

## AN UNUSUAL GAHNITE-FORMING REACTION, GECO BASE-METAL DEPOSIT, MANITOUWADGE, ONTARIO

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### ABSTRACT

Gahnite, together with nigerite and högbomite of unusual composition, is present in phlogopite-staurolite-cordierite schists within the Geco base-metal deposit, Manitouwadge, Ontario. These minerals are enclosed within cordierite and a vermicular cordierite-corundum intergrowth and are nowhere in contact with tin-bearing phlogopite. Högbomite and nigerite are rarely enclosed in zincian staurolite. Textural and chemical evidence suggests that gahnite was produced at upper amphibolite - lower granulite grade by the reaction: zincian staurolite + tin-bearing phlogopite = cordierite + corundum + gahnite + nigerite + högbomite + tin-poor phlogopite.

*Keywords:* gahnite, nigerite, högbomite, zincian staurolite, tin-bearing phlogopite, Geco deposit, Ontario, electron-microprobe analyses.

### SOMMAIRE

On trouve la gahnite associée à de la nigérite et de la högbomite de composition bizarre, dans des schistes à phlogopite-staurotide-cordiérite dans le gisement Cu-Zn de Geco (Manitouwadge, Ontario). Ces minéraux sont inclus dans la cordiérite et dans une intercroissance vermiculaire de cordiérite + corindon; ils ne sont nulle part en contact avec la phlogopite stannifère. Högbomite et nigérite se présentent rarement sous forme d'inclusions dans la staurotide zincifère. Les indices texturaux et chimiques portent à croire que la gahnite apparaît au faciès amphibolite supérieur ou granulite inférieur comme produit de la réaction: staurotide zincifère + phlogopite stannifère = cordiérite + corindon + gahnite + nigérite + högbomite + phlogopite appauvrie en Sn.

(Traduit par la Rédaction)

*Mots-clés:* gahnite, nigérite, högbomite, staurotide zincifère, phlogopite stannifère, gisement de Geco, Ontario, analyses à la microsonde électronique.

### INTRODUCTION

Gahnite is believed to have formed by a variety of processes including (1) desulfidation of sphalerite during metamorphism (*e.g.*, Frost 1973), (2) precipitation from a metamorphic-hydrothermal solution (Wall 1977), (3) deriva-

tion from a primary ZnO phase during metamorphism (*e.g.*, Segnit 1961), (4) dehydration of zinc-enriched staurolite during metamorphism (Stoddard 1976, 1979, Atkin 1978), and (5) formation from residual ZnO that was produced during a silicate reaction (Dietvorst 1980). Gahnite at the Geco mine, an Archean Cu-Zn massive-sulfide deposit located at Manitouwadge, 200 km east of Thunder Bay, Ontario, was probably formed by more than one of the above mechanisms (Spry, in prep.). The present contribution concerns only that gahnite considered to have resulted from the breakdown of zincian staurolite and tin-bearing phlogopite. The pre-metamorphic origin of the Geco deposit was first recognized by Suffel *et al.* (1971). Metamorphic mineral assemblages suggest that Geco has been metamorphosed to upper amphibolite or lower granulite grade (Petersen & Friesen 1982).

### PETROGRAPHY

The specimens containing gahnite were collected adjacent to the 4/2 ore zone on the 2850 level within a weakly foliated phlogopite-staurolite-cordierite schist. This particular rock-type is one of several that constitute the sericite schist group of the mine series (Bakker 1979). Gahnite, corundum, pyrrhotite, högbomite and nigerite are minor constituents of the rocks, which consist primarily of phlogopite, staurolite, cordierite, pyrite and chalcopyrite. Other minerals present in small amounts are sericite, zircon and chlorite.

In some specimens, staurolite occurs as embayed porphyroblasts surrounded by a rim of cordierite. Staurolite is never in contact with phlogopite, the most common mafic phase. Phlogopite is generally bladed, but where in contact with cordierite, phlogopite has a ragged appearance. Pyrite and chalcopyrite commonly occur within phlogopite and along grain boundaries. In other specimens, staurolite is extremely corroded and partly replaced by a vermicular intergrowth of cordierite and corundum

(Fig. 1a). Subhedral gahnite, up to 0.8 mm in length, occurs within cordierite, commonly in embayments within staurolite (Fig. 1b). Brown nigerite and brown högbomite, anhedral to euhedral and up to 0.6 mm across, are not only associated with the vermicular cordierite–corundum intergrowth (Fig. 1c), but also occur as inclusions within cordierite. Rare inclusions of högbomite and nigerite, some of which are associated with fractures, occur within staurolite. Nigerite commonly occurs as inclusions or overgrowths on gahnite (Fig. 1d).

#### MINERAL CHEMISTRY

Analyses of the major and minor oxides and silicates were carried out with a Jeol 733 Superprobe and an ARL electron microprobe (Table 1); the excitation potentials were 15 and 20 kV, respectively. The standards used were natural and synthetic spinels for Zn, Fe, Mg and Al, amphibole for Mg, Fe, Si and Al, biotite

for K, Mg, Al, Si and Fe, wollastonite for Ca and Si, rhodonite for Mn, rutile for Ti and synthetic cassiterite for Sn.

The gahnite is enriched in  $MgAl_2O_4$  and  $FeAl_2O_4$  and depleted in  $ZnAl_2O_4$  relative to zincian spinel found elsewhere in the Geco deposit (unpubl. data) and in other deposits that have been ascribed to formation *via* desulfidation mechanisms (Spry & Scott 1982).

Högbomite has a generalized formula (proposed by Zakrzewski 1977) of  $R^{2+}_{2-2x}Ti_xR^{3+}_4O_8$ , in which  $R^{2+}$  represents  $Mg^{2+}$ ,  $Zn^{2+}$ ,  $Mn^{2+}$  and  $Fe^{2+}$ , and  $R^{3+}$  represents  $Al^{3+}$  and  $Fe^{3+}$ . Tin and silicon may substitute for titanium. Högbomite was previously reported by Chew (1977) in a sample found in the Willroy base-metal deposit 2 km west of Geco. Except for Chew's (1977) and Mancktelow's (1981) analytical results, in which  $Fe/(Fe + Mg) = 0.72$  (atomic ratio), other examples of högbomite reported in the literature show  $Fe/(Fe + Mg)$  in the range 0.02 to 0.62. Unlike the högbomite from Willroy,

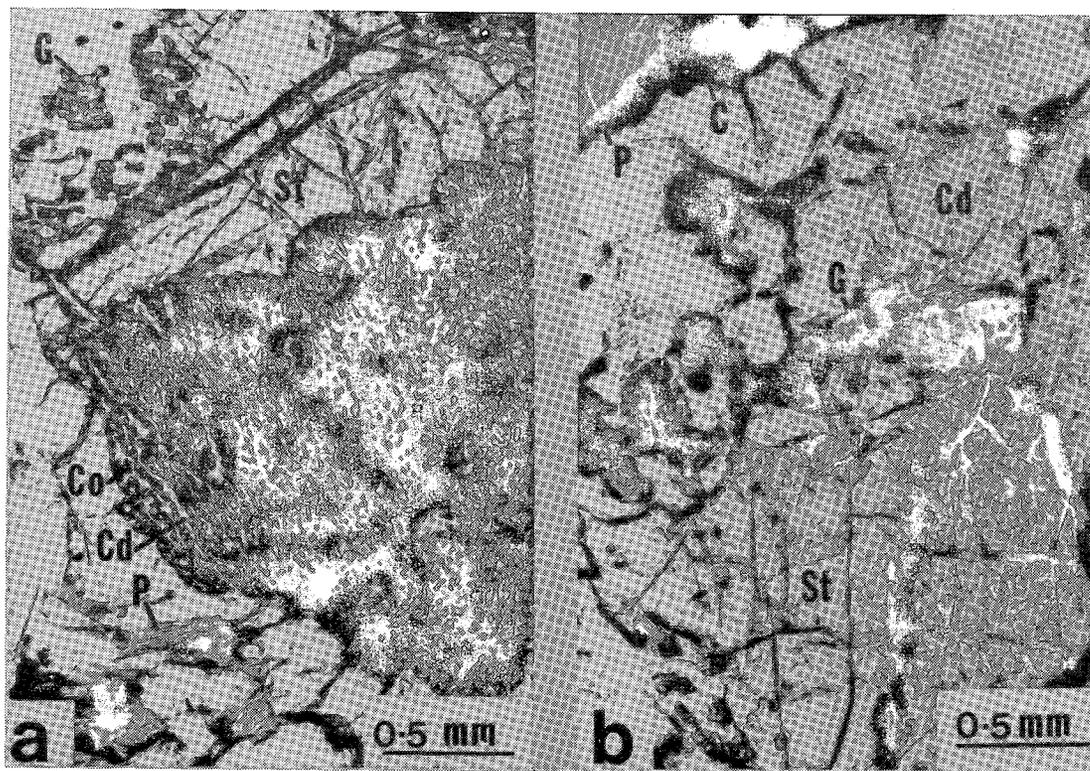
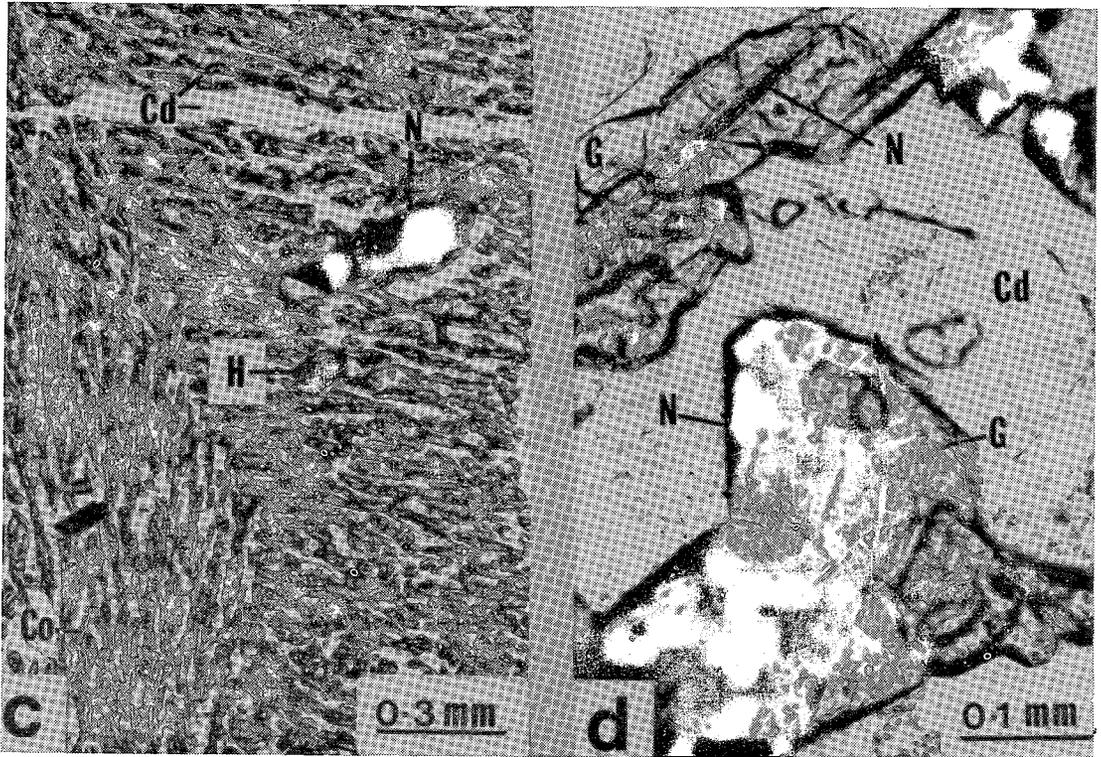


FIG. 1a. Staurolite St and a vermicular cordierite Cd–corundum Co intergrowth separated from phlogopite P by a rim of cordierite. Note the gahnite G in cordierite. b. Gahnite and adjacent embayed staurolite separated from phlogopite and chalcopyrite C by a rim cordierite. c. Högbomite H and nigerite N within a vermicular cordierite – corundum intergrowth. d. Cordierite with nigerite that rims (outlined in black) and is included in gahnite.



which contains less than 1 wt. % ZnO, that from Geco contains, on average, 10.2 wt. % ZnO. Such unusually zinc-rich h ogbomite had previously been reported only by Moleva & Myasnikov (1952), who described h ogbomite that contains 11.1 wt. % ZnO from the U.S.S.R.

Nigerite, which has a formula analogous to h ogbomite, namely  $R^{2+}_{2-2x}R^{4+}_xR^{3+}_4(O,OH)_8$ , in which  $R^{2+}$  represents  $Mg^{2+}$ ,  $Zn^{2+}$ ,  $Fe^{2+}$  and  $Mn^{2+}$ ,  $R^{3+}$  represents  $Al^{3+}$  and  $Fe^{3+}$ , and  $R^{4+}$  represents  $Ti^{4+}$ ,  $Sn^{4+}$  and  $Si^{4+}$ , was recognized previously at Geco by Essene *et al.* (1982) and Petersen *et al.* (1982). Petersen *et al.* analyzed several samples of nigerite from Geco and found a wide range in their Sn content. Their revised abstract (E.U. Peterson, pers. comm. 1982) describes nigerite compositions having the highest Mg, Zn and Ti contents as well as the lowest Sn content ever recorded for this mineral. Nigerite samples reported here have compositions that are similar to these.

#### DISCUSSION

Bannerjee (1974) initially recorded the presence of cassiterite in the Geco deposit. Essene *et al.* (1982) noted that cassiterite occa-

sionally coexists with nigerite and that rutile or ilmenite (or both) coexist with h ogbomite, suggesting that cassiterite may be a source for the tin in nigerite, and rutile or ilmenite (or both) may be a source for the titanium in h ogbomite. Cassiterite, ilmenite and rutile, however, are not present in the samples studied here. Although phlogopite does not appear to have been produced during the gahnite-forming reaction, phlogopite contains Ti and Sn, and probably constitutes the source of Ti and Sn for nigerite and h ogbomite in these samples.

At Geco, the common association of gahnite, nigerite and h ogbomite with cordierite or a cordierite-corundum intergrowth, together with the evidence that where gahnite (with or without nigerite) and staurolite are present, the staurolite is embayed or corroded, suggests that these minerals are genetically related. The presence of zinc in staurolite, gahnite, h ogbomite and nigerite, in addition to the textural evidence, suggests that the following prograde reaction has been involved in the formation of gahnite: zincian staurolite + tin-bearing phlogopite = cordierite + corundum + gahnite + nigerite + h ogbomite + tin-poor phlogopite.

Experimental work by Richardson (1968)

TABLE 1. CHEMICAL COMPOSITIONS OF MINERALS FROM PHLOGOPITE-STAUROLITE-CORDIERITE SCHIST, GECO MINE

	1	2	3	4	5	6	7**	8
MgO	7.33	5.86	5.77	5.57	2.60	20.60	11.01	0.03
Al <sub>2</sub> O <sub>3</sub>	60.80	59.84	61.74	60.52	54.37	18.30	34.18	99.04
SiO <sub>2</sub>	0.06	0.20	0.07	---	---	28.57	39.60	0.10
K <sub>2</sub> O	---	---	---	---	---	---	8.65	---
TiO <sub>2</sub>	0.00	2.45	4.03	5.94	0.18	0.75	0.00	0.00
MnO	0.46	0.46	0.47	0.03	1.12	0.08	0.69	0.00
FeO*	12.09	12.05	14.95	25.79	9.36	7.90	3.02	0.57
ZnO	19.88	8.94	10.43	0.73	1.88	0.05	---	0.11
SnO	---	8.79	1.06	---	---	0.23	---	0.00
Anhydrous	100.62	98.59	98.52	98.58	98.08	96.16	98.00	99.85
Total								
ATOMIC PROPORTIONS								
O + OH	24	24	24	24	69	24	18	24
Mg	1.82	1.49	1.42	1.36	1.60	4.74	1.63	0.01
Al	11.96	11.89	12.01	11.70	26.38	3.33	4.01	15.92
Si	0.01	0.04	0.01	---	11.76	6.11	4.89	0.01
K	---	---	---	---	---	1.70	---	---
Ti	0.00	0.32	0.50	0.73	0.05	0.09	0.00	0.00
Mn	0.07	0.06	0.07	0.01	0.39	0.09	0.06	0.00
Fe	1.69	1.63	2.06	3.54	3.22	1.02	0.25	0.06
Zn	2.45	1.11	1.27	0.09	0.57	0.01	---	0.01
Sn	---	0.59	0.07	---	---	0.02	---	---

\* Total Fe as FeO. \*\* Composition of rim cordierite is not significantly different from that of cordierite in the vermicular cordierite-corundum intergrowth. Compositions were determined by electron microprobe. 1. Gahnite (average of 6 points). 2. Nigerite (average of 9 points). 3. Högbomite (average of 5 points). 4. Högbomite from Willroy (Chew 1977). 5. Staurolite (average of 7 points). 6. Phlogopite (average of 6 points). 7. Cordierite (average of 7 points). 8. Corundum (average of 4 points).

shows that, in the presence of quartz, Fe-staurolite is stable to 680–690°C. In natural assemblages, Mg and Zn may stabilize staurolite to slightly higher temperatures (e.g., Ashworth 1975). Staurolite analyzed here contains, on average, 2.60 wt. % MgO and 1.88 wt. % ZnO. However, this may be insufficient to stabilize staurolite, even in the absence of quartz, at the upper-amphibolite to lower-granulite grade of metamorphism attained at Geco. It is unclear why, in some cases, staurolite that is associated with phlogopite breaks down to a cordierite-corundum intergrowth, whereas in other instances, staurolite of similar composition in the same thin section does not break down in this way. Owing to the two apparent states of equilibrium within short distances (of the order of millimetres), no attempt has been made to balance the proposed equation. The presence of rare inclusions of nigerite and högbomite within staurolite might suggest that they are not products of the breakdown of staurolite. Some of these inclusions occur along fractures and may be the result of Zn diffusion from staurolite in addition to Sn and Ti diffusion from phlogopite along zones of weakness.

Even though pyrite, chalcopyrite and pyrrothite are present, sphalerite is absent in gahnite-högbomite-nigerite samples. Therefore, there is no textural or chemical evidence that the gahnite was produced by desulfidation of sphalerite.

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