COMPOSITIONAL ZONING IN ZINCIAN SPINEL

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ABSTRACT

Zincian spinel (Zn, Fe, Mg)Al$_2$O$_4$ has been examined for compositional zoning. The samples come from fifty-two widely scattered localities, in metamorphosed massive-sulfide deposits, pegmatites, aluminous metasediments, and rocks of other geological settings; it results primarily from partitioning 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$_2$O$_4$, 20 mole % FeAl$_2$O$_4$ and 7 mole % MgAl$_2$O$_4$. 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.

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$_{3-4}$Fe$_{0.5}$Mg$_{0.5}$)Al$_2$O$_4$ 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$_2$O$_4$ and less hercynite FeAl$_2$O$_4$ and spinel MgAl$_2$O$_4$ 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 zinian spinel from the Bodenmais deposit (Bavaria), Boctor (1978) analyzed zinian spinel with a biotite rim on one side and pyrrhotite on the other. This zinian spinel has a stronger depletion in hercynite and enrichment in garnethn toward the contact with pyrrhotite than it does with biotite. Zinian spinel in contact with cor- dierite and muscovite is homogeneous. The steeper gradient in the hercynite component toward pyrrho-
tite does with biotite. Zincian spinel in contact with cor-

This study documents the nature of compositional zoning in zinian spinel, the relationship between compositional zoning in zinian spinel and the geological environment, and provides an assessment of possible causes of compositional zoning in zinian 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, zinian spinel coexisting with garnet to give possible insight into the factors determining compositional variations in spatially related zinian spinel.

**TABLE 1. CHEMICAL COMPOSITIONS OF ZONED ZINCIAN SPINEL**

<table>
<thead>
<tr>
<th>Component</th>
<th>Formula</th>
<th>Weight</th>
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</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>57.88</td>
<td>58.46</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>MgO</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>1.07</td>
<td>2.40</td>
</tr>
<tr>
<td>MnO</td>
<td>31.29</td>
<td>33.64</td>
</tr>
<tr>
<td>FeO</td>
<td>98.92</td>
<td>101.66</td>
</tr>
<tr>
<td>MgO</td>
<td>1.98</td>
<td>2.09</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>MnO</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>FeO</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>MgO</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

**ELECTRON-MICROPROBE DATA**

The chemical composition of the zinian 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-

**GEOLOGICAL SETTING**

Zinian 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 zinian 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.
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 zinian spinel from fifty-two localities studied here are given in Spry (1934). Nine occurrences of zinian 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 \( \text{ZnAl}_2\text{O}_4 \), \( \text{FeAl}_2\text{O}_4 \) and \( \text{MgAl}_2\text{O}_4 \). The most common pattern is for zinian spinel to show an increase in \( \text{ZnAl}_2\text{O}_4 \) and a decrease in \( \text{FeAl}_2\text{O}_4 \) and \( \text{MgAl}_2\text{O}_4 \) 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 zinian spinel to exhibit an increase \( \text{ZnAl}_2\text{O}_4 \) and a decrease in \( \text{MgAl}_2\text{O}_4 \) with no significant change in \( \text{FeAl}_2\text{O}_4 \) (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 \( \text{Al}^{3+} \) content of a spinel is less than twelve, \( \text{Fe}^{3+} \) is assumed to make up the difference.

The content of \( \text{Fe}_2\text{O}_3 \) and \( \text{FeO} \) (weight %) was subsequently determined from the relative proportions of \( \text{Fe}^{2+} \) and \( \text{Fe}^{3+} \). Owing to the presence of \( \text{Fe}^{2+} \) and \( \text{Fe}^{3+} \), the proportion of Fe-bearing end-member spinels will depend on the algorithm used to compute them. I have arbitrarily chosen to place all \( \text{Fe}^{2+} \) in the magnetite end-member unless there is insufficient \( \text{Fe}^{2+} \) to balance \( \text{Fe}^{3+} \). 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 zinian spinel in the Mineral District, Virginia, is homogeneous in composition. However, one zinian spinel from the Sulphur deposit exhibits a compositional variation from core to edge of 3.7 mole % decrease in garnet component, 1.3 mole % increase in hercynite and 2.3 mole % increase in spinel sensu stricto. Zinian spinel in this sample coexists with quartz, biotite, pyrrhotite and chalcopyrite. Zinian spinel from the Davis deposit, Massachusetts, coexists with muscovite, quartz, pyrite, ilmenite, garnet and chalcopyrite and shows a marked decrease in garnite, 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 zinian spinel comes from the Broken Hill deposit, Australia (Anal. 2, Table 1; Fig. 1a). Zinian spinel in the deposit shows an enrichment in garnite and a depletion in hercynite and spinel sensu stricto from the centre to the edge.

### Table 2. Mineral Assemblages Associated with Zoned Zinian Spinel*

| Anal. | Sample No. | Locality          | Assemblage
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>POS-147</td>
<td>Marshall Lake, Ontario</td>
<td>Qts, Spl, Sp, Bt, Crn, Chi(^4), Ccp, Bil(^b)</td>
</tr>
<tr>
<td>2</td>
<td>532-296</td>
<td>Broken Hill, Australia</td>
<td>Qts, Grt, Spl, Bt(^4), St(^4), Chi(^4), Sp</td>
</tr>
<tr>
<td>3</td>
<td>POS-74/1</td>
<td>Inc claim, Northwest Territories</td>
<td>Qts, Mc, Sp, Po, Spl, Ap, Bt, Ccp, Ms(^2), Ep</td>
</tr>
<tr>
<td>4</td>
<td>POS-45</td>
<td>Betty, Colorado</td>
<td>Chl, Mh, Spl, Ath, Qts, Sp, Ccp(^b)</td>
</tr>
<tr>
<td>5</td>
<td>POS-49</td>
<td>Umanmed deposit, Round Mountain</td>
<td>Cal, Chn, Spl, Chl, Fo, Se(^3), Gn, Mag, Ilm(^b), Hem(^b)</td>
</tr>
<tr>
<td>6</td>
<td>POS-97</td>
<td>Nontfjell, Norway</td>
<td>Hbl, Ath, Qts, Spl, Py, Grt, Ged, Sp, Cdr, Rb(^4), Ilm(^b)</td>
</tr>
<tr>
<td>7</td>
<td>R12518</td>
<td>Davis, Massachusetts</td>
<td>Ms, Qts, Spl, Py, Ilm, Grt, Ccp(^b)</td>
</tr>
<tr>
<td>8</td>
<td>24627**</td>
<td>Bossost, Spain</td>
<td>Qts, Spl, Sp, Chi(^b), Sa(^b)</td>
</tr>
<tr>
<td>9</td>
<td>M2714800</td>
<td>Orkjärvi, Finland</td>
<td>Qts, Spl, Gn</td>
</tr>
</tbody>
</table>

*listed in Table 1; \( ^{a} \) 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; Cdp chalcopyrite; Chl chlorite; Chn clinohumite; Cdr cordierite; Crn corundum; Ep epidote; Fo forsterite; Gn galena; Grt garnet; Ged gedrite; Hbl hornblende; Hem hematite; Hu hunsdie; Ilm ilmenite; Mag magnetite; Mc microcline; Ms muscovite; Po pyrrhotite; Py pyrite; Qts quartz; Rb rutile; Sa saiburgerite; Bil silimanite; Sp sphalerite; SpL zinian spinel; St staurolite; \( ^{a} \) Smithsonian Institute Catalogue number; ** Museum of Natural History Catalogue number; \( ^{b} \) Royal Ontario Museum Catalogue number
Most grains of garnet coexisting with zinckian 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 zinckian-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).

Zinckian-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 zinckian 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 zinckian spinel from the Broken Hill deposit (Anal. 2, Table 1).

Zinckian spinel from the Betty deposit, Colorado, and an unnamed deposit near Round Mountain, Colorado, is associated with members of the humite group. Zinckian 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. Zinckian 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 zinckian spinel from the Nonsfjellet deposit, Norway (Anal. 6, Table 1, Fig. 1b). Zinckian 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 zinckian 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 ZINCKIAN SPINEL

In order to evaluate the possible causes of compositional zoning in zinckian spinel, the following factors must be considered: 1) Of the fifty-two spinel localities studied here, only nine contain zinckian spinel that is compositionally zoned. 2) These nine localities are metamorphosed massive-sulfide deposits. However, zoned zinckian spinel has also been reported in other geological environments, including a granite from New Zealand (Iulloch 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 zinckian 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 asym-

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**TABLE 3. COMPOSITIONS OF ZONED GARNET**

<table>
<thead>
<tr>
<th></th>
<th>RD-80-47</th>
<th>PGS-10</th>
<th>PGS-97</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Centre</td>
<td>Edge</td>
<td>Edge</td>
</tr>
<tr>
<td>S离子</td>
<td>3.90</td>
<td>5.92</td>
<td>5.88</td>
</tr>
<tr>
<td>Al</td>
<td>3.91</td>
<td>4.02</td>
<td>3.98</td>
</tr>
<tr>
<td>Fe⁺⁺</td>
<td>0.09</td>
<td>0.00</td>
<td>0.02</td>
</tr>
<tr>
<td>Fe⁺⁺</td>
<td>4.06</td>
<td>4.26</td>
<td>4.00</td>
</tr>
<tr>
<td>Mg</td>
<td>1.25</td>
<td>0.90</td>
<td>0.43</td>
</tr>
<tr>
<td>Ca</td>
<td>0.36</td>
<td>0.53</td>
<td>0.11</td>
</tr>
<tr>
<td>Ch</td>
<td>0.43</td>
<td>0.37</td>
<td>1.58</td>
</tr>
</tbody>
</table>

| 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  | 23.3 | 13.0 | 19.7 | 6.7  | 7.2  |
| Pyrope    | 3.9  | 8.7  | 8.7  | 1.8  | 1.9  | 1.8  | 1.7  |
| 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, Davey, Massachusetts; 2, Broken Hill, Australia; 3, Nonsfjellet; Norway
metrical 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):

\[ \text{[Fe}_2\text{Al}_2\text{Si}_3\text{O}_{12}] \text{ in garnet} + [\text{ZnS}] \text{ in sphalerite} + \frac{5}{2}\text{S}_2 = [\text{ZnAl}_2\text{O}_4] \text{ in spinel} + 3\text{FeS}_2 + 3\text{SiO}_2 + \text{O}_2 \]

(1)

\[ \text{[Fe}_2\text{Al}_2\text{Si}_3\text{O}_{12}] \text{ in garnet} + [\text{ZnS}] \text{ in sphalerite} + \text{S}_2 = [\text{ZnAl}_2\text{O}_4] \text{ in spinel} + 3\text{FeS} + 3\text{SiO}_2 + \text{O}_2 \]

(2)

\[ [\text{ZnS}] \text{ in sphalerite} + [\text{FeS}] \text{ in pyrrhotite} + 2\text{Al}_2\text{SiO}_5 + \text{O}_2 = [\text{ZnAl}_2\text{O}_4] \text{ in spinel} + [\text{FeAl}_2\text{O}_4] \text{ in spinel} + 2\text{SiO}_2 + \text{S}_2 \]

(3)

\[ [\text{ZnS}] \text{ in sphalerite} + [\text{FeS}] \text{ in pyrrhotite} + 2\text{Al}_2\text{O}_3 + \text{O}_2 = [\text{ZnAl}_2\text{O}_4] \text{ in spinel} + [\text{FeAl}_2\text{O}_4] \text{ in spinel} + \text{S}_2 + \text{O}_2 \]

(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 garnetite (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:

\[ \text{FeS} + \frac{1}{2}\text{S}_2 = \text{FeS}_2 \]

(5)

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

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**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 garnetite in the garnetite–hercynite solid solution. The composition of garnetite has arbitrarily been assigned a value \( X_{\text{Alm}} = 0.34 \). 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 garnetite.
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 % ZnAl₂O₄ at 600°C and 2 kbar, 75 mole % ZnAl₂O₄ at 700°C and 2 kbar, and 84 mole % ZnAl₂O₄ 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

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**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 zinccian 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 zinccian 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 zinccian 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 garnet components in zinccian 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 garnet, like that in associated garnet, formed during a prograde metamorphic event.

DISCUSSION

An increase in garnet 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 zinccian spinel. In conformity with earlier suggestions by Dietvorst (1980) and Tulloch (1981), this pattern is attributed to the stabilizing effect of Zn on the garnet–hercynite solid solution at lower temperatures. Theoretical considerations and textural relations suggest that in the case of zinccian 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 zinccian spinel by desulfurization of sphalerite during a period of retrograde metamorphism.

Whereas compositional zoning may be present in zinccian spinel from a variety of environments, this phenomenon is most common, but not ubiquitous, in metamorphosed massive-sulfide deposits. Zinccian 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 zinccian 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 zinccian 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 zinccian 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 zinccian spinel.

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