

Zinc-rich hercynite in high-grade metamorphic rocks: a product of the dehydration of staurolite

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Abstract

Ternary spinels in the system $(\text{Fe,Zn,Mg})\text{Al}_2\text{O}_4$ are apparently relatively common and widespread constituents of some metamorphic rocks in the amphibolite and granulite facies. Two new occurrences, one from granulite facies metapelitic gneiss, and one from cordierite-orthoamphibole (metavolcanic?) rock, illustrate the two major lithologies in which such spinels occur. Compositions of associated phases in both parageneses are consistent with spinel formation as a result of the dehydration of Zn-enriched staurolite.

Introduction

The origin of natural spinels in the series $(\text{Fe,Mg,Zn})\text{Al}_2\text{O}_4$ has commonly been ascribed to high-*T*/low-*P* metamorphism of silica-poor rocks such as emery, impure carbonates, and ultramafics, or to zinc ore bodies or pegmatites enriched in Zn (see, e.g., Rumble, 1976).

However, such spinels also have been reported from two other parageneses: (1) pelitic metasedimentary rocks which have undergone high-grade regional metamorphism (Gable and Sims, 1969, p. 19; Frost, 1973; Wagner and Crawford, 1975) or contact metamorphism (Loomis, 1972; Atkin, 1978); and (2) mafic metavolcanic or metasedimentary rocks rich in cordierite and gedrite (Robinson and Jaffe, 1969; Gable and Sims, 1969, p. 30; James *et al.*, 1978). Although rocks in both parageneses commonly contain quartz, the spinel is not in direct contact with quartz and, at least in some cases, it is restricted to portions of the rock with anomalously high Al/Si (e.g., Robinson and Jaffe, 1969). Nevertheless, some workers consider these spinels to be in equilibrium with quartz (e.g., Wagner and Crawford, 1975). All such spinels reported in the literature (Table 1, analyses 4-8) contain appreciable ZnO, and it appears probable that this stabilized them in the presence of quartz.

New occurrences

Two new occurrences of zincian hercynite are described here. The first is in granulite facies metapelitic gneisses from the northwest Adirondacks, New

York, the second in amphibolite facies cordierite + amphibole rocks from the Old Woman Mountains, southeastern California.

Northwest Adirondacks

Small green translucent crystals of spinel are present in pelitic Grenville paragneiss interlayered with other metasediments and with mafic metavolcanics in the West Parishville synform, about five km northeast of the town of Colton, New York (Stoddard, 1976a). Spinel-bearing rocks contain the assemblage: quartz + plagioclase + perthitic K-feldspar + garnet + biotite + sillimanite + spinel + ilmenite \pm rutile \pm cordierite. The spinel is not in direct contact with quartz; it occurs most commonly in the cores of segregations of coarse prismatic sillimanite with ilmenite \pm rutile. These segregations are surrounded by zones rich in plagioclase and biotite or garnet (Fig. 1). Other specimens contain granoblastic cordierite and spinel. Chemically, the Adirondack spinels are ternary solutions, containing 20 to 30 mole percent each of MgAl_2O_4 and ZnAl_2O_4 , the remainder being FeAl_2O_4 (Table 1, analyses 1, 2).

Old Woman Mountains

Green spinel was also studied in rocks of probable Precambrian age from Sweetwater Wash in the Old Woman Mountains, a north-south trending range located in the eastern Mojave Desert about 60 km southwest of Needles, California. Spinel-bearing rocks occur within a large ($\sim 50 \times 500$ m) block of

Table 1. Chemical analyses of zinc-bearing spinels in metamorphic rocks

	1	2	3	4	5	6	7	8
SiO ₂	0.04	0.05	0.05	0.22	na	0.51	0.29	na
TiO ₂	0.01	0.03	0.08	na	0.02	0.03	0.16	na
Al ₂ O ₃	58.71	56.83	57.46	58.55	56.2	55.10	54.76	60.45
Cr ₂ O ₃	0.18	2.86	na	na	0.02	0.00	na	na
FeO*	20.56	24.23	18.66	33.88	16.6	26.36	36.05	15.70
MgO	5.90	7.44	4.44	1.59	2.36	9.9	2.67	4.59
MnO	0.03	0.03	0.14	0.02	0.02	0.02	0.07	na
ZnO	14.63	9.66	19.78	3.45	24.0	1.25	7.02	21.74
Total	100.06	101.13	100.61	97.72	99.37	93.17	101.02	102.48
Cations per formula unit based on 4 oxygens								
Si	0.001	0.002	0.001	0.007	--	0.015	0.011	--
Ti	0.000	0.001	0.004	--	0.006	0.001	0.003	--
Al	1.967	1.883	1.948	2.012	1.969	1.907	1.851	1.995
Cr	0.004	0.064	--	--	0.000	0.000	--	--
Fe ³⁺	0.028	0.050	0.047	--	0.025	0.077	0.139	0.005
Fe ²⁺	0.461	0.520	0.409	0.826	0.390	0.570	0.737	0.362
Mg	0.250	0.312	0.190	0.069	0.105	0.433	0.110	0.191
Mn	0.001	0.001	0.004	0.001	0.001	0.001	0.003	--
Zn	0.307	0.200	0.420	0.074	0.527	0.028	0.150	0.449

*Total Fe as FeO; Fe³⁺ calculated assuming (Si+Ti+Al+Cr+Fe³⁺) = 2.000.
na: not analyzed

Analyses 1-3 by electron microprobe at U.C.L.A. by the author; analyses 4-8 from other sources.

1. Northwest Adirondacks, assemblage qtz+plag+Kspar+gar+sill+biot+rut+ilm+spl.
2. Northwest Adirondacks, qtz+plag+Kspar+gar+sill+cord+biot+rut+ilm+spl.
3. Old Woman Mountains, cord+gedrite+anthoph+plag+biot+ilm+qtz+staur+spl.
4. Southern Spain, qtz+Kspar+gar+cord+biot+sill+spl+plag (Loomis, 1972).
5. Wyoming, qtz+biot+gar+plag+ilm+spl (Frost, 1973).
6. Colorado, qtz+cord+gedrite+biot+plag+spl+ilm+gar (Gable and Sims, 1969).
7. Co. Donegal, Eire, qtz+plag+biot+gar+sill+fibro+cord+spl+staur+graph+ilm+pyrrhot (Atkin, 1978).
8. Southeastern Pennsylvania, qtz+ky+spl+rut+hem(?) (Wagner and Crawford, 1975; Wagner, personal comm.).

metamorphics engulfed by late Mesozoic granite plutons (Miller, 1977). The spinel (Table 1, analysis 3) is closely associated with calcic plagioclase (An₈₈), staurolite, and in some cases ilmenite and/or corundum. These minerals are included within cordierite porphyroblasts (see Fig. 2). Similar associations without spinel also occur. The mineral assemblage of the host rock is generally cordierite + gedrite + antho-

phyllite + intermediate to calcic plagioclase + biotite + ilmenite ± quartz ± rutile ± staurolite (Stoddard and Miller, 1979). These rocks are virtually identical to some of those described by Robinson and Jaffe (1969) from New Hampshire, and by James *et al.* (1978) from south-central Ontario. They are characterized by an unusually Al-rich mafic bulk composition, possibly the result of low-temperature alteration

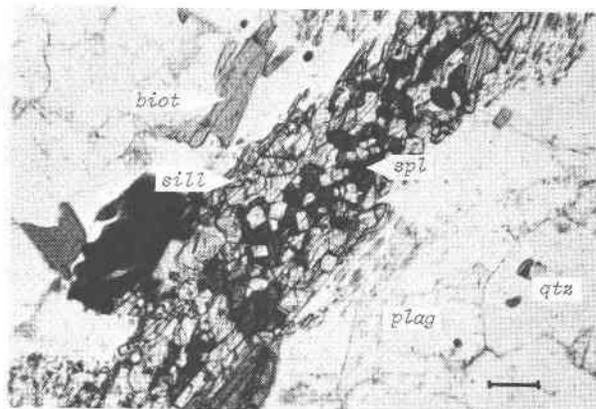


Fig. 1. Sillimanite-spinel segregation in pelitic gneiss, north-west Adirondacks (specimen 1, Table 1); complete assemblage is qtz + plag + Kspar + gar + sill + biot + rut + ilm + spl. Plane polarized light; bar is 0.5 mm in length.

of basalt prior to metamorphism (e.g., Vallance, 1967).

The compositions of all spinels are plotted for comparison in Figure 3.

Host-rock Zn content

The possibility that the formation of the spinels was controlled by unusually high Zn contents of the host rocks was evaluated. Duplicate analyses (XRF) for Zn were run on four metapelites from the north-west Adirondacks, and on three cordierite-amphibole rocks from the Old Woman Mountains. Analyzed specimens from each locality occur interlayered and contain similar mineral assemblages and modes, with the exception that some of the ana-

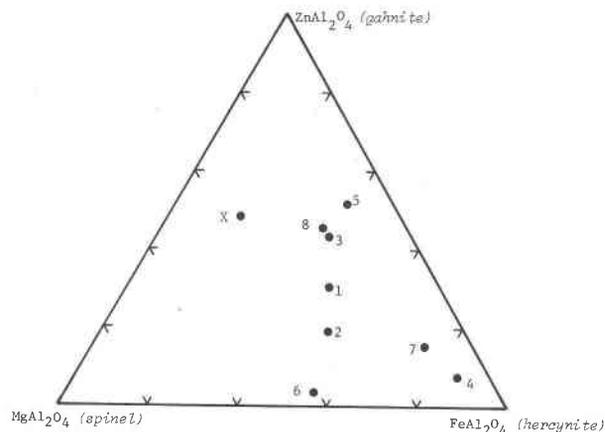


Fig. 3. Ternary plot of metamorphic spinels in the compositional range $(\text{Fe,Zn,Mg})\text{Al}_2\text{O}_4$. Numbers refer to the analyses compiled in Table 1; X was also reported by Wagner and Crawford (1975). These spinels contain less than seven mole percent of all other spinel end-members.

lyzed rocks contain spinel, and the others are spinel-free. Results (Table 2) indicate no systematic relationship between host-rock Zn and occurrence of spinel in these rocks. Furthermore, the Adirondack rocks fall well within the range of Zn contents reported in the literature for rocks and sediments of pelitic composition (50–200 ppm) (e.g., Flanagan, 1973; Turekian and Wedepohl, 1961). In contrast, the California rocks all contain much greater abundances of Zn than unaltered basalt (Flanagan, 1973; Turekian and Wedepohl, 1961); they may have been enriched in the element during low-temperature submarine alteration (Vallance, 1967).

Zn in staurolite

Zinc partitions strongly into staurolite in amphibolite facies metapelites. Residual staurolite progressively concentrates Zn as the mineral reacts somewhat below the sillimanite + K-feldspar isograd (Guidotti, 1970), beyond which high Zn content may cause it to persist (Hollister, 1969; Ashworth, 1975). Albee (1972) reports staurolite in pelitic schist (quartz + kyanite + muscovite + paragonite + staurolite + chloritoid + chlorite + hematite ± garnet) from Vermont with 5.5 weight percent ZnO; Griffen and Ribbe (1973) present analyses of staurolite from North Carolina with nearly 6.9 weight percent ZnO. Sillimanite-zone staurolites (in quartz + muscovite + biotite + oligoclase + sillimanite + staurolite + ilmenite ± garnet ± pyrrhotite schists) from Maine (Guidotti, 1970) are progressively en-

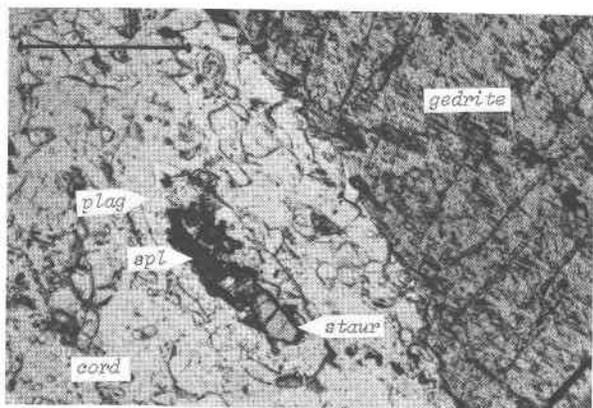


Fig. 2. Spinel and staurolite with calcic plagioclase in cordierite-orthoamphibole rock, Old Woman Mountains, California (specimen 3, Table 1); complete assemblage is cord + gedrite + anthoph + plag + biot + ilm + qtz + staur + spl. Plane polarized light; bar is 0.5 mm in length.

riched in zinc up to 2.7 weight percent ZnO at highest metamorphic grade.

The strong partitioning of Zn into staurolite has been explained by Albee (1972), who noted the tendency of Zn to form sp^3 hybrid bonds, which require a tetrahedrally-coordinated cation site. Furthermore, the ionic radius of Zn^{2+} is very close to that of IV-fold coordinated Fe^{2+} (0.60 and 0.63Å, respectively; Shannon and Prewitt, 1969). Zn^{2+} would therefore be expected to substitute into an $Fe^{2+,IV}$ site. Staurolite tends to concentrate available Zn because it is the only common metamorphic mineral with such a cation site (Griffen and Ribbe, 1973). Zn^{2+} also prefers the tetrahedral sites in the (normal) spinel structure; this has been explained by Burns (1970, p. 110) in terms of crystal field theory.

During metamorphism below the stability region of staurolite, minerals with the appropriate cation site are not present, and so Zn is not partitioned strongly into any particular phase but is highly dispersed. Staurolite then performs the function of collecting and concentrating Zn. As temperature increases and staurolite eventually dehydrates, its Zn would be re-dispersed into other phases, unless another mineral with the $Fe^{2+,IV}$ site were present. In many cases, staurolite may therefore be a direct precursor of Zn-rich hercynite, as has been suggested by Loomis (1972), Stoddard (1976b), and Atkin (1978).

Grenville pelites in southeastern Ontario

Although staurolite is absent from the Adirondack Grenville lowlands, it is common in lower-temperature (amphibolite facies), possibly correlative units of adjacent Ontario (Hounslow and Moore, 1967; T. Rivers, University of Ottawa, written communication, 1976; J. F. Chappell, Carleton University, written communication, 1977), and sillimanite-zone staurolites there are moderately enriched in Zn (0.20–0.40 wt.% ZnO) when compared to those from the staurolite zone (0.00–0.05 wt. %) (analyses by the author). In addition, sillimanite + spinel assemblages have been reported from granulite facies equivalents in Ontario (Wynne-Edwards, 1967).

Thus, although it is not possible to continuously trace Zn-staurolite + sillimanite assemblages into Zn-spinel + sillimanite assemblages in the Adirondacks, the complete transition is apparently present in Ontario, and it seems reasonable to suppose that the Adirondack geotherm also passed through the stability field of staurolite.

Table 2. Zn contents* of host rocks

Specimen	1	2	3	4
Zn(ppm)	122	113	138	136
spinel-bearing?	no	yes	no	yes

Specimen	5	6	7
Zn(ppm)	624	599	1093
spinel-bearing?	yes	no	no

*X-ray fluorescence analyses; estimated analytical accuracy $\pm 20\%$.

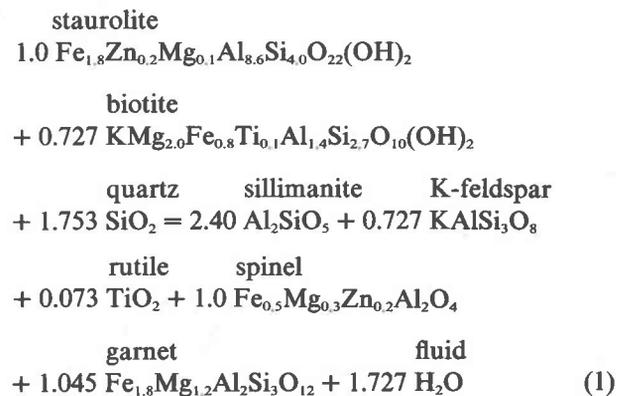
1–4. Northwest Adirondack metapelites.

5–7. Old Woman Mountains cordierite-amphibole rocks.

Postulated mineral equilibria

Virtually all analyzed staurolites have molar Fe/(Fe+Mg) greater than 0.7 (e.g., Griffen and Ribbe, 1973; Guidotti, 1970, 1974). Most of the spinels listed in Table 1 have lower ratios; therefore, if they were produced during staurolite breakdown, a relatively Mg-enriched reactant phase and/or an Fe-enriched product phase must have been involved, along with staurolite, in the spinel-producing reaction. Table 3 lists compositions of phases coexisting with the three spinels reported here.

For the Adirondack specimens, hypothetical Zn-enriched staurolite, together with the phases listed in Table 3 (neglecting minor components), are consistent with staurolite breakdown and spinel formation by a univariant reaction such as



In addition to its agreement with the observed Fe/(Fe+Mg) ratios, reaction (1) is also consistent with

Table 3. Compositions of phases associated with spinel*

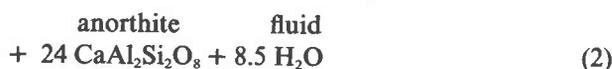
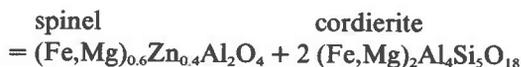
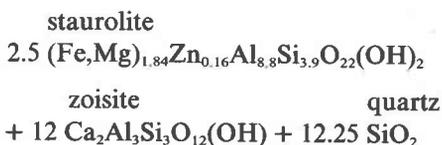
Specimen (from Table 1)	1	1	2	2	2	3	3
phase	garnet	biotite	garnet	biotite	cordierite	staurolite	cordierite
SiO ₂	38.68	36.79	38.47	37.9	48.29	26.92	48.21
TiO ₂		4.39		4.5		0.57	0.02
Al ₂ O ₃	21.86	16.95	22.07	16.2	31.81	52.43	33.92
Cr ₂ O ₃			0.00				
FeO**	28.65	10.07	28.86	13.0	4.80	12.04	5.66
MgO	9.12	16.55	9.67	15.2	10.49	2.64	9.94
MnO	0.47	0.01	0.41		0.02	0.14	0.09
ZnO			0.06		0.01	3.03	0.09
CaO	1.12	0.06	0.97		0.06	0.09	0.12
K ₂ O		10.10		10.1	0.02		0.09
Na ₂ O		0.06		0.02			0.41
anhydrous total	99.91	94.98	100.51	96.9	95.52	98.07	98.56
mol. Fe/(Fe+Mg)	0.636	0.255	0.621	0.325	0.185	0.719	0.242

*electron microprobe analyses by the author

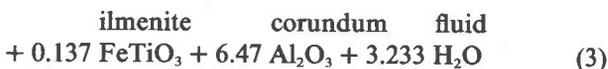
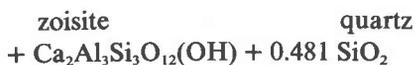
**total Fe as FeO

well-documented prograde dehydration and progressive development of K-feldspar and sillimanite in the pelites of the northwest Adirondack lowlands (Engel and Engel, 1960; Stoddard, 1976a). Where present, cordierite appears to be indifferent to the reaction, and may have formed later.

In the Old Woman Mountains specimen, the situation is more complex. The calcic plagioclase is the only high-calcium phase in the rock, and its presence suggests that it was preceded by a different Ca-rich mineral at lower metamorphic temperatures (perhaps zoisite, which has been reported in association with staurolite, Zn-spinel, cordierite, and orthoamphibole by James *et al.*, 1978). Furthermore, spinel and staurolite have virtually identical Fe/(Fe+Mg), but the other mafic silicates in the rock are more magnesian. However, if the excess mafic components produced by the breakdown of staurolite and the formation of Zn-rich spinel went into solution in cordierite, then one could speculate that the curious enclave may have formed as the result of a reaction such as:



In other cases, corundum [*cf.* reaction (9), Robinson and Jaffe, 1969, p. 418] and ilmenite may have been produced by the breakdown of the relatively Ti-rich staurolite:



Reactions analogous to (2) and (3) involving calcite instead of zoisite can also be written.

Conclusion

Although zinc is generally present in only trace or minor amounts in most rock types, its strong preference for tetrahedral, divalent cation sites causes it to partition very strongly into minerals possessing such sites. In metamorphic rocks, staurolite and (normal) spinel have such sites, and they appear to have acted as sinks for available Zn^{2+} during metamorphic diffusion. Information provided by textures and by mineral assemblages indicates that, in many cases, spinel represents a breakdown product of staurolite, and has been stabilized in silica-rich rocks by its zinc content. Zincian hercynite or spinel may be fairly common in high-grade pelites and aluminous amphibolites during or after the breakdown of staurolite. In some cases, it may have been overlooked because of its small size.

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