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ZINCIAN SPINEL AND STAUROLITE AS GUIDES TO ORE IN THE APPALACHIANS AND SCANDINAVIAN CALEDONIDES

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ABSTRACT

Zincian spinel or gahnite $(Zn,Fe, Mg)Al_2O_4$ occurs in metamorphosed massive-sulfide deposits, aluminous metasediments, pegmatites, quartz veins, and metamorphosed oxide–silicate deposits in at least forty localities within the Appalachians and Scandinavian Caledonides. Most occurrences are associated with metamorphosed massive-sulfide deposits, in which gahnite is considered to form predominantly by desulfurization reactions involving a member of the system Fe–S–O and either sphalerite and garnet or sphalerite and aluminosilicate. Spinel in quartz veins and pegmatites is thought to be a product of metamorphic–hydrothermal solutions and magmatic processes, respectively. Spinel in aluminous metasediments was probably derived from the metamorphism of metalliferous shales, in which rocks Zn may originally have been linked to organic material. Although gahnite in some sulfide deposits coexists with zincian staurolite, textural evidence suggests that staurolite did not act as a precursor to spinel. The high Zn content in staurolite is likely the result of desulfurization reactions. Staurolite from the Bleikvassli deposit (Norway) contains up to 8.77 wt.% ZnO and is thought to be the most Zn-rich yet recorded. Both gahnite and staurolite are most Zn-rich where associated with sulfides and may constitute an exploration guide for massive-sulfide deposits in metamorphosed terranes.

Keywords: zincian spinel, gahnite, zincian staurolite, Appalachians, Scandinavian Caledonides, electron-microprobe data, exploration guide.

SOMMAIRE

Le spinelle zincifère ou gahnite se présente dans les gîtes de sulfure massif métamorphiques, métasédiments alumineux, pegmatites, filons de quartz et gîtes oxyde–silicate métamorphiques. On l'a trouvé dans au moins quarante endroits dans les Appalaches et les Calédonides scandinaves. La plupart des gîtes sont associés à des sulfures massifs métamorphiques, dans lesquels on admet que la gahnite s'est formée surtout par des réactions de désulfurisation, impliquant un pôle du système Fe–S–O et de la sphalérite (blende) ainsi que du grenat ou un aluminosilicate. Le spinelle des filons de quartz est considéré comme produit de solutions hydrothermales-métamorphiques, celui des pegmatites, comme résultant de processus magmatiques. Le spinelle des métasédiments dérive probablement du métamorphisme de schistes (sédimentaires), roches dans lesquelles il se peut que le Zn ait été combiné à des composés organiques. Quoique la gahnite et la staurotide zincifère coexistent dans certains gîtes de sulfures, les observations texturales font douter que la staurotide soit l'avant-coureur du spinelle. La haute teneur en Zn de la staurotide résulte vraisemblablement des réactions de désulfurisation. La staurotide du gîte de Bleikvassli (Norvège), dont la teneur en ZnO atteint jusqu'à 8.77% (en poids), passe pour la plus riche en Zn connue à ce jour. Gahnite et staurotide sont toutes deux les plus riches en Zn là où elles sont associées aux sulfures; elles peuvent donc guider la prospection pour gîtes de sulfures massifs en terrain métamorphique.

(Traduit par la Rédaction)

Mots-clés: spinelle zincifère, gahnite, staurotide zincifère, Appalaches, Calédonides scandinaves, données de microsonde électronique, guide à la prospection.

INTRODUCTION

Zincian spinel, or gahnite $(Zn,Fe,Mg)Al_2O_4$, is widely distributed in the Appalachian–Caledonide orogen; based on experience here (Sandhaus 1981, Sundblad 1982) and elsewhere (Sheridan & Raymond 1977, 1984, Spry & Scott 1982, Spry 1984), this phase has potential as a guide in the exploration for metamorphosed massive-sulfide deposits. Among the various associations of zincian spinel observed, that with metamorphosed sulfide deposits is the most common. This has prompted the suggestion (*e.g.*, Sangster & Scott 1976) that such zincian spinel is a product of desulfurization of sphalerite during metamorphism. Spinel in and around metamorphosed massive-sulfide deposits forms a solid solution between $ZnAl_2O_4$ and $FeAl_2O_4$ predominantly and is commonly spatially associated with sphalerite in addition to pyrite, pyrrhotite or magnetite (or various combinations of these minerals). Calculation of $f(O_2)$–$f(S_2)$ relations in the system Zn–Fe–Al–Si–S–O by Wall & England (1979), Spry & Scott (1983a) and Spry (1984), and experiments by Spry (1984) on a simplified SiO_2-free system, demonstrate that gahnite can indeed form by the breakdown of sphalerite coexisting with either an aluminosilicate or garnet. However, considering the assortment of environ-

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ments in which gahnite is found, other theories have also been proposed to account for the formation of gahnite. These include: (1) reaction of Zn-bearing silicates [*e.g.*, biotite and staurolite to form spinel during metamorphism (Stoddard 1979, Dietvorst 1980)]; (2) precipitation of spinel from a metamorphic-hydrothermal solution (Wall 1977); and (3) formation from a primary Zn-oxide phase during metamorphism (Segnit 1961).

The zincian-spinel-bearing rocks of the Appalachian–Caledonide orogen also contain staurolite that is amongst the most Zn-rich yet recorded (*e.g.*, Sandhaus 1981, Spry & Scott 1983b). Zincian staurolite spatially associated with zincian spinel is thought to be the precursor of spinel in some metamorphic rocks (Atkin 1978, Stoddard 1979, Spry 1982).

This paper documents some of the spinel-bearing localities in the Appalachians and Scandinavian Caledonides. We discuss the origin of the spinel in the light of calculations of stability, experiments, textural evidence and field associations, its potential as a guide to sulfide mineralization and the reason for the anomalous content of Zn in staurolite with which it is spatially associated.

ELECTRON-MICROPROBE DATA

The chemical composition of the spinel and of coexisting phases was determined at the University of Toronto (Etec Autoprobe and ARL–EMX electron microprobe equipped with Kevex and Ortec energy-dispersion silicon detectors, respectively), and at the University of Adelaide (JEOL wavelength-dispersion Superprobe, model 733).

Operating conditions of the Etec Autoprobe and ARL–EMX electron microprobe included accelerating voltages of 20 kV and beam currents of 100 nA. Natural and synthetic spinels were used as standards for Zn, Fe, Mg and Al, garnet for Mg, Mn, Ca, Fe, Si and Al, rutile for Ti, synthetic pyrrhotite for Fe and S, synthetic sphalerite for Zn, Fe and S, synthetic chalcopyrite for Cu, synthetic alabandite for Mn, and synthetic cadmium sulfide for Cd. These electron microprobes are connected to a PDP/11 computer system providing on-line reduction of energy-dispersion data by a modified version of the PESTRIPS program. The techniques used in the program were described by Statham (1975).

Operating conditions of the JEOL Superprobe included an accelerating voltage of 15 kV and a beam

TABLE 1. ZINCIAN SPINEL LOCALITIES IN THE APPALACHIANS

Locality No.^{a}	Name	Geological Setting	Geological Province	Reference
1	A, Quebec	mmsd	N.E.	Chevé et al. (1983)
2	Auburn, Me	pegmatite	N.E.	this study
3	Topsham, Me	?pegmatite	N.E.	this study
4	Davis, Mass	mmsd	N.E.	Dana (1885), Bwerinofa (1972), Field & Haggerty (1984)
5	Charlemont, Mass	sulfides in a.s.	N.E.	Flint (1908)
	Lord's Hill, Mass	?pegmatite	N.E.	exact location unknown
6	Middleton, Conn	pegmatite	P	this study
7	Franklin, NJ	mzod	P	Frondel & Klein (1965)
8	Sterling Hill, NJ	mzod	P	Carvalho & Sclar (1979)
9	S.E. Pennsylvania	as	P	Wagner & Crawford (1975)
10	Springfield, Md	mmsd	P	Shannon (1923)
11	Mineral Hill, Md	mmsd	P	Shannon (1923)
12	Patapsco, Md	mmsd	P	Shannon (1923)
13	Valzinco, Va	mmsd	P	Ross (1935)
14	Sulphur, Va	mmsd, qv	P	Craig (1980), Sandhaus (1981)
15	Cofer, Va	mmsd	P	Miller (1978), Sandhaus (1981)
16	Arminius, Va	mmsd	P	Cox (1979), Sandhaus (1981)
17	Julia, Va	mmsd	P	Craig (1980), Sandhaus (1981)
18	Johnson, Va	mmsd, qv	P	this study
19	Andersonville (#18), Va	mmsd, qv	P	this study
20	Stratford, NC	as	B.R.	Brannock (1971)
21	Ore Knob, NC	mmsd	B.R.	Ross (1935)
22	Elk Knob, NC	mmsd	B.R.	Ross (1935)
23	Deake, NC	as	B.R.	Genth (1891)
24	Spruce Pine, NC	pegmatite	B.R.	this study
25	Cullowhee, NC	mmsd	B.R.	Ross (1935)
26	Savannah, NC	mmsd	B.R.	Ross (1935)
27	Wayhutta, NC	mmsd	B.R.	Ross (1935)
28	Otto, NC	mmsd	B.R.	Ross (1935)
29	Standard, Ga	sulfide veins in as	B.R.	Lindgren (1906)
30	Magruder, Ga	sulfide veins in as	B.R.	Cofer (1953)
31	Canton, Ga	mmsd	B.R.	Genth (1862), Ross (1935)
32	Little Bob, Ga	mmsd	B.R.	Cook (1970), Abrams & McConnell (1984)
33	Villa Rica, Ga	mmsd	B.R.	Cook (1970), Neathery & Hollister (1984)

a. Deposit shown in Fig. 1; N.E. New England; P. Piedmont; B.R. Blue Province; mmsd metamorphosed massive sulfide deposit; as aluminous metasediment; qv quartz vein; mzod metamorphosed zinc-oxide deposit.

TABLE 2. ZINCIAN SPINEL LOCALITIES IN THE SCANDINAVIAN CALEDONIDES

Locality No.[a]	Name	Geological Setting	Tectonic Unit	Reference
1	Bleikvassli, Nor.	mmsd	Rödingsfjället Nappe	Vokes (1962)
2	Graskevardo Ripudden, Swe.	mmsd	Rödingsfjället Nappe	Sundblad (1982)
3	Mofjell, Nor.	mmsd	Rödingsfjället Nappe	Sundblad (1982)
4	Thermos, Nor.	mmsd	Rödingsfjället Nappe	Sundblad (1982)
5	Nonsfjellet, Nor.	mmsd	Beiarn Nappe	Sundblad (1982)
6	Skårnesdalen, Nor.	mmsd	Rödingsfjället Nappe	Juve (1967)
7	Villdalsfjell, Niingen, Nor.		Beiarn Nappe	Vokes (1962)

a. Deposit shown in Fig. 2; Nor. Norway; Swe. Sweden; mmsd metamorphosed massive sulfide deposit.

current of 200 nA. Natural spinels, simple oxides and metals were used as standards. The JEOL Superprobe is connected to a PDP/11 computer, which reduced data by a FORTRAN IV program using a type of correction proposed by Duncumb & Reed (1968).

ZINCIAN SPINEL IN THE APPALACHIAN - SCANDINAVIAN CALEDONIDE OROGEN

Zincian spinel is known from at least forty localities in metamorphosed volcanic and sedimentary rocks in the Appalachians and Scandinavian Caledonides (Tables 1, 2) but, in general, is poorly described and treated as a mineralogical curiosity. Occurrences in the U.S. Appalachians are found in metamorphosed massive-sulfide deposits, aluminous metasediments, pegmatites, quartz veins and Zn-rich oxide bodies within the Blue Ridge and Piedmont geological provinces and in the probable extension of the Piedmont province in New England (Fig. 1). The only reported locality of gahnite in the Canadian Appalachians is that by Chevé *et al.* (1983), who noted its occurrence in the small stratiform massive A sulfide deposit, Eastern Townships, Quebec.

According to Sunblad (1982), all known gahnite localities of the Scandinavian Caledonides are associated with metamorphosed massive-sulfide deposits contained within the Rödingsfjället and Beiarn Nappes of Norway and Sweden (Table 2). These nappes predominantly consist of gneisses and marbles that were metamorphosed to the amphibolite grade. Gahnite-bearing massive-sulfide deposits in the Rödingsfjället Nappe include the Bleikvassli, Mofjell, Thermos and Skårndesdalen deposits of Norway and the Graskevardo and Ripudden deposits of Sweden (Fig. 2). The Villdalsfjell and Niingen deposits are located in the Beiarn Nappe.

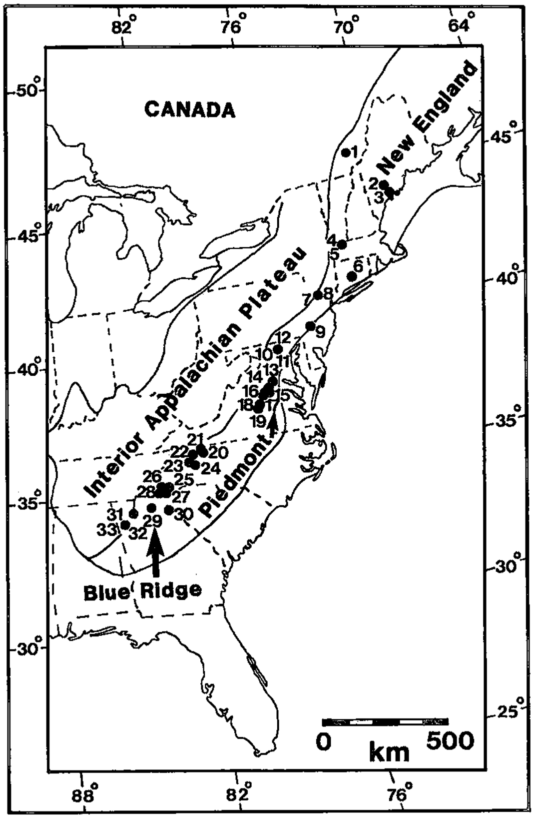


FIG. 1. Location of zincian spinel occurrences in the Appalachians. Names of deposits are in Table 1.

Field and textural relations

Of the various geological settings in the Appalachian–Caledonide orogen in which gahnite is found, the association between gahnite and metamorphosed massive-sulfides is the most common. Gahnite is most often contained within sulfide zones; however, it is also found in quartz veins crosscutting sulfide zones and in aluminous rocks surrounding sulfides. Because of the variable nature of

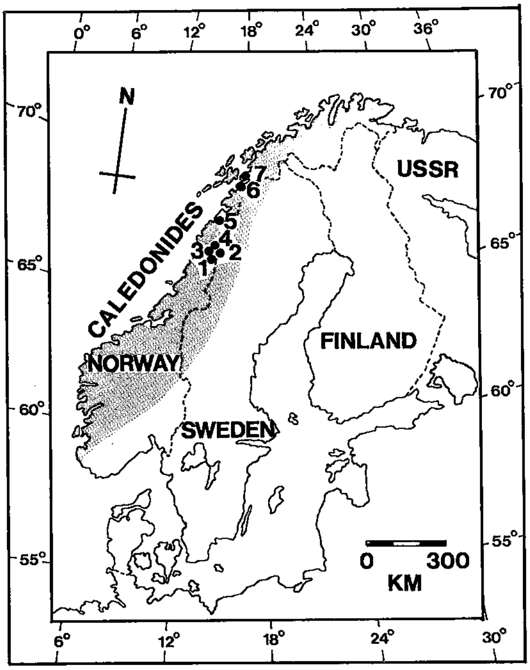


FIG. 2. Location of zincian spinel occurrences in the Scandinavian Caledonides (modified after Sundblad 1982). Names of deposits are in Table 2.

TABLE 3. MINERAL ASSEMBLAGES OF ZINCIAN SPINEL- AND ZINCIAN STAUROLITE-BEARING SAMPLES

Sample No.	Locality	Assemblage*
PGS-54[a]	Bleikvassli	qz,py,sp,ph,st,cp,ga,mu,spl[d],gn[d],po[d],cl[de]
PGS-55(1)[b]	Bleikvassli	py,ph,st, cl[e],sp,spl[d],ru[d],zr[d]
PGS-55(2)[b]	Bleikvassli	qz,sp,py,po,cp,spl[d]
PGS-55(3)[b]	Bleikvassli	qz,st,mu,spl[d],py[d],gn[d],bi[d]
PGS-56(1)[bc]	Bleikvassli	py,qz,spl,gn,sp,st,bi,cp[d],po[d],pl[d]
PGS-56(2)[b]	Bleikvassli	qz,sp,st,mu,py,po,bi,gn,spl[d],cp[d],fi[d]
PGS-56(3)[b]	Bleikvassli	st,bi,mu,po,spl,gn[d],cp[a],pl[a]
PGS-65[b]	Bleikvassli	qz,sp,py,bi,gn,cp[a],cl[de]
PGS-67[b]	Bleikvassli	st,qz,sp,ph,po,py
PGS-68[b]	Bleikvassli	po,sp,qz,ph,spl,py,gn
PGS-69[b]	Bleikvassli	sp,qz
PGS-70[b]	Bleikvassli	qz,py,bi,sp,ga,po,spl,cp,mu
PGS-97[a]	Nonsfjellet	hb,an,qz,sp,py,ga,gd,spl,cd,ru[d],il[d]
PGS-98[a]	Thermos	qz,sp,py,hb,ga,ma,cp,ru[d]
PGS-96[a]	Skårnesdalen	qz,ga,mu,sp,spl,bi,gn,pl
M4513[a]	Auburn	pl,mu,ga,sp
M19160[a]	Topsham	qz,pl,sp
PGS-24[a]	Andersonville	qz,py,bi,sp,hb[a],spl,ser[e],ep[d],pl[d]
PGS-72[b]	Andersonville	qz,sp
PGS-85[b]	Andersonville	qz,sp
PGS-84[a]	Johnson	qz,sp,il
143573[b]	Sterling Hill	hd,ca,sp,ga,pyr
145056[b]	Sterling Hill	ca,sp,rh,spl,cl[e]
47896[c]	Franklin	rh,sp,ca,kn,ma
R12531[b]	Davis	mu,qz,sp,py,il,ga,cp[d]
M21317[b]	Davis	py,qz,sp,cp
Mass-104[b]	Davis	sp,cp,py,qz,ca
RG-80-46[b]	Davis	py,spl,ga,sp,po,qz,bi,cp
RG-80-47[b]	Davis	py,qz,sp,spl,ga,po,cl[e],cp
RG-80-6[b]	Davis	qz,py,mu,pl,sp,spl[e]
RG-80-26[b]	Davis	qz,py,mu,ga,sp,ma
RG-80-45[b]	Davis	qz,mu,py,spl,sp,cp[e]
1286303[b]	Charlemont	qz,sp
39306[a]	Lord's Hill	pl,qz,mu,cr,sp
R1955[a]	Mineral Hill	sp,pl,ma,bi,ep,qz,cp,mu,cl[e],spl,ch
94677[a]	Springfield	sp,qz,ma,cl[e],bi
84718-2[b]	Mitchell Co.	sp
R1957[b]	Siskoe Ridge	sp,mu,qz
120967-5[ac]	Stratford	sp,qz,st,hm,po
79522[ac]	Canton	qz,cp,py,st,sp,spl,gn,ch[de]

* listed in approximate order of abundance; a analyses of gahnite listed in Table 4; b analyses of gahnite listed in Spry (1984); c analysis of staurolite listed in Table 5; d mineral present in trace amounts; e mineral is secondary; an anthophyllite; bi biotite; ca calcite; cd cordierite; ch chalcocite; cl chlorite; cp chalcopyrite; cr cryolite; ep epidote; fi fibrolite; fr franklinite; ga garnet; gd gedrite; gn galena; hb hornblende; hd hedenbergite; hm hematite; il ilmenite; kn knebelite; ma magnetite; mu muscovite; ph phlogopite; pl plagioclase; po pyrrhotite; py pyrite; pyr pyrophanite; qz quartz; rh rhodonite; ru rutile; ser sericite; sp zincian spinel; spl sphalerite; st staurolite; zr zircon.

the geological settings, it is hardly surprising that gahnite is associated with a variety of minerals (Table 3). Representative compositions of spinel from several deposits, determined by electron microprobe, are presented in Table 4. Additional compositions are listed in Spry (1984).

The most detailed study to date on gahnite in the Appalachians is by Sandhaus (1981), who determined its distribution, chemistry and possible origin in the Arminius, Cofer, Julia and Sulphur deposits in the Mineral District, Virginia. These deposits are located in a sequence of metapelitic sedimentary and mafic to felsic volcanic rocks (Southwick *et al.* 1971) within the Piedmont geological province. Although gahnite is distributed throughout the sulfide deposits, Sandhaus (1981) noted that it is most abundant near ore–wallrock contacts. According to Sandhaus, gahnite in ore zones is predominantly associated with quartz, biotite, garnet, pyrite, sphalerite, chalcopyrite and galena. Magnetite, pyrrhotite, staurolite, kyanite, amphibole, chlorite and muscovite are associated with gahnite in lesser amounts. Sandhaus (1981) reported that gahnite coexists with sphalerite; however, an antipathetic relationship between these minerals is suggested by the distribution within the deposits. Despite this relationship, gahnite is poikiloblastic and uncorroded where in contact with other phases, including sphalerite.

The Davis mine, Massachusetts, is one of several mines and pits that lie along a vaguely defined mineral belt within volcanic and sedimentary rocks metamorphosed to the lower or middle amphibolite grade (Bwerinofa 1972). Gahnite is associated with pyrite in massive sulfides and magnetite in sulfide-bearing chlorite–mica schists surrounding the deposit (Bwerinofa 1972), as well as with pyrite quartzites and quartz–albite metatuffs (Slack *et al.* 1983). At Bleikvassli, Norway, spinel occurrences are confined to massive sulfides, quartz veins and quartz-rich schists in the ore zone (Vokes 1962). In massive sulfides, gahnite coexists with sphalerite, pyrite, pyrrhotite, quartz and garnet, whereas in quartz-rich muscovite schists it coexists with quartz, phlogopite, muscovite, zincian staurolite, garnet, sphalerite, pyrite and pyrrhotite. There is a particularly close association between gahnite, garnet, quartz and Fe sulfides (pyrite or pyrrhotite, or both) and sphalerite in samples from the Davis and Bleikvassli deposits. Sillimanite, although rare, may also coexist with gahnite at the Bleikvassli deposit. Gahnite and garnet exhibit euhedral grain-shapes and noncorroded contacts where in contact with the other members of the system Zn-Fe-Al-Si-S-O (Figs. 3a, b).

Juve (1967) reported on gahnite in lead–zinc deposits in the Håfjell syncline, Norway. This gahnite occurs in the ore zone and its immediate wallrocks, with the grain size and frequency of spinel decreasing away from the ore zone. As with the

TABLE 4. REPRESENTATIVE COMPOSITIONS OF SPINEL FROM THE APPALACHIANS AND SCANDINAVIAN CALEDONIDES[a]

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
SiO_2%	0.00	0.00	0.00	0.00	0.05	0.00	0.00	0.05	0.06	0.00	0.00	0.15	0.07	0.05	0.04	0.03
TiO_2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.02	0.02	0.04
Al_2O_3	56.42	56.06	57.09	47.47	53.71	56.47	56.17	56.83	57.24	58.08	55.78	57.34	57.69	56.25	57.37	57.80
FeOx	9.61	7.46	6.41	10.91	5.29	5.39	5.77	5.20	7.29	7.60	4.39	5.19	6.06	5.89	5.45	5.42
MnO	0.36	0.35	0.29	0.61	0.12	0.00	0.00	0.03	0.12	0.00	0.00	0.00	0.14	0.02	0.07	0.07
MgO	0.00	0.16	0.83	0.00	1.14	1.54	1.16	1.66	1.76	1.93	1.09	1.72	1.90	0.59	1.92	1.71
CoO	nd	nd	nd	nd	nd	0.23	1.34	nd	nd	nd	nd	nd	nd	nd	nd	nd
ZnO	32.94	37.00	35.29	40.49	40.89	37.65	36.88	35.76	33.42	32.95	40.46	35.43	36.81	35.36	35.64	35.56
Total	99.33	101.03	99.91	99.48	101.20	101.28	101.32	99.53	99.89	100.58	101.72	100.83	101.69	99.16	100.51	100.63
Atomic proportions (oxygen basis 24)																
Si	0.000	0.000	0.000	0.000	0.008	0.000	0.000	0.009	0.010	0.000	0.000	0.026	0.011	0.009	0.006	0.006
Ti	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.003	0.003	0.003	0.002
Al	11.818	11.638	12.060	10.703	11.538	11.857	11.824	11.857	12.010	11.926	11.785	11.965	11.946	12.031	11.991	12.063
Fe	1.428	1.098	0.961	1.747	0.810	0.804	0.862	0.768	1.085	1.107	0.659	0.768	0.889	0.894	0.509	0.797
Mn	0.054	0.052	0.044	0.099	0.018	0.000	0.002	0.005	0.018	0.000	0.000	0.000	0.020	0.004	0.011	0.009
Mg	0.000	0.040	0.221	0.000	0.310	0.408	0.357	0.437	0.466	0.492	0.289	0.454	0.495	0.161	0.506	0.474
Co	—	—	—	—	—	0.032	0.165	—	—	—	—	—	—	—	—	nd
Zn	4.323	4.809	4.668	5.721	5.507	4.959	4.864	4.676	4.393	4.236	5.356	4.762	4.648	4.872	4.667	4.652

1 M4513+ Auburn, Maine; 2 M19160+ Topsham, Maine; 3 39306** Lord's Hill, Massachusetts; 4 47896++ Franklin, New Jersey; 5 145056++ Sterling Hill, New Jersey; 6 94677++ Springfield, Maryland; 7 R1955++ Mineral Hill, Maryland; 8 PGS-24 Andersonville, Virginia; 9 PGS-84 Johnson, Virginia; 10 120967-5++ Stratford, North Carolina; 11 R1957++ Siskoe Ridge, North Carolina; 12 79522++ Canton, Georgia; 13 PGS-54 Bleikvassli, Norway; 14 PGS-96 Skårnesdalen, Norway; 15 PGS-97 Nonsfjellet, Norway; 16 PGS-98 Thermos, Norway; + Royal Ontario Museum Catalogue no.; ++ Smithsonian Institute Catalogue no.; ** American Museum of Natural History Catalogue no.; x Total Fe as FeO; nd not determined; a mineral assemblages listed in Table 1.

aforementioned Mineral District, Davis and Bleikvassli deposits, gahnite and garnet from the Håfjell syncline form porphyroblasts that appear to be in textural equilibrium with quartz, Fe sulfides and sphalerite. According to Ross (1935), gahnite was commonly observed in sulfides associated with the Ore Knob, Wayhutta and Valzinco deposits in the southern Appalachians. Samples were not investigated in this study; therefore, the textural relations between sulfides and gahnite are unknown.

In the Thermos deposit, gahnite occurs within pyroxene–amphibole–garnet-rich layers (Vik 1977, Sundblad 1982) and at Nonsfjellet, gahnite appears in garnet–mica schists (Sundblad 1982). Coarse euhedral spinel at Thermos formed in rocks containing pyrite, quartz, garnet and hornblende. The spinel–amphibole association is also present at Nonsfjellet, where porphyroblastic zincian spinel coexists with gedrite, anthophyllite and hornblende (Figs. 3d, 4a) and in Swedish deposits, where Sundblad (1982) noted that gahnite coexists with anthophyllite and cummingtonite.

Zn spinel has been found in aluminous metasediments adjacent to metamorphosed sulfide deposits in Bleikvassli, Davis and the Mineral District, with disseminated sulfides at Charlemont (Flint 1908) and Stratford, in sulfide-free metasedimentary rocks in southeastern Pennsylvania (Wagner & Crawford 1975) and the Deake mica mine (Genth 1891). Gahnite at Stratford is associated with quartz, staurolite, hematite and pyrrhotite, whereas according to Flint (1908), gahnite at Charlemont coexists with tremolite, chloritoid, feldspar and quartz.

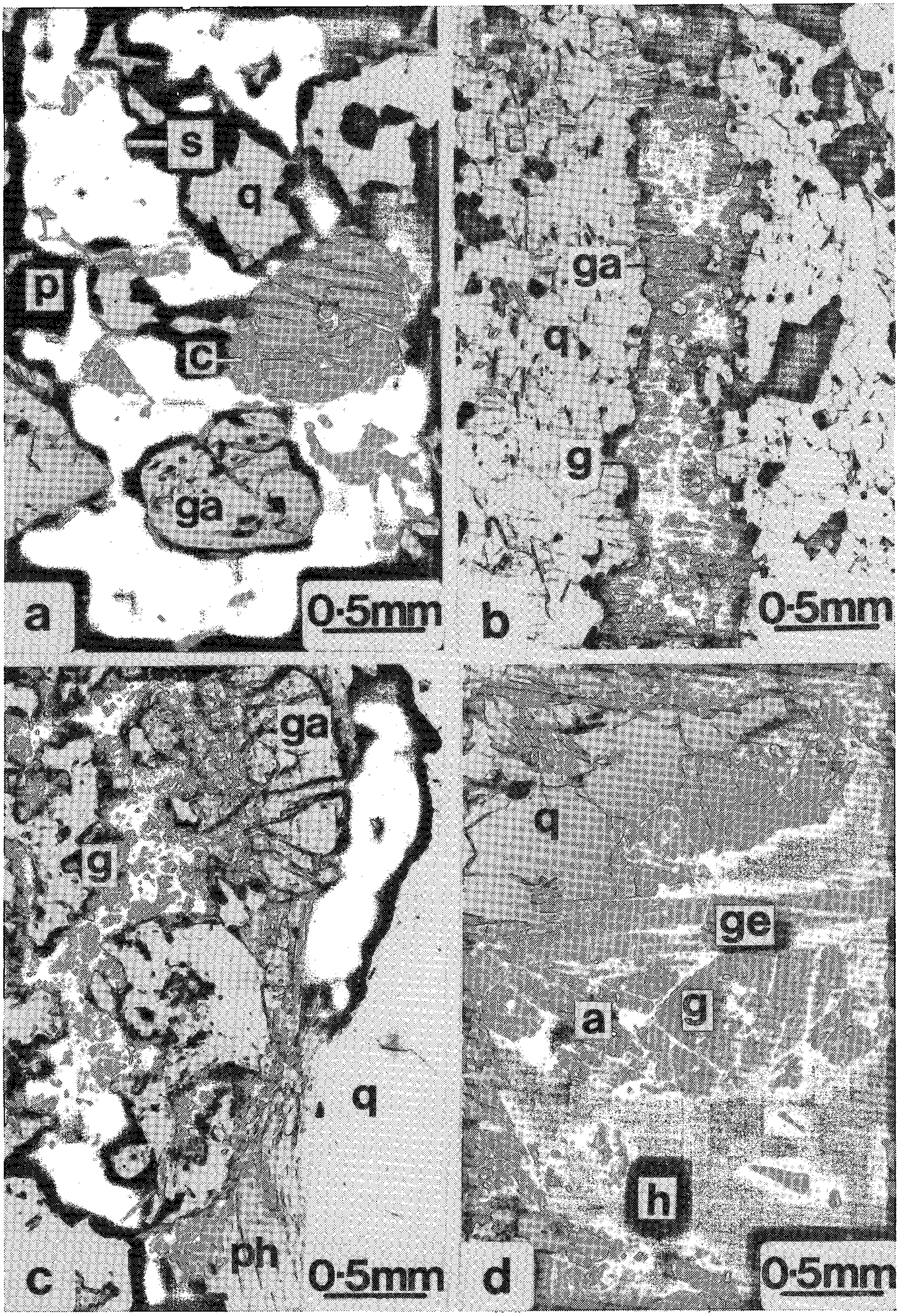
Although gahnite at Ore Knob, Wayhutta and Valzinco is commonly spatially associated with sulfides, it is also associated with quartz veins or as a replacement of quartz–plagioclase segregations. Similar sulfide-free associations occur at Andersonville, Johnson, Magruder and Standard mines. Gahnite is coarse grained and euhedral where in contact with quartz and plagioclase. Pegmatites at Auburn (Maine), Topsham (Maine) and Spruce Pine (North Carolina) contain gahnite coexisting with quartz, muscovite, plagioclase and other accessory minerals. The granoblastic intergrowth among all of these minerals suggests that gahnite is a primary phase rather than a secondary mineral.

An unusual and rare blue Co-bearing spinel is reported from the Mineral Hill, Springfield and Patapsco Cu mines, Maryland, by Shannon (1923). One of his analyses of spinel from the Mineral Hill deposit gave 1.48 wt.% CoO. Spinel analyzed by us from the Mineral Hill and Springfield mines contains 1.34 and 0.23 wt.% CoO, respectively (Table 4). Magnetite in the latter deposit contains 0.83 wt.% CoO.

Phase relations

Since occurrences of gahnite in the Appalachian–Scandinavian Caledonide orogen are most often associated with metamorphosed massive sulfides, it is pertinent to look at phase relations in the system Zn-Fe-Al-Si-S-O to determine whether gahnite could conceivably have been formed by a desulfurization mechanism in some localities. This simplified system does not take into account all phases that may be involved in desulfurization mechanisms, but it does incorporate common phases such as gahnite, almandine, aluminosilicate, quartz, sphalerite, pyrrhotite, pyrite and magnetite.

A Schreinemakers analysis (Schreinemakers 1965) for the system Zn-Fe-Al-Si-S-O (Fig. 5) can be compared with calculated phase-relations using two natural examples, Mineral District and Bleikvassli, where gahnite is intimately associated with sulfides. For the Mineral District, calculated phase-relations for the system Zn-Fe-Al-Si-S-O are projected onto the $f(O_2)$-$f(S_2)$ plane of Fe–S–O (Fig. 6) for peak metamorphic conditions of 465°C, 4.6 kbar, $X^{garnet}_{Fe_3Al_2Si_3O_{12}} = 0.55$ [based upon the average of Sandhaus's (1981) microprobe data on garnet co-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existing with gahnite] and taking into account the a_{ZnS}, a_{FeS} and the thermal expansion and compressibility of sulfide phases. Peak metamorphic conditions of 465°C and 4.6 kbar are based upon garnet-biotite geothermometry and sphalerite geobarometry (Craig 1980). For the Bleikvassli deposit, phase relations (Fig. 7) assume peak metamorphic conditions of 505°C and 3.8 kbar and $X^{garnet}_{Fe_3Al_2Si_3O_{12}} = 0.56$ [based upon the average of Spry's (1984) microprobe data on garnet coexisting with gahnite]. The presence of both kyanite and sillimanite at Bleikvassli requires a minimum temperature and pressure of 505°C and 3.76 kbar (Holdaway 1971). This temperature agrees with a mean value of 487°C ($\pm$31°C) obtained by Sen & Mukherjee (1972) from sulfur isotope geothermometry. Sphalerite coexisting with pyrrhotite or pyrite + pyrrhotite from a number of samples has a composition ranging from 9 to 12 mole % FeS. Such compositions yield pressures in excess of 7.6 kbar and appear to be the result of re-equilibration upon cooling. Calculations for Figures 6 and 7 were made using standard free-energy values obtained from Robie *et al.* (1978) for kyanite, corundum, quartz, magnetite, hematite, iron and sphalerite, from Jacob (1976) for gahnite (from the oxides) and zinc oxide, from Richardson & Jeffes (1952) for troilite, and the standard Gibbs free-energy change for the reaction:

$$FeS + 0.5S_2 = FeS_2 \qquad (1)$$

from Froese & Gunter (1976). The standard free-energy for almandine was derived using the technique of Froese (1973). The free-energy change in the oxidation of almandine (data from Froese) is based on the magnetite–wüstite buffer of Eugster & Wones (1962) and on the quartz–fayalite–magnetite buffer of Wones & Gilbert (1969). So as to remain internally consistent, values of free energy of almandine from Froese (1973) were rederived using free-energy values of magnetite from Robie *et al.* (1978). An ideal ionic-solution model was assumed for the almandine- and spessartine-rich garnet based on the results of Ganguly & Kennedy (1974).

Four studies (Pillay *et al.* 1960, Rezukhina *et al.* 1963, McLean & Ward 1966, Chan *et al.* 1973) have derived values of the free energy of formation of hercynite. The close agreement in the values of standard-state entropy at 298 K of Rezukhina *et al.* (1963) and Chan *et al.* (1973) using electrochemical techniques with that derived from calorimetric measurements by King (1956) would appear to indicate the superiority of these thermodynamic data to those of Pillay *et al.* (1960) and McLean & Ward (1966), where the agreement is not as good. Pillay *et al.* determined free-energy values for hercynite by equilibration of liquid Fe, corundum and hercynite with H_2–H_2O gas mixtures, whereas McLean & Ward derived values by measuring the oxygen concentration of liquid Fe in equilibrium with hercynite. Despite a preference for data derived using electrochemical techniques, there is excellent agreement between calculated chemical compositions of spinel on the $ZnAl_2O_4$–$FeAl_2O_4$ join using Jacob's (1976) free-energy data for gahnite with data for hercynite from Pillay *et al.* and McLean & Ward, assuming ideality for the gahnite–hercynite solid solution, and the experimentally derived spinel compositions of Spry (1984). The ideal nature of the gahnite–hercynite solution is proposed because extremely low values of excess enthalpy are obtained (Spry 1984, Spry & Scott, in prep.) utilizing the procedure of Jacob & Alcock (1977). This procedure estimates cation distributions using octahedral site-preference energies. The apparent absence of gahnite–hercynite exsolutions in natural assemblages, although not diagnostic, supports the view that the excess enthalpy-of-mixing term is small, and the gahnite–hercynite solid solution is close to being ideal. Spry (1984) showed that computed spinel compositions using the data of Pillay *et al.* (1960) and McLean & Ward (1966) are almost identical. The data of McLean & Ward have been used in this study.

In constructing Figures 6 and 7, the alm–sph–sp boundary in the pyrrhotite field is calculated by solving two equilibria:

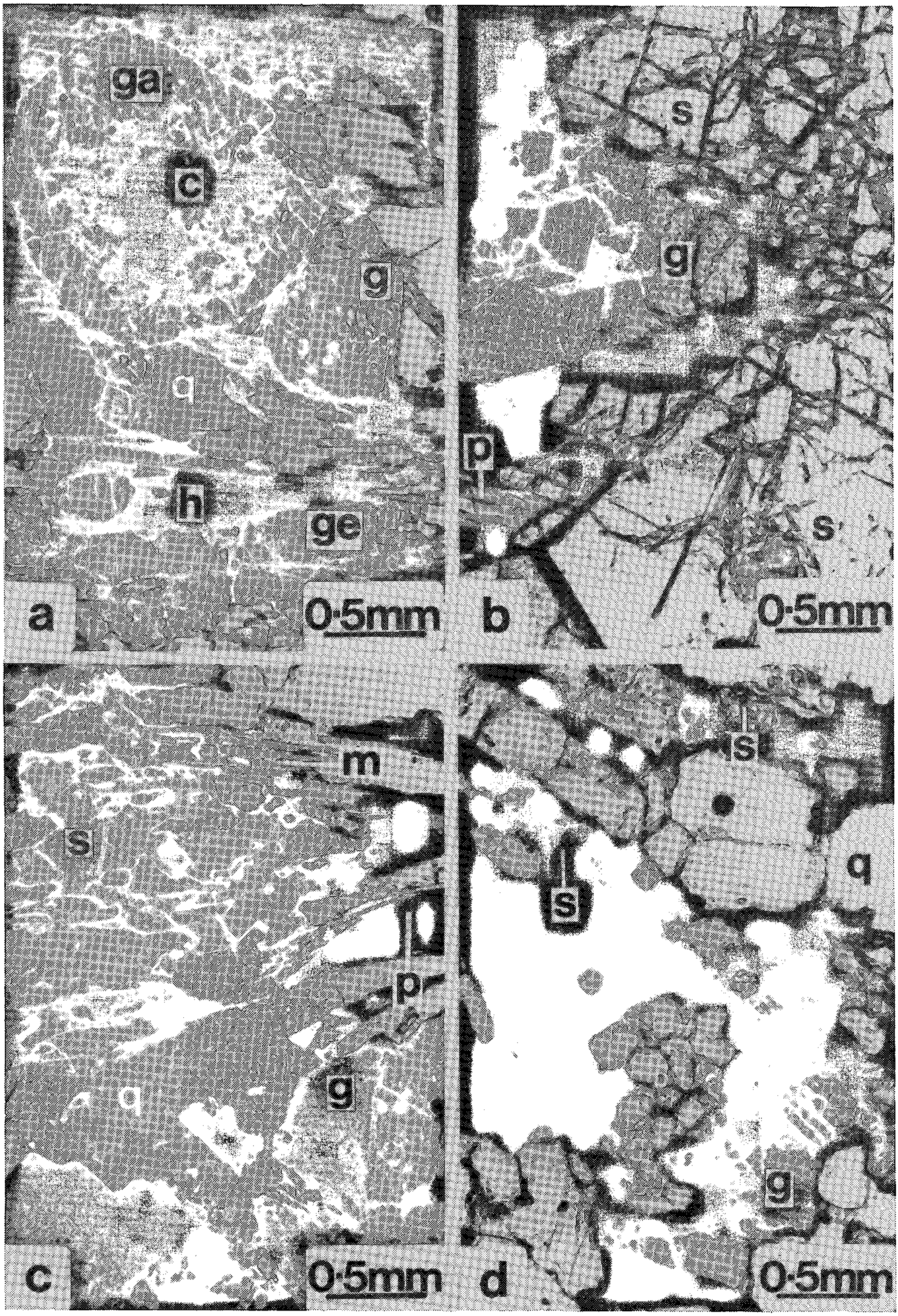
$$Fe_3Al_2Si_3O_{12} + ZnS + S_2 = ZnAl_2O_4 + 3FeS + 3SiO_2 + O_2 \qquad (2)$$

$$Fe_3Al_2Si_3O_{12} + S_2 = FeAl_2O_4 + 2FeS + 3SiO_2 + O_2 \qquad (3)$$

To obtain the alm–al boundary, the following equilibrium is used:

$$Fe_3Al_2Si_3O_{12} + 1.5S_2 = 3FeS + Al_2SiO_5 + 2SiO_2 + 1.5O_2 \qquad (4)$$

FIG. 3. a. Gahnite (g) and garnet (ga) porphyroblasts in a pyrite (p), sphalerite (s) and quartz matrix. Chlorite (c) formed as a retrograde product; Davis mine, Massachusetts. b. Gahnite–garnet layers in quartz-rich sulfide schists. The opaque mineral is pyrite; Davis mine, Massachusetts. c. Garnet appears to have replaced gahnite in a rock rich in quartz, phlogopite (ph) and sulfide. The sulfide (opaque) consists of pyrite, pyrrhotite and sphalerite; Bleikvassli, Norway. d. Subhedral porphyroblasts of gahnite intergrown with gedrite (ge), anthophyllite (a), hornblende (h) and quartz. The opaque mineral is pyrite; Nonsfjellet, Norway.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whereas for the sp–al–sph boundary the following two equilibria are solved:

$$ZnAl_2O_4 + SiO_2 + 0.5S_2 = ZnS + Al_2SiO_5 + 0.5O_2 \quad (5)$$

$$FeAl_2O_4 + SiO_2 + 0.5S_2 = FeS + Al_2SiO_5 + 0.5O_2 \quad (6)$$

The association of magnetite–pyrrhotite–pyrite in the Arminius and Sulphur deposits, Mineral District, provided buffering of $f(S_2)$ and $f(O_2)$ at about $10^{-5.2}$ and $10^{-22.6}$ bars, respectively (Fig. 6). A slightly lower value of $f(O_2)$ and a similar value of $f(S_2)$ are likely in the Julia deposit, where pyrite and pyrrhotite, but not magnetite, coexist. Magnetite does occur in the deposit but is corroded, suggesting that $f(O_2)$ and $f(S_2)$ conditions may initially have been close to the pyrite–pyrrhotite–magnetite (PPM) triple point but subsequently declined (Sandhaus 1981). A common assemblage described by Sandhaus is that involving gahnite, garnet, sphalerite and quartz. According to Figure 6, this assemblage would be expected at relatively high $f(O_2)$ conditions. The coexistence of gahnite, garnet, quartz, sphalerite and pyrrhotite (Sandhaus 1981) suggests $f(O_2)$ – $f(S_2)$ conditions on the alm–sph–sp boundary. Despite this, there is no textural evidence to suggest that garnet and sphalerite are breaking down. One assemblage described by Sandhaus (1981) that involves gahnite, kyanite, pyrite, sphalerite and quartz implies that $f(O_2)$ – $f(S_2)$ conditions were in some places on the equilibrium boundary defined by the following:

$$2Al_2SiO_5 + ZnS + FeS_2 + O_2 = ZnAl_2O_4 + FeAl_2O_4 + 2SiO_2 + 1.5S_2 \quad (7)$$

Pyrite and pyrrhotite are commonly associated with gahnite in the Bleikvassli deposit, whereas magnetite is an uncommon, but locally abundant, mineral. The presence of pyrite, pyrrhotite and magnetite requires that $f(O_2)$ – $f(S_2)$ conditions were close to those expected at the PPM triple point (Fig. 7). The presence of the assemblages pyrite, sphalerite, gahnite, pyrrhotite and garnet (Fig. 3c) and pyrite, sphalerite, pyrrhotite, gahnite and sillimanite supports this prediction.

A Schreinemakers analysis (Schreinemakers 1965) for the system Zn–Fe–Al–Si–S–O in $f(O_2)$ – $f(S_2)$ space shows that five univariant reactions have slopes of one-to-one and intersect at an invariant point (Fig. 5). Using Sandhaus's (1981) microprobe data for gahnite from the Mineral District and normalizing the gahnite and hercynite contents to 100% yield a ratio of 83 mole % gahnite to 17 mole % hercynite, which disagrees with the ratio of 98 mole % gahnite to 2 mole % hercynite predicted at the pyrite-pyrrhotite boundary (Fig. 6). Our calculations also predict a value of 90 mole % gahnite (10 mole % hercynite) for spinel from Bleikvassli along the pyrite–pyrrhotite join (Fig. 7), whereas analyzed compositions normalized to 100% contain approximately 80 mole % gahnite (20 mole % hercynite). In addition to the lack of agreement between calculated and natural compositions, reactions involving gahnite, garnet, aluminosilicate, pyrrhotite and quartz do not intersect at an invariant point (Figs. 6, 7) as predicted in Figure 5. These disagreements are probably due to uncertainties in the free-energy determinations of gahnite, hercynite and almandine when extrapolated to the lower- to middle-amphibolite grades. Spry (1984) has documented the excellent agreement between calculated and natural compositions of zincian spinel at upper amphibolite to granulite grades. Furthermore, the sequence of reactions in Figure 7 is inconsistent with that shown in Figure 5. This inconsistency results from the uncertainty in free energies of formation of gahnite, hercynite and almandine and the fact that the alm–al and alm–sph–sp boundaries will shift in $f(O_2)$ – $f(S_2)$ space depending on the choice of the activity of almandine in garnet (a^{gar}_{alm}), whereas the sp–al–sph boundary will remain fixed regardless of a^{gar}_{alm}.

Genetic speculations

Speculations concerning precursors to gahnite depend on the preservation of unmetamorphosed or slightly metamorphosed Zn-bearing rocks at grades below the stability of gahnite. Despite the apparent absence of obvious precursors to gahnite, the association of sphalerite and pyrrhotite or pyrite makes these sulfides likely. It is also likely that aluminosilicate or garnet breaks down to provide Al and, in the case of garnet, Fe and Mg, for the formation of gahnite.

FIG. 4. a. Subhedral gahnite (g) and garnet (ga) porphyroblasts intergrown with quartz (q), gedrite (ge) and hornblende (h). Chlorite (c) has replaced garnet; Nonsfjellet, Norway. b. Intergrowth of subhedral gahnite and staurolite (s) with phlogopite (p) and pyrite (opaque); Bleikvassli, Norway. c. Corroded staurolite in a layer rich in phlogopite, muscovite and quartz adjacent to a gahnite–quartz–pyrite layer. The opaque mineral is pyrite; Bleikvassli, Norway. d. Corroded staurolite and gahnite intergrown with sulfide (opaque) and quartz. Sulfide consists of pyrite, chalcopyrite and sphalerite; Canton mine, Georgia.

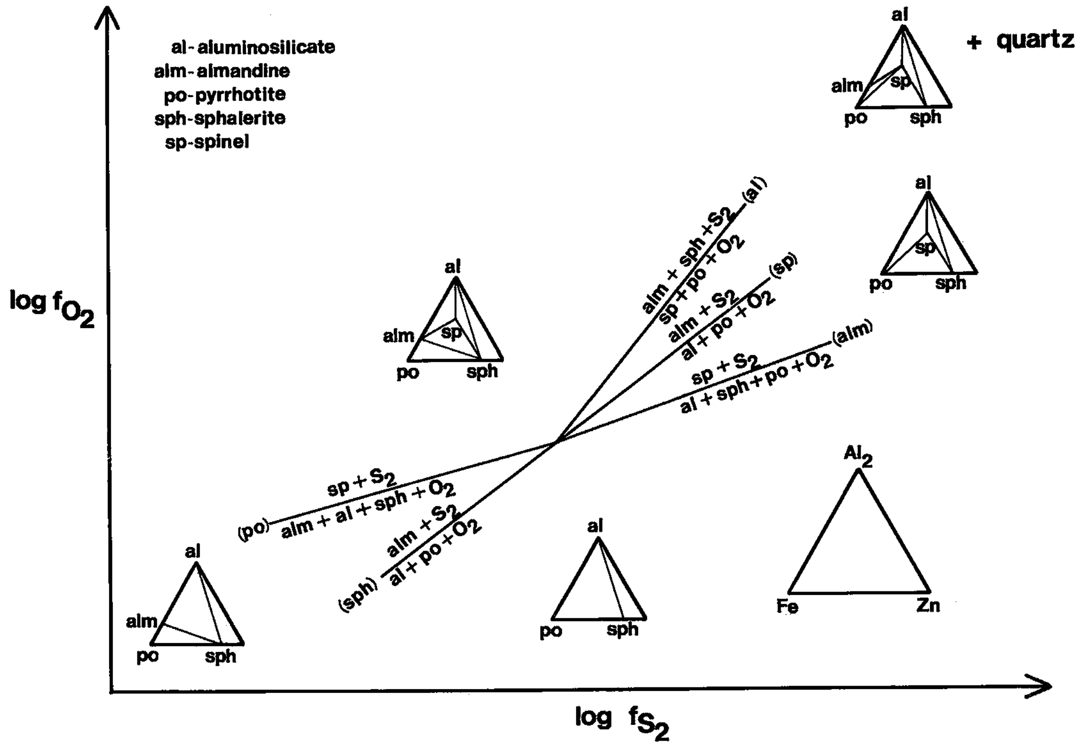

FIG. 5. Schreinemakers analysis of the system Zn–Fe–Al–Si–S–O in $f(O_2)$ – $f(S_2)$ space.

In proposing a mechanism for the formation of gahnite at Broken Hill, Australia, Segnit (1961) suggested a reaction between kaolinite and adsorbed Zn oxide. A slightly modified form of Segnit's reaction is:

$$Al_2Si_2O_5(OH)_4 + ZnO = ZnAl_2O_4 + 2SiO_2 + 2H_2O \quad (8)$$

Although this reaction could conceivably account for the formation of gahnite in aluminous metasediments, there is no documentation of ZnO being adsorbed onto clays. The available literature on metalliferous shales suggests that Zn may have originally been linked to organic material (*e.g.*, Vine & Tourtelot 1970, Coveney 1979, Coveney & Martin 1983) or phosphate material (Coveney 1979). These materials may subsequently have been removed and the remaining Zn reacted with sulfur to form sphalerite. Although no examples have been documented in the literature, sphalerite may subsequently react with aluminous clays (*e.g.*, kaolinite) to form gahnite. In this context, it is significant to note that slates in the Venn–Stavelot Massif (Kramm 1977) contain gahnite that is intimately associated with viridine. In an earlier study, Kramm (1973) showed on the basis of textural evidence that viridine and andalusite formed directly from kaolinite. Metamorphism has obliterated precursor phases to gahnite in aluminous metasediments in the Appalachian–Swedish Caledonide orogen; however, it is conceivable that Zn originally linked to organic or phosphatic matter formed sphalerite and subsequently reacted with aluminous clays (*e.g.*, kaolinite) to form gahnite by the following reaction:

$$Al_2Si_2O_5(OH)_4 + ZnS + 0.5O_2 = ZnAl_2O_4 + 2SiO_2 + 2H_2O + 0.5S_2 \quad (9)$$

There is a strong possibility that gahnite in pegmatite at Auburn, Topsham and Spruce Pine crystallized directly from peraluminous granitic melts because there is no textural evidence to suggest that gahnite formed as a secondary product. Similar spinel has been reported in acid volcanic rocks elsewhere (*e.g.*, Phillips *et al.* 1981, Tulloch 1981).

Gahnite in quartz veins that cut across massive sulfide zones are not spatially related to acid igneous

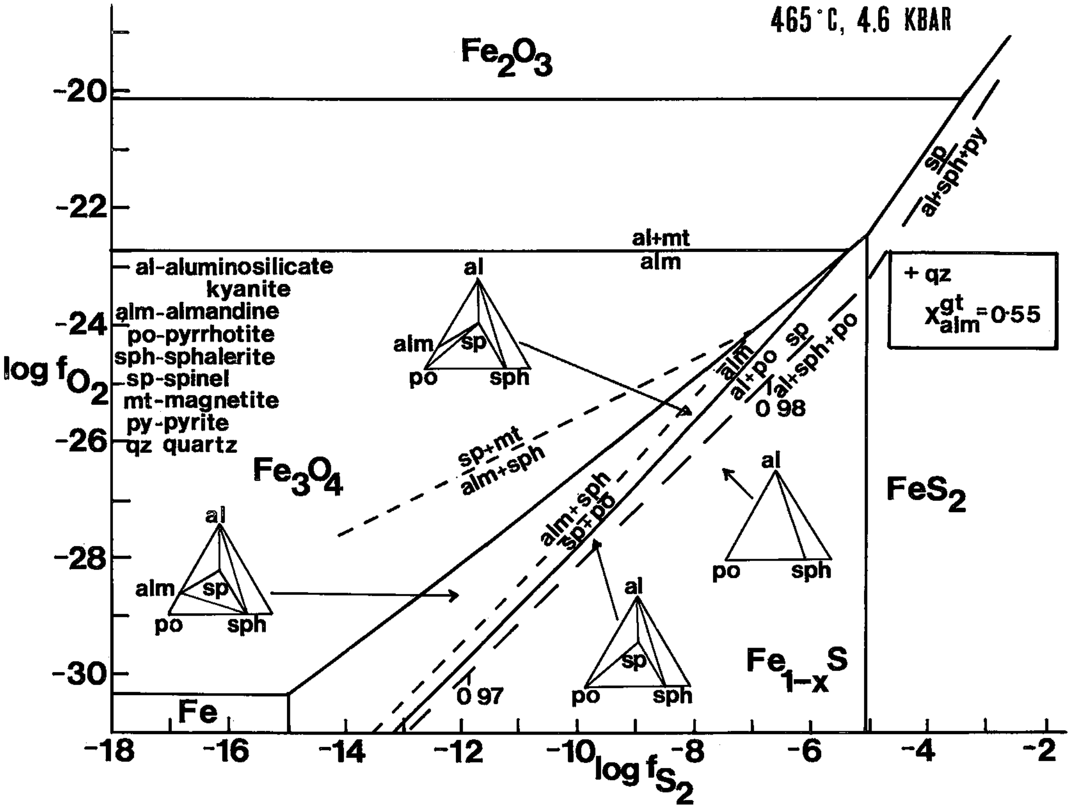

FIG. 6. Calculated phase-relations for the system Zn–Fe–Al–Si–S–O projected onto the Fe–S–O plane as a function of $f(S_2)$ and $f(O_2)$ for peak metamorphic conditions (465°C, 4.6 kbar) affecting the Mineral District, Virginia. See text for sources of data used in the calculations. Mole % $ZnAl_2O_4$ for the gahnite–hercynite solid solution is indicated on the broad dashed line.

rocks and are thought to have precipitated from a Si-rich hydrothermal solution during metamorphism.

Zincian Staurolite in the Appalachian – Scandinavian Caledonide Orogen

According to synthesis experiments on Zn- and Zn–Fe-staurolite by Griffen (1982), there is no limitation to the amount of Zn that can be incorporated in staurolite. Despite this, in natural specimens Zn content has been previously reported to range only from 0 to 7.7 wt.% ZnO. The incorporation of Zn stabilizes staurolite to the upper amphibolite grade in sulfide-free rocks (*e.g.*, Ashworth 1975). However, the most Zn-rich staurolite appears in sulfide-bearing assemblages that have been metamorphosed to the lower or middle amphibolite grade. Anomalously Zn-rich staurolite is found in a number of deposits in the Appalachian–Scandinavian Caledonide orogen. For example, in the Mineral District, staurolite coexisting with zincian spinel and sphalerite contains up to 6.9 wt.% ZnO (Sandhaus 1981). Representative compositions of staurolite that coexist with spinel and sulfide from three localities in the Appalachian–Scandinavian Caledonide orogen are listed in Table 5. Additional compositions are given by Spry (1984). Included in Table 5 for comparison are data for staurolite from the Kiipu deposit, Finland, which occurs in Precambrian volcanic and sedimentary rocks metamorphosed to the lower amphibolite grade.

Field and textural observations

Mineral assemblages of Zn-staurolite-bearing rocks studied are included in Table 3. Zincian staurolite from the Bleikvassli deposit contains up to 8.77 wt.% ZnO and is believed to be the most Zn-rich yet recorded. Such staurolite commonly occurs in contact with gahnite and pyrite at Bleikvassli; there does not appear to be any reaction between the Zn-bearing phases (Fig. 4b). In some specimens, moreover, corroded staurolite in layers rich in mus-

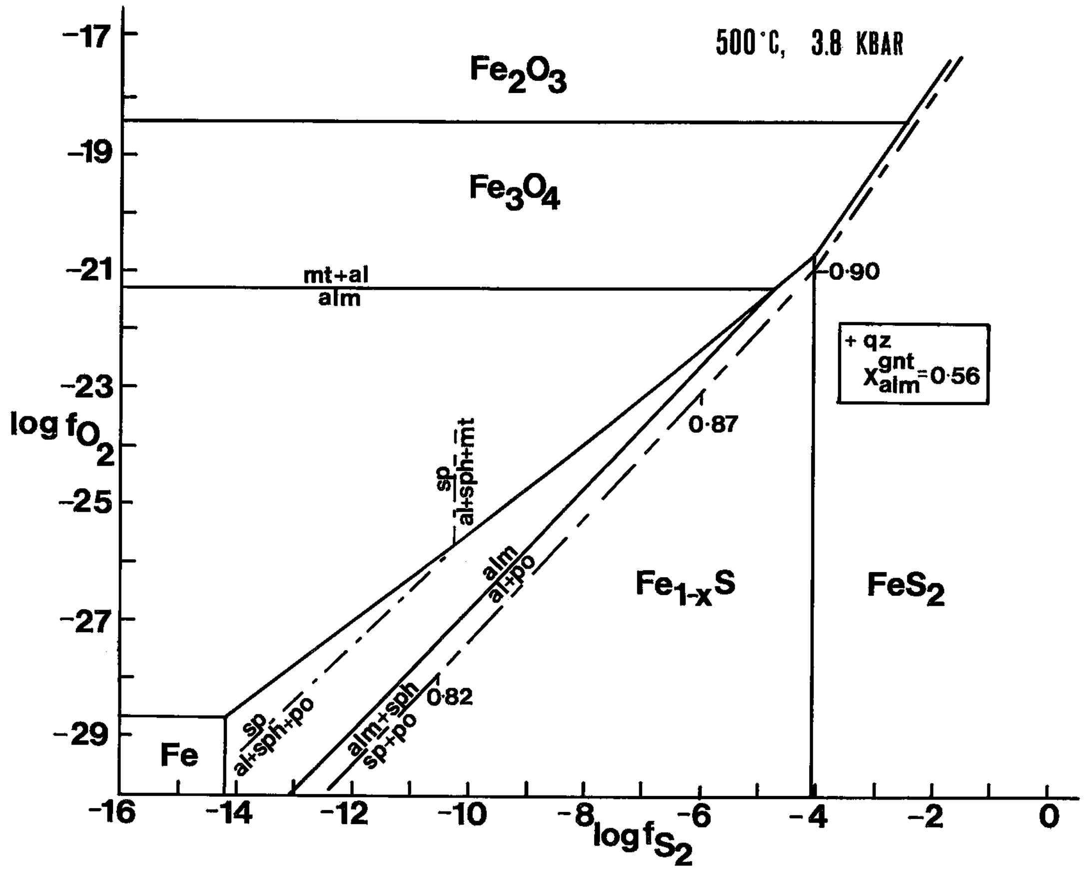

FIG. 7. Calculated phase-relations for the system Zn–Fe–Al–Si–S–O projected onto the Fe–S–O plane as a function of $f(S_2)$ and $f(O_2)$ for peak metamorphic conditions (500°C, 3.8 kbar) affecting the Bleikvassli deposit, Norway. Spinel compositions are given in mole % $ZnAl_2O_4$ for gahnite-hercynite solid solutions. See Figure 6 for the explanation of symbols.

covite and phlogopite is isolated from subhedral grains of spinel that are confined to quartz-sulfide layers (Fig. 4c). Although staurolite and gahnite appear to be corroded in the Canton deposit (Fig. 4d), coexisting subhedral staurolite, gahnite, quartz and pyrite appear to be a stable assemblage at Stratford and at Kiipu.

Genetic speculations

Gahnite - zincian staurolite reactions have been proposed elsewhere (*e.g.*, Atkin 1978, Stoddard 1979, Spry 1982); however, there does not appear to be any reaction between these phases at Bleikvassli, Canton, Stratford and Kiipu. Rather than staurolite breaking down to gahnite at Bleikvassli, the presence of corroded staurolite and muscovite, euhedral garnet and rare sillimanite in the biotite-muscovite layers suggests the following reaction (Thompson & Norton 1968):

$$\text{staurolite} + \text{muscovite} + \text{quartz} = \text{sillimanite} + \text{almandine} + \text{biotite} + H_2O \qquad (10)$$

Part of the Zn released from the breakdown of staurolite is incorporated into biotite; however, where the remainder of Zn goes is unknown.

There is no textural evidence to support the formation of zincian staurolite by desulfurization of sphalerite and pyrite; however, by analogy, it is possible that staurolite, like gahnite, formed by desulfurization reactions, for example:

$$[2ZnS] \text{ in sphalerite } + [2FeS] \text{ in pyrrhotite } + 9Al_2Si_5 + H_2O + 2O_2 = [Zn_2Al_9Si_4O_{23}(OH)] \text{ in staurolite } + [Fe_2Al_9Si_4O_{23}(OH)] \text{ in staurolite } + SiO_2 + 2S_2 \qquad (11)$$

TABLE 5. CHEMICAL COMPOSITIONS OF ZINCIAN STAUROLITE

	1	2	3	4
SiO_2%	28.23	27.07	26.24	28.55
TiO_2	0.40	0.38	0.41	0.34
Al_2O_3	52.77	51.91	51.73	51.86
FeO*	6.31	7.52	8.89	6.67
MnO	0.28	0.11	0.00	0.43
MgO	2.08	1.64	2.41	2.2.
ZnO	8.77	7.73	6.84	7.27
Total**	98.84	96.33	96.52	97.32
Atomic proportions (oxygen basis 69)				
Si	11.642	11.589	11.267	12.020
Ti	0.127	0.124	0.132	0.106
Al	25.938	26.226	26.191	25.734
Fe	2.194	2.700	3.194	2.349
Mn	0.098	0.043	0.000	0.152
Mg	1.297	1.049	1.544	1.389
Zn	2.703	2.447	2.171	2.226

* Total Fe as FeO; ** Total is anhydrous total; 1 PGS-56(1) Bleikvassli, Norway (average of 5 points); 2 79522+ Canton, Georgia (average of 4 points); 3 120967-5+ Stratford, North Carolina (average of 3 points); 4 PGS-61 Kiipu, Finland (average of 10 points); assemblage contains staurolite, quartz, pyrite, biotite, gahnite, pyrrhotite^x, chlorite^x, galena, chalcopyrite muscovite^{xx}; + Smithsonian Institute catalogue number; x secondary; xx trace amount.

Significantly, the most Zn-rich staurolite, that at Bleikvassli, coexists with sphalerite. This is to be expected in view of the phase relations shown in Figure 8. Increasing $f(S_2)$ at constant $f(O_2)$ would shift the tie lines so that Zn-rich staurolite coexists with Zn-rich sphalerite.

DISCUSSION

Calculations of spinel compositions that should be in equilibrium with associated sulfides in the Mineral District and Bleikvassli deposit disagree by as much as 15 mole % $ZnAl_2O_4$ with those actually determined from natural assemblages (Figs. 6, 7). Part of the explanation for this difference lies in the extremely high sensitivity of calculated spinel compositions, at given $f(O_2) - f(S_2)$ conditions, to the free energy of hercynite. At 600°C and 2 kbar, for example, a difference in free energy of formation of hercynite of 31.4 kJ or only 1.9% of the value of McLean & Ward (1966) produces a huge (71 mole %) shift in the computed composition of spinel at the pyrrhotite–pyrite boundary. The 31.4 kJ is the difference between the free-energy data for hercynite formation of McLean & Ward (1966) and those of Pillay *et al.* (1960). We have chosen to use the value of McLean & Ward because it gives compositions of spinel closer to our experimental results and naturally observed compositions (Spry & Scott 1983a, in prep., Spry 1984), but clearly the free energy of formation of hercynite is not well established.

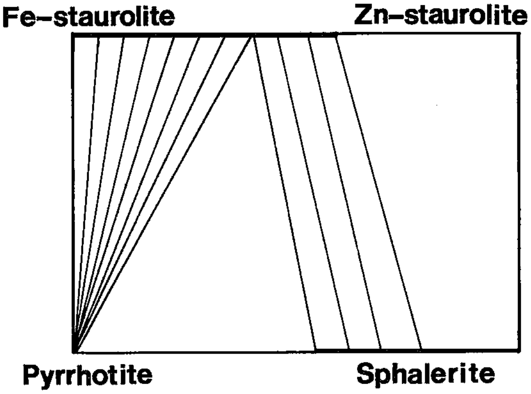

FIG. 8. The composition of Fe- and Zn-staurolite coexisting with sphalerite and pyrrhotite (schematic).

Sundblad (1982) claimed that the critical factors controlling the occurrence of gahnite in the Scandinavian Caledonides are metamorphic grade and composition of the local rock. The rocks at all gahnite localities have been metamorphosed to the amphibolite grade. Massive-sulfide deposits in the same terrane that were metamorphosed to the greenschist grade are apparently devoid of gahnite. At first glance, this would appear to rule out gahnite as an exploration guide for massive sulfides in lower-grade metamorphic rocks. However, zincian spinel has been reported from three greenschist terranes (Franklin *et al.* 1975, Kramm 1977, Hicks *et al.* 1985). Kramm (1977) recognized spinel grains that are only 8 to 10 μm in length in slates, which raises the possibility that gahnite is more widespread in low-grade terranes than commonly believed but may not have been recognized because of its grain size. Spinel associated with metamorphosed massive-sulfide deposits tend to be Zn-rich (*e.g.*, Vokes 1962, Juve 1967, Sandhaus 1981, Sundblad 1982, Spry 1984) and can, in general, be distinguished on the basis of composition from spinel associated with aluminous metasedimentary rocks, which are Fe-rich (Spry & Scott 1983a, in prep., Spry 1984). However, Kramm (1977) and Hicks *et al.* (1985) have shown that aluminous metasedimentary rocks in Belgium and South Africa, respectively, contain Zn-rich spinel simply because of the stabilizing effects of Zn on spinel at low metamorphic grades. Because of such effects, caution must be utilized if spinel composition is to be used as an exploration guide for massive-sulfide deposits in low-grade metamorphic terranes. The presence of Zn-enriched spinel does not necessarily indicate Zn-rich rocks under such conditions because, for example, Kramm (1977) demonstrated that some of the most Zn-enriched spinels recorded to date occur in rocks with only 50 ppm Zn.

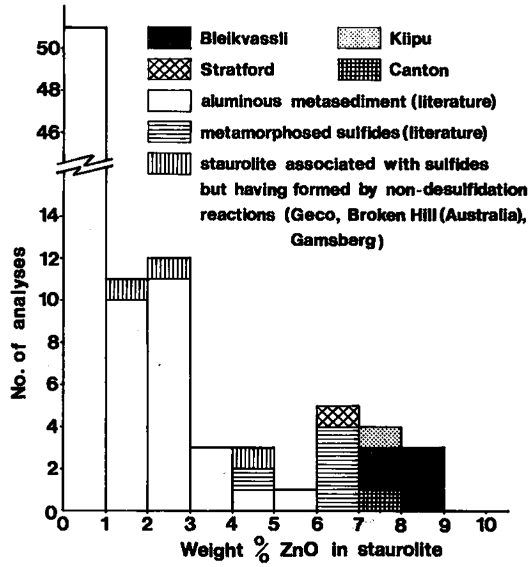

FIG. 9. The Zn content of staurolite in aluminous metasediments and metamorphosed sulfides.

In Figure 9, the Zn content of staurolite from the Bleikvassli, Kiipu, Stratford and Canton deposits is plotted together with published compositional data for staurolite in aluminous metasedimentary rocks and metamorphosed sulfide deposits. Although there is some overlap in the Zn content of staurolite from these two settings, the most Zn-rich are from metamorphosed massive-sulfide deposits. It is unclear whether all Zn-rich staurolite from massive-sulfide zones has formed by desulfurization of Fe and Zn sulfides; however, staurolite that did not form by desulfurization mechanisms (*e.g.*, Broken Hill, Australia; Gamsberg, South Africa and Geco, Ontario), even though adjacent to sulfide zones, contains less than 6 wt.% ZnO. Textural evidence suggests that staurolite in retrograde shear-zones that cut across mineralized zones at Broken Hill formed by the breakdown of almandine, sillimanite and biotite (Laing 1977). Staurolite occurs in cordierite-anthophyllite rocks (Spry 1982) along the margin of the Geco deposit. Although the identity of precursors to this staurolite is unknown, the widespread occurrence of staurolite in gneisses throughout the area suggests that sphalerite is an unlikely precursor. At Gamsberg, staurolite is present in sphalerite-free magnetite - hercynite - garnet - sillimanite rocks that overlie the economic C-unit of the Gams iron formation (Spry 1984). Textural evidence suggests that staurolite may have formed by the breakdown of garnet and sillimanite.

Staurolite in aluminous metasediments contains up to 6 wt.% ZnO. That in rocks metamorphosed to the upper amphibolite grade, in general, contains more Zn (*e.g.*, Ashworth 1975) than staurolite in rocks from lower-grade metamorphic terranes, regardless of the Zn content of the host rock. However, staurolite that probably formed by desulfurization mechanisms generally contains more than 6 wt.% ZnO (Fig. 9). Therefore, the Zn content of staurolite may be a useful guide in exploration for metamorphosed sulfide ores, in analogous fashion to zincian spinel.

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