Zincian högbomite as an exploration guide to metamorphosed massive sulphide deposits

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Abstract

Zincian högbomite (ZnO 3.5–10.5 wt.%) occurs as an accessory phase in garnet quartzite that is intimately associated with the Broken Hill and Black Mountain Cu–Pb–Zn–Ag deposits, Aggeneys, South Africa. Högbomite coexists with a number of minerals including quartz, gahnite, sillimanite, sphalerite, pyrrhotine, pyrite, magnetite, and ilmenite, suggesting that högbomite may have formed by sulphidation and oxidation reactions. Such reactions may account for the high Zn content of högbomite. Where associated with metamorphosed massive sulphide deposits högbomite is enriched in Zn relative to that found in ultramafics, Fe–Ti deposits, Fe ores, aluminous metasediments, and skarns. This enrichment in högbomite constitutes a potential exploration guide for metamorphosed massive sulphide deposits.

KEYWORDS: zincian högbomite, sulphidation-oxidation reactions, Aggeneys, South Africa, massive sulphides, exploration guide.

Introduction

HÖGBOMITE, $R_{8-2x}^{2+}R_{16}^{3+}$ Ti_xO₃₂, where $R^{2+} = Mg$, Fe, Zn, Mn, Co, $R^{3+} = Al$, Fe, Cr, and $x \approx 1$ (Petersen, 1986), although generally considered rare has been found in a wide variety of geological environments including aluminous-rich metasediments (e.g. Teale, 1980; Mancktelow, 1981), ultramafics (e.g. Michel-Levy and Sandrea, 1953), Fe-Ti deposits (e.g. Zakrzewski, 1977; Devaraju *et al.*, 1981), skarns (e.g. McKie, 1963) and Fe ores (Marcotty, 1984; Petersen *et al.*, 1988). Although usually Fe- or Mg-rich, there are a number of examples where högbomite contains variable amounts of Zn (Moleva and Myasnikov, 1952; Wilson, 1977; Mancktelow, 1981; Spry, 1982; Spry and Scott, 1986a; Beukes *et al.*, 1986; Petersen, 1986; Petersen *et al.*, 1988).

Van Zyl (1986) and Beukes *et al.* (1986) have recently reported the occurrence of högbomite in cordierite-gedrite-phlogopite schist, hornblendite and massive amphibolite in the Bushmanland Group, Namaqualand Metamorphic Complex, South Africa. The hornblendite sample occurs

Mineralogical Magazine, April 1989, Vol. 53, pp. 263–9 © Copyright the Mineralogical Society adjacent to the Big Syncline Zn-Pb deposit at Aggeneys. In studies of gahnite associated with the Aggeneys base metal deposits (Broken Hill, Black Mountain, and Big Syncline), Spry (1986) documented additional occurrences of högbomite in garnet quartzite spatially associated with the Black Mountain and Broken Hill deposits. Spry and Scott (1986a) have also reported its occurrence in the Gams iron formation intimately associated with the Gamsberg Zn deposit, 15 km east of Aggeneys.

The Black Mountain and Broken Hill deposits are contained in a sequence of Proterozoic metasediments and metavolcanics known as the Bushmanland Group in the Namaqualand Metamorphic Complex of the Northwestern Cape Province, Aggeneys, South Africa. Detailed mapping by Ryan et al. (1982) has shown that the deposits are hosted by a paragneiss sequence known as the Aggeneys Subgroup, which is dominated by pelitic mica-sillimanite schists, quartzites and leucogneisses. A variety of minor rock types is also spatially associated with mineralization including garnet quartzite, amphibolite, calc-

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TABLE 1.	Mineral assemblages of zincian högbomite-bearing rocks
	associated with metamorphosed massive sulphide deposits

Sample Number	Deposit	Assemblage*				
PS84-20	Black Mountain	Qtz, Grt, Mag, Bt, ZSpl, Hög				
PS84-42	Black Mountain	Grt, Qtz, ZSpl, Sp, Mag, Bt, Po, Ccp, Py, I1m ^x , Hög ^x				
PS82-120	Broken Hill	Bt, Grt, Mag, ZSpl, Opx, Ap, Chl ⁺ , Ms ^{x+} , Hög, Ccp ^x , Po ^x , Gn ^x , Sil ^x				
PS84-130	Broken Hill	Qtz, Grt, Bt, Ch1 ⁺ , Mag, ZSp1, Hög ^x				
PS84-132	Broken Hill	Grt, Mag, Qtz, Sil, ZSpl, Hög ^x				
M56 ²	Geco, Ontario	Ph, Crd, St, ZSpl, Gd, Crn, Ru, Py, Ccp, Zr, Hög, Nig				
M652 ²	Geco, Ontario	Ph, Crd, St, Gd, Mag, Ilm, Py, Po, Ap, Zr, Hög				
M177 ²	Geco, Ontario	Ph, Crd, St, ZSpl, Gd, Mag, Ilm, Py, Po, Ccp, Zr, Hög				
PGS-100 ¹	Geco, Ontario	Crd, Ph, St, ZSp1, Ccp, Py, Crn, Po, Ser ^{X+} , Hög, Nig				
PGS-107 ³	Gamsberg	Qtz, Mag, Po, ZSpl, St, Sil, Gn, Mu ^{x+} , Hög ^x , Cu				

*listed in approximate order of abundance; x mineral present in trace amounts; + mineral is secondary; Ap apatite; Bt biotite; Ccp chalcopyrite; Chl chlorite; Crd cordierite; Crn corundum; Cu cummingtonite; Gn galena; Grt garnet; Cd gedrite; Hog högbomite; Ilm ilmenite; Nag magnetite; Mu muscovite; Nig nigerite; Opx orthopyroxene; Ph phlogopite; Po pyrthotine; Py pyrite; Qtz quartz; Ru rutile; Ser sericite; Sil sillimanite; Sp sphalerite; St staurolite; ZSpl zincian spinel; Zr zircon; l Spry (1982); 2 Petersen (1984); 3 Spry and Scott (1986a)

silicates, iron formation, pyritic and graphitic schists, conglomerate, sillimanite-rich rocks and cordierite-anthophyllite gneisses (Moore, 1984). Ryan *et al.* (1982) proposed that the Aggeneys Ore Formation is equivalent to the Gams Iron Formation, which hosts the Gamsberg deposit. The deposits have been metamorphosed to the upper amphibolite grade (Ryan *et al.*, 1982; Blignault *et al.*, 1983).

The present study documents the petrography and composition of högbomite in garnet quartzite at Black Mountain and Broken Hill and the potential of högbomite as a guide in the exploration for metamorphosed massive sulphide mineralization in general.

Petrography and mineral chemistry

The garnet quartzite consists primarily of garnet, magnetite, zincian spinel, quartz, biotite, orthopyhroxene, apatite, sillimanite, sphalerite, pyrrhotine, pyrite, chalcopyrite and secondary chlorite. Minerals present in trace amounts are högbomite, ilmenite and galena (Table 1). Högbomite, brown in colour and up to 0.4 mm in length, predominantly occurs along the interface between green zincian spinel and magnetite (Fig. 1a). However, it also occurs in contact with biotite and quartz and as inclusions in magnetite (Fig. 1b).

In a thermodynamic treatment of the stability of högbomite, Petersen *et al.* (1988) proposed a number of högbomite-forming reactions that included the breakdown of magnetite and spinel. The association between spinel and högbomite had previously been recognized by a number of workers including Friedman (1952), Wilson (1977), and Teale (1980), and led them to suggest that högbomite formed at the expense of spinel. Despite these associations there is no textural evidence to suggest that högbomite formed by the breakdown of these minerals. On the contrary, these minerals form a stable assemblage with högbomite.

The compositions of högbomite and its associated phases were determined using an ARL-EMX electron microprobe equipped with a Kevex energy-dispersion silicon detector.

Average analyses of coexisting högbomite and spinel are given in Table 2 and representative analyses of associated biotite and garnet in Table 3. Högbomite from the Broken Hill and Black Mountain deposits contains significant Zn and Fe with sample PS84-132 displaying a ZnO content of 10.47 wt.% (Table 2). A ternary plot of the Zn + Mn, Mg, and total Fe content of högbomite from Broken Hill and Black Mountain, along with data from a large number of worldwide localities show that högbomite from Broken Hill and Black Mountain are amongst the most Zn- and Fe-rich yet reported (Fig. 2). The most Zn-rich högbomite is that from the Gamsberg deposit (Spry and Scott, 1986a). A similar plot of the högbomite and coexisting spinel compositions listed in Table 2 demonstrates a close compositional relationship between these phases (Fig. 3). Spinel in högbomite-free assemblages at Broken Hill and Black Mountain, however, is considerably more Zn-rich than spinel in högbomite-bearing assemblages



FIG. 1. Photomicrographs of (a) högbomite (h) along the interface between zincian spinel (z) and magnetite (m). The colourless phase is quartz (q) (Black Mountain); (b) högbomite inclusions within magnetite (Broken Hill).

	PS84-20			PS84-120			PS84-130			PS84-132		
	Н8g (Зр)	Spin (3p)	Mag (2p)	H8g (6p)	Spin (3p)	Mag (2p)	Н8g (4р)	Spin (2p)	Mag (3p)	Н8g (5р)	Spin (4p)	Mag (2p)
S102	n.d.	n.d.	n.d.									
T102	5.41	0.03	0.07	5.17	0.04	0.25	6.38	0.00	0.20	3.64	0.08	0.06
A1203	60.25	57.46	0.32	57.88	55.19	0.35	57.81	54.59	0.61	57.00	56.40	0.42
FeÕ	27,65	31.96	86.70	26.85	27.76	90.49	26.07	27.62	91.53	24.95	27.73	90.09
MnO	0.10	0.16	0.03	0.14	0.24	0.13	0.13	0.16	0.00	0.42	0.59	0.03
MgO	2.51	2.34	0.35	1.26	1.34	0.06	2.66	3.17	0.04	3.47	3.18	0.00
ZnO	3.46	8.07	0.27	7.70	15.69	0.76	6.15	13.28	0.00	10.47	11.64	0.09
TOTAL	99.38	100.02	87.74	99.00	100.26	92.05	99.20	98.82	92.38	99.95	99.62	90.69
					Оху	gen basi	32					
Si	n.d.	n.d.	n.d.									
Ti	0.901	0.005	0.018	0.888	0.007	0.056	1.809	0.000	0.047	0.624	0.013	0.014
A1	15.764	15.617	0.122	15.565	15.260	0.129	15.331	15.124	0.223	15.316	15.404	0,156
Fe	5.133	6.163	23.502	5.121	5.479	23,455	4.905	5.431	23.554	4.755	5.375	23.708
Mn	0.020	0.031	0.008	0.028	0.047	0.033	0.025	0.032	0.000	0.080	0.116	0.008
Mg	0.829	0.804	0.168	0.429	0.468	0.028	0.892	1.109	0.016	1.179	1.110	0.000
Zn	0.567	1.380	0.064	1,299	2.741	0.175	1.021	2,305	0.000	1.764	1.993	0.022

TABLE 2. Composition of högbomite and coexisting spinels

(3p) 3 points analysed



FIG. 2. Ternary plot showing the composition of högbomite from worldwide localities in terms of Zn + Mn, Mg, and total Fe. Open circles represent högbomite from massive sulphide deposits (Gamsberg, Geco, Black Mountain and Broken Hill): crosses represent högbomite from the Benson iron mine (Petersen *et al.*, 1988); closed circles represent högbomite from aluminous metasediments, ultramafic rocks, calcic skarns, Fe-Ti deposits and calc-silicate granulites and the open square, högbomite from an unknown host rock (Moleva and Myasnikov, 1952). Other sources of data: Nel (1949); McKie (1963); Cech *et al.* (1976); Woodford and Wilson (1976); Chew (1977); Wilson (1977); Zakrzewski (1977); Teale (1980); Coolen (1981); Devaraju *et al.* (1981); Mancktelow (1981); Gatehouse and Grey (1982); Spry (1982); Ackermand *et al.* (1983); Petersen (1984); Angus and Middleton (1985); Beukes *et al.* (1986); Gieré (1986); Petersen (1986); Spry and Scott (1986b); Petersen *et al.* (1988); Grew (1987); this paper.

(Spry and Scott, 1986a). Biotite and magnetite in contact with högbomite and zincian spinel contain up to 0.56 and 0.35 wt.% ZnO, respectively (Tables 3 and 2). Although biotite shows variable Mg/Fe ratios, garnet is generally Fe-rich in högbomite-bearing samples (Table 3). Also, it is significant to note that the Mg/Fe ratio of högbomite is almost the same as that in coexisting spinel in sulphide-bearing deposits, whereas in non-sulphide settings their Mg/Fe ratios are generally dissimilar (Fig. 3).

Applications to exploration

At Black Mountain, Ryan *et al.* (1982) have proposed that garnet quartzite represents an alteration zone in the footwall of the deposit. Although not all garnet quartzites at Aggeneys

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	Garnet PS84-20	Garnet PS84-120	Garnet PS84-130	Garnet PS84-132	Biotite PS84-20	Biotite PS84-120	Biotite PS84-130
Si02	37.65	36.56	36.81	37.54	36.41	35.80	34.29
T102	n.d.	n.d.	n.d.	n.d.	0.88	1.06	2.86
A1203	20.73	20.28	20.69	21.09	21.07	18.77	21.38
Fe0	38.37	36.55	35.46	31.88	20.36	21.62	25.22
Mn0	2.70	4.93	4.61	5.11	0.02	0.08	0.13
Mg0	2.10	1.26	1.31	4.44	9.27	10.47	3.48
ZnO	n.d	n.d	n.d	n.d	0.37	0.56	0.40
Ca0	0.16	0.43	1,46	0.31	0.02	0.00	0.01
Na ₂ 0	n.d	n.d	n.d	n.d	0.09	0.14	0.00
к ₂ Ö	n.d	n.d	n.d	n.d	9.27	8.38	9.05
TOTAL	101.72	100.01	100.35	100.36	97.27	96.88	96.82
			Oxygen	basis 24			
Si	6.038	6.008	5,998	5.997	5.882	5.884	5.749
Ti	n.d.	n.d.	n.d.	n.d.	0.107	0.131	0.360
A1	3.918	3.926	3.993	3.968	4.011	3.636	4.224
Fe	5.146	5.022	4.832	4.256	2.750	2.971	3.536
Mn	0.367	0.686	0.636	0.691	0.003	0.012	0.019
Mg	0.503	0.306	0.320	1.056	2.233	2,515	0.869
Zn	n.d.	n.d.	n.d.	n.d.	0.045	0.063	0.049
Ca	0.028	0.076	0.254	0.052	0.004	0.000	0.002
Na	n.d.	n.d.	n.d.	n.d.	0.028	0.046	0.000
K	n.d.	n.d.	n.d.	n.d.	1.911	1.757	1,935

TABLE 3. Representative chemical analysis of garnet and biotite associated with högbomite at Black Mountain and Broken Hill

represent alteration pipes, garnet quartzites, some of which contain högbomite, are spatially related to sulphide zones (Spry, in preparation).

Average högbomite compositions from a variety of localities are plotted in Fig. 2 and distinguished on the basis of geological setting. Högbomite associated with metamorphosed sulphide deposits (Broken Hill, Black Mountain, Geco and Gamsberg) are enriched in Zn and Fe whereas that associated with calc-silicate granulites, aluminous metasediments, Fe ores and Fe-Ti deposits are depleted in Zn and show variable Mg and Fe contents. Although högbomites in some ultramafic rocks are enriched in Zn, they show lower Fe/Mg ratios than those related to metamorphosed massive sulphides (e.g. Coolen, 1981). Furthermore, zincian spinel that coexists with högbomite is consistently more enriched in Zn relative to högbomite in massive sulphide occurrences. This contrasts with spinel in non-sulphide occurrences where Zn may be either enriched, depleted or the same as that in coexisting högbomite.

A number of reactions relating spinel and högbomite in non-sulphide occurrences have been suggested by a number of workers (Ackermand *et al.*, 1983; Grew *et al.*, 1987; Petersen *et al.*, 1988). Petersen *et al.* (1988) have proposed that högbomite in sulphide occurrences may form by sulphidation and oxidation reactions. Their reactions suggest that the Mg/Fe ratio of högbomite will increase with increasing f_{O_2} and f_{S_2} conditions. Because of the low Mg/Fe ratio of högbomite from Black Mountain and Broken Hill, it is unlikely that högbomite formed by sulphidation and oxidation reactions of the type proposed by Petersen *et al.* (1988).

There is no textural evidence to support the formation of högbomite at Black Mountain and Broken Hill by desulphidation of sphalerite and pyrrhotine; however, it is possible that zincian högbomite may have formed by desulphidation reactions, for example:

[5FeS] in pyrrhotine + [5ZnS] in sphalerite + $16Al_2SiO_5 + ZnTiO_3 + FeTiO_3 + 5O_2 =$ [Zn₆Al₁₆TiO₃₂] in högbomite + [Fe₆Al₁₆ TiO₃₂] in högbomite + $16SiO_2 + 5S_2$ (1)

and

[6FeS] in pyrrhotine + [6ZnS] in sphalerite
+
$$16Al_2SiO_5 + 2TiO_2 + 6O_2 = [Zn_6Al_{16}$$

TiO₃₂] in högbomite [Fe₆Al₁₆TiO₃₂] in högbo-
mite + $16SiO_2 + 5S_2$ (2)

Corresponding oxidation reactions can also be written. The above sulphidation reactions are comparable to those proposed by Spry and Scott (1986a,b) for the formation of zincian spinel and zincian staurolite in massive sulphide deposits and may partly account for the high Zn content of högbomite in these deposits. Sulphidation reactions involving zincian spinel and högbomite may also account for the constant Mg/Fe ratio between these coexisting phases. As a conse-



FIG. 3. Ternary plot showing the composition of högbomite and coexisting zincian spinel in terms of Zn + Mn, Mg, and total Fe. Open and closed triangles represent spinel and högbomite, respectively in massive sulphide deposits; and open and closed circles represent spinel and högbomite, respectively in non-sulphide forming environments. Data: Zakrzewski (1977); Coolen (1981); Spry (1982); Petersen (1984, 1986); Angus and Middleton (1985); Beukes et al. (1986); Gieré (1986); Spry and Scott (1986a); Grew (1987); this paper.

quence of this explanation, coexisting spinel and högbomite that did not form by sulphidation and oxidation reactions should have variable Mg/Fe ratios (Fig. 3).

At the Geco deposit, Ontario, högbomite occurs in cordierite-gedrite gneisses which represent hydrothermally altered mafic volcanics that have been metamorphosed (Petersen *et al.*, 1988). The common presence of magnetite and pyrite (\pm ilmenite or rutile) indicates that these gneisses were highly oxidized and likely formed from rocks that were originally highly oxidized (Petersen and DePangher, 1987). Cordierite-gedrite gneisses of both mafic and felsic protoliths occur only in the footwall of the Geco massive sulfide deposit

where they comprise part of the feeder system for that deposit. These originally hydrated, oxidized and highly altered rocks have the appropriate geochemical characteristics to permit the formation of zincian högbomite during metamorphism. Spry (1982) and Petersen *et al.* (1988) have suggested that högbomite at Geco has formed by reactions not involving sulphides. The high levels of Zn are attributed to both the availability of Zn and the dramatic enrichment of Fe over Mg in the rocks during alteration (Petersen and DePangher, 1987). In view of the Zn-rich nature of högbomite that is spatially related to metamorphosed massive sulphide deposits at Aggeneys, Gamsberg, and Geco, it is proposed that the Zn

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content of högbomite may be a useful guide in exploration, in analogous fashion to zincian spinel (Spry and Scott, 1986*a*) and zincian staurolite (Spry and Scott, 1986*b*).

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