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COMPOSITIONAL ZONING IN ZINCIAN SPINEL

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ABSTRACT

Zincian spinel (Zn, Fe, Mg)Al_2O_4 has been examined for compositional zoning. The samples come from fifty-two widely scattered localities, in metamorphosed massive-sulfide deposits, pegmatites, aluminous metasediments, metamorphosed oxide–silicate deposits, a marble, and a syenite. Most zoned crystals of zincian spinel exhibit an enrichment in Zn, with depletion in Fe and Mg, from the core to the rim. This pattern is more common in samples from metamorphosed massive-sulfide deposits than any other geological settings; it results primarily from partitioning Zn and Fe between their sulfides and zincian spinel, by sulfurization and oxidation reactions, during retrograde metamorphism. In some of these deposits and some aluminous metasediments, zoning in zincian spinel is due to partitioning of Zn, Fe and Mg between zincian spinel and adjacent ferromagnesian silicates. Zincian spinel from the Broken Hill metamorphosed massive-sulfide deposit (Australia) varies up to 30 mole % $ZnAl_2O_4$, 20 mole % $FeAl_2O_4$ and 7 mole % $MgAl_2O_4$. Spinel from other localities, however, shows a less pronounced compositional variation. The uncommon opposite trend noted in zincian spinel, *i.e.*, increase in Fe and Mg with decrease in Zn from core to rim, may be due to growth during prograde metamorphism.

Keywords: zincian spinel, gahnite, compositional zoning, electron-microprobe data.

SOMMAIRE

Le spinelle zincifère (Zn, Fe, Mg)Al_2O_4 a été étudié au point de vue du zonation en composition. Les spécimens proviennent de 52 localités, réparties dans le monde entier, dans des gîtes de sulfures massifs métamorphisés, des pegmatites, des métasédiments alumineux, des gîtes oxydes–silicates métamorphisés, un marbre et une syénite. La majorité des cristaux zonés de spinelle zincifère montrent un enrichissement en Zn, avec appauvrissement en Fe et Mg, du centre vers la périphérie. Ce type de variation domine dans les spécimens provenant de gîtes de sulfures massifs métamorphisés, en comparaison de tout autre mode de gisement; il résulte surtout du partage de Zn et Fe entre leurs sulfures et le spinel zincifère, par réactions de sulfurisation et d'oxydation, au cours du métamorphisme rétrograde. Dans quelques-uns de ces gîtes de sulfures et certains métasédiments alumineux, le zonage des cristaux de spinelle est dû au partage de Zn, Fe et Mg entre spinelle zincifère et silicates ferromagnésiens contigus. Le spinelle zincifère de Broken Hill (Australie), dans un gîte de sulfures massifs métamorphisé, varie jusqu'à 30 mole % $ZnAl_2O_4$, 20 mole % $FeAl_2O_4$ et 7 mole % $MgAl_2O_4$. Les spinelles d'autres endroits, cependant, présentent une variation de composition moins prononcée. La tendance opposée, c'est-à-dire accroissement en Fe et Mg avec diminution du Zn du centre vers l'extérieur, a été notée, plutôt rarement, dans le spinelle zincifère; ce phénomène peut être attribué à une croissance pendant le métamorphisme prograde.

(Traduit par la Rédaction)

Mots-clés: spinelle zincifère, gahnite, zonation en composition, microsonde électronique (données de).

INTRODUCTION

Numerous electron-microprobe studies have demonstrated the importance of compositional zoning in metamorphic minerals, particularly garnet and chromite (*e.g.*, Bliss & MacLean 1975, Tracy 1982). However, compositional zoning of zincian spinel (Zn,Fe,Mg)Al_2O_4 has been documented to a lesser extent (Spry 1978, Dietvorst 1980, Tulloch 1981). Where zoned, zincian spinel generally contains more of the component gahnite $ZnAl_2O_4$ and less hercynite $FeAl_2O_4$ and spinel $MgAl_2O_4$ at the edge of the grain relative to the centre, but there are exceptions. For example, Sandhaus (1981) analyzed zincian spinel from the metamorphosed Sulphur massive-sulfide deposit in the Mineral District, Virginia, that shows the reverse trend.

Spry (1978) studied zincian spinel from five localities in South Australia and New South Wales and concluded that compositional zoning reflects temperature variations during crystal growth. Dietvorst (1980) hypothesized that compositional zoning in zincian spinel from metapelites in Finland was produced by a retrograde metamorphic event. Dietvorst supported his argument by noting 1) the presence of retrograde chlorite after prograde biotite, and 2) the similarity of compositional zoning in the coexisting garnet to that expected in garnet formed as temperature decreases. A similar conclusion was reached by Tulloch (1981) to explain compositional zoning in zincian spinel from a granite in New Zealand. Both Tulloch (1981) and Dietvorst (1980) have surmised that hercynite, which is unstable in the presence of quartz below about 750°C (Richardson 1968, Frost 1973, Wall & England 1979), is stabilized by zinc at lower temperatures. If they are right, the gahnite content is expected to increase and hercynite decrease from the centre to the edge of the grain, as is commonly observed. In a study of zincian spinel from the Bodenmais deposit (Bavaria), Boctor (1978) analyzed zincian spinel with a biotite rim on one side and pyrrhotite on the other. This zincian spinel has a stronger depletion in hercynite and enrichment in gahnite toward the contact with pyrrhotite than it does with biotite. Zincian spinel in contact with cordierite and muscovite is homogeneous. The steeper gradient in the hercynite component toward pyrrhotite than toward biotite may be a result of desulfurization. Although Boctor did not discuss the cause for the zoning, it is consistent with growth during cooling. A period of retrogression after peak metamorphism led to the formation of chlorite and muscovite in the country rocks adjacent to the Bodenmais deposit (Schreyer *et al.* 1964). It follows from Boctor's study that at the conditions of metamorphism that affected the spinel-bearing assemblages, the composition of the zincian spinel depended upon the nature of the phase in contact with it.

This study documents the nature of compositional zoning in zincian spinel, the relationship between compositional zoning in zincian spinel and the geological environment, and provides an assessment of possible causes of compositional zoning in zincian spinel from fifty-two world-wide occurrences. Since some of the factors determining compositional zoning in garnet are known (Tracy 1982), I have chosen, where possible, zincian spinel coexisting with garnet to give possible insight into the factors determining compositional variations in spatially related zincian spinel.

GEOLOGICAL SETTING

Zincian spinel is found in a wide variety of geological settings. The four most common, in order of abundance, are metamorphosed massive-sulfide deposits, aluminous metasediments, pegmatites, and marbles (Spry 1984). Of the fifty-two localities studied here, thirty-two represent metamorphosed massive-sulfide deposits, ten are pegmatites, six are aluminous metasediments, two are metamorphosed oxide–silicate deposits, one a marble and one a spinel-bearing syenite. Although three occurrences of zincian spinel have been reported in rocks metamorphosed to only greenschist grade (Franklin *et al.* 1975, Kramm 1977, Hicks *et al.* 1985), all localities studied here, except for the pegmatites and the syenite, have been metamorphosed to amphibolite or granulite grade.

ELECTRON-MICROPROBE DATA

The chemical composition of the zincian spinel 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 were: accelerating voltage of 20 kV and beam current of 100 μA. Natural and synthetic spinels were used as standards. These electron microprobes are connected to a PDP/11 computer system providing on-line reduc-

TABLE 1. CHEMICAL COMPOSITIONS OF ZONED ZINCIAN SPINEL

	PGS-147		532-296		PGS-74/1		PGS-45		PGS-49		PGS-97		R12531@		24627*		M27148#	
	1		2		3		4		5		6		7		8		9	
	Centre	Edge	Centre	Edge	Centre	Edge	Centre	Edge	Centre	Edge	Centre	Edge	Centre	Edge	Centre	Edge	Centre	Edge
SiO_2 %	0.00	0.00	0.00	0.00	0.00	0.00	0.46	0.31	0.00	0.00	0.03	0.04	0.00	0.00	0.00	0.00	0.00	0.00
TiO_2	0.00	0.00	0.04	0.08	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	0.00
Al_2O_3	57.88	58.46	57.63	57.98	57.97	57.76	60.18	59.19	64.85	64.26	57.47	57.70	56.87	57.39	58.38	57.96	58.38	58.34
Fe_2O_3	0.00	0.00	0.98	0.23	0.08	0.00	2.65	3.61	5.88	5.57	0.90	0.00	0.83	0.75	0.00	0.00	0.00	0.00
FeO	9.82	7.71	16.46	11.05	10.00	7.77	6.28	5.85	0.00	0.71	4.95	5.34	5.15	6.70	7.28	4.30	16.10	14.83
MnO	0.00	0.00	0.17	0.09	0.36	0.36	0.00	0.00	0.43	0.46	0.09	0.06	0.00	0.00	0.18	0.00	0.20	0.00
MgO	1.07	0.75	2.40	1.83	2.69	1.89	9.79	8.89	21.67	22.42	2.48	1.36	1.35	2.40	2.30	2.29	0.00	0.00
ZnO	31.29	33.64	22.79	29.29	29.14	31.47	21.82	24.03	6.50	7.60	35.53	36.35	37.27	33.77	32.28	35.07	25.81	27.01
TOTAL	100.06	100.56	100.47	100.55	100.24	99.25	101.18	101.88	99.34	100.31	101.45	100.85	101.47	101.01	100.42	99.62	100.49	100.18
Atomic proportions (cation basis 18)																		
Si	0.00	0.00	0.00	0.00	0.00	0.00	0.08	0.05	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00
Ti	0.00	0.00	0.00	0.10	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	0.00
Al	12.14	12.24	11.87	11.97	11.99	12.14	11.67	11.55	11.34	11.37	11.88	12.08	11.89	11.90	12.10	12.15	12.00	12.24
Fe^{3+}	0.00	0.00	0.13	0.03	0.01	0.00	0.33	0.45	0.66	0.63	0.12	0.79	0.11	0.10	0.00	0.00	0.00	0.00
Fe^{2+}	1.46	1.14	2.42	1.62	1.47	1.16	0.87	0.81	0.00	0.09	0.73	0.00	0.76	0.99	1.07	0.64	2.35	2.21
Mn	0.00	0.00	0.03	0.01	0.05	0.06	0.00	0.00	0.06	0.06	0.01	0.01	0.00	0.00	0.03	0.00	0.03	0.00
Mg	0.28	0.20	0.62	0.48	0.70	0.50	2.40	2.20	5.22	5.01	0.65	0.36	0.35	0.63	0.61	0.60	0.00	0.00
Zn	4.12	4.42	2.93	3.79	3.78	4.14	2.65	2.94	0.72	0.84	4.60	4.75	4.88	4.38	4.19	4.61	3.62	3.55
Spinel proportions																		
Magnetite	0.0	0.0	1.1	0.3	0.1	0.0	2.8	3.8	0.0	1.5	1.0	0.0	0.9	0.8	0.0	0.0	0.0	0.0
Hercynite	24.9	19.8	39.3	27.2	24.4	19.8	11.9	9.8	0.0	0.0	11.2	13.4	11.8	15.7	18.2	10.9	39.2	38.4
Galaxite	0.0	0.0	0.5	0.2	0.8	1.0	0.0	0.0	1.0	1.0	0.2	0.2	0.0	0.0	0.5	0.0	0.5	0.0
Spinel	4.8	3.5	10.3	8.1	11.7	8.5	40.5	37.0	87.0	83.4	10.9	6.1	5.8	10.5	10.3	10.3	0.0	0.0
Gahnite	70.3	76.7	48.8	64.2	63.0	70.7	44.8	49.4	6.5	10.3	76.7	80.3	81.5	73.0	71.0	78.8	60.3	61.6
Franklinite	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	5.5	3.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

1, Marshall Lake, Ontario; 2, Broken Hill, Australia; 3, Inc claims, Northwest Territories; 4, Betty, Colorado; 5, Unnamed deposit near Round Mountain, Colorado; 6, Nonsfjellet, Norway; 7, Davis, Massachusetts; 8, Bossost, Spain; 9, Orijärvi, Finland; # Royal Ontario Museum catalogue number; @ Smithsonian Institute catalogue number; * Museum of Natural History catalogue number tion 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 were: an accelerating voltage of 15 kV and a beam current of 200 μA. Natural spinels and simple oxides 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).

Compositional Zoning in Zincian Spinel and Petrography

The mineral assemblages and compositions of zincian spinel from fifty-two localities studied here are given in Spry (1984). Nine occurrences of zincian spinel, all from metamorphosed massive-sulfide deposits, show compositional zoning. Compositions of the centre and edge of grains from these localities are listed in Table 1, and the associated mineral assemblages are in Table 2. Three compositional patterns can be identified based on the relative distribution of $ZnAl_2O_4$, $FeAl_2O_4$ and $MgAl_2O_4$. The most common pattern is for zincian spinel to show an increase in $ZnAl_2O_4$ and a decrease in $FeAl_2O_4$ and $MgAl_2O_4$ from the centre to the edge of grains (Anal. 1–4, 8 and 9; Table 1). However, the opposite trend is also observed (Anal. 7). The third distribution is for zincian spinel to exhibit an increase $ZnAl_2O_4$ and a decrease in $MgAl_2O_4$ with no significant change in $FeAl_2O_4$ (Anal. 5 and 6; Table 1).

Note that the atomic proportions in Table 1 have been calculated assuming a cation basis of eighteen. Where the Al^{3+} content of a spinel is less than twelve, Fe^{3+} is assumed to make up the difference. The content of Fe_2O_3 and FeO (weight %) was subsequently determined from the relative proportions of Fe^{3+} and Fe^{2+}. Owing to the presence of Fe^{2+} and Fe^{3+}, the proportion of Fe-bearing end-member spinels will depend on the algorithm used to compute them. I have arbitrarily chosen to place all Fe^{3+} in the magnetite end-member unless there is insufficient Fe^{2+} to balance Fe^{3+}. The proportion of the franklinite component was determined only (Anal. 5) where Zn^{2+} was required to balance Fe^{3+}.

Sandhaus (1981) showed that most zincian spinel in the Mineral District, Virginia, is homogeneous in composition. However, one zincian spinel from the Sulphur deposit exhibits a compositional variation from core to edge of 3.7 mole % decrease in gahnite component, 1.3 mole % increase in hercynite and 2.3 mole % increase in spinel *sensu stricto*. Zincian spinel in this sample coexists with quartz, biotite, pyrrhotite and chalcopyrite. Zincian spinel from the Davis deposit, Massachusetts, coexists with muscovite, quartz, pyrite, ilmenite, garnet and chalcopyrite and shows a marked decrease in gahnite, an increase in the proportions of hercynite and spinel *sensu stricto* from the centre to the edge of grains (Anal. 7, Table 1). Garnet increases in pyrope and almandine and decreases in andradite and spessartine proportions from the centre to the edge of grains (Anal. 1, Table 3), and is probably a product of growth during prograde metamorphism (*e.g.*, Tracy 1982).

The most spectacular example of compositional zoning within a single grain of zincian spinel comes from the Broken Hill deposit, Australia (Anal. 2, Table 1; Fig. 1a). Zincian spinel in the deposit shows an enrichment in gahnite and a depletion in hercynite and spinel *sensu stricto* from the centre to the edge

TABLE 2. MINERAL ASSEMBLAGES ASSOCIATED WITH ZONED ZINCIAN SPINEL*

Anal.	Sample No.	Locality	Assemblages#
1	PGS-147	Marshall Lake, Ontario	Qtz, Spl, Sp, Bt, Crn, Chl[a], Ccp, Sil[b]
2	532-296	Broken Hill, Australia	Qtz, Grt, Spl, Bt[a], St[a], Chl[a], Sp
3	PGS-74/1	Inc claim, Northwest Territories	Qtz, Mc, Sp, Po, Spl, Ap, Bt, Ccp, Ms[a], Ep
4	PGS-45	Betty, Colorado	Chl, Hu, Spl, Ath, Qtz, Sp, Ccp[b]
5	PGS-49	Unnamed deposit, Round Mountain	Cal, Chu, Spl, Chl, Fo, Se[a], Gn, Mag, Ilm[b], Hem[b]
6	PGS-97	Nonsfjellet, Norway	Hbl, Ath, Qtz, Spl, Py, Grt, Ged, Sp, Crd, Rt[b], Ilm[b]
7	R12531@	Davis, Massachusetts	Ms, Qtz, Spl, Py, Ilm, Grt, Ccp[b]
8	24627**	Bossost, Spain	Qtz, Spl, Sp, Chl[b], Se[b]
9	M27148##	Orijärvi, Finland	Qtz, Spl, Gn

*listed in Table 1; # listed in approximate order of abundance; a mineral is secondary; b mineral is present in trace amounts; Ath anthophyllite; Ap apatite; Bt biotite; Cal calcite; Ccp chalcopyrite; Chl chlorite; Chu clinohumite; Crd cordierite; Crn corundum; Ep epidote; Fo forsterite; Gn galena; Grt garnet; Ged gedrite; Hbl hornblende; Hem hematite; Hu humite; Ilm ilmenite; Mag magnetite; Mc microcline; Ms muscovite; Po pyrrhotite; Py pyrite; Qtz quartz; Rt rutile; Se sericite; Sil sillimanite; Sp sphalerite; Spl zincian spinel; St staurolite; @ Smithsonian Institute Catalogue number; ** Museum of Natural History Catalogue number; ## Royal Ontario Museum Catalogue number

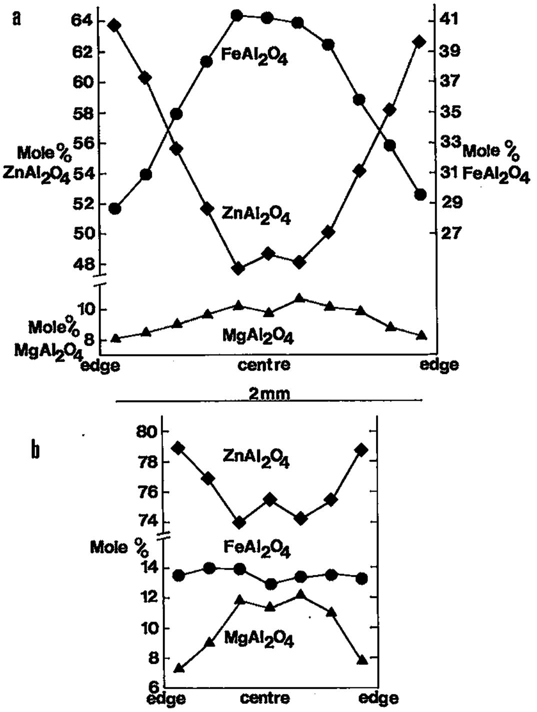

FIG. 1. a. Compositional profile across zincian spinel in sample 532–296, Broken Hill, Australia. b. Compositional profile across zincian spinel in sample PGS–97, Nonsfjellet, Norway.

of grains. This distribution is opposite to that observed in zincian spinel from the Davis and Sulphur deposits. Where zoned, zincian spinel from Broken Hill is commonly surrounded by ferromagnesian silicates (*i.e.*, staurolite, biotite and chlorite) that formed during a retrograde metamorphic event.

TABLE 3. COMPOSITIONS OF ZONED GARNET

		RG-80-47		PGS-10			PGS-97	
		1		2			3	
		Centre	Edge	Centre	Edge[a]	Edge[b]	Centre	Edge
SiO_2	%	36.21	36.30	36.61	36.24	36.49	37.46	36.62
Al_2O_3		20.31	20.91	21.02	20.92	20.79	20.90	20.90
Fe_2O_3		0.73	0.00	0.17	0.00	0.41	0.59	0.51
FeO		29.83	31.31	29.80	34.13	30.12	24.19	27.26
MnO		9.07	6.51	3.17	3.71	3.82	7.58	5.77
MgO		1.47	2.19	0.48	0.46	0.49	5.42	4.57
CaO		2.42	2.13	9.20	4.53	7.20	2.98	3.06
TOTAL:		100.04	99.35	100.45	99.99	99.32	99.12	98.69
		Atomic proportions (cation basis 16)						
Si		5.90	5.92	5.88	5.91	5.96	5.96	6.03
Al		3.91	4.02	3.98	4.02	3.95	3.93	3.94
Fe^{3+}		0.09	0.00	0.02	0.00	0.05	0.07	0.06
Fe^{2+}		4.06	4.26	4.00	4.66	4.13	3.21	3.65
Mn		1.25	0.90	0.43	0.51	0.53	1.04	0.73
Mg		0.36	0.53	0.11	0.12	0.11	1.28	1.07
Ca		0.43	0.37	1.58	0.79	1.26	0.51	0.52
		Garnet proportions						
Almandine		66.1	70.3	65.4	76.6	68.5	53.2	61.2
Andradite		2.2	0.0	0.5	0.0	1.2	1.7	1.5
Grossular		4.9	6.1	25.3	13.0	19.7	6.7	7.2
Pyrope		5.9	8.7	1.8	1.9	1.8	17.2	17.9
Spessartine		20.9	14.9	7.0	8.5	8.8	21.2	12.2

a in contact with sphalerite; b - in contact with quartz;
1, Davis, Massachusetts; 2, Broken Hill, Australia; 3, Nonsfjellet; Norway

Most grains of garnet coexisting with zincian spinel are unzoned (Spry 1978), much like those found throughout the Broken Hill district, which has been metamorphosed to the upper amphibolite to granulite facies (Chenhall 1976). However, in some zincian-spinel-bearing samples, garnet in contact with sphalerite (Anal. 2a, Table 3) shows greater zoning than where in contact with quartz (Anal. 2b, Table 3).

Zincian-spinel-bearing samples from the Bossost (Anal. 8, Table 1), Spain, and Marshall Lake deposits (Anal. 1, Table 1), Ontario, and Inc claims (Anal. 3, Table 1), Northwest Territories, contain retrograde chlorite, sericite or muscovite. Coexisting zincian spinel, usually in contact with Fe and Zn sulfides or ferromagnesian silicates (*e.g.*, biotite, garnet), exhibits the same pattern of compositional zonation that occurs in zincian spinel from the Broken Hill deposit (Anal. 2, Table 1).

Zincian spinel from the Betty deposit, Colorado, and an unnamed deposit near Round Mountain, Colorado, is associated with members of the humite group. Zincian spinel and either humite or chondrodite are corroded and separated by Mg-rich chlorite. Quartz, sphalerite and Fe sulfides are generally absent from these rocks. Zincian spinel shows an increase in the gahnite component and a decrease in the spinel *sensu stricto* component from the centre to the edge of grains (Anal. 4, 5; Table 1). The same pattern also exists in zincian spinel from the Nonsfjellet deposit, Norway (Anal. 6, Table 1, Fig. 1b). Zincian spinel in this deposit is in contact with garnet and Mg-rich phases, gedrite, anthophyllite and chlorite. It is not clear from textural relations whether the zincian spinel broke down to form any of these phases or whether it is part of the original mineral assemblage.

THE ORIGIN OF COMPOSITIONAL ZONING IN ZINCIAN SPINEL

In order to evaluate the possible causes of compositonal zoning in zincian spinel, the following factors must be considered: 1) Of the fifty-two spinel localities studied here, only nine contain zincian spinel that is compositionally zoned. 2) These nine localities are metamorphosed massive-sulfide deposits. However, zoned zincian spinel has also been reported in other geological environments, including a granite from New Zealand (Tulloch 1981), sulfide-free and sulfide-bearing aluminous metasediments in Finland (Dietvorst 1980), a marble from Czechoslovakia (Ulrych 1971), and a pegmatite from the Willyama Complex, Australia (Spry 1978). 3) Zoned zincian spinel is best developed where in contact with Fe and Zn sulfides and ferromagnesian silicates. The zonation pattern is generally weak and concentric; however, it may be asymmetrical if one side of the grain is in contact with Fe and Zn sulfides and ferromagnesian silicates and the other side is in contact with a Mg-, Zn-, or Fe-free mineral.

Theoretical and field studies by Wall & England (1979), Spry (1984), Spry & Scott (1986a, b) and results of experiments by Spry (1984) and Spry & Scott (1986a) suggest that zincian spinel associated with metamorphosed massive-sulfide deposits is a product of desulfurization of sphalerite during metamorphism. Spinel-forming reactions involve phases in the system Zn–Fe–Al–Si–S–O and include (Spry 1984, Spry & Scott 1986a):

$[Fe_3Al_2Si_3O_{12}]$ in garnet + [ZnS] in sphalerite + $5/2S_2$ = $[ZnAl_2O_4]$ in spinel + $3FeS_2$ + $3SiO_2$ + O_2 (1)

$[Fe_3Al_2Si_3O_{12}]$ in garnet + [ZnS] in sphalerite + S_2 = $[ZnAl_2O_4]$ in spinel + 3FeS + $3SiO_2$ + O_2 (2)

[ZnS] in sphalerite + [FeS] in pyrrhotite + $2Al_2SiO_5$ + O_2 = $[ZnAl_2O_4]$ in spinel + $[FeAl_2O_4]$ in spinel + $2SiO_2$ + S_2 (3)

[ZnS] in sphalerite + [FeS] in pyrrhotite + $2Al_2O_3$ + O_2 = $[ZnAl_2O_4]$ in spinel + $[FeAl_2O_4]$ in spinel + S_2 (4)

Phase relations in the system Zn–Fe–Al–Si–S–O can be calculated and projected onto the plane of Fe–S–O in terms of $f(O_2)$ and $f(S_2)$ at any temperature and pressure using the technique proposed by Spry (1984) and Spry & Scott (1986a). Those phase relations at 650°C and 5.9 kbar are shown in Figure 2. Free-energy values utilized in the construction of Figure 2 were obtained from Robie *et al.* (1978) for the aluminosilicate (sillimanite), corundum, quartz, magnetite, iron and sphalerite; from Jacob (1976) for gahnite (from the oxides) and zinc oxide; from McLean & Ward (1966) for hercynite; from Richardson & Jeffes (1952) for troilite, and the standard Gibbs free-energy change for the reaction:

$$FeS + ½S_2 = FeS_2 \quad (5)$$

from Froese & Gunter (1976). The standard free-

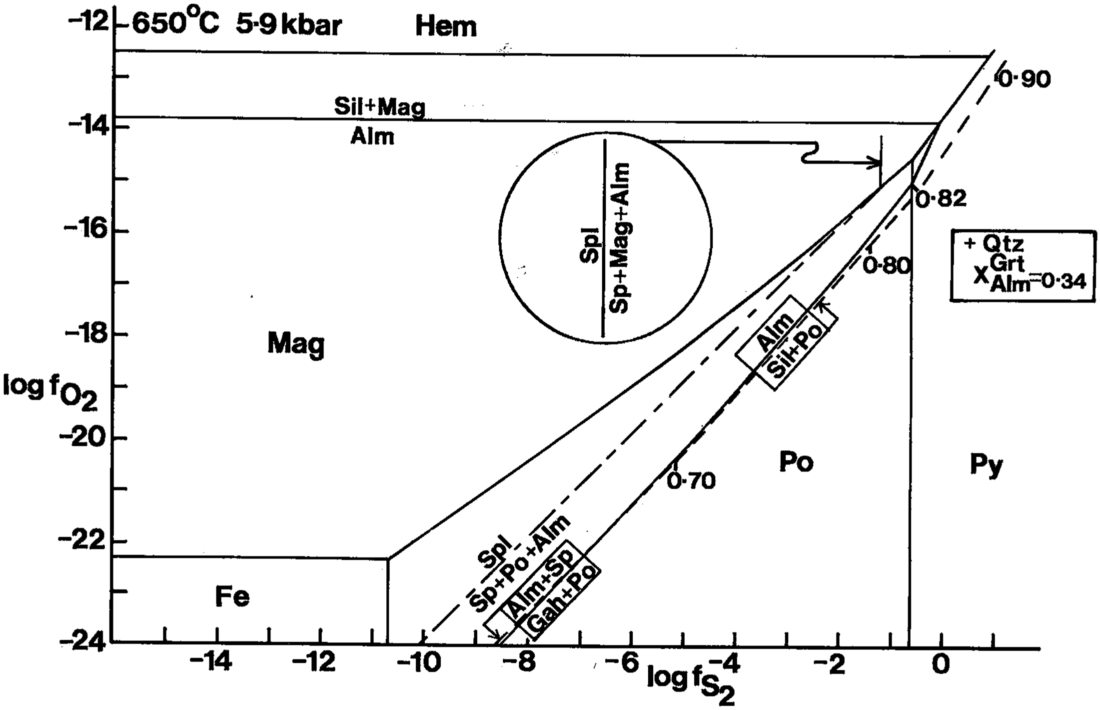

FIG. 2. Calculated phase-relations in the system Zn–Fe–Al–Si–S–O projected onto the Fe–S–O plane as a function of $f(S_2)$ and $f(O_2)$. The composition of spinel is indicated and given in terms of the mole fraction of gahnite in the gahnite–hercynite solid solution. The composition of garnet has arbitrarily been assigned a value X^{grt}_{alm} = 0.34. See text for sources of data used in the construction of the diagram. Abbreviations of mineral names are in Table 1. In addition, Gah is gahnite.

energy for almandine was derived using the technique of Spry & Scott (1986a, b), which is a slight modification of the technique of Froese (1973). Ideal ionic models are assumed for the almandine–spessartine and gahnite–hercynite solid solutions. In the construction of Figure 2, the composition of Zn–Fe spinel in equilibrium with sphalerite and one or two phases of the system Fe–S–O is calculated. At 650°C and 5.9 kbar the composition of spinel in the gahnite–hercynite solid solution in equilibrium with sphalerite, pyrrhotite and pyrite is 82 mole % gahnite (Fig. 2). It was shown by Spry (1984) and Spry & Scott (1986a) that the composition of spinel coexisting with sphalerite, pyrrhotite and pyrite is 81 mole % $ZnAl_2O_4$ at 600°C and 2 kbar, 75 mole % $ZnAl_2O_4$ at 700°C and 2 kbar, and 84 mole % $ZnAl_2O_4$ at 600°C and 5 kbar. The mole fraction of gahnite in the gahnite–hercynite solid solution in equilibrium with these sulfides has been calculated at a number of other pressures and temperatures and contoured on a pressure–temperature grid (Fig. 3). Although relatively insensitive to changes in pressure and temperature, the composition of spinel coexisting with these sulfides is expected to decrease slightly in the proportion of gahnite during prograde metamorphism. Theoretically this decrease will occur at thermal gradients greater than 5°C/km. A thermal gradient of 20°C/km is shown in Figure 3 for reference.

Owing to the coexistence of spinel with garnet, sphalerite, pyrrhotite and pyrite in some samples from the Davis and Sulphur deposits, it is conceivable that the zoning observed in spinel from these localities was produced as the spinel grew during a prograde metamorphic event *via* reactions (1) and (2) at the pyrrhotite–pyrite buffer. The pattern of compositional zoning in garnet coexisting with spinel at the Davis deposit (Anal. 1, Table 2) is typical of that which has developed during such an event.

An increase in gahnite and a decrease in hercynite and spinel *sensu stricto* from the centre to the edge of grains occur in spinel from the Broken Hill, Bossost, and Marshall Lake deposits and the Inc claims (Anal. 2, 8, 1 and 3, respectively; Table 1). The presence of retrograde phases, such as staurolite (*e.g.*, Broken Hill, Spry & Scott 1986b), sericite, chlorite and muscovite, in contact with gahnite suggests that it may have been subjected to a period of retrograde metamorphism after a prograde metamorphic event. Zoning in spinel coexisting with garnet at Broken Hill may be the result of spinel forming *via* reaction (1) during a retrograde metamorphic event.

Zincian spinel from the Inc claims is unzoned where in contact with quartz. However, where in contact with sphalerite, zincian spinel exhibits an 8 mole % increase in gahnite, a 5 mole % decrease in hercynite and a 3 mole % decrease in spinel *sensu*

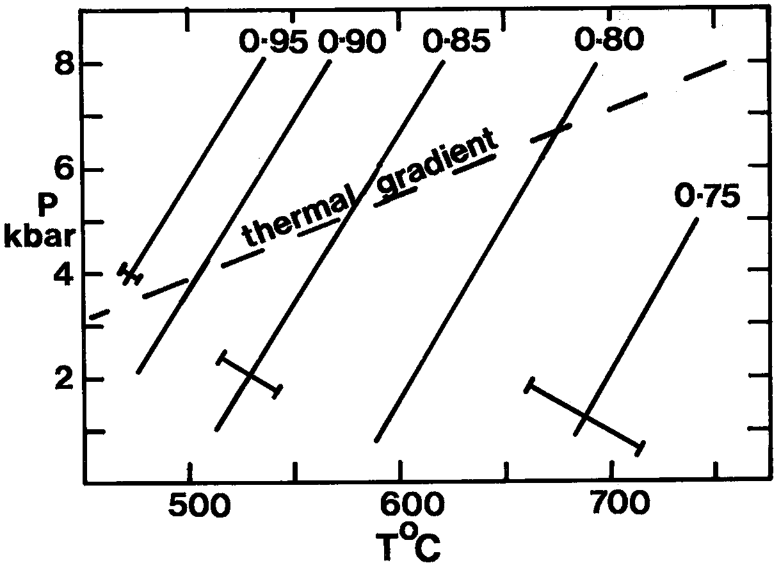

FIG. 3. Plot of spinel composition (mole fraction of gahnite in gahnite – hercynite solid solution) at the sphalerite – pyrrhotite – pyrite equilibria as a function of pressure and temperature. The dashed line represents a thermal gradient of 20°C/km. Note that the contours of spinel composition are steeper than the thermal gradient and that they decrease with increasing temperature and pressure. Errors in calculated values of the composition of spinel are indicated with bars.

stricto from centre to edge. The absence of compositional zoning in zincian spinel where in contact with quartz may be the result of having no Fe–Mg–Zn mineral in close enough proximity for exchange to be established. The pattern of zonation in zincian spinel where in contact with sphalerite may be the result of spinel growth *via* desulfurization of sphalerite during a retrograde metamorphic event. Alternatively, it may be the result of a back reaction between zincian spinel and sphalerite, similar in type to that which occurs between biotite and garnet when these phases grow during a period of retrograde metamorphism.

Sympathetic patterns of zonation between spinel *sensu stricto* and gahnite components in zincian spinel from the Betty deposit and an unnamed deposit near Round Mountain, Colorado are *not* believed to be the product of the formation by desulfurization of sphalerite. Rather, they seem to be the result of Mg depletion from spinel and humite to form Mg-chlorite, which separates corroded spinel and humite. Textural relations do not indicate whether the chlorite-forming reaction occurred during a prograde or retrograde metamorphic event.

The phase relations between spinel, garnet, anthophyllite, gedrite and chlorite at Nonsfjellet, Norway are equivocal. However, the compositional variation within garnet is typical of garnet that has grown during a prograde metamorphic event, *i.e.*, the spessartine component decreases and the almandine component increases from the centre to edge of the grains. Furthermore, secondary minerals that may have formed during a retrograde metamorphic event are absent. It is probable, therefore, that the zonation pattern in gahnite, like that in associated garnet, formed during a prograde metamorphic event.

DISCUSSION

An increase in gahnite component, a decrease in hercynite and, to a lesser extent, a decrease in spinel *sensu stricto* from centre to edge is the most common pattern of compositional zonation in grains of zincian spinel. In conformity with earlier suggestions by Dietvorst (1980) and Tulloch (1981), this pattern is attributed to the stabilizing effect of Zn on the gahnite–hercynite solid solution at lower temperatures. Theoretical considerations and textural relations suggest that in the case of zincian spinel in metamorphosed massive-sulfide deposits, this pattern is most pronounced where in contact with pyrite, pyrrhotite or sphalerite and is the product of formation of zincian spinel by desulfurization of sphalerite during a period of retrograde metamorphism.

Whereas compositional zoning may be present in zincian spinel from a variety of environments, this phenomenon is most common, but not ubiquitous, in metamorphosed massive-sulfide deposits. Zincian spinel that is compositionally zoned is less commonly encountered in aluminous metasediments, pegmatites and marbles because suitable phases for partitioning Zn are absent. It is more difficult, however, to explain why zoned grains of zincian spinel are absent from many metamorphosed massive-sulfide deposits. Part of the answer may relate to the $f(O_2)$ and $f(S_2)$ conditions at which the zincian spinel equilibrated. Using Figure 2, for example, it is apparent that relatively large changes in $f(O_2)$ and $f(S_2)$ are required to significantly alter the composition of spinel in equilibrium with sphalerite and a member of the system Fe–S–O. This feature will be maintained regardless of changes in P and T. The apparent absence of zoning in many cases and the preservation of patterns of weak compositional zonation in zincian spinel are also probably due to high rates of diffusion of Fe, Zn and Mg through the spinel lattice relative to growth rates at metamorphic conditions (greenschist to granulite grade) that are required for the growth of zincian spinel.

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REFERENCES

BLISS, N.W. & MACLEAN, W.H. (1975): The paragenesis of zoned chromite from central Manitoba. *Geochim. Cosmochim. Acta* 39, 973-990.

BOCTOR, N.Z. (1978): Evaluation of sphalerite geobarometry in Bodenmais ore, Bavaria. *Carnegie Inst. Wash. Year Book* 77, 880-886.

CHENHALL, B.E. (1976): Chemical variation of almandine and biotite with progressive regional metamorphism of the Willyama Complex, Broken Hill, New South Wales. *J. Geol. Soc. Aust.* **23**, 235-242.

DIETVORST, E.J.L. (1980): Biotite breakdown and the formation of gahnite in metapelitic rocks from Kemio, southwest Finland. *Contr. Mineral. Petrology* **75**, 327-337.

DUNCUMB, P. & REED, S.J.B. (1968): The calculation of stopping power and backscatter effects in electron probe microanalysis. *In* Quantitative Electron Probe Microanalysis (K.F.J. Heinrich, ed.). *Nat. Bur. Standards, Spec. Publ.* **298**, 133-154.

FRANKLIN, J.M., KASARDA, J. & POULSEN, K.H. (1975): Petrology and chemistry of the alteration zone of the Mattabi massive sulfide deposit. *Econ. Geol.* **70**, 63-79.

FROESE, E. (1973): The oxidation of almandine and iron cordierite. *Can. Mineral.* **11**, 991-1002.

______ & GUNTER, A.E. (1976): A note on the pyrrhotite - sulfur vapor equilibrium. *Econ. Geol.* **71**, 1589-1594.

FROST, B.R. (1973): Ferroan gahnite from quartz - biotite - almandine schist, Wind River Mountains, Wyoming. *Amer. Mineral.* **58**, 831-834.

HICKS, J.A., MOORE, J.M. & REID, A.M. (1985): The co-occurrence of green and blue gahnite in the Namaqualand metamorphic complex, South Africa. *Can. Mineral.* **23**, 535-542.

JACOB, K.T. (1976): Gibbs free energies of formation of $ZnAl_2O_4$ and $ZnCr_2O_4$. *Thermochim. Acta* **15**, 79-87.

KRAMM, U. (1977): Gahnite in the Venn-Stavelot Massif and its petrologic significance. *Ann. Soc. Géol. Belg.* **100**, 199-201.

MCLEAN, A. & WARD, R.G. (1966): Thermodynamics of hercynite formation. *J. Iron Steel Inst.* **204**, 8-11.

RICHARDSON, F.D. & JEFFES, J.H.E. (1952): The thermodynamics of substances of interest in iron and steel making. III. Sulfides. *J. Iron Steel Inst.* **171**, 165-175.

RICHARDSON, S.W. (1968): Staurolite stability in a part of the system Fe–Al–Si–O–H. *J. Petrology* **9**, 467-488.

ROBIE, R.A., HEMINGWAY, B.S. & FISHER, J.R. (1978): Thermodynamic properties of minerals and related substances at 298.15K and 1 bar (10^5 pascals) pressure and at higher temperatures. *U.S. Geol. Surv. Bull.* **1452**.

SANDHAUS, D.J. (1981): *Gahnite in Metamorphosed Volcanogenic Massive Sulfides of the Mineral District, Virginia.* M.S. thesis, Virginia Polytechnic Inst. and State Univ., Blacksburg, Virginia.

SCHREYER, W., KULLERUD, G. & RAMDOHR, P. (1964): Metamorphic conditions of ore and country rock of the Bodenmais, Bavaria, sulfide deposit. *Neues Jahrb. Mineral. Abh.* **101**, 1-26.

SPRY, P.G. (1978): *The Geochemistry of Garnet-Rich Lithologies Associated with the Broken Hill Orebody, N.S.W., Australia.* M.S. thesis, Univ., Adelaide, Adelaide, Australia.

______ (1984): *The Synthesis, Stability, Origin and Exploration Significance of Zincian Spinels.* Ph.D. thesis, Univ. Toronto, Toronto, Ont.

______ & SCOTT, S.D. (1986a): The stability of zincian spinels in sulfide systems and their potential as exploration guides for metamorphosed massive sulfide deposits. *Econ. Geol.* **81**, 1446-1463.

______ & ______ (1986b): Zincian spinel and staurolite as guides to ore in the Appalachians and Scandinavian Caledonides. *Can. Mineral.* **24**, 147-163.

STATHAM, P.J. (1975): *Quantitative X-ray Energy Spectrometry: the Application of Si(Li) Detector to Electron Microprobe Analysis.* Ph.D. thesis, Univ. Cambridge, Cambridge, England.

TRACY, R.J. (1982): Compositional zoning and inclusions in metamorphic minerals. *In* Characterization of Metamorphism Through Mineral Equilibria (J.M. Ferry, ed.). *Mineral. Soc. Amer., Rev. Mineral.* **10**, 355-393.

TULLOCH, A.J. (1981): Gahnite and columbite in an alkali-feldspar granite from New Zealand. *Mineral. Mag.* **44**, 275-278.

ULRYCH, J. (1971): Zinc spinel from Lukovská hora Hill near Moravské Budějovice. *Čas. Mineral. Geol.* **16**, 419-422.

WALL, V.J. & ENGLAND, R.N. (1979): Zn–Fe spinel–silicate–sulphide reactions as sensors of metamorphic intensive variables and processes. *Geol. Soc. Amer. Abstr. Programs* **11**, 354.

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