The occurrence of högbomite in high-grade metamorphic rocks *

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Abstract. Högbomite has generally been considered to be a rare accessory phase in metamorphic rocks. While investigating high-grade peraluminous metamorphites in the Benson Mine District, Adirondack Mountains, New York and the Manitouwadge Massive Sulfide District, Ontario, Canada, we have found several högbomite occurrences and believe that högbomite is more widespread in high-grade aluminous rocks than previously recognized. At Benson Mine, an iron-rich högbomite (Hög) occurs with K-feldspar-magnetite (Mt)-ilmenite (Ilm)-biotite-almandine (Alm)-sillimanite (Sil)-quartz (Qz)-hercynite (Hc)-corundum (Cor)-rutile (Ru). At Manitouwadge, Fe−Zn högbomite is found with gedrite-cordierite-staurolite-hercynite-magnetite ± quartz ± ilmenite ± rutile ± biotite ± cassiterite. Because composition varies with structure type, it is essential to determine the structure of högbomite utilized in specific reactions. Högbomite from Benson Mine has an 8H structure type, while that at Manitouwadge has a complex mixed structure. Both are more iron-rich than previously reported högbomites, and their composition can be approximated by the ideal formula $Fe_5Al_{16}TiO_{30}(OH)_2$. Proposed reactions for 8H-högbomite are $Hög = Ilm + Hc + Cor + V$, $Hög = Ru + Hc + Cor + V$, $Hög + Ru = Ilm + Cor + V$, and $Hög + Ilm = Ru + Hc + V$. These reactions can be combined with the experimentally determined reactions $Alm + Sil = Hc + Qz$ and $Ru + Alm = Ilm + Sil + Qz$ to derive reactions in the system $FeO − Al_2O_3 − TiO_2 − SiO_2 − H_2O$ that limit the stability of the assemblages $Hög + Alm$ and $Hög + Sil$. Oxidation-sulfidation reactions define a wedge-shaped stability field for högbomite that is closed on the high fS_2 side.

Introduction

Since its characterization by Gavelin (1916), the mineral högbomite has been observed in many widely varying parageneses. It was originally thought to be a rare accessory phase, but it has since been observed with increasing frequency in high-grade metamorphosed peraluminous or mafic rocks (Table 1). In this paper we review the literature concerning högbomite to highlight aspects of its crystal chemistry that are poorly understood, present mineralogical

data on two new högbomite localities, and consider possible phase equilibria involving högbomite.

Identification of högbomite has probably been obscured by its optical resemblance to rutile, because högbomite (like rutile) is dark brown and uniaxial negative. Högbomite can be distinguished from rutile by its lower relief, distinct pleochroism, hexagonal cross-section when found in euhedral grains and tendency to be intergrown with spinel. Rutile is readily distinguished from högbomite by its brilliance in reflected light. Thin hexagonal plates of ilmenite may occasionally be confused with högbomite but can be distinguished by its greater reflectivity.

Gavelin's (1916) data show högbomite to be a hexagonal $Mg − Ti − Al$ oxide. Several general formulae have been proposed for högbomite (Table 1). Zakrzewski (1977) has suggested that the cation/anion ratio of högbomite is explicitly related to the Ti content by the relation $R_{2-2x}^{2+}R_4^{3+}Ti_xO_8$; this converts to $R_6^{2+}R_{16}^{3+}TiO_{32}$ for Ti = 1 on an anhydrous oxygen basis. The formulae of Nel (1949), Michel-Levy and Sandrea (1953), McKie (1963), and Gatehouse and Grey (1982) are basically the same and, normalized to 32 anions, simplify to $R_6^{2+}R_{16}^{3+}TiO_{32}$ or to $R_5^{2+}R_{16}^{3+}TiO_{30}(OH)_2$, and where $R^{2+} = Mg$, Fe^{2+}, Zn, Mn, Co ... and $R^{3+} = Al$, Fe^{3+}, Cr. In the formula derived for 8 H-högbomite by Gatehouse and Grey (1982) the six R^{2+} cations are reduced to five in order to charge balance the substitution of two hydroxyl for two oxygen anions. The structure analysis of Gatehouse and Grey (1982) shows that the cation to anion ratio of 8H-högbomite is 22:32. McKie (1963) first proposed the presence of water in the högbomite structure based on the water content reported by Nel (1949), although Nel attributed the water to contamination of the sample by chlorite. Gatehouse and Grey (1982) also inferred the presence of some hydroxyl, the amount of which may depend on the valence states of the metal cations surrounding the site that hydrogen may occupy. This permits partial occupancy of that site – i.e., högbomite may be variably hydrated (Gatehouse and Grey 1982). Gatehouse and Grey's infrared analyses, however, show no peaks indicative of any H_2O, OH^- or H^+ in their sample. Zakrzewski (1977) also performed infrared analyses on a högbomite from Liganga, Tanzania, and found no water. Thus the inconsistency remains: detailed structural analysis leads crystallographers to infer that högbomite is an hydroxyl-bearing phase, yet infrared and wet-chemical analysis have not conclusively demonstrated the presence of hydroxyl.

Also unknown is the ferrous/ferric ratio of högbomite.

Table 1. Occurrences of högbomite

Reference	Occurrence	Structure (nHR)	General Formula
Gavelin (1916)	Magmatic iron ores, Ruoutevare, Sweden	4H	
Onay (1949)	Emery deposit in marble, S.W. Anatolia, Turkey		
Nel (1949)	Transvaal, S. Africa	B:18R; A:5H	$(Mg, Fe^{2+})_6(Al, Fe^{3+})_{16}TiO_{32}$
Friedman (1952)	Emery hornfels, Cortlandt Twnp., Westchester Co., N.Y.	6H	
	Emery hornfels, Whittles Pittsylvania Co., Va.	4H	
	Emery hornfels, Macon Co., N. Carolina	5H	
Moleva and Myasnikov (1952)	Chlorite-epidote amphibolite, Russia		$(Mg, Fe^{2+}, Mn)_7(Al, Fe^{3+}Cr)_{20}TiO_{39}$
Michel-Levy and Sandrea (1953)	Metamorphosed ulbrabasics, Frain, Czechslovakia		$(Fe^{2+}, Mg)_6(Al, Fe^{3+})_{16}TiO_{32}$
Belov (1964)	Russia		$(R^{2+}, Ti, R^{3+})_6(O, OH)_8$
Leake (1965)	Hornfelsed pelitic xenolith in norite, N. Connemara, Co. Galway, Ireland		
McKie (1963)	Enstatite-tremolite-chlorite skarns, Mautia Hill Tanzania, Tanganyika	5H	$R^{2+}_{1.0-1.6}Ti_{0.2-0.4}R^{3+}_{3.7-4.0}O_{7.6-8.0}(OH)_{0.0-0.4}$
Woodford and Wilson (1976)	Sapphirine-kornerupine-surinamite-bearing aluminous granulite, N.E. Strangways Range, Central Australia		R_xO_{40}; where $\Sigma R^{4+} = 1.0-1.7$, $\Sigma R^{3+} = 19.9-20.6$[a] $\Sigma R^{2+} = 7.0-7.6$, $\Sigma R = 28.7-28.8$
Cech et al. (1976)	Co-rich cordierite-anthophyllite amphibolite, Lusaka, Zambia	4H	R_xO_8; where $\Sigma R^{4+} = 0.26$, $\Sigma R^{3+} = 3.828$[a], $\Sigma R^{2+} = 1.74$ $\Sigma R = 5.81$
Wilson (1977)	Phlogopite-spinel-corundum-chlorite amphibolite, Strangways Range, Australia	4H	$(Mg, Fe^{2+}, Zn...)_6(Al, Fe^{3+}, Ti...)_{17}O_{32}$
Zakrzewski (1977)	Titanomagnetite ore lenses in anorthosite, Liganga, Tanzania	5H	$R^{2+}_{2-2x}Ti_xR^{3+}_4O_8$; where $\Sigma R^{4+} = 0.21-0.39$, $\Sigma R^{2+} = 1.21-1.58$, $\Sigma R = 5.60-5.79$
Teale (1980)	Upper amphibolite spinel-phlogopite schist, cordierite-sillimanite gneisses, Mount Painter Province, Australia	5H?	$R^{2+}_xR^{3+}_4Ti_yO_8$; where $\Sigma R^{4+} = 0.20-0.24$, $\Sigma R^{2+} = 1.52-1.61$, $\Sigma R = 5.76-5.80$
Mancktelow (1981)	Aluminous segregations in migmatite zone of Reedy Creek, S. Australia (640° C, 3.7 Kb)		R_xO_8; where $\Sigma R^{4+} = 0.08-0.177$, $\Sigma R^{3+} = 3.92-4.04$[a] $\Sigma R^{2+} = 1.65-1.77$, $\Sigma R = 5.84-5.90$
Devaraju et al. (1981)	Magmatic Fe−Ti ores, Madangere, Ankola Taluk, Karnataka, India	18R	R_xO_8; where $\Sigma R^{4+} = 0.24-0.28$, $R^{3+} = 3.84-3.81$[a] $\Sigma R^{2+} = 1.77-2.01$, $\Sigma R = 5.82-5.81$
Coolen (1981)	Calcsilicate granulite, Furua, Tanzania (600–700° C, 5–7 Kb) Granulite-metamorphosed garnet pyroxenite, Gali-Ruoutevare, Sweden (see Gavelin, 1916, above)		See Zakrzewski (1977); where $\Sigma R^{4+} = 0.19-0.31$, $\Sigma R^{2+} = 1.39-1.62$, $\Sigma R = 5.70-5.81$
Ding (1982)	Contact metamorphism, Yanshianian Granite, Hunan Province, China	4H	$(Mg, Sn, Al)_{5.9}O_{8.5}$
Gatehouse and Grey (1982)	Strangways Range, Australia (see Wilson, 1977)	8H	$R^{2+}_5R^{3+}_{16}TiO_{30}(OH)_2$
Spry (1982)	Amphibolite-granulite gedrite-cordierite schist, Manitouwadge, Ontario		R_xO_{24}; where $\Sigma R^{4+} = 0.58$, $\Sigma R^{3+} = 12.01$[a], $\Sigma R^{2+} = 4.82$ $\Sigma R = 17.41$
Ackermand et al. (1983)	Granulite facies sapphirine rocks, Fiskenqesset, W. Greenland		R_xO_{31}; where $\Sigma R^{4+} = 0.83-1.20$, $\Sigma R^{3+} = 14.78-15.14$[a] $\Sigma R^{2+} = 6.40-6.69$, $\Sigma R = 22.35-22.61$

Table 1. (continued)

Reference	Occurrence	Structure (nHR)	General Formula
Giere (1986)	Contact aureole, Bergell Intrusive, Switzerland		$R^{2+}_{2-2x}Ti_xR^{3+}_4O_8$
Beukes et al. (1986)	Amphibolite facies mafic volcanics Bushmanland, South Africa	4H; 5H	
Grew et al. (1987)	Kornerupine-sillimanite gneisses, India		$R^{2+}_5 R^{3+}_{16} TiO_{30}(OH)_2$
This study	Benson Mine, New York	8H	$R_{22}O_{30}(OH)_2$; where $\Sigma R^{4+} = 0.60\text{-}1.03$,
	Manitouwadge, Ontario	8H/10H	$\Sigma R^{3+} = 15.95\text{-}16.80$, $\Sigma R^{2+} = 4.60\text{-}5.02$

 [a] All Fe treated as FeO

The small amount of högbomite in most rocks precludes separation of enough material to perform Mossbauer or wet-chemical analyses that would permit determination of Fe^{2+}/Fe^{3+}. The refractory character of högbomite may also complicate wet chemical analyses.

X-ray crystallographic data have been reported for högbomite by Michel-Levy and Sandrea (1953), Mikheev (1957), McKie (1963), Cech et al. (1976), Zakrzewski (1977), Bovin (1981), Devaraju et al. (1981), Ding (1981), Gatehouse and Grey (1982), and Beukes et al. (1986). Using single crystal X-ray data, McKie (1963) identified a series of högbomite polytypes and designated them as nH or nR (where n equals c/4.6 Å, H = hexagonal, R = rhombohedral). These arise from variations in the stacking sequence of a basic högbomite hexagonal cell with dimensions of a = 5.72 Å, c = 4.6 Å. Polytypes observed to date are 4H, 5H, 6H and 18R. Peacor (1967) has introduced a nomenclature which is adhered to in this report, in which n equals the number of closest-packed oxygen layers per unit cell. Thus McKie's (1963) 4H-högbomite now becomes 8H-högbomite. With this nomenclature, the structures of 24R-nigerite and 4H-taaffeite are analogous to those of the corresponding högbomite polytypes (Anderson et al. 1951; McKie 1963; Pen and Van 1963; Grey and Gatehouse 1979; Gatehouse and Grey 1982). Gatehouse and Grey (1982) propose that the högbomite structure can be modeled as having parallel layers of a spinel-like structure and a nolanite-like structure alternating along the c-axis. Mixed "polytypes" of högbomite, högbomite-spinel (högbomite (0001) parallel to spinel (111): this study, Fig. 1A and B) and högbomite-taaffeite (Teale 1980) intergrowths have been observed and are compatible with this model. Such intergrowths make crystallographic and compositional analysis very difficult, because separation of the two phases is almost impossible.

In deriving the crystal structure of nigerite, Grey and Gatehouse (1979) outlined the principles underlying the crystal structures of both the nigerite and högbomite "polytypes" and then applied those principles to creating a successful model of the structure of 8H-högbomite (Gatehouse and Grey 1982). They showed that the nigerite and högbomite structures are composed of three separate kinds of cation layers, designated O, T_1 and T_2. Each layer sequence (e.g., 8H) is characterized by a given cation sequence. The formulae of the so-called polytypes are different because each cation layer has a different structure and composition. Thus the various stacking modifications of högbomite are better designated as "mixed-layer" structures than as poly-

types, because the term polytype implies identity of composition. It is therefore essential to determine the detailed structural relations in order to properly interpret chemical analytical data, especially where formulae are used in chemical reactions. For 8H-högbomite from Manitouwadge and högbomite from Benson Mine, which is dominantly 8H, the formula is expected to be $M_{22}O_{30}(OH)_2$.

It is likely that a correlation exists between compositional ranges of specific cations and specific mixed-layer sequences. The corundum-rutile-spinel-hercynite tetrahedron sectioned such that the apices of the ternary can be expressed as $Fe_2Al_4O_8$ (hc), $Mg_2Al_4O_8$ (sp), and $TiAl_4O_8$ (hypothetical phase; $TiO_2 + 2\ Al_2O_3$ is shown in Fig. 2. Analyses of 8H-högbomites show approximately one Ti atom per 32 oxygens, while many analyses of 10H-högbomites (Nel 1949; McKie 1963; Zakrzewski 1977) show ratios closer to 2/32. A correlation between Ti content and högbomite structure type should be considered. The similar Fe/Mg ratios of coexisting högbomite and spinel further highlight the structural similarity of these minerals.

Knowledge of the water content and the FeO/Fe_2O_3 ratio of högbomite are important to the determination of its field of stability. Both primary and secondary modes of origin have been proposed for högbomite based upon textural considerations. Högbomite frequently occurs rimming, along cracks in, or intergrown with green spinel (Fig. 1A and B), or enclosed within magnetite (Fig. 1A and C). These textures have been interpreted frequently as primary spinel altering to secondary högbomite by addition of H_2O, Ti or Al (e.g. Friedman 1952; Leake 1965). These textures may also be formed by "exsolution" during oxidation of an initially homogeneous titanian spinel without introduction of externally derived Ti or Al (Appel 1986). Others have considered högbomite to be the product of a retrograde or second metamorphic episode of amphibolite grade imposed on granulite facies rocks (e.g. Woodford and Wilson 1976; Wilson 1977; Coolen 1981; Angus and Middleton 1985). Högbomite that occurs as idiomorphic, isolated crystals in high-grade spinel-bearing rocks (Gavelin 1916; Zakrzewski 1977; Teale 1980; Mancktelow 1981; Spry 1982; Petersen 1986) appears to be in equilibrium with surrounding minerals (Fig. 1E and F). However, the range of stability of högbomite in $P-T-X_{fluid}$ space remains to be determined.

The recently discovered occurrences at the Benson Iron Mine, Adirondacks, New York, and at Manitouwadge, Ontario, are appropriate for the investigation of some of these
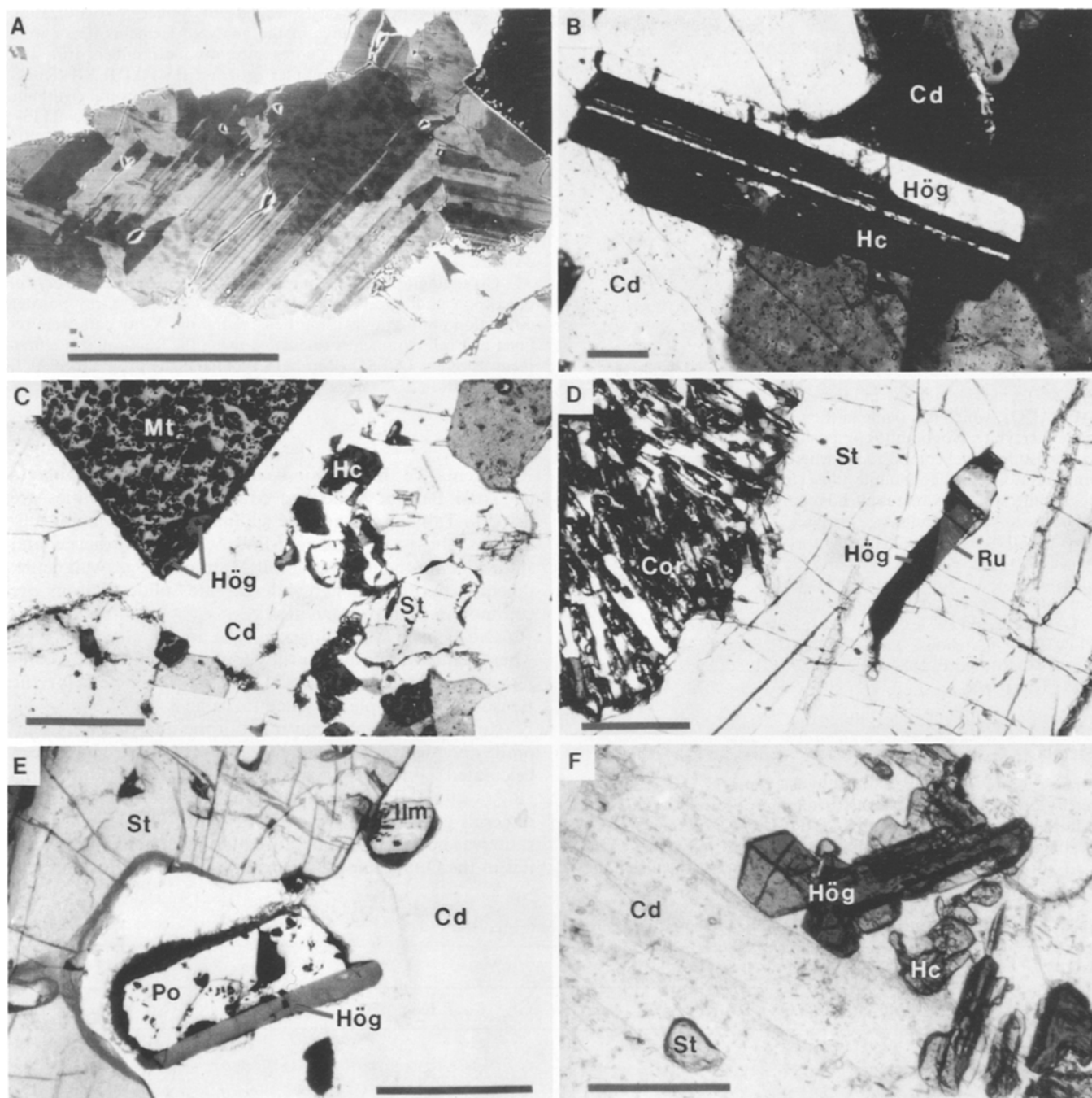
Fig. 1A–F. Photomicrographs of Benson Mine and Manitouwadge högbomite. *Scale bar* represents 200 μ unless otherwise noted. Abbreviations: *Alm*, almandine; *Hög*, högbomite; *Hc*, hercynite; *Hm*, hematite-ilmenite; *Cor*, corundum, *Cd*, cordierite; *St*, staurolite; *Po*, pyrrhotite; *Ilm*, ilmenite; *Mt*, magnetite. **A** Backscattered electron image showing a complex spinel (light grey) – högbomite (dark grey) intergrowth contained in magnetite (white). Dark area on right is perthite. Areas in intergrowths surrounded by white are holes. Note terminations of spinel and högbomite lamellae. Blotchy areas in both spinel and högbomite show no correlation with chemistry and may be artifacts of the coating process. Benson Mine sample BM80-48. *Bar scale* = 100 μ; **B** Högbomite-hercynite intergrowth. Cross-polarized transmitted light. Manitouwadge sample M495; **C** Högbomite-magnetite intergrowth with cordierite and hercynite. Plane-polarized transmitted and reflected light. Mantiouwadge sample M651; **D** Högbomite-rutile composite grain in staurolite with corundum and cordierite. Cross-polarized transmitted light and reflected light. Manitouwadge sample M56; **E** Högbomite lath in cordierite with staurolite. Cross-polarized transmitted light and reflected light. Manitouwadge sample M652; **F** Euhedral högbomite in cordierite with hercynite. Plane polarized transmitted light. Note incipient pinite alteration in cordierite. Manitouwadge sample M651

questions. Benson Mine högbomite occurs mantling and intergrown with spinel in magnetite, in magnetite alone, and included in garnet and garnet-magnetite intergrowths (Marcotty 1984; Fig. 1A). At Manitouwadge högbomite is invariably associated with the district-wide cordierite-ged-

rite gneisses, where it forms idiomorphic crystals associated with cordierite, staurolite, hercynite and corundum (Fig. 1C, D, E, and F). A study of these högbomite occurrences has been made to consider relationships between chemistry, structure type and possible phase equilibria.
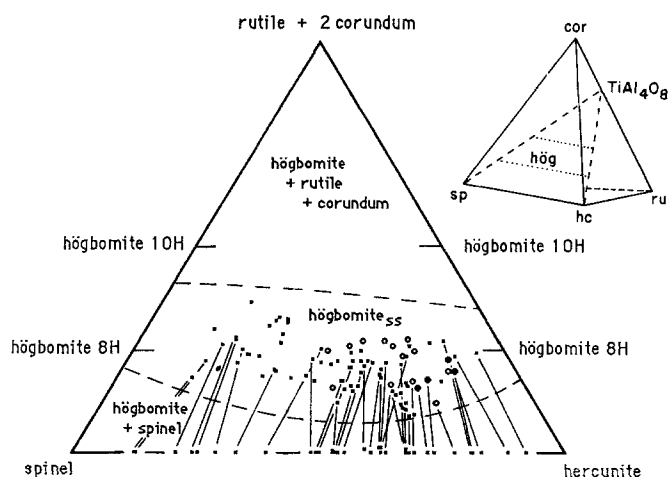
Fig. 2. Ternary diagram in the system $TiAl_4O_8 - Mg_2Al_4O_8 - Fe_2Al_4O_8$, which is a plane in the tetrahedron corundum-rutile-spinel-hercynite. Högbomite compositions are plotted with tie lines to coexisting spinel compositions where known. *Open circles* represent Manitouwadge högbomite, *filled circles* represent Benson Mine högbomite, and dots represent högbomite from a variety of other localities. All högbomite analyses were renormalized to $M_{22}O_{30}(OH)_2$ assuming 8H structures. Sources of högbomite and spinel data: Gavelin 1917; Nel 1949; Onay 1949; Moleva and Myasnikov 1952; Kuz'min 1960; Maaskant 1970; Cech et al. 1976; Karpova 1976; Woodford and Wilson 1976; Chew 1977; Wilson 1977; Zakrzewski 1977; Coolen 1981; Devaraju et al. 1981; Mancktelow 1981; Gatehouse and Grey 1982; Spry 1982; Ackermand et al. 1983; Marcotty 1984; Petersen 1984, 1986; Spry and Petersen 1989; This paper

Methods

Analyses were initially performed by EUP and L-AM on the University of Michigan ARL-EMX-S microprobe analyzer equipped with three spectrometers and LiF, ADP, and TAP crystals. An accelerating potential of 15 kV, emission current of 150 μa, and specimen current of 0.01 μa on wollastonite were used with current digitized counting periods of 15 seconds or longer. "Volatilization checks" showed no change in the analyzed elements. Data were corrected for absorption, fluorescence, atomic number, drift, and backgrounds using the computer program EMPADR VII (Rucklidge and Gasparrini 1969). Standards used were synthetic $MnFe_2O_4$, Al_2O_3, $MgTiO_3$, SnO_2, ZnS and almandine R1137. Because many analytical totals were unacceptably high (102–105 weight percent), the Manitouwadge samples were reanalyzed by EJE with the University of Michigan Cameca CAMEBAX electron microprobe. Standards used were synthetic $MgAl_2O_4$, $MgTiO_3$, $Ca_3Cr_2Si_3O_{12}$, SnS, ZnS and natural ilmenite, rhodonite and clinopyroxene. Acceptable totals (98–102) were obtained with those procedures.

Crystallographic data were obtained from both single-crystal precession photographs using CuK_α and Gandolfi X-ray powder diffraction photographs using FeK_α radiation. X-ray data were refined and cell parameters calculated using the least-squares refinement program LCLSQ (Burnham 1966) and the program SPACE for calculation of d-values.

Results

Representative högbomite-bearing minerals assemblages from the Benson Mine and Manitouwadge localities are listed in Table 2. Garnet and sillimanite are the major aluminous phases at Benson Mine, whereas cordierite and staurolite are the major ones at Manitouwadge. Magnetite, ilmenite, pyrite, and hercynite-gahnite solid solutions are common in both parageneses.

The Benson Mine högbomite is an 8H structure type, whereas the Manitouwadge högbomite is composed of complex, mixed structure types. Unit cell parameters for the Benson Mine sample are listed in Table 3.

Representative electron microprobe analyses for högbomite and nigerite are given in Table 4. Formulae have been calculated on the basis of 22 cation equivalents $[R_{22}O_{30}(OH)_2]$, assuming all analyses were obtained on minerals grains having the 8H structure. The ferrous/ferric ratio was not estimated because of the remaining uncertainties in the O/OH and in the expected formulae for different

Table 2. Högbomite-bearing mineral assemblages from Benson Mine and Manitouwadge

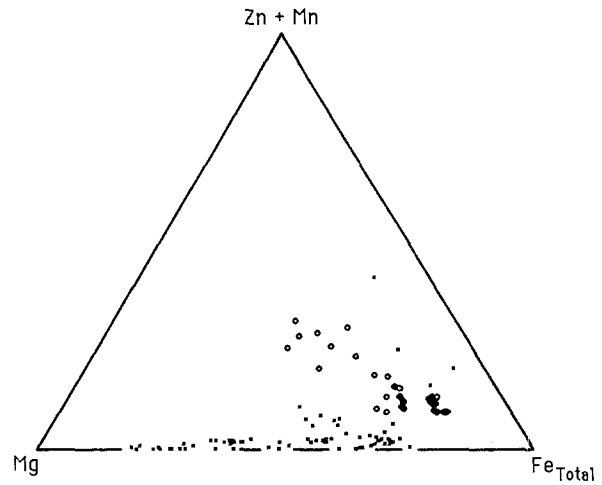| Sample No.	Assemblage																					
	Gn	Sil	Cd	St	Bi	Qz	Kfs	Pl	Gd	Mt	Ilm	Gh	Cor	Hög	Ng	Ru	Cs	Py	Po	Cpy	Sph	Ap	Zr
BM81-48	X	X			X	X	X	X		X	X	X	X	X				X		X		X	
BM81-49	X	X			X	X	X			X	X	X	X	X				X		X		X	
BM81-52	X				X	X	X			X	X	X	X	X				X		X		X	
BM81-25	X				X	X	X			X	X	X	X	X		X		X	X	X		X	
BM81-301	X	X			X	X	X			X	X	X		X				X		X			
BM80-5	X	X			X	X	X			X	X	X	X	X								X	
BM80-9	X	X			X	X	X			X		X	X	X								X	
M56			X	X	X				X	X		X	X	X	X	X	X	X	X	X			X
M177			X	X	X				X	X	X	X		X				X	X	X			X
M306	X	X	X	X	X	X			X	X	X	X		X	X		X	X	X	X			X
M495		X	X	X	X					X		X		X						X			X
M610			X	X	X				X	X		X		X						X			X
M651			X	X	X				X	X	X	X		X				X	X	X	X		X
M652			X	X	X				X	X	X	X		X			X	X	X	X		X	X
M660	X		X	X	X	X			X	X	X			X				X					X
M664			X	X	X	X			X	X	X			X				X	X	X			X
M723			X	X	X	X			X	X	X			X				X		X		X	X

Abbreviations: Gn, garnet; Sil, sillimanite; Cd, cordierite; St, staurolite; Bt, biotite; Qz, quartz; Kfs, K-feldspar; Pl, plagioclase; Gd, gedrite; Mt, magnetite; Ilm, ilmenite; Gh, gahnite; Cor, corundum; Hög, högbomite; Ng, nigerite; Ru, rutile; Cs, cassiterite; Py, pyrite; Po, pyrrhotite; Cpy, chalcopyrite; Sph, sphalerite; Ap, apatite; Zr, zircon

Table 3. Comparison of unit cell parameters of Benson Mine högbomite (BM81-49) with Strangways högbomite

Unit Cell Parameters	This study	Gatehouse and Grey (1982)
a (Å)	5.75 (2)	5.734 (3)
c (Å)	18.29 (1)	18.389 (8)
V (Å³)	523.7 (4)	523.6 (9)

Fig. 3. $(Zn + Mn) - Mg - Fe_{Total}$ ternary diagram for known högbomite compositions. *Open circles* are högbomite from Manitouwadge. *Filled circles* represent högbomite from Benson Mine. Dots represent högbomite from a variety of other settings

högbomite polytypes that may be mixed with spinel and integrated by the probe beam. The occasional high totals may have resulted in part from the inclusion of two moles of OH in the analyses, and they may indicate that these högbomite have less than the inferred OH. Noting that F commonly substitutes for OH in hydrous minerals, a Manitouwadge högbomite (M56) that coexists with a fluorine-bearing biotite (1.33 wt. % F, $X_F = 0.15$) was analyzed for fluorine by electron microprobe. Högbomite M56 contains 0.09 ± 0.02 wt.% fluorine. Representative electron microprobe analyses for minerals coexisting with högbomite and nigerite are given in Table 5.

The Benson Mine and Manitouwadge occurrences are unusual in that Benson Mine högbomite contains significant Mn and Manitouwadge högbomite contains substantial Zn (Table 4, Fig. 3). A ternary plot of the R^{2+} cations of the available chemical analyses shows that högbomite is characterized principally by $Mg - Fe$ solid solution and that the Benson Mine and Manitouwadge högbomite are among

the most iron-rich reported (Fig. 3). Solid solution with Mn and Zn at Benson Mine and Manitouwadge, respectively, is consistent with their respective geochemical settings. Spessartine-rich garnets occur at Benson Mine, while gahnite and zincian staurolite are intimately associated with högbomite at Manitouwadge.

Manitouwadge högbomite contains variable amounts of

Table 4. Electron microprobe analyses of Benson Mine and Manitouwadge högbomite (H) and nigerite (N). Oxides in weight percent

Mineral Sample	Benson Mine		Manitouwadge											
	H 81-49	H 81-52	H 306-1	N 306-2	N 306-3	H 652-1	H 652-2	H 177-1	H 177-2	N 56-1	N 56-2	N 56-3	H 56-4	H 56-5
SiO₂	–	–	0.02	0.26	0.24	0.08	0.03	0.00	0.00	0.10	0.12	0.06	0.03	0.05
SnO₂	–	–	3.06	14.04	8.96	5.16	1.73	0.29	1.83	8.46	11.31	6.55	0.10	1.25
TiO₂	4.44	5.42	1.86	3.15	2.52	5.48	3.10	3.84	5.36	3.76	3.54	4.12	5.10	2.83
Al₂O₃	61.66	61.26	57.22	55.85	56.18	57.06	59.27	60.02	59.89	59.36	57.51	59.88	59.83	61.40
Cr₂O₃	–	–	0.02	0.00	0.03	0.00	0.01	0.07	0.01	0.00	0.01	0.00	0.00	0.00
FeO	26.60	27.18	18.18	12.65	13.98	17.75	18.81	24.14	22.31	11.08	10.43	11.67	14.66	14.33
MnO	1.06	1.08	0.00	0.06	0.00	0.18	0.17	0.12	0.16	0.49	0.55	0.53	0.57	0.57
MgO	2.81	2.94	2.96	2.90	2.48	4.56	4.98	4.91	4.70	5.92	5.50	5.86	6.98	6.99
CaO	–	–	0.00	0.00	0.09	0.00	0.00	0.06	0.03	0.00	0.00	0.00	0.00	0.00
ZnO	3.22	2.44	17.53	10.33	14.16	8.13	12.64	5.16	3.16	9.13	8.44	8.43	10.80	12.85
Sum	99.79	100.32	100.85	99.24	98.64	98.40	100.74	98.61	97.45	98.30	97.41	97.10	98.07	100.27
H₂O[a]	1.44	1.44	1.40	1.31	1.34	1.38	1.44	1.43	1.40	1.38	1.35	1.38	1.44	1.46
Sum	101.23	101.76	101.25	100.55	99.98	99.78	102.18	100.04	98.85	99.68	98.76	98.58	99.51	101.73
Cations and anions														
Si	–	–	0.00	0.06	0.05	0.02	0.01	0.00	0.00	0.02	0.03	0.02	0.00	0.01
Sn	–	–	0.26	1.28	0.80	0.45	0.14	0.03	0.15	0.73	1.01	0.67	0.01	0.10
Ti	0.70	1.05	0.30	0.54	0.43	0.89	0.48	0.60	0.85	0.61	0.59	0.57	0.80	0.44
Al	15.12	14.83	14.46	14.98	14.86	14.61	14.58	14.81	15.14	15.17	15.10	15.28	14.73	14.85
Cr	–	–	0.01	0.00	0.01	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00
Fe	4.62	4.67	3.26	2.41	2.65	3.23	3.28	4.21	3.85	2.01	1.94	2.12	2.56	2.46
Mn	0.19	0.19	0.00	0.01	0.00	0.03	0.03	0.02	0.03	0.09	0.11	0.10	0.10	0.10
Mg	0.87	0.90	0.94	0.98	0.83	1.47	1.54	1.52	1.48	1.91	1.83	1.89	2.13	2.10
Ca	–	–	0.00	0.00	0.02	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.00
Zn	0.50	0.37	2.77	1.74	2.35	1.30	1.94	0.79	0.49	1.46	1.39	1.35	1.67	1.94
OH	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
O	29.26	30.48	29.80	30.37	29.72	29.67	28.92	29.04	30.57	29.95	30.17	29.90	29.18	28.99

[a] Calculated assuming 2(OH)/22 cations

Table 5. Electron microprobe analyses of minerals coexisting with högbomite and nigerite. Oxides in weight percent

| Mineral[a] | Gh | St | Cs | St | Gh | St | Hc | Cs | Gh | Ru | St | Hc | Mt |
Sample	306-1	306-2	306-3	652-1	652-2	177-1	177-1	56-2	56-3	56-4	56-4	56-5	56-5
SiO_2	0.02	30.45	0.00	30.29	0.04	30.29	0.03	0.00	0.00	0.02	30.88	0.01	0.17
SnO_2	0.00	0.05	99.34	0.00	0.04	0.00	0.00	98.51	0.00	0.21	0.00	0.00	0.00
TiO_2	0.00	0.48	0.34	0.50	0.04	0.37	0.02	0.01	0.00	99.40	0.31	0.04	0.00
Al_2O_3	58.24	52.05	0.02	52.84	59.72	52.69	59.03	0.03	60.24	0.00	51.99	57.98	0.45
Cr_2O_3	0.00	0.00	0.07	0.00	0.01	0.04	0.01	0.05	0.00	0.00	0.00	0.15	0.02
FeO	17.32	11.17	0.17	11.25	15.86	12.13	26.21	1.62	11.81	0.27	8.54	30.38	94.22
MnO	0.06	0.03	0.00	0.34	0.17	0.11	0.08	0.06	0.58	0.04	0.99	0.26	0.00
MgO	2.78	1.94	0.01	2.74	5.05	2.76	5.71	0.01	6.82	0.01	3.77	7.81	0.03
CaO	0.01	0.00	0.00	0.01	0.00	0.01	0.00	0.00	0.00	0.01	0.00	0.00	0.00
ZnO	23.03	3.14	0.20	2.42	20.60	0.88	8.67	0.10	20.82	0.16	2.40	2.35	0.00
Sum	101.46	99.31	100.15	100.39	101.53	99.28	99.76	100.39	100.27	100.12	98.88	98.78	94.89
Sum[b]	101.56	100.91	–	101.99	–	100.88	99.93	–	100.30	–	100.48	99.19	101.80

Cations and anions

Si	0.00	8.46	0.00	8.34	0.00	8.36	0.00	0.00	0.00	0.00	8.55	0.00	0.01
Sn	0.00	0.01	0.98	0.00	0.00	0.00	0.00	0.96	0.00	0.00	0.00	0.00	0.00
Ti	0.00	0.10	0.01	0.11	0.00	0.08	0.00	0.00	0.00	0.99	0.06	0.00	0.00
Al	1.98	17.04	0.00	17.16	1.98	17.14	1.96	0.00	1.99	0.00	16.95	1.91	0.02
Cr	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe^{3+}	0.02	–	–	–	–	–	0.04	–	0.01	–	–	0.08	1.96
Fe^{2+}	0.39	2.60	0.01	2.59	0.37	2.80	0.58	0.04	0.27	0.01	1.98	0.63	1.01
Mn	0.00	0.01	0.00	0.08	0.01	0.02	0.00	0.00	0.01	0.00	0.23	0.01	0.00
Mg	0.12	0.80	0.00	1.13	0.21	1.13	0.24	0.00	0.29	0.00	1.56	0.32	0.00
Ca	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Zn	0.49	0.64	0.00	0.49	0.43	0.18	0.18	0.00	0.43	0.00	0.49	0.05	0.00
Cations	3.00	(25.50)	1.00	(25.50)	3.00	(25.50)	3.00	1.00	3.00	1.00	(25.50)	3.00	3.00
O	4.00	46.75	1.99	46.93	3.99	46.86	4.00	1.96	4.00	1.99	46.91	4.00	4.00

[a] *Gh*, gahnite; *St*, staurolite; *Cs*, cassiterite; *Hc*, hercynite; *Ru*, rutile; *Mt*, magnetite
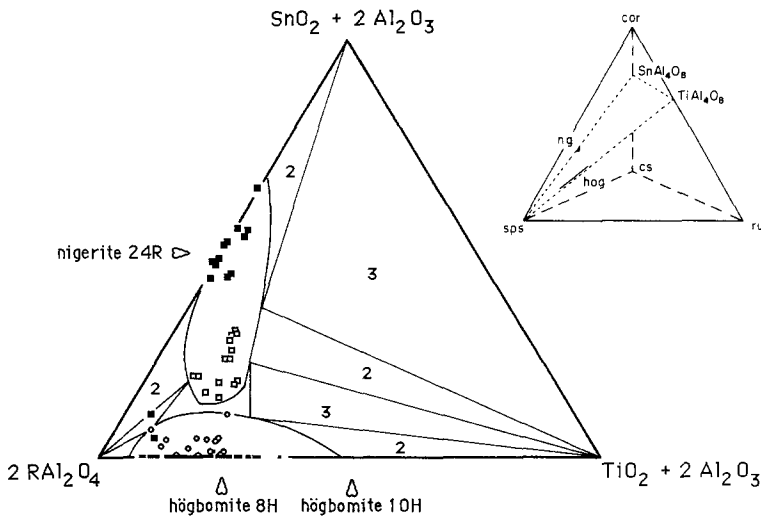[b] Sum corrected for estimated Fe^{3+} in spinels and for 1.60 wt.% H_2O for staurolites

Fig. 4. Ternary diagram in the system SnO_2 $+2 Al_2O_3 - 2 RAl_2O_4 - TiO_2 + 2 Al_2O_3$, which is a plane in the tetrahedron corundum-cassiterite-rutile-spinels. Commonly reported assemblages are illustrated. *Open squares* and *circles* represent Manitouwadge nigerite and högbomite, respectively. *Filled squares* and *dots* represent nigerite and högbomite from other localities, respectively. Sources of nigerite data: Bannister 1947; Ginsburg et al. 1963; van Tassel 1965; Chukhrov and Bonshtedt-Kupletskaya 1967; Kloosterman 1974; Burke et al. 1977; Cech et al. 1978; Grey and Gatehouse 1979; Spry 1982; Petersen 1986; Schumacher et al. 1987; This paper. The two R^{4+} deficient nigerites are from Falun

tin (Table 4), suggesting solid solution toward nigerite ($Fe_4Sn_2Al_{16}O_{32}$), a structurally related mineral with which it occurs in several samples (Essene et al. 1982; Petersen 1986). Coexisting nigerite has extensive substitution of titanium for tin (Petersen 1986; Table 4). Falun nigerite (Schumacher et al. 1987) spans the nigerite-högbomite compositional boundary with Sn/(Sn+Tn) ratios of 0.63–0.34 ($\Sigma R^{4+} = 0.58 - 0.67$; 32 anion basis). The relationship between högbomite and nigerite is illustrated on a ternary diagram which represents a section through the corundum-cassiterite-rutile-spinels tetrahedron (Fig. 4). A complete solid solution (Sn to Ti) between nigerite and högbomite may exist at Manitouwadge temperatures based on the wide variations observed in Sn/Ti of nigerite and högbomite in sample M56 (Table 4). It is possible that titanian nigerite and stannian högbomite may contain mixed layers of nigerite, spinel and högbomite, and that any observed solid solutions and compositional gaps simply relate to the ratios of submicroscopic layers. Careful TEM and AEM measurements may be able to provide tests of these relations.

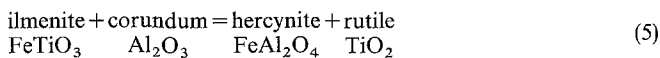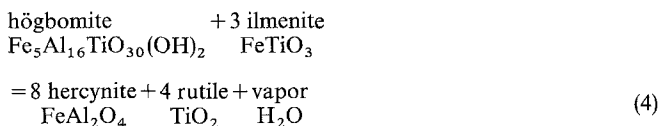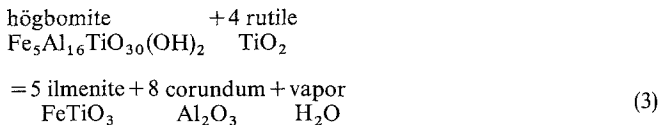**Table 6.** Thermodynamic data for selected solids in the system $FeO - Al_2O_3 - SiO_2 - TiO_2 - H_2O$

Phase	Formula	Abbreviation	S^0_{298} (J/m^0 K)	V^0_{298} (J/bar)
Almandine	$Fe_3Al_2Si_3O_{12}$	Alm	342.6[1]	11.52[1]
Corundum	Al_2O_3	Cor	50.92[2]	2.558[2]
Hercynite	$FeAl_2O_4$	Hc	106.3[2]	4.075[2]
Ilmenite	$FeTiO_3$	Ilm	108.9[3]	3.169[2]
Quartz	SiO_2	Qz	45.51[4]	2.269[2]
Rutile	TiO_2	Ru	50.3[2]	1.882[2]
Sillimanite	Al_2SiO_5	Sil	96.11[2]	4.990[2]
Högbomite	$Fe_5Al_{16}TiO_{30}(OH)_2$	Hög	837.2[5]	31.55[5]

[1] Metz et al. (1983), [2] Robie et al. (1978), [3] Anovitz et al. (1985), [4] Robinson et al. (1982), [5] This study
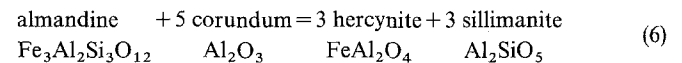
Discussion

Phase equilibria

Several mineral reactions are suggested both by observations of natural mineral assemblages. These reactions are:

högbomite
$Fe_5Al_{16}TiO_{30}(OH)_2$

$$= \text{ilmenite} + 4 \text{ hercynite} + 4 \text{ corundum} + \text{vapor} \quad (1)$$
$$FeTiO_3 \quad FeAl_2O_4 \quad Al_2O_3 \quad H_2O$$

högbomite
$Fe_5Al_{16}TiO_{30}(OH)_2$

$$= \text{rutile} + 5 \text{ hercynite} + 3 \text{ corundum} + \text{vapor} \quad (2)$$
$$TiO_2 \quad FeAl_2O_4 \quad Al_2O_3 \quad H_2O$$

högbomite $+ 4$ rutile
$Fe_5Al_{16}TiO_{30}(OH)_2 \quad TiO_2$

$$= 5 \text{ ilmenite} + 8 \text{ corundum} + \text{vapor} \quad (3)$$
$$FeTiO_3 \quad Al_2O_3 \quad H_2O$$

högbomite $+ 3$ ilmenite
$Fe_5Al_{16}TiO_{30}(OH)_2 \quad FeTiO_3$

$$= 8 \text{ hercynite} + 4 \text{ rutile} + \text{vapor} \quad (4)$$
$$FeAl_2O_4 \quad TiO_2 \quad H_2O$$

$$\text{ilmenite} + \text{corundum} = \text{hercynite} + \text{rutile} \quad (5)$$
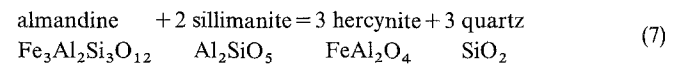$$FeTiO_3 \quad Al_2O_3 \quad FeAl_2O_4 \quad TiO_2$$

Mineral formulae, abbreviations, and thermodynamic data for the above phases are shown in Table 6. Entropy and molar volume were estimated for högbomite in order to approximate the relative slopes for högbomite-bearing reactions. The molar volume, calculated from the measured unit cell volumes of a Strangways Range högbomite (Gatehouse and Grey 1982) and a Benson Mine Ferich högbomite, are almost identical. Therefore, the molar volume of an idealized Fe end-member högbomite was approximated by this value. The entropy of Fe-högbomite was estimated from chemically similar oxides ($S_{hog} = 5\ S_{hc} + 2\ S_{cor} + 2\ S_{diaspore} + S_{ru}$) with a volume correction $[0.6 \times (V_{products} - V_{reactants})]$; Fyfe et al. 1958). The entropy and volume of water at 730° C and 7.5 kb (Burnham et al. 1969) have been used since those are the independently determined temperature and pressure of formation of the Benson Mine rocks (Marcotty 1984). Decomposition reactions (1) and (2) limit the stability field of högbomite. These reactions are virtually pressure-independent, with högbomite stable on the low temperature side of the reactions, breaking down to form a titanium phase, hercynite and corundum (Fig. 5A).

Reactions (3) and (4) lie within the högbomite field and limit its stability with rutile and ilmenite. Reaction (5) is högbomite-absent and therefore anhydrous. All of these reactions have anhydrous analogues with similar relations (Essene et al. 1982).

Reaction (1) is of particular interest. In combination with the reaction

$$\text{almandine} + 5 \text{ corundum} = 3 \text{ hercynite} + 3 \text{ sillimanite} \quad (6)$$
$$Fe_3Al_2Si_3O_{12} \quad Al_2O_3 \quad FeAl_2O_4 \quad Al_2SiO_5$$

which can be calculated using an experimentally determined reaction

$$\text{almandine} + 2 \text{ sillimanite} = 3 \text{ hercynite} + 3 \text{ quartz} \quad (7)$$
$$Fe_3Al_2Si_3O_{12} \quad Al_2SiO_5 \quad FeAl_2O_4 \quad SiO_2$$

(Bohlen et al. 1986a, b), a second set of equilibria is obtained limiting the stability of the assemblage Hög + Alm. Figure 5B shows the topology of these equilibria in P − T space. Reaction (1) extends to higher pressure and generates a second invariant point, yielding the additional reactions:
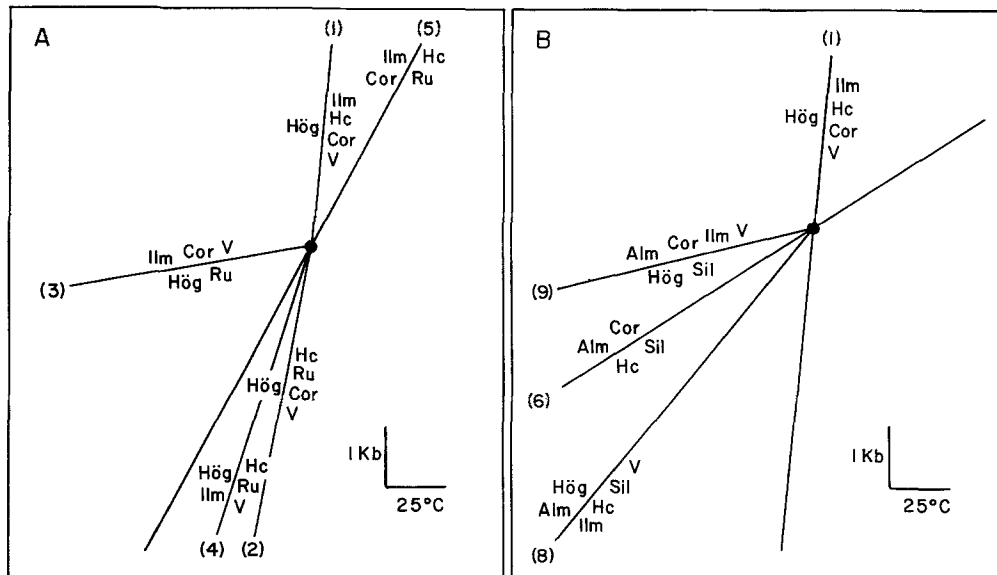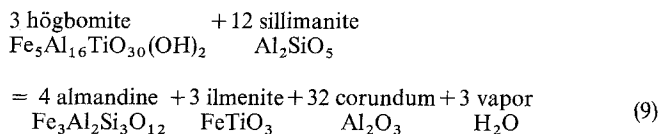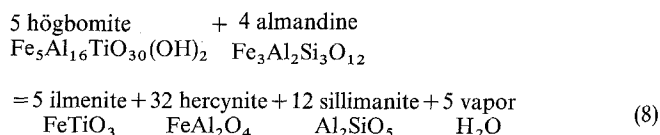

Fig. 5A, B. Schematic pressure-temperature phase diagram for the system $FeAl_2O_4 - Al_2O_3 - TiO_2 - H_2O$. **A** reactions 1–5; **B** reactions 6–8

5 högbomite   + 4 almandine
$Fe_5Al_{16}TiO_{30}(OH)_2$ $Fe_3Al_2Si_3O_{12}$

$$= 5 \text{ ilmenite} + 32 \text{ hercynite} + 12 \text{ sillimanite} + 5 \text{ vapor} \qquad (8)$$
$FeTiO_3$ $FeAl_2O_4$ Al_2SiO_5 H_2O

3 högbomite   + 12 sillimanite
$Fe_5Al_{16}TiO_{30}(OH)_2$ Al_2SiO_5

$$= 4 \text{ almandine} + 3 \text{ ilmenite} + 32 \text{ corundum} + 3 \text{ vapor} \qquad (9)$$
$Fe_3Al_2Si_3O_{12}$ $FeTiO_3$ Al_2O_3 H_2O

Reaction (9) is a backbending reaction with vapor stable on the high-pressure side, consistent with the high entropy and the small amount of vapor in högbomite. The assemblage Hög + Alm is limited to the high-pressure, low-temperature area of the diagram.

Assemblages observed at Benson Mine and Manitouwadge are consistent with the proposed phase equilibria. At Benson Mine, högbomite is hosted by ilmenite and magnetite and frequently rims or is interlayered with hercynite (Fig. 1A). Rutile is not common in Benson Mine rocks but has been observed in some thin sections, apparently having exsolved from the opaques. Corundum is an accessory phase in two samples and occurs in contact with högbomite. Almandine sometimes encloses högbomite and less commonly is in contact with external grains of högbomite. Textural determination of equilibrium is usually ambiguous; almandine is the phase which most frequently appears to be in equilibrium with högbomite. Peak metamorphic conditions of 730° C and 7.5 kb have been determined for Benson Mine rocks (Marcotty 1984).

At Manitouwadge, slightly lower conditions of 650° C and 6 kb (Petersen and Essene 1989) have produced gedrite-cordierite-staurolite gneisses in which högbomite is associated with corundum, cordierite, and rutile (Fig. 1D, E, and F). The minerals cordierite, gedrite, and staurolite have also been found associated with högbomite in other localities (Woodford and Wilson 1976; Wilson 1977; Ackermand et al. 1983; Beukes et al. 1986; Grew et al. 1987) and indicate a more complex set of reactions involving cordierite, gedrite, staurolite and rutile.

The reported occurrences of högbomite (Table 1) are in high temperature skarns and xenoliths or in rocks which have been metamorphosed to the amphibolite or granulite facies of regional metamorphism. In skarns and xenoliths högbomite is likely to form by metasomatic processes, but in regionally metamorphosed rocks it is more likely that högbomite forms from pre-existing minerals at temperatures lower than those for the reported occurrences. Because no low-temperature occurrences of högbomite have been described it is not possible to define the lower stability limit of högbomite or propose the mineral reactions by which it might form. It should be noted that the known occurrences are in relatively coarsely crystalline rock, and that in these rocks högbomite crystals are commonly less than 200 μ in diameter. In finer grained lower temperature rocks högbomite might be easily overlooked. Particularly appropriate rocks, in which lower temperature occurrences might be found, occur in the footwall of massive sulfide deposits hosted by mafic volcanics that have only been moderately metamorphosed.

Oxidation-sulfidation equilibria

Högbomite-bearing minerals assemblages commonly include magnetite and ilmenite, and/or rutile as well as pyrite
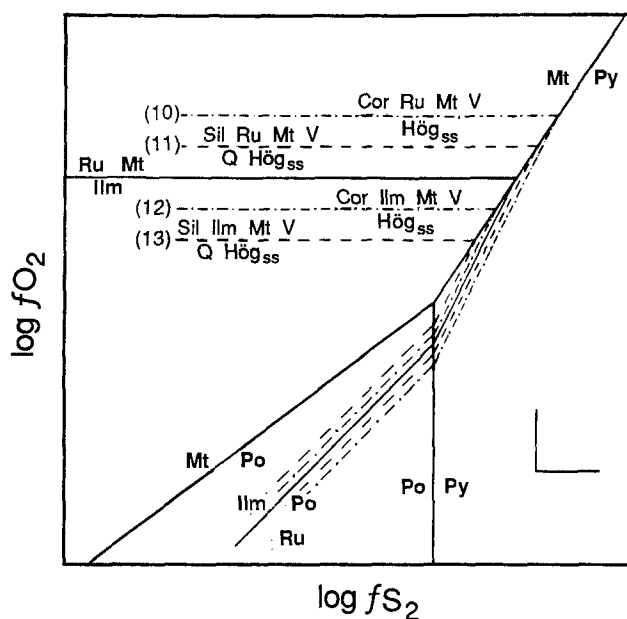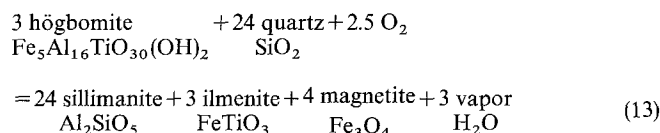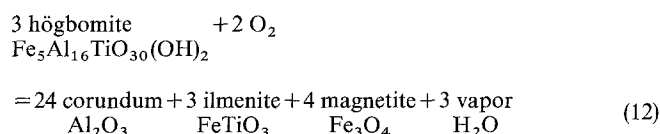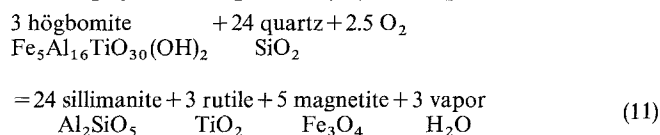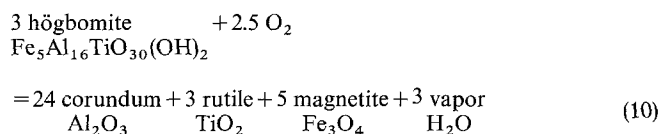

Fig. 6. Topology of oxidation-sulfidation reactions in the system Fe−Al−Ti−Si−S−O−H. One log unit in $\int O_2$ and $\int_2$ are indicated in the inset axes

or pyrrhotite (Table 2). Simple oxidation-sulfidation reactions involving these phases can be written for quartz saturated and quartz undersaturated systems:

3 högbomite   + 2.5 O_2
$Fe_5Al_{16}TiO_{30}(OH)_2$

$$= 24 \text{ corundum} + 3 \text{ rutile} + 5 \text{ magnetite} + 3 \text{ vapor} \qquad (10)$$
Al_2O_3 TiO_2 Fe_3O_4 H_2O

3 högbomite   + 24 quartz + 2.5 O_2
$Fe_5Al_{16}TiO_{30}(OH)_2$ SiO_2

$$= 24 \text{ sillimanite} + 3 \text{ rutile} + 5 \text{ magnetite} + 3 \text{ vapor} \qquad (11)$$
Al_2SiO_5 TiO_2 Fe_3O_4 H_2O

3 högbomite   + 2 O_2
$Fe_5Al_{16}TiO_{30}(OH)_2$

$$= 24 \text{ corundum} + 3 \text{ ilmenite} + 4 \text{ magnetite} + 3 \text{ vapor} \qquad (12)$$
Al_2O_3 $FeTiO_3$ Fe_3O_4 H_2O

3 högbomite   + 24 quartz + 2.5 O_2
$Fe_5Al_{16}TiO_{30}(OH)_2$ SiO_2

$$= 24 \text{ sillimanite} + 3 \text{ ilmenite} + 4 \text{ magnetite} + 3 \text{ vapor} \qquad (13)$$
Al_2SiO_5 $FeTiO_3$ Fe_3O_4 H_2O

Reactions (10)−(13), together with the corresponding sulfidation reactions, are shown schematically in Fig. 6. Oxidation reactions (10) and (11) limit the stability field of högbomite in the presence of magnetite + rutile whereas reactions (12) and (13) limit the stability field of högbomite within the ilmenite field. The stability field of högbomite + quartz closely approximates the stability field of ilmenite. The topology shown in Fig. 6 is general and similar to those that could be constructed employing other hydrous högbomite formulae. Oxidation-sulfidation diagrams constructed using anhydrous formulae for högbomite are significantly more complex because reactions including hercynite must be incorporated. In addition, reactions involving both ilmenite and rutile are possible. In spite of these complexities, these diagrams also are characterized by a wedge-shaped, though

more restricted, högbomite field that is closed on the high fS_2 side.

The common occurrence of pyrite and magnetite with högbomite also suggests that högbomite forms under relatively oxidizing conditions, consistent with the observations of Grew (1987). At Manitouwadge högbomite occurs in extremely hydrothermally altered basaltic rocks which were then subject to high-grade regional metamorphism. These rocks were highly oxidized from the outset.

Summary

From the available petrographic and chemical evidence högbomite is more widespread in high-grade metamorphic assemblages than has generally been recognized. Its consistent association with other aluminous (corundum, spinel, garnet, cordierite, gedrite, staurolite, sillimanite) and titanian (rutile, ilmenite) minerals has been used to infer a set of reactions relating these phases. If these equilibria can be experimentally located, they may be useful as geobarometer/thermometers in the study of metamorphosed peraluminous rocks.

The H_2O content and FeO/Fe_2O_3 must be determined before högbomite equilibria can be more precisely constrained, and the effect of metamorphic fluids determined. Any relation between högbomite composition and crystal structure can only be discovered by chemical analysis and crystallographic identification of a variety of structures. Any occurrence of högbomite should be examined in light of its possible significance to the petrology of peralumininous metamorphic systems.

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