formation. Associated with the zincian högbomite and green spinel are corundum, chlorite, ilmenite, apatite, and a pale green mica (preiswerkite). The chlorite and mica are generally intergrown or interfingered.

The disseminated, large, brown-colored grains of högbomite in specimen D-225 make up about 50 vol% of the rock. Also abundant are chlorite (I + II), zoisite, margarite, and diaspore. Chlorite I is always associated with högbomite. Chlorite II is chiefly found as an alteration product of calcic amphibole, högbomite, or phlogopite. The högbomite alters to diaspore + chlorite II + Ti-oxides. Epidote and apatite are common. In this sample, spinel is rare and was observed in only one thin section, as a very fine-grain inclusion in högbomite. The near total absence of spinel relicts and the coarse grain size of högbomite suggest that it was not formed by alteration or retrograde of spinel. This textural type has been interpreted by Gavelin (1916) and Zakrzweski (1977) to be a primary one.

X-RAY DATA

Mckie (1963) reported that högbomite forms a series of polytypes, designated *n*H or *n*R with hexagonal or rhombohedral lattices and hexagonal unit-cell dimensions of $a = 5.72$ Å, $c = 4.6 \times n$Å. Högbomite grains, separated from sample D-225, have been studied by X-ray diffraction. The following intense *d* spacings correspond to the rhombohedral *18R* polytype of Mckie (1963): 2.93, 2.87, 2.69, 2.55, 2.44, 2.36, 2.08, 1.99.

MINERAL CHEMISTRY

Analyses of högbomite, spinel, and associated minerals were carried out with an ARL-SEMQ electron microprobe operated at 15-KeV accelerating voltage, 0.03-μA sample current and 20-s counting time, at the Institute of Mineralogy and Petrography, University of Innsbruck. The standards used were natural minerals: spinel, chromite, gahnite, tephroite, kaersutite, tremolite, jadeite, garnet, and orthoclase. The matrix effects were corrected according to Bence and Albee (1968).

Högbomite and zincian högbomite. Representative electron-microprobe analyses of högbomite and zincian högbomite are presented in Table 1. A series of analyses of högbomite grains of specimen D-225 display no chemical zonation, whereas zincian högbomite of sample D-136 is somewhat zoned. Compared to the zincian högbomite (D-136), högbomite (D-225) has higher TiO_2 and

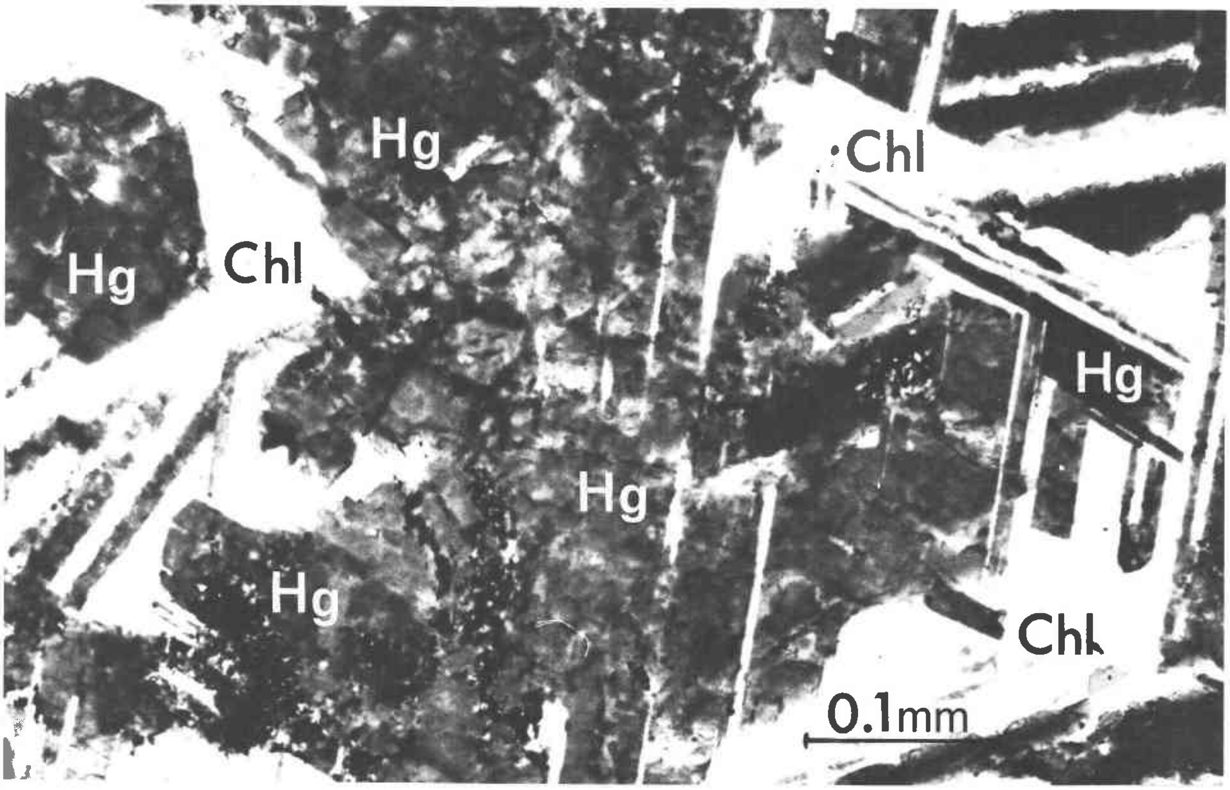

Fig. 2. Twinned högbomite (Hg) and chlorite (Chl) intergrowth in sample D-225. Parallel nicols.

MgO and lower FeO and ZnO. The amount of SiO_2 is less than 0.05 wt%.

Zakrzweski (1977) proposed a general formula for högbomite: $R^{2+}_{2-2x}Ti_xR^{3+}_4O_8$ where R^{2+} = Mg, Fe^{2+}, Zn, Ni; R^{3+} = Fe^{3+}, Al, V, Cr; and x = 0.2–0.4. Schumacher et al. (1987) have formulated a method analogous to that of Zakrzweski to calculate the formula of nigerite (structurally similar to högbomite) and suggested a general formula for högbomite: $CAT_c = (24.CAT_u)/(CAT_u + R^{4+}_u)$, where CAT_u and R^{4+} are respectively the cation total and the sum of Sn + Ti^{4+} in a microprobe analysis that is based on 32 oxygens and with all Fe treated as Fe^{2+}. The analysis must then be normalized to the number of CAT_c cations (where CAT_c is the correct number of cations in

Table 1. Representative electron-microprobe analyses

	D-225				D-136		
	Hg	Hg	Gh (rim)	Sp (core)	Zn-Hg	Zn-Hg	Hc
TiO_2	6.11	6.13	0.10	0.07	4.78	5.49	0.00
Al_2O_3	60.63	60.85	58.63	62.50	58.28	58.53	55.62
FeO*	20.30	20.00	10.68	21.21	29.47	28.30	34.75
MnO	0.15	0.15	0.08	0.16	0.22	0.21	0.25
ZnO	0.60	0.68	23.91	1.23	1.99	1.95	3.53
MgO	11.14	11.57	6.01	14.24	4.78	4.76	5.73
Total	98.93	99.38	99.41	99.41	99.92	99.24	99.88
Oxygens	8	8	32	32	8	8	32
Ti	0.24	0.24	0.02	0.01	0.20	0.23	0.00
Al	3.74	3.73	15.86	15.54	3.77	3.78	14.85
Fe^{3+}	0.26	0.27	0.00	0.44	0.23	0.22	1.14
Fe^{2+}	0.63	0.60	2.05	3.31	1.13	1.08	5.44
Mn	0.01	0.01	0.01	0.03	0.01	0.01	0.05
Zn	0.02	0.03	4.05	0.19	0.08	0.08	0.59
Mg	0.87	0.90	2.06	4.48	0.39	0.39	1.93
Total	5.77	5.78	24.05	24.00	5.81	5.79	24.00
$Fe_{tot}/(Fe_{tot} + Mg)$	0.51	0.49	0.50	0.46	0.78	0.77	0.77

Note: Abbreviations are högbomite (Hg), spinel (Sp), gahnite (Gh), zincian högbomite (Zn-Hg), and hercynite (Hc).
* Fe_{tot} as FeO.

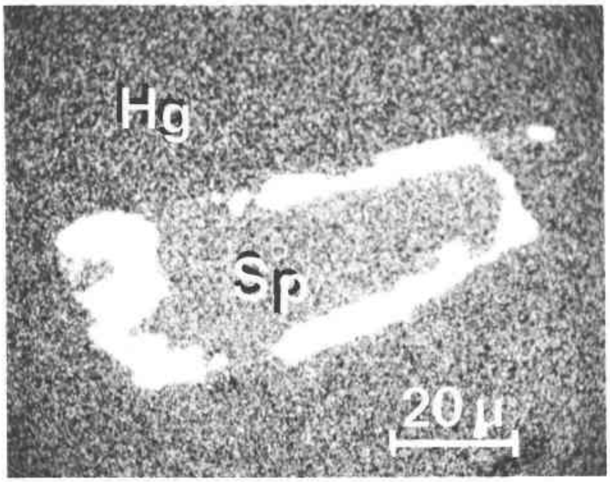

Fig. 3. Electron-beam scanning image of Zn distribution in the spinel (Sp) inclusion in högbomite (HG). The spinel core contains 1.23 wt% ZnO, the gahnite rim 24 wt% ZnO, and högbomite contains only 0.7 wt% ZnO. Sample D-225.

a stoichiometric högbomite). Since CAT_c is less than CAT_u, the oxygen total in the CAT_c formula is brought to 32 by converting Fe^{2+} to Fe^{3+}, which gives a stoichiometric formula corrected for Fe^{3+}.

Grey and Gatehouse (1979) reported a partially vacant site resulting in a cation total between 21.1 and 21.5 calculated on the basis of 30O + 2OH in nigerite-*24R*. Gatehouse and Grey (1982) found 22 cations per 30O + 2OH in högbomite-*8H*. In recalculating högbomite analyses from an assumed *8H* polytype, Grew et al. (1987) reported a total cation sum of 22, based on 30O + 2OH, although they did not establish whether their högbomite (from Ellammankovilpatti, Tamil Nadu, India) was an *8H* polytype. They suggested that this formula is more appropriate than Zakrzweski's (1977) formula.

Using the method of Gatehouse and Grey (1982), the calculated högbomite formula from Botswana gives a total cation sum of more than 22, similar to that reported for three högbomites belonging to the *36R* and *10H* polytypes of Nel (1949) and Mckie (1963). The Gatehouse and Grey (1982) formula does not seem to apply for this polytype. Thus the högbomite and zincian högbomite formulae presented in Table 1 are those calculated using the method of Zakrzweski (1977). The zincian högbomite (D-136) of Botswana with a relatively constant $Fe_{tot}/(Fe_{tot} + Mg)$ values of 0.77–0.78 are comparable to those of Angus and Middleton (1985), making them among the most Fe-rich zincian högbomites thus far reported in the literature.

Spinel. Representative electron-microprobe analyses of spinels in samples D-225 and D-136 are given in Table 1. Specimen D-225 contains a very small grain of green spinel and occurs in only one of several thin sections that have been studied. The analyses and the X-ray distribution photo of Zn (Fig. 3) show a discontinuous zonation with a sharp increase of ZnO from 1.2 wt% in the core to about 24 wt% at the rim. Since the large högbomite grains, which make up over 50 vol% of the rock, contain an average amount of 0.6 wt% ZnO, the reason for the high concentration of ZnO only in the very fine rim of a small green spinel is not clear. Spinel D-136 is a zincian hercynite.

Chlorite. In both samples the chemistry of the chlorites varies considerably. The variation in the MgO/MgO + FeO) ratio is from 0.80 (Chl I) to 0.59 (Chl II) in sample D-225 and from 0.54 (Chl I) to 0.32 (Chl II) in sample D-136 (Table 2). The chlorite chemistry plots in the sheridanite and corundophyllite fields of Hey (1954). X-ray diffraction of powdered sample D-136 shows two different chlorites at 7 and 14 Å. The 7 Å corresponds to the highly aluminous chlorite (Table 2, D-136 Chl II) with a septichlorite (amesite) structure.

Margarite. It is found only in specimen D-225 as an alteration product commonly associated with chlorite, diaspore, zoisite, and högbomite. The analysis of margarite (Table 2) reveals that it is highly sodian with 34% Na/(Na + Ca).

Epidote and zoisite. These are products of an original plagioclase–calcic amphibole assemblage. No relict plagioclase has been observed, but pargasite is enclosed in chlorite and phlogopite.

Calcic amphibole. The calcic amphibole in sample D-225 (Table 2) is pargasite (Leake, 1978) comparable to the amphiboles of the central Oetztal, eastern Alps (Mogessie et al., 1986).

Phlogopite and preiswerkite. Specimen D-225 contains phlogopite in intimate contact with högbomite, chlorite, and pargasite. The analysis of phlogopite (Table 2) reveals that the phlogopite is aluminous and silica deficient. In sample D-136, the assemblage spinel + högbomite + corundum + chlorite + apatite + preiswerkite + ilmenite + magnetite is found. A preiswerkite analysis (Table 2) compares well with the original data of Keusen and Peters (1980).

BULK CHEMISTRY

The major- and trace-element chemistries of the two rock specimens are set out in Table 3. Both are Fe-Mg-Al–rich, Si-poor rocks. These differences are reflected by the highly aluminous but silica-deficient mineral associations in the rocks. During metamorphism of the Vumba schist belt, metasomatism seems to have taken place between the thin felsic interlayers (representative samples D-225, D-136) and the ultrabasic rocks, resulting in the unusual chemical patterns of these högbomite-bearing rocks.

DISCUSSION

Depending on the mineral parageneses associated with högbomite in the different rock types and localities, several possible reactions for the formation of högbomite have been suggested. Most of these reactions are documented by Grew et al. (1987). As suggested in the preceding pages, the högbomite of sample D-225 is consid-

TABLE 2. Representative electron-microprobe analyses of associated minerals from the högbomite assemblage (D-225) and the (zincian högbomite + hercynite)–bearing assemblage (D-136)

	D-225								D-136				
	Phlog	Marg	Hbl	Chl I	Chl II	Ep	Zoi	Ilm	Chl I	Chl II	Cor	Ilm	Prw
SiO_2	36.57	31.06	39.51	25.76	25.24	37.26	40.36	0.09	24.09	18.86	0.02	0.11	28.37
TiO_2	1.08	0.09	0.96	0.07	0.18	0.02	0.00	53.06	0.02	0.00	0.00	52.64	0.03
Al_2O_3	19.45	51.07	20.28	24.87	22.84	28.95	33.68	0.49	26.35	32.31	98.64	0.49	35.83
Fe_2O_3	—	—	—	—	—	7.20	1.34	—	—	—	1.13	—	—
FeO^*	7.37	0.82	7.24	7.83	17.77	—	—	43.56	17.25	21.09	—	44.47	9.74
MnO	0.03	0.00	0.09	0.00	0.05	0.02	0.00	2.31	0.09	0.11	0.02	1.14	0.00
MgO	22.65	2.05	14.33	28.77	21.61	0.13	0.46	0.34	20.20	14.65	0.02	0.81	15.16
CaO	0.02	8.57	12.57	0.03	0.09	24.15	22.80	0.10	0.03	0.17	0.01	0.02	0.16
K_2O	7.87	0.04	0.35	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.20
Na_2O	0.76	2.45	2.23	0.00	0.00	0.00	0.00	0.00	0.00	0.20	0.00	0.00	7.06
F	0.20	0.21	0.13	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
O≡F	0.08	0.09	0.05	—	—	—	—	—	—	—	—	—	—
Total	95.92	96.27	97.64	87.33	87.78	97.73	98.64	99.95	88.03	87.39	99.84	99.68	96.55
Oxygens	24	24	24	28	28	25	25	6	28	28	6	6	22
Si	5.20	4.07	5.69	4.97	5.11	5.82	6.05	0.01	4.84	3.92	0.00	0.01	3.95
Al^{IV}	2.80	3.93	2.31	3.03	2.89	2.18	1.95	0.03	3.16	4.08	3.97	0.03	4.05
Al^{VI}	0.45	3.96	1.13	2.63	2.55	3.16	3.99	0.00	3.07	3.83	0.00	0.00	1.83
Ti	0.12	0.01	0.10	0.01	0.03	0.00	0.00	2.00	0.00	0.00	0.00	1.99	0.00
Fe^{3+}	—	—	—	—	—	0.85	0.15	—	—	—	0.03	—	—
Fe^{2+}	0.88	0.09	0.87	1.26	3.01	—	—	1.82	2.90	3.67	—	1.87	1.14
Mn	0.00	0.00	0.01	0.00	0.01	0.00	0.00	0.10	0.02	0.02	0.00	0.05	0.00
Mg	4.80	0.40	3.08	8.28	6.52	0.03	0.10	0.03	6.05	4.54	0.00	0.06	3.15
Ca	0.00	1.20	1.94	0.01	0.02	4.05	3.66	0.01	0.01	0.04	0.00	0.00	0.02
K	1.42	0.01	0.06	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.04
Na	0.21	0.62	0.62	0.00	0.00	0.00	0.00	0.00	0.00	0.08	0.00	0.00	1.91
Total	15.88	14.29	15.81	20.19	20.14	16.06	15.90	4.00	20.00	20.18	4.00	4.01	16.09
F	0.09	0.09	0.06	—	—	—	—	—	—	—	—	—	—
OH_{calc}	3.92	3.92	1.94	—	—	—	—	—	—	—	—	—	—

Note: Chl = chlorite, Ep = epidote, Zoi = zoisite, Ilm = ilmenite, Phlog = phlogopite, Marg = margarite, Hbl = hornblende, Cor = corundum, Prw = preiswerkite.

* Fe_{tot} as FeO.

ered to be primary. However, the presence of a very fine grain of chemically zoned spinel in a large brown, twinned högbomite may imply a secondary origin. If so, the following probably has taken place, according to the alteration process suggested by Gieré (1986) in marble skarns: original spinel is metasomatically altered in three subsequent steps involving successive formation of (1) högbomite or corundum + magnetite, (2) chlorite, then (3) margarite.

TABLE 3. Bulk-rock and trace-element chemistry of högbomite-bearing samples

	D-136	D-225		D-136	D-225
SiO_2	10.57	21.06	Ba	75	15
TiO_2	1.18	3.27	Ce	112	215
Al_2O_3	46.17	35.81	Co	552	170
Fe_2O_3	27.41	11.87	Cr	66	96
MnO	0.23	0.11	Cu	34	9
MgO	8.44	14.43	La	47	171
CaO	0.48	5.21	Nb	4	18
Na_2O	1.81	0.25	Ni	948	975
K_2O	0.08	0.03	Pb	5	27
P_2O_5	0.34	0.32	Rb	12	13
SO_3	0.00	0.09	Sc	5	61
ZnO	1.97	0.29	Sr	387	2018
L.O.I.	0.55	6.56	Th	6	21
Total	99.23	99.21	U	7	3
			V	217	100
			Y	17	82
			Zr	308	358

Note: Major elements in wt%, trace elements in ppm.

Based on the textural features, the zincian högbomite of D-136 is of secondary origin, formed from green spinel. The $Fe_{tot}/(Fe_{tot} + Mg)$ ratio of coexisting zincian högbomite and spinel is found to be almost the same (Table 1), supporting the idea that the zincian högbomite is an alteration product of spinel, possibly formed by the reaction spinel + ilmenite ± rutile + O_2 = högbomite + corundum, similar to the reaction proposed by Teale (1980).

Several authors have considered the conditions of högbomite formation. Wilson (1977), Teale (1980), Mancktelow (1981), Spry (1982), and Beukes et al. (1986), among others, suggested that högbomite is a stable component of an upper-amphibolite-facies metamorphic event, subsequent to an earlier high-grade amphibolite-facies or granulite-facies metamorphism. Angus and Middleton (1985) proposed that two high-grade metamorphic episodes appear to be necessary for högbomite growth, whereby the first determines the essential chemical composition, which is a mineral assemblage rich in Fe, Mg, and Al, accompanied by Ti and Zn. The second metamorphic event is instrumental in producing the appropriate physical parameters and presumably high oxygen fugacity, necessary for högbomite development.

The Vumba schist belt in which these högbomites occur is polymetamorphic; grades range from granulite to amphibolite to greenschist facies (Litherland, 1975; Rammlmair et al., in prep.). The formation of högbomite in this polymetamorphic terrane seems to be related not only to the Al-Fe-Mg–rich bulk rock chemistry, but also to the high-grade metamorphism of the region. It is suggested that the högbomites were formed during the granulite to amphibolite retrogressive phase of M2, similar to the conditions of högbomite formation proposed by Angus and Middleton (1985).

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