

## A GAHNITE-GARNET RETROGRADE REACTION FROM THE PINNACLES DEPOSIT, BROKEN HILL, NEW SOUTH WALES, AUSTRALIA

JOANNA PARR

*Department of Geology, University of Newcastle, Newcastle, New South Wales 2308, Australia*

### ABSTRACT

A retrograde reaction involving the breakdown of the zincian spinel *gahnite* [(Zn,Fe,Mg)Al<sub>2</sub>O<sub>4</sub>] to almandine garnet occurs in samples from the Pinnacles mine, southwest of Broken Hill, New South Wales, Australia. Grains of prograde *gahnite* are rimmed by a retrograde corona of garnet in a quartz matrix. The *gahnite* grains exhibit no compositional zoning, which suggests that homogenization occurred during prograde metamorphism. The retrograde rim of garnet, however, exhibits some compositional zoning away from the *gahnite* - garnet interface and contains trace amounts of Zn. The assemblage was probably created by the formation of garnet from *gahnite* in the presence of solutions enriched in Fe, Mn, Mg, Ca, Na and Si, with the loss of Zn. These observations, together with sillimanite-bearing pelitic assemblages, are consistent with isobaric cooling during retrograde metamorphism.

*Keywords:* zincian spinel, *gahnite*, electron-microprobe data, retrograde metamorphism, Broken Hill, Australia.

### SOMMAIRE

Une réaction rétrograde impliquant la déstabilisation de la *gahnite* [(Zn,Fe,Mg)Al<sub>2</sub>O<sub>4</sub>] pour donner un grenat riche en almandin fait l'objet de cette contribution à la minéralogie de la mine Pinnacles, au sud-ouest de Broken Hill, au New South Wales, en Australie. Les cristaux de *gahnite*, d'origine prograde, ont une couronne de grenat rétrograde dans une matrice de quartz. L'absence de zonation en composition dans la *gahnite* fait penser qu'il y a eu homogénéisation lors d'un épisode de métamorphisme prograde. Les liserés de grenat, par contre, montrent une zonation à partir de l'interface *gahnite* - grenat, et contiennent des traces de zinc. L'assemblage résulterait de la formation du grenat au dépens de la *gahnite* en présence de solutions enrichies en Fe, Mn, Mg, Ca, Na et Si, et capables de mobiliser le Zn. Ces observations, et la présence de sillimanite dans les assemblages pélitiques, concordent avec un modèle de refroidissement isobare pendant le métamorphisme rétrograde.

(Traduit par la Rédaction)

*Mots-clés:* spinelle zincifère, *gahnite*, données à la microsonde électronique, métamorphisme rétrograde, Broken Hill, Australie.

### INTRODUCTION

The spinel *gahnite* represents the zincian end-member of the *gahnite* - hercynite solid-solution series [(Zn,Fe,Mg)Al<sub>2</sub>O<sub>4</sub>]. Although *gahnite* is relatively rare in nature, it has been reported in association with metamorphosed massive sulfide deposits (Plimer 1977, Williams 1983, Sheridan & Raymond 1984, Spry & Scott 1986, Spry 1987a, b). The high Zn content of the spinel, together with its hardness (8) and stability in metamorphic rocks, make it a potential indicator mineral in base-metal exploration programs (Sheridan & Raymond 1984, Spry & Scott 1986). Several theories have been proposed for the formation of *gahnite* in metamorphic rocks. These include the desulfurization of sphalerite (Sangster & Scott 1976), the breakdown of Zn-bearing silicates such as biotite (Dietvorst 1980) and staurolite (Stoddard 1979) during prograde metamorphism, and the metamorphism of opaline silica and hydrothermal clays with adsorbed Zn and zincian carbonate (Plimer 1988).

Quartz - *gahnite* rock is the most common *gahnite*-bearing lithology in the Willyama Supergroup, New South Wales; other rock types include psammitic to pelitic metasediments and quartz - feldspar - biotite - garnet - *gahnite* gneisses (Barnes *et al.* 1983). *Gahnite* is commonly observed as a gangue mineral in the base-metal ores of the Broken Hill deposit, within the Willyama Supergroup (*e.g.*, Segnit 1961, Richards 1966, Plimer 1976, 1977, Spry 1978, 1984, 1987a, Barnes *et al.* 1983). In the main Broken Hill lode, there are at least two distinct *gahnite*-bearing assemblages: quartz - *gahnite* - pyrrhotite - galena - garnet - biotite ( $\pm$  staurolite, muscovite, ilmenite, sphalerite) and garnet - biotite - chlorite - sphalerite - *gahnite* - galena - pyrrhotite - quartz ( $\pm$  ilmenite); muscovite, chlorite and staurolite are retrograde minerals (Spry 1978). This contribution documents one particularly unusual occurrence of *gahnite* from the Pinnacles Mine Sequence, New South Wales, in which retrograde reactions in sulfur-poor quartz - garnet - *gahnite* - biotite pelites (sillimanite-deficient) have produced a garnet rim on grains of *gahnite*. The association of retrograde garnet and prograde *gahnite* in sillimanite- and

sphalerite-deficient rocks has not been described previously and allows some speculation on metamorphic conditions in the Broken Hill area.

#### GEOLOGICAL SETTING

The Pb–Zn Pinnacles mine lies 15 km southwest of Broken Hill, western New South Wales (Fig. 1), in the Proterozoic Willyama Supergroup. The mine is the largest “Broken Hill”-type deposit in the Broken Hill Block, after Broken Hill itself: approximately 200,000 tonnes of ore have been extracted, with average grades of 10% Pb, 420 g/t Ag and 2.5% Zn in the main lead lode, and 3.5% Pb, 100 g/t Ag and 7.5–11.5% Zn, in the smaller Zn lodes. Remaining ore-reserves are estimated at 200,000 to 600,000 tonnes (Department of Mineral Resources 1981). The deposit consists of a series of highly deformed stratabound sulfide lenses hosted in pelitic schists. Stratigraphically, it lies approximately 700 m below the main Broken Hill

deposit, in the Cues Formation of the early Proterozoic Willyama Supergroup (Willis *et al.* 1983).

The Willyama Supergroup has undergone two events of high-grade metamorphism and deformation, followed by at least one later retrograde event (Rutland & Etheridge 1975, Glen *et al.* 1977, Laing *et al.* 1978, Corbett & Phillips 1981, Stevens *et al.* 1988). Prograde regional metamorphism in the Willyama Supergroup increases from andalusite grade in the northeast, through sillimanite – muscovite and sillimanite – K-feldspar zones, to two-pyroxene grade in the southwest (Phillips 1978, 1980) (Fig. 1). The Pinnacles deposit lies in the two-pyroxene zone and is characterized by high-temperature, low- to intermediate-pressure mineral assemblages. Retrograde metamorphism is most strongly developed within, but not confined to, zones of retrograde schists that transect the Willyama Supergroup (Stevens 1986). There is a transition from lower-grade chloritoid-bearing assemblages in the central and northern regions, to staurolite-bearing assemblages in the central and southern regions, and zones of kyanite-bearing retrograde schist in the south (Corbett & Phillips 1981). In the Pinnacles area, the geology is dominated by the kyanite – staurolite-bearing Thackaringa–Pinnacles Retrograde Shear Zone to the south of the deposit (Stevens 1986). The deposit itself also is cross-cut by several retrograde shear zones.

#### ANALYTICAL PROCEDURE

The chemical compositions of 35 gahnite and approximately 250 garnet crystals were determined using a JEOL JSM840 scanning electron microscope fitted with a TRACOR TN5500 energy-dispersion spectroscopy EDS system. An accelerating potential of 15 kV and an emission current of 2 nA were used. The spectra were analyzed using the following standards: wollastonite (Si, Ca), corundum (Al), hematite (Fe), rutile (Ti), rhodonite (Mn), periclase (Mg), anorthoclase (Na, K), willemite (Zn),  $V_2O_5$  (V) and chromite (Cr). Representative compositions are given in Tables 1 and 2.

#### PETROGRAPHY AND MINERAL CHEMISTRY

Within the Pinnacles Mine Sequence, gahnite-bearing pelites are associated with the wallrocks to both the galena-rich and sphalerite-rich orebodies. The pelites form stratiform units with distinct compositional layering, interpreted as primary bedding ( $S_{0,1}$ ) and defined by relative abundances of garnet, gahnite, quartz and feldspar. Two foliations ( $S_2$  and  $S_3$ ) can be defined by the alignment of sillimanite and retrograde muscovite

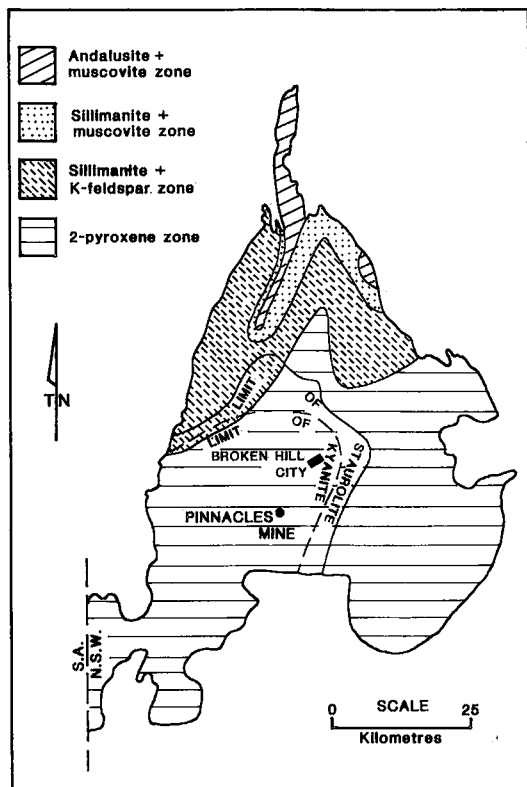


FIG. 1. Outline of the Broken Hill Block showing prograde metamorphic zones (after Phillips 1978), retrograde metamorphic zones and location of the Pinnacles mine; modified after Stevens (1986).

TABLE 1. REPRESENTATIVE CHEMICAL COMPOSITIONS OF GAHNITE

Sample	Gh3	Gh4	Gh14	Gh16	Gh17	Gh18	Gh31	Gh32	Gh33			Gh1		
									center	edge	edge	center	edge	
wt%														
SiO <sub>2</sub>	0.00	0.00	0.00	0.17	0.18	0.00	0.18	0.35	0.25	0.22	0.00	0.00	0.12	0.00
TiO <sub>2</sub>	0.00	0.00	0.00	0.15	0.00	0.00	0.00	0.00	0.14	0.00	0.00	0.00	0.00	0.00
Al <sub>2</sub> O <sub>3</sub>	54.70	55.02	56.30	54.96	56.06	55.34	56.22	56.67	56.54	56.94	55.45	55.48	55.09	55.20
Cr <sub>2</sub> O <sub>3</sub>	0.00	0.00	0.58	1.17	0.00	0.00	0.15	0.00	0.00	0.00	0.00	0.00	0.00	0.00
FeO*	10.89	12.55	9.82	10.22	13.84	11.86	13.58	13.70	14.05	14.06	13.67	13.60	14.01	14.11
MnO	0.00	0.20	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MgO	0.00	0.31	0.64	0.84	1.12	0.29	0.91	0.66	0.64	0.48	0.29	0.44	0.16	0.27
ZnO	33.08	31.28	33.57	32.40	28.62	31.07	28.83	29.52	28.88	28.88	29.51	29.63	29.68	29.45
TOTAL	98.83	99.36	100.93	99.91	99.82	98.86	100.06	100.89	100.70	100.75	98.92	99.28	99.05	99.20
Cation proportions (based on 4 oxygen atoms)														
Si	0.00	0.00	0.00	0.01	0.01	0.00	0.01	0.01	0.01	0.01	0.00	0.00	0.00	0.00
Ti	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	1.98	1.97	1.98	1.95	1.97	1.99	1.98	1.98	1.98	1.99	1.99	1.98	1.98	1.98
Cr	0.00	0.00	0.01	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe <sup>2+</sup>	0.28	0.32	0.24	0.26	0.35	0.30	0.34	0.34	0.35	0.35	0.35	0.34	0.36	0.36
Mn	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mg	0.00	0.01	0.03	0.04	0.05	0.01	0.04	0.03	0.03	0.02	0.01	0.02	0.01	0.01
Zn	0.75	0.70	0.74	0.72	0.63	0.70	0.63	0.65	0.63	0.63	0.66	0.66	0.67	0.66

\* Total Fe as FeO

TABLE 2. REPRESENTATIVE CHEMICAL COMPOSITIONS OF GARNET

Sample	Gt139	Gt142	Gt203	Gt204		Gt201			Gt202					
				(gahnite)	(quartz)	(core)	(edge)	(core)	(edge)					
wt%														
SiO <sub>2</sub>	35.76	35.74	36.06	35.76	35.88	35.86	36.41	36.10	36.32	35.99	36.24	36.37	35.91	35.86
TiO <sub>2</sub>	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 <sub>2</sub> O <sub>3</sub>	20.04	20.37	21.11	20.97	21.02	20.81	21.27	20.57	21.16	20.66	21.06	20.88	21.00	20.68
FeO	37.11	36.66	36.10	37.03	36.87	35.83	36.16	36.28	36.60	36.72	36.84	36.22	36.15	35.57
MnO	3.74	3.48	4.10	3.28	3.36	3.54	3.19	3.03	3.02	3.30	3.02	3.09	3.06	2.97
MgO	1.07	1.17	1.37	1.32	1.23	1.34	1.66	1.65	1.65	1.61	1.66	1.59	1.71	1.53
CaO	1.28	1.28	1.36	1.39	1.36	1.25	1.29	1.41	1.40	1.45	1.29	1.24	1.41	1.31
NaO	0.00	0.00	0.18	0.31	0.28	0.00	0.00	0.00	0.38	0.00	0.17	0.00	0.21	0.27
ZnO	0.00	0.66	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TOTAL	99.00	99.37*	100.27	100.06	100.00	98.64	99.59	99.22	100.53	99.72	100.28	99.38	99.45	98.20
Cations proportions (based on 12 oxygen atoms)														
Si	2.98	2.96	2.95	2.94	2.95	2.97	2.97	2.95	2.96	2.96	2.98	2.95	2.98	2.98
Ti	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	1.97	1.99	2.03	2.03	2.03	2.03	2.04	2.00	2.03	2.00	2.02	2.02	2.03	2.02
Fe	2.58	2.54	2.47	2.54	2.53	2.48	2.46	2.50	2.49	2.52	2.51	2.49	2.48	2.47
Mn	0.26	0.24	0.28	0.23	0.23	0.25	0.22	0.21	0.21	0.23	0.21	0.22	0.21	0.21
Mg	0.13	0.15	0.17	0.16	0.15	0.17	0.20	0.20	0.20	0.20	0.20	0.19	0.21	0.19
Ca	0.11	0.11	0.12	0.12	0.12	0.11	0.11	0.12	0.12	0.13	0.11	0.11	0.12	0.12
Na	0.00	0.00	0.02	0.05	0.04	0.00	0.00	0.00	0.06	0.00	0.03	0.00	0.10	0.04
Zn	0.00	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

replacing prograde sillimanite in both S<sub>2</sub> and S<sub>3</sub> (Fig. 2a).

The pelites comprise quartz, garnet, biotite, K-feldspar and gahnite, with varying amounts of sillimanite, calcite, apatite, rutile, magnetite, tourmaline and zircon, and retrograde muscovite and staurolite. Sulfides present in these wallrocks include sphalerite, galena, pyrrhotite, pyrite and arsenopyrite. The gahnite occurs as dark green crystals less than 0.5 mm in diameter. It seems to be unaltered and commonly occurs as subhedral

crystals with an inclusion-rich core (Fig. 2b), similar to that in grains of prograde garnet in the pelites. The inclusions commonly consist of quartz, but also include subhedral biotite, rutile and sphalerite. The rim is generally inclusion-free, although commonly a crystal's margin has been partially corroded and removed, leaving only the inclusion-rich core. The gahnite generally has retrograded to white mica (*cf.* Corbett & Phillips 1981), a reaction that is particularly prevalent in sulfide-bearing assemblages. A common association is a gahnite

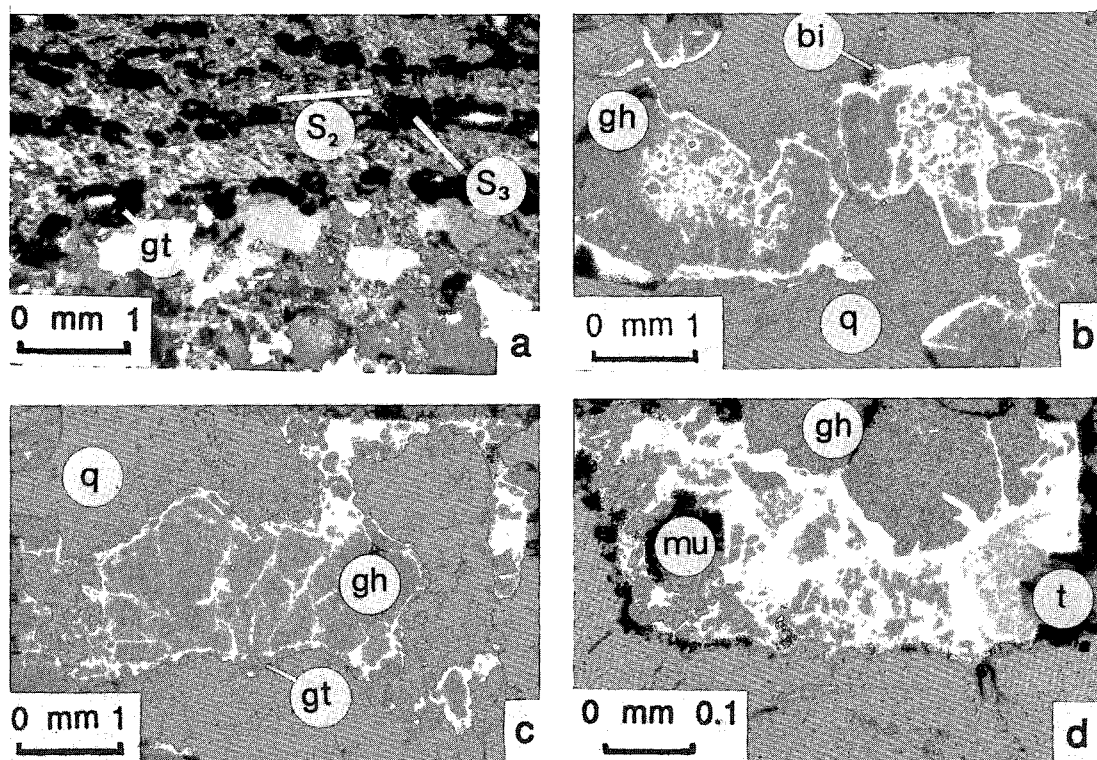


FIG. 2. (a) Photomicrograph showing the pre- $S_2$  nature of garnet crystallization. Isotropic crystals of garnet (gt) are aligned in  $S_1$  and partially resorbed along subparallel  $S_2$  foliation ( $S_2$ ). Sillimanite is retrograded to muscovite, which is aligned parallel to the  $S_3$  fabric ( $S_3$ ). (b) Photomicrograph of prograde gahnite crystals (gh), each with a core rich in quartz inclusions. Crystals have embayed contacts with matrix quartz (q) and are partially rimmed by biotite crystals (bi) aligned in  $S_2$ . (c) Photomicrograph of prograde gahnite crystals (gh) with retrograde garnet (gt) corona in subequigranular quartz (q). Note the sharp contact between the mineral phases. (d) Photomicrograph of tourmaline crystal (t) within a retrograde muscovite rim (mu) to a gahnite crystal (gh). Tourmaline also is a minor component in muscovite-free gahnite-garnet-quartz assemblages.

core with a muscovite rim in a sphalerite host. The muscovite is fine grained, mostly aligned in  $S_1$ , but is also observed as a cross-cutting, axial planar,  $S_2$  fabric.

Less micaceous, sulfur-poor pelites make up a minor, but important, component of the mine sequence and are the subject of this study. They are dominated by the assemblage quartz - garnet - gahnite, with minor biotite and apatite. Retrograde reactions observed in these sulfur-poor pelites include the formation of a garnet corona around gahnite crystals (Fig. 2c), a garnet (inclusion-free) corona around garnet (inclusion-rich) grains, and the minor breakdown of garnet to biotite. A garnet corona separates most examples of gahnite in this rock from the quartz matrix. The coronas are 30 to 150  $\mu\text{m}$  thick, form a complete boundary between quartz and gahnite, and contain

few inclusions. The boundary between the two phases is sharp and without intermediate phase or symplectitic intergrowth; this is confirmed by back-scattered imagery and electron-microprobe analyses (see below). Tourmaline (<1% by volume) is present in some garnet coronas and also is associated with a muscovite rim on gahnite crystals elsewhere in the sequence (Fig. 2d). The role of these small, subhedral tourmaline crystals is unclear, but they may indicate boron enrichment in the late-stage fluids that induced retrogression. Recently, Slack & Robinson (1990) reported the breakdown of tourmaline during retrograde metamorphism in tourmaline - quartz - garnet - biotite - sillimanite - ilmenite (minor gahnite, plagioclase and apatite) assemblages at Broken Hill; this may also be the case in pelites from the Pinnacles Mine Sequence.

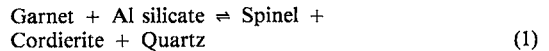
The gahnite crystals have a significant hercynite component (up to 13.7% FeO) but have low Mg content and are virtually Mn-free (Table 1). The average composition is  $(Zn_{0.68}Fe_{0.30}Mg_{0.02})Al_{1.98}O_4$ , which is consistent with other compositions of gahnite from pelitic metasediments (*cf.* Spry & Scott 1986). Some gahnite also contains high trace amounts of Cr (up to 1.17%  $Cr_2O_3$ ), indicating a minor chromite component in the gahnite. There is no systematic chemical zoning across the gahnite crystals (Table 1: Gh 33, Gh 1), indicating that any primary growth-zoning, if present, was removed by homogenization during prograde metamorphism, a state that remained unchanged during the later retrograde event. The lack of zoning is also observed in garnet in pelites elsewhere in the mine succession and is reported for garnet from the Broken Hill deposit (Spry & Wonder 1989).

The garnet coronas on gahnite grains consist of Fe-rich almandine (Table 2) with an average composition  $(Fe_{2.57}Mn_{0.24}Mg_{0.14}Ca_{0.13}Na_{0.02})Al_2Si_3O_{12}$ . Garnet elsewhere in the same pelites, in inclusion-rich cores and as an inclusion-free rim (retrograde?) on garnet cores, have a similar composition [average:  $(Fe_{2.51}Mn_{0.21}Mg_{0.12}Ca_{0.19}Na_{0.01})Al_2Si_3O_{12}$ ]. Compositional profiles across

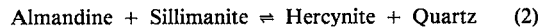
typical garnet coronas show some small-scale and consistent zoning involving Fe, Mn, Ca and Mg (variations < 2%; Fig. 3). Relative depletions of Fe and Mn occur at the garnet - gahnite interface and at the outer margin of the garnet corona where, conversely, there is enrichment in Mg and Ca. Variations are not large and suggest either that partial metamorphic homogenization of these coronas occurred, or that changes in chemical composition during crystallization were only minor. The garnet coronas also contain trace amounts of Zn (up to 0.66% ZnO; Table 2), suggesting that Zn from the gahnite partially substituted for Fe and Mn during retrogression.

## DISCUSSION

P-T fields of stability for hercynite, the ferroan spinel end-member, have been calculated according to the prograde reactions:



(Loomis 1976) and:



(Wall & England 1979). The equilibria indicate that hercynite - quartz is a high-temperature (>750°C), medium- to high-pressure (2-8 kbar) assemblage, characteristic of granulite-facies terranes (Bohlen *et al.* 1986). The presence of Zn in the crystal structure is considered to increase the field of stability of the spinel into the amphibolite-facies domain (Frost 1973, Dietvorst 1980, Montel *et al.* 1986).

The mineral assemblage observed (quartz - garnet - gahnite with minor biotite) is simple, which suggests either 1) completion of the metamorphic reactions above with the removal of cordierite or sillimanite (or both), or 2) a different reaction that does not involve an aluminosilicate. Cordierite is not observed in other garnet-bearing pelites at the Pinnacles mine; Mg-bearing pyroxene, also a metamorphic product in the sillimanite - spinel - cordierite - garnet - orthopyroxene system (with excess quartz) for pelitic rocks (Vielzeuf 1983), is rare in these rocks, suggesting that neither of these two phases were present prior to the occurrence of these reactions. Sillimanite, on the other hand, is a common constituent in many pelites within the mine sequence, although it is nearly always retrograded to muscovite, which is consistent with hydration during retrograde metamorphism (Corbett & Phillips 1981). It is possible, therefore, that the observed texture of garnet corona around gahnite crystal in a quartz matrix, with only minor biotite and apatite, represents the incomplete

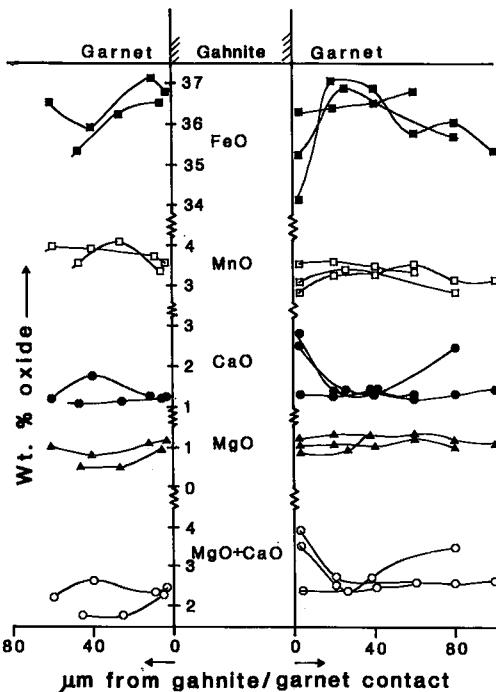


FIG. 3. Compositional profiles of garnet coronas surrounding prograde gahnite, including that shown in Fig. 2c.

prograde reaction of Wall & England (1979) (reaction 2) after the removal of sillimanite. However, evidence such as the sharp contacts between corona and core, the lack of muscovite in this rock, the minor occurrence of retrograde biotite associated only with prograde garnet, and the similar chemistries of garnet coronas to both gahnite and garnet crystals, indicates that this reaction is a retrograde one that induced the formation of garnet during the breakdown of gahnite.

The formation of garnet as a product of the breakdown of hercynite during retrograde metamorphism is predicted (*e.g.*, Vielzeuf 1983) but not widely documented in the literature. Muscovite is the more commonly observed product of retrograde metamorphism in gahnite-bearing pelites; it is observed elsewhere in the mine sequence and is widely reported for the Willyama Supergroup (*e.g.*, Barnes *et al.* 1983). In many of the gahnite-bearing, garnet-rich pelitic assemblages of the Pinnacles Mine Sequence, garnet crystals are subhedral, with an inclusion-rich core and an inclusion-free corona, similar to the gahnite crystals described above. In these rocks, both garnet coronas and garnet cores are partially resorbed along the  $S_2$  foliation, which suggests a pre- $S_2$  crystallization. Both cores and rims have the same almandine chemistry (Table 2) as do the garnet coronas to the gahnite crystals described above, which suggests that garnet grains and garnet coronas formed in close succession and, therefore, both represent metamorphic events during  $S_2$ .

The lack of muscovite and sillimanite in association with the quartz - garnet - gahnite (minor biotite and apatite) assemblage described here could be interpreted as a result of a gahnite - garnet reaction, representing destabilization during retrograde metamorphism of a quartz - gahnite assemblage in an anhydrous environment. A retrograde reaction in an anhydrous environment would, however, be unusual, especially as evidence for fluid migration is common elsewhere in the sequence (*e.g.*, in late-stage shear zones). Alternatively, the assemblage may represent a reaction in the absence of significant amounts of Al. The reaction involving the observed phases must include the addition of Fe with minor amounts of Mn, Mg, Ca and Na, and the removal of Zn. Therefore, the retrograde metamorphism took place in the presence of Fe- and Si-rich fluids that contained minor concentrations of Mn, Mg, Ca, and Na, but involved the removal of Zn away from the immediate assemblage. Possible "sinks" for the mobile Zn include staurolite, biotite and sphalerite. Stoddard (1979) observed the prograde formation of gahnite from staurolite in granulite-facies metapelites and amphibolite-facies cordierite -

amphibole rocks from North America; in the Pinnacles Mine Sequence, the reverse appears to be true. Staurolite is observed in several specimens of pelitic schists, but not in those exhibiting the gahnite - garnet reaction. The staurolite is Zn-enriched (up to 4.2 wt.% ZnO) and forms pseudomorphs of gahnite crystals; therefore, staurolite probably formed by the retrograde breakdown of prograde gahnite. Biotite is a common retrograde product of the Fe-rich spinel hercynite in hydrous conditions (Montel *et al.* 1986). In the Pinnacles Mine Sequence, retrograde biotite contains only trace amounts of Zn (0.6 wt.% ZnO detected in one microprobe analysis), suggesting that Zn was not preferentially hosted in this mica. Sphalerite, however, is common in rocks of the mine sequence, although not in the immediate vicinity of the retrograde textures described here. Consequently, the Zn seems to have been transported by hydrothermal fluids associated with retrograde metamorphism and was deposited in sulfur-rich reducing environments as sphalerite. Kyanite- and staurolite-bearing late-stage shear zones in the Pinnacles area (the Thackaringa-Pinnacles Shear Zone; Stevens 1986) indicate that high-pressure conditions were maintained during the late-stage metamorphic event that caused the formation of a garnet rim on gahnite grains as described in this paper. The reaction of Wall & England (1979) (reaction 2), which has a steep positive gradient on a P-T diagram (Bohlen *et al.* 1986), also is observed in the micaceous schists within the mine sequence. The transition from gahnite to garnet in the absence of sillimanite is thermodynamically unconstrained, but it seems to represent conditions in which temperature decreased more rapidly than pressure (*cf.* petrogenetic grids for sillimanite-bearing rocks of Bohlen *et al.* 1986 and Montel *et al.* 1986). All these factors support an isobaric retrograde event. Such an interpretation is consistent with regional P-T calculations that suggest an anticlockwise P-T-t path with final isobaric cooling (Corbett & Phillips 1981, Phillips & Wall 1981).

#### ACKNOWLEDGEMENTS

This work forms part of an ongoing research project at the Pinnacles mine supported by the N.E.R.C. (UK). I thank Messrs E. and C. Williams of the Pinnacles mine for their help, D. Phelan at the University of Newcastle (NSW) for help with the electron-microprobe analyses, and W. Crebert for drafting the diagrams. The manuscript has benefited from discussion with I.R. Plimer and R. Offler, and comments from P.G. Spry and J.M. Montel.

## REFERENCES

- BARNES, R.G., STEVENS, B.P.J., STROUD, W.J., BROWN, R.E., WILLIS, I.L. & BRADLEY, G.M. (1983): Zinc, manganese and iron-rich rocks and various minor rock types. *Geol. Surv. New South Wales Records* 21, 289-323.
- BOHLEN, S.R., DOLLASE, W.A. & WALL, V.J. (1986): Calibration and application of spinel equilibria in the system FeO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>. *J. Petrol.* 27, 1143-1156.
- CORBETT, G.J. & PHILLIPS, G.N. (1981): Regional retrograde metamorphism of a high grade terrain: the Willyama Complex, Broken Hill, Australia. *Lithos* 14, 59-73.
- DEPARTMENT OF MINERAL RESOURCES (1981): *Mining and Exploration at Broken Hill - a Review*. New South Wales Department of Mineral Resources, Sydney, Australia.
- DIETVORST, E.J.L. (1980): Biotite breakdown and the formation of gahnite in metapelitic rocks from Kemiö, southwest Finland. *Contrib. Mineral. Petrol.* 75, 327-337.
- FROST, B.R. (1973): Ferroan gahnite from quartz-biotite-almandine schist, Wind River Mountains, Wyoming. *Am. Mineral.* 58, 831-834.
- GLEN, R.A., LAING, W.P., PARKER, A.J. & RUTLAND, R.W.R. (1977): Tectonic relationships between the Proterozoic Gawler and Willyama Orogenic domains, Australia. *J. Geol. Soc. Aust.* 24, 125-150.
- LAING, W.P., MARJORIBANKS, R.W. & RUTLAND, R.W.R. (1978): Structure of the Broken Hill mine area and its significance for the genesis of the orebodies. *Econ. Geol.* 73, 1112-1136.
- LOOMIS, T.P. (1976): Irreversible reactions in high-grade metapelitic rocks. *J. Petrol.* 17, 559-588.
- MONTEL, J.-M., WEBER, C. & PICHAVANT, M. (1986): Biotite-sillimanite-spinel assemblages in high-grade metamorphic rocks: occurrences, chemographic analysis and thermobarometric interest. *Bull. Minéral.* 109, 555-573.
- PHILLIPS, G.N. (1978): *Metamorphism and Geochemistry of the Willyama Complex, Broken Hill*. Ph.D. thesis, Monash Univ., Melbourne, Australia.
- \_\_\_\_\_ (1980): Water activity changes across an amphibolite-granulite facies transition, Broken Hill, Australia. *Contrib. Mineral. Petrol.* 75, 377-386.
- \_\_\_\_\_ & WALL, V.J. (1981): Evaluation of prograde regional metamorphic conditions: their implications for the heat source and water activity during metamorphism in the Willyama Complex, Broken Hill, Australia. *Bull. Minéral.* 104, 801-810.
- PLIMER, I.R. (1976): Zinc spinel from Broken Hill, NSW. *Aust. Mineral.* 5, 17-18.
- \_\_\_\_\_ (1977): The mineralogy of the high grade metamorphic rocks enclosing the Broken Hill orebodies, Australia. *Neues Jahrb. Mineral. Abh.* 131, 115-139.
- \_\_\_\_\_ (1988): Broken Hill, Australia and Bergslagen, Sweden - why God and Mammon bless the Antipodes! *Geol. Mijnbouw* 67, 265-278.
- RICHARDS, S.M. (1966): The banded iron formations at Broken Hill, Australia, and their relationship to the lead-zinc orebodies. I. *Econ. Geol.* 61, 72-96.
- RUTLAND, R.W.R. & ETHERIDGE, M.A. (1975): Two high grade schistositys at Broken Hill and their relation to major and minor structures. *J. Geol. Soc. Aust.* 22, 259-274.
- SANGSTER, D.F. & SCOTT, S.D. (1976): Precambrian, stratabound, massive Cu-Zn-Pb sulfide ores of North America. In *Handbook of Stratabound and Stratiform Ore Deposits* 6 (K.N. Wolf, ed.). Elsevier, Amsterdam (129-222).
- SEGNIT, E.R. (1961): Petrology of the zinc lode, New Broken Hill Consolidated Ltd., Broken Hill, New South Wales. *Austral. Inst. Min. Metall. Proc.* 199, 87-112.
- SHERIDAN, D.M. & RAYMOND, W.H. (1984): Preliminary data on some Precambrian deposits of zinc-copper-lead sulfides and zinc spinel (gahnite) in Colorado. *U.S. Geol. Surv., Open-File Rep.* 77-607.
- SLACK, J.F. & ROBINSON, G.R., JR. (1990): Retrograde metamorphic breakdown of tourmaline at Broken Hill, Australia. *Geol. Soc. Am., Abstr. Programs* 22, A126.
- SPRY, P.G. (1978): *The Geochemistry of Garnet-Rich Lithologies Associated with the Broken Hill Orebody, N.S.W., Australia*. M.Sc. thesis, Univ. Adelaide, Adelaide, Australia.
- \_\_\_\_\_ (1984): *The Synthesis, Stability, Origin and Exploration Significance of Zincian Spinel*. Ph.D. thesis, Univ. Toronto, Toronto, Ontario.
- \_\_\_\_\_ (1987a): Compositional zoning in zincian spinel. *Can. Mineral.* 25, 97-104.
- \_\_\_\_\_ (1987b): The chemistry and origin of zincian spinel associated with the Aggeney's Cu-Pb-Zn-Ag deposits, Namaqualand, South Africa. *Miner. Deposita* 22, 262-268.

- \_\_\_\_ & SCOTT, S.D. (1986): The stability of zincian spinels in sulfide systems and their potential as exploration guides for metamorphosed massive sulfide deposits. *Econ. Geol.* **81**, 1446-1463.
- \_\_\_\_ & WONDER, J.D. (1989): Manganese-rich garnet rocks associated with the Broken Hill lead-zinc-silver deposit, New South Wales, Australia. *Can. Mineral.* **27**, 275-292.
- STEVENS, B.P.J. (1986): Post-depositional history of the Willyama Supergroup in the Broken Hill Block, NSW. *Aust. J. Earth Sci.* **33**, 73-98.
- \_\_\_\_, BARNES, R.G., BROWN, R.E., STROUD, W.J. & WILLIS, I.L. (1988): The Willyama Supergroup in the Broken Hill and Euriovie Blocks, New South Wales. *Precamb. Res.* **40/41**, 297-327.
- STODDARD, E.F. (1979): Zinc-rich hercynite in high-grade metamorphic rocks: a product of the dehydration of staurolite. *Am. Mineral.* **64**, 736-741.
- VIELZEUF, D. (1983): The spinel and quartz associations in high grade xenoliths from Tallante (S.E. Spain) and their potential use in geothermometry and barometry. *Contrib. Mineral. Petrol.* **82**, 301-311.
- WALL, V.J. & ENGLAND, R.N. (1979): Zn-Fe spinel - silicate - sulphide reactions as sensors of metamorphic intensive variables and processes. *Geol. Soc. Am., Abstr. Programs* **11**, 534.
- WILLIAMS, P.J. (1983): The mineralogy and metamorphism of some gahnite-bearing silicate inclusions in massive sulphides from Fornas, north-west Spain. *Mineral. Mag.* **47**, 233-235.
- WILLIS, I.L., BROWN, R.E., STROUD, W.J. & STEVENS, B.P.J. (1983): The Early Proterozoic Willyama Supergroup: stratigraphic subdivision and interpretation of high to low-grade metamorphic rocks in the Broken Hill Block, New South Wales. *J. Geol. Soc. Aust.* **30**, 195-224.

Received November 20, 1990, revised manuscript accepted May 22, 1991.