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Högbomite from the Aldan Shield, Eastern Siberia, USSR

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Högbomite from the Aldan Shield, Eastern Siberia, USSR

HÖGBOMITE, a complex oxide of Al, Fe, Mg, and Ti, is an important constitutent of some iron ores and emery deposits as well as an infrequent accessory in aluminous high-grade rocks (e.g. Grew *et al.*, 1987). The recent increase in reports of new localities (e.g. Rammlmair *et al.*, 1988) suggests that högbomite may be more widespread than is generally perceived. We report here högbomite from the Aldan Shield, Eastern Siberia. This högbomite is remarkable for the wide variation in composition measured in a single thin section. Our report is only the second from the USSR of högbomite for which chemical data are given. Reports of högbomite other than Moleva and Myasnikova's (1952) well-documented description of högbomite from the Urals are based only on optical properties (Bobrovnik, 1955; Sinitsa, 1957; Sudovikov *et al.*, 1962); the third citation includes mentions of högbomite in pelitic gneisses from unspecified localities in the Aldan Shield. In the present paper we present details of the paragenesis and chemistry of högbomite and several associated minerals; the reader is referred to Drugova *et al.* (in press) for a general account of the högbomite-bearing rock and its geological and geochemical significance.

Högbomite is found in a biotite–plagioclase–corundum–spinel schist cropping out 2 km east of the Aldan River at a point 1 km north of its tributary Ayyannaakh Creek (approximately 120 km southwest of the city of Aldan). The högbomite-bearing rock is part of a metasedimentary unit consisting largely of quartzite with layers of pelitic gneisses and schists; associated rocks include orthopyroxene-bearing plagiogneiss. These rocks were metamorphosed in the granulite facies, subsequently migmatized during two events in the amphibolite facies, and intruded by microcline granite (Drugova *et al.*, in press).

The högbomite-bearing rock is a biotite–plagioclase schist containing well-aligned cylindrical nodules of corundum, magnetite, and spinel up to 10 cm long and 6 cm across as well as disseminated grains of corundum, magnetite, rutile(?) and högbomite. The oxide nodules constitute up to 30 or 40% of the rock and are found over an area of 20 or 30 m^2 in outcrop. The matrix to the nodules is a medium-grained rock (mostly 0.5–3 mm) consisting of dark biotite, plagioclase, subordinate magnetite, rare clinozoisite, and minor secondary muscovite. The plagioclase (An 40–46 in the section analysed with the microprobe, Drugova *et al.*, in press) is locally zoned. The nodules generally have a core of corundum up to 12 mm across, surrounded by a mantle of spinel, magnetite, and corundum. Adjacent to the corundum core is an inner rim of magnetite. Spinel is commonly dominant in the remainder of the mantle; magnetite, rarely in association with ilmenite, occurs as isolated grains. The spinel also contains abundant blebs of exsolved magnetite in distinct planar arrays. Towards the margin of the mantle are biotite and patches of corundum riddled with magnetite. This corundum is in places dichroic in blue. In the analysed section, the oxide nodule has a corona of fine-grained pale biotite. Discrete biotite flakes near this corona are in places pale brown or green. Other minerals in the nodule-bearing rocks are apatite, zircon, allanite, monazite, pyrrhotite, and rutile (Drugova *et al.*, in press); of these, only zircon was found in the analysed section.

Högbomite is found in both the matrix and in the nodules; its distribution is irregular. Grains are mostly 0.05 to 0.2 mm across, locally up to 0.35 mm, and range from nearly equant to planar. In the matrix, högbomite is closely associated with magnetite and forms aggregates contiguous to irregular magnetite grains; in some cases, högbomite appears to have replaced magnetite; in others, textural relations are ambiguous. Near some högbomite, magnetite appears to be replaced by a fine-grained mineral resembling rutile (leucoxene?). In the nodules, högbomite occurs mostly in and near spinel and locally with magnetite or corundum and, in places, touches biotite. Högbomite is moderate brown (nodule) to dark brown (matrix) and is dichroic.

One grain of the nodule högbomite and three grains (in two aggregates) of the matrix högbomite, together with spinel (in two spots) and associated minerals, were analysed in a single thin section within a 1×1.5 cm area with a Cameca 'Camebax-micro' electron microprobe at the Institute of Geology, Yakutsk (selected analyses listed Table 1). The nodule and matrix högbomite differ most in Ti, total Fe, and Mg. Matrix högbomites also vary in composition from grain to grain and within a grain (e.g. TiO_2, 4.6–5.6%; ZnO, 0.8–1.8%), and the nodule högbomite grain also appears to be zoned in Ti. In formulae recalculated assuming 22 cations, 30 oxygens and 2 hydroxyls (Gatehouse and Grey, 1982; Grew *et al.*, 1987), most of the Fe in the matrix högbomite is Fe^{2+} and that in the nodule högbomite, Fe^{3+}, and the two compositions can be related by the substitutions $Ti + Fe^{2+} = 2\,Fe^{3+}$ ($Ti\,Fe_{-1}$, ilmenite-hematite type) and Mg = Fe ($Mg\,Fe_{-1}$); Al contents in the formulae are nearly identical. However, these formulae were calculated assuming the *8H* polytype, apparently a rare polytype (Beukes *et al.*, 1986), and thus may not be valid for either or both of the Aldan högbomites. Indeed, the excessively high analytical totals calculated for the nodule högbomites (e.g. 102.4%, Table 1) indicate that this calculation results in an excessive estimate of Fe^{3+} content. On the other hand, the Zakrzewski (1977) formula for recasting högbomite analyses yields Fe^{3+}/Total Fe ratios of 0.07 and 0.08 for the matrix högbomite and <0 and 0.05 for the nodule högbomite. These values seem too low, because the corresponding ratios in spinel are calculated to be 0.10 to 0.13. In the absence of detailed crystallographic studies of different högbomite polytypes, it is not possible to reliably recast analyses and estimate Fe^{3+}/Fe^{2+} ratios, nor is it possible to determine water contents. We have calculated a value of H_2O using the Gatehouse and Grey (1982) formula in order to call attention to this potentially critical component of högbomite.

Magnetite (5 analyses) in the matrix and nodules contain 0.2–0.3% Cr_2O_3 and 0–0.2% TiO_2, Al_2O_3, MnO, MgO, and ZnO (for example, Table 1), with the exception of one spot with 3.1% Al_2O_3 in the matrix. The averaged spinel analyses in Table 1 are representative of the 4 analyses in Cr_2O_3 contents (0.08–0.12%) and X(Fe)T(0.35–0.36), while ZnO in the unlisted analyses reaches 1.68%. Corundum (4 analyses) in the spinel mantle contains 0.37–0.99% Fe_2O_3 and 0.18–0.24% Cr_2O_3. The dark biotites of the matrix (4 flakes analysed; average of 2 in Table 1) are titanian (2.8–3.1% TiO_2), and relatively

Table 1. Composition of Minerals in Sample 0206B, Ayyannaakh Stream, Aldan Shield, USSR

	Biotite			Högbomite			Spinel	Magnetite		Corundum
	Matrix	Corona		Matrix		Nodule	Nodule	Nodule	Matrix	Nodule
Number of Analyses	5	1	1	1	1	2	2	1	1	1
SiO_2	35.82	37.16	38.48	0.0	0.05	0.01	0.0	0.0	0.0	0.0
TiO_2	3.12	0.38	0.24	5.30	5.55	2.95	0.0	0.0	0.0	0.0
Al_2O_3	17.57	21.52	19.10	61.20	60.74	64.67	65.40	0.21	0.15	99.04
Cr_2O_3	0.06	0.07	0.06	0.25	0.20	0.17	0.10	0.18	0.29	0.19
FeO[1]	13.54	7.22	7.43	24.26	25.30	17.10	17.29	87.88	87.74	0.99
MnO	0.11	0.12	0.08	0.25	0.34	0.27	0.39	0.0	0.03	0.01
MgO	13.65	19.43	20.48	5.97	5.47	13.14	17.57	0.0	0.0	0.01
ZnO	—	—	—	1.35	0.83	0.94	0.63	0.15	0.03	—
CaO	0.0	0.03	0.02	0.0	0.01	0.0	0.0	0.0	0.0	0.02
Na_2O	0.15	0.16	0.13	0.07	0.02	0.02	0.03	0.08	0.0	0.0
K_2O	10.36	10.30	10.04	0.0	0.05	0.0	0.0	0.02	0.0	0.0
H_2O[2]	3.98	4.22	4.21	1.45	1.45	1.55	—	—	—	—
Total	98.36	100.61	100.27	100.10[3]	100.01[4]	100.82[5]	101.41[6]	88.52[7]	88.24[8]	100.26
					Formulae					
Oxygens	22	22	22	31	31	31	4	4	4	3
Si	5.398	5.278	5.478	0.0	—	—	0.0	0.0	0.0	0.0
Al^{IV}	2.602	2.722	2.522	—	—	—	—	—	—	—
Al	—	—	--	14.871	14.839	14.790	1.950	0.010	0.007	1.985
Al^{VI}	0.518	0.880	0.683	—	—	—	—	—	—	—
Cr	0.007	0.008	0.007	0.041	0.033	0.026	0.002	0.006	0.009	0.003
Ti	0.354	0.041	0.026	0.822	0.865	0.430	0.0	0.0	0.0	0.0
Fe^{2+}	1.706	0.858	0.885	2.738	2.988	0.452	0.317	0.996	0.998	—
Fe^{3+}	—	—	—	1.445	1.398	2.323	0.048	1.984	1.983	0.013
Mn	0.014	0.014	0.010	0.044	0.060	0.044	0.008	0.000	0.001	—
Mg	3.067	4.114	4.346	1.835	1.690	3.800	0.663	0.000	0.000	—
Total	5.666	5.915	5.957	—	—	—	—	—	—	—
Ca	0.0	0.005	0.004	—	—	—	—	—	--	—
Na	0.045	0.044	0.036	—	—	—	—	—	0.0	—
K	1.991	1.866	1.823	—	—	—	—	—	0.0	—
Total	2.036	1.915	1.863	—	—	—	—	—	—	0.0
Zn	—	—	—	0.206	0.127	0.134	0.012	0.004	0.001	—
Total	15.702	15.830	15.820	22.002	22.000	21.999	3.0	3.000	2.999	2.001
X(Fe)T[9]	0.36	0.17	0.17	0.70	0.72	0.42	0.36	—	—	—

Notes.

Dash - Not analysed or not calculated.

1. All Fe as FeO, except for corundum, for which all Fe as Fe_2O_3. In formulae, Fe^{2+} and Fe^{3+} calculated from stoichiometry.
2. Calculated assuming ideal hydroxyl contents for högbomite (2(OH) and 22 cations, Gatehouse and Grey, 1982) and for biotite.

3-8. Calculated weight %: 3- FeO=15.88, Fe_2O_3=9.31; Total=101.03, 4- FeO=17.24, Fe_2O_3=8.96, Total=100.91; 5- FeO=2.79, Fe_2O_3=15.91, Total=102.42; 6- FeO=15.00, Fe_2O_3=2.54, Total=101.66; 7-FeO = 29.36, Fe_2O_3 = 65.04, Total = 95.04; 8- FeO = 29.37, Fe_2O_3 = 64.87, Total = 94.74.

9. X(Fe)T = total Fe/(Mg + Total Fe)

Microprobe Operating Conditions: 20 kV, 40 nA.

iron rich ($X_{Fe} = 0.35–0.37$), while the fine-grained biotites in the corona (7 analyses) are almost free of Ti (0–0.4% TiO_2), aluminous (19–23% Al_2O_3) and magnesian ($X_{Fe} = 0.15–0.17$).

The present mineralogy and chemistry of the högbomite-bearing rocks is due to a complex metamorphic history to which Drugova *et al.* (in press) assigned 3 stages. The X_{Fe}'s of the matrix biotite, which is interpreted to have formed during the granulite-facies event, and spinel are approximately equal, that is $K_D = [Fe/Mg(Spl)]/[Fe/Mg(Bt)] = 0.91–1.00$, in marked contrast to equilibrium spinel–biotite pairs, for which $K_D \geqslant 3.7$ (Lal *et al.*, 1978; Waters and Moore, 1985). Consequently, the analysed spinel probably did not equilibrate with the matrix biotite, whose rather constant composition from grain to grain is presumed to be little changed since original crystallization in the granulite facies. The spinel–magnetite–corundum intergrowths in the mantles of the nodules could have resulted from exsolution, breakdown, and possibly oxidation of a homogeneous hercynite-rich member of the spinel group that had equilibrated with the matrix biotite. Högbomite in the nodule probably formed during this breakdown, drawing on Ti and Zn in the original homogeneous spinel. By analogy with other högbomite occurrences (e.g. Grew *et al.*, 1987), appearance of högbomite suggests interaction of the secondary spinel, magnetite, and corundum with hydrous fluids. Alternatively Ti for högbomite could have originated from the matrix biotite, which released Ti, its remaining constituents forming the corona biotite. The K_D (Mg–Fe) of 2.5–3.1 for spinel and corona biotite is closer to the presumably equilibrium values cited above. Thus högbomite formation in the nodules, breakdown of a hercynite-rich phase into spinel, magnetite, and corundum, and crystallization of corona biotite could be coeval and closely related to either intrusion of microcline granite or retrogression in the amphibolite facies.

The matrix högbomite is presumed to have formed coevally with the nodule högbomite and could have formed from magnetite, but there is no obvious source of Al. Alternatively the present magnetite–högbomite ± rutile (?) aggregates could have resulted from the recrystallization (and oxidation?) of a pre-existing Fe–Mg–Ti–Al ± Zn spinel phase (+ ilmenite?). In any case, given its different composition, the matrix högbomite must have formed from a different mix of oxide phases from those in the nodule, thereby implying that compositional factors, including oxygen fugacity, rather than pressure and temperature, are the main controls on högbomite chemistry.

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