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A SIMS INVESTIGATION OF *REE* CHEMISTRY OF GARNET IN GARNETITE ASSOCIATED WITH THE BROKEN HILL Pb–Zn–Ag OREBODIES, AUSTRALIA

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ABSTRACT

The concentration of the rare-earth elements (*REE*) in metamorphic garnet from garnetite associated with the Broken Hill (Australia) Pb–Zn–Ag orebodies was determined by secondary ion mass spectrometry (SIMS). *REE* signatures for whole-rock samples of garnetite are enriched in *LREE* relative to chondrites, and the samples have a high *LREE/HREE* ratio. Individual grains of garnet have very low *LREE/HREE* values. The *HREE* are contained in the garnet, whereas the *LREE* are contained in an exotic intergranular material consisting of an amorphous phase, chlorite, chlorides, and a titanium-rich phase. Samples of Ca-rich garnet are enriched in *LREE* relative to Ca-poor garnet. Samples of garnet taken adjacent to the Pb–Zn–Ag orebodies have a positive Eu anomaly. Samples of garnet located several kilometers from the mineralized area have a negative Eu anomaly. The rim of garnet grains is slightly enriched in *HREE* relative to the core. The *REE* signatures of the garnet seem to reflect a protolithic origin, *i.e.*, enrichment before the appearance of garnet as a result of metamorphism, rather than during post-garnet-growth hydrothermal alteration.

Keywords: secondary ion mass spectrometry, garnet, rare-earth elements, crystal-chemical control, Broken Hill, Australia.

SOMMAIRE

La teneur en terres rares du grenat métamorphique provenant de garnetite associée au gisement à Pb–Zn–Ag de Broken Hill, en Australie, a été déterminée par spectrométrie de masse des ions secondaires. Les roches totales font preuve d'un enrichissement en terres rares légères par rapport aux chondrites, et d'un rapport élevé des concentrations de terres rares légères à celles des terres rares lourdes. Par contre, les grains individuels de grenat montrent un faible rapport des concentrations des terres rares légères à celles des terres rares lourdes. Les terres rares lourdes sont incorporées dans la structure du grenat, tandis que les terres rares légères sont présentes sous forme de matériau intergranulaire exotique contenant une phase amorphe, chlorite, chlorures et une phase titanifère. Le grenat plus calcique est enrichi en terres rares légères par rapport aux terres rares lourdes. Le grenat situé près des gisements possède une anomalie positive en Eu. Le grenat prélevé à plusieurs kilomètres de la zone minéralisée possède une anomalie négative en Eu. La bordure des grains est légèrement enrichie en terres rares lourdes par rapport au coeur. Le schéma d'enrichissement relatif des terres rares semble résulter des caractéristiques du protolithe avant les réactions métamorphiques responsables de la production du grenat, plutôt que d'une altération hydrothermale postérieure à la croissance du grenat.

Mots-clés: spectrométrie de masse des ions secondaires, grenat, terres rares, contrôle cristallochimique, Broken Hill, Australie.

INTRODUCTION

Garnet is a common mineral in metamorphic and igneous rocks, and is an important host for many trace elements, in both rock types. Most examples of igneous (Irving & Frey 1978, Shimizu 1975) and metamorphic (Hickmott *et al.* 1987) garnet exhibit very low ratios of light rare-earth elements (*LREE*) to heavy rare-earth elements (*HREE*) relative to most other silicate minerals and melts. In contrast to these observations, Lottermoser (1988) described a suite of garnet samples from garnetite bodies (Spry & Wonder 1989) associated with the Pb–Zn–Ag orebodies of Broken Hill, Australia, that have anomalously high values of the ratio *LREE/HREE* based on instrumental neutron-activation analyses (INAA) of hand-picked mineral separates. Based on this observation, Lottermoser (1988) concluded that there is no crystal-chemical control over the incorporation of the *REE* in garnet, that the *REE* occur in interstitial and crystallographic sites, and that the *REE* signatures

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suggest an exhalative origin for the protolith of the garnetite. If these conclusions are correct, they would have important implications concerning the behavior of trace elements in metamorphic systems, and specifically the mechanism of incorporation of *REE* in garnet-group minerals.

Replicate samples of Lottermoser's suite were obtained for investigation by secondary ion mass spectrometry (SIMS), in order to address the following questions: 1) Do the INAA data represent the *REE* chemistry of the garnet? 2) Where do the *LREE* reside, if not within the garnet structure? 3) Do the grains of garnet contain any zonal distribution of the trace elements? 4) What are possible petrogenetic explanations for the trace-element signatures of individual grains of garnet *versus* whole-rock signatures of the garnetite? Microanalytical techniques like SIMS are especially useful to address problems of this nature, because the interpretation of the trace-element chemistry of metamorphic minerals is complicated by chemical zoning, microinclusions, fluid inclusions, fine grain-size, and grain-boundary material.

THE GEOLOGY OF BROKEN HILL

Individual grains of garnet used in this investigation were selected from samples of garnetite that are associated with the Broken Hill Pb–Zn–Ag orebodies in Australia (Fig. 1) (Lottermoser 1989, Spry & Wonder 1989, Plimer 1984). Small grains of garnet less than 0.5 mm in diameter are cemented together with an intergranular material typically only a few μm thick. Modally, the garnetite at Broken Hill consists of between 80 to 95% garnet. The other 5 to 20%, mostly intergranular material, consists of quartz, scheelite, ilmenite, galena, gahnite, biotite, pyrite, and other Fe–Mg silicates (Lottermoser 1988, Spry & Wonder 1989, Plimer 1984).

The garnetite units overlie the lead ore zones, occur as blocks within the ore, and are strike-equivalents of the lead-rich orebodies (Plimer 1984, Spry & Wonder 1989). The Broken Hill sulfide orebodies and the associated garnetite occur within the Broken Hill Group of the Proterozoic Willyama Supergroup (Stevens *et al.* 1988). The Broken Hill orebodies consist of seven distinct stacked lenses that are concordant with host-rock layering (Laing *et al.* 1978), and are hosted by schistose pelitic and psammitic metasedimentary and metavolcanic rocks and gneisses (Stevens *et al.* 1988). The Willyama Supergroup has undergone at least three phases of deformation and metamorphism. The metamorphic history consists of two granulite-grade prograde events and at least one retrograde event of amphibolite to greenschist grade (Parr 1992, Stevens *et al.* 1988, Laing *et al.* 1978). The growth of garnet grains is considered to have occurred primarily during the late stages of prograde metamorphism or early stages of retrograde metamorphism (Stanton & Williams 1978, Plimer 1984, Stevens *et al.* 1988).

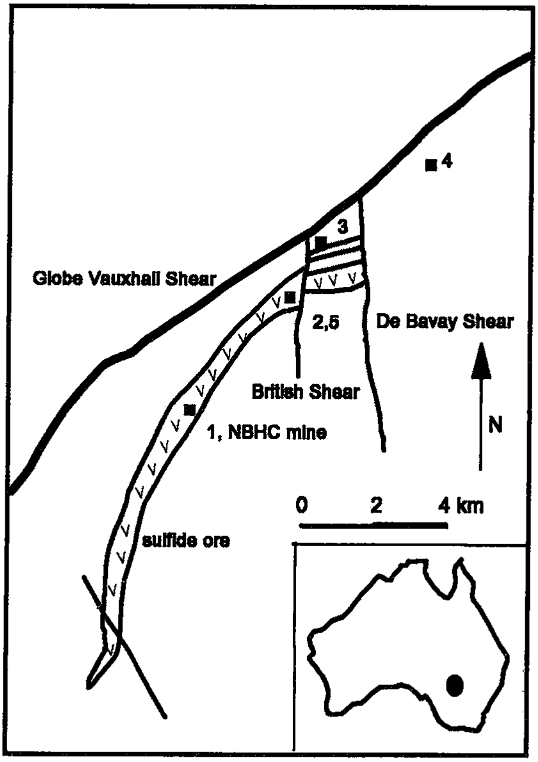

FIG. 1. Generalized map of Broken Hill ore zone, Australia (modified from Lottermoser 1991), shown by the shaded area. Locations of the garnetite samples are numbered, and major shear-zones are labeled.

The origin of the Broken Hill Pb–Zn–Ag mineralization and associated units of garnetite has been debated for more than 100 years (Plimer 1985, Plimer & Lottermoser 1988, Willis *et al.* 1988). Current explanations for the genesis of ores and associated garnetite range from metamorphism of submarine exhalative deposits, or mantle-derived chemical precipitates (Plimer 1984, 1985, 1986, Plimer & Lottermoser 1988), to formation from pore fluids in a sedimentary basin (Wright *et al.* 1987, 1988). Evidence seems to be most convincing for the rift-related chemical precipitate models (Plimer & Lottermoser 1988). As a result, the exotic rock-types, like the garnetite, are referred to as exhalites (Plimer 1984, Lottermoser 1988, 1989).

The exhalites are enriched in *REE* relative to chondrites and relative to the associated sulfide ores. Exhalites proximal to the base metal lodes have a high *LREE/HREE* value and a positive europium anomaly. The distal exhalites have a low *LREE/HREE* value and a negative Eu anomaly (Lottermoser 1989). The similarity of the high *LREE/HREE* values and positive Eu anomalies to those in recent submarine hydrothermal

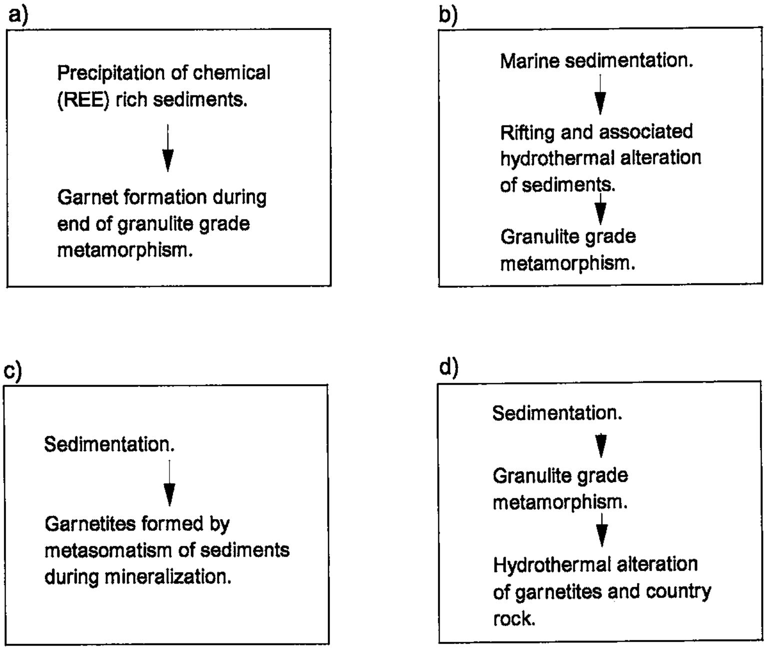

FIG. 2. Schematic presentation of four petrogenetic models (a–d).

fluids and metalliferous sediments of the East Pacific Rise, the Salton Sea, and the Red Sea supports the "chemical precipitate" hypothesis, in the opinion of Lottermoser (1991).

Hypotheses for garnet growth include: 1) regional isochemical metamorphism of *REE*-rich hydrothermal chemical precipitates (Lottermoser 1988, 1989, Richards 1966), 2) hydrothermal *LREE* enrichment of protolith sediments followed by garnet-producing regional metamorphism (Hodgson 1975), 3) metasomatism of lode and sedimentary wallrocks during mineralization (Hodgson 1975), and 4) variable contamination and overprinting of post-granulite-grade garnet by hydrothermal alteration (our suggestion). These alternative models are illustrated schematically in Figures 2a–d.

Chemical analysis of bulk-rock or bulk-mineral samples provides chemical signatures that cannot easily distinguish between these petrogenetic processes. In contrast, microbeam analysis of mineral phases provides greater discrimination.

ANALYTICAL TECHNIQUES

Lottermoser (1988) collected samples both proximal and distal relative to the main orebodies. Figure 1 illustrates the general locations of Lottermoser's samples on a generalized map of the Broken Hill area. Figure 3 shows chondrite-normalized *REE* abundances in hand-picked garnet separates from samples 1, 2, 3, and 4. Samples 1, 2, and 3 are proximal to the orebodies, occurring within the ore zones, and sample 4 is distal, a few kilometers from the mineralized area. Lottermoser (1988) used instrumental neutron activation to obtain data on the *REE*.

We obtained replicate garnetite samples 1, 2, 3, 4 and 5 (5 is an additional proximal sample, collected about 10 m from sample 2: Lottermoser, pers. comm.) from B.G. Lottermoser and I.R. Plimer. The replicates were prepared as polished thin sections for SIMS analysis.

Concentrations of the rare-earth elements La, Ce, Nd, Sm, Eu, Dy, Er, and Yb were measured by spot analysis at garnet core and rim positions. The data were obtained with a Cameca IMS 3F ion microprobe housed at the Woods Hole Oceanographic Institution. The diameter of the primary beam was approximately 20 µm. Five cycles of counts were used for increased precision. Element counts are normalized to silicon counts to offset instrument instability during different counting runs. Accuracy is within 15%, and precision is mostly within 10% (Shimizu & Hart 1982).

Concentrations of the major elements were determined using a JEOL 733 Superprobe electron-microprobe analyzer. Operating conditions were 15 kV, 20 nA beam current, and a 2-µm beam. Counting times were up to 20 seconds for major elements and 40 seconds for minor elements.

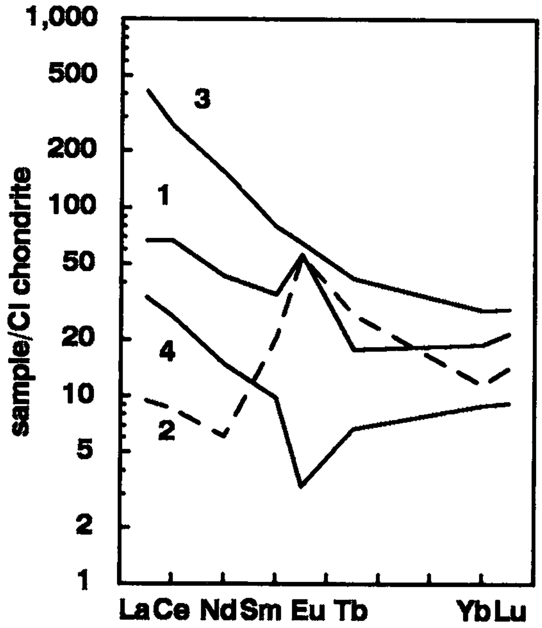

FIG. 3. Chondrite-normalized abundances of the rare-earth elements in acid-washed bulk separates of garnet, from Lottermoser (1988). Note the variation in *LREE/HREE* values among samples.

Transmission electron microscopy (TEM) analysis of the cement or grain boundary material was carried out on a JEOL 2000FX analytical TEM operating at 200 kV. *In situ* quantitative analytical data were obtained using a TN 5500 EDS system.

RESULTS

The combined major- and trace-element data for each sample of garnetite are presented in Table 1. In terms of major-element chemistry, the garnet is homogeneous, both within grains and within each sample of garnetite. Sample 2 was not analyzed with SIMS, and is omitted. Figure 4 shows the compositions of samples 1, 3, 4 and 5 in terms of occupancy of the dodecahedrally coordinated site. Proximal samples 1, 3 and 5 are spessartine-rich, whereas distal sample 4 is distinctly more almandine-rich.

Chondrite-normalized abundances of the *REE* are presented in Figures 5a–d. A SIMS analysis reveals that garnet in the Broken Hill samples has a very low *LREE/HREE* value. Relative to the other *REE*, europium is much more variable in its abundance. In addition, the garnet grains seem to exhibit some zoning in the *HREE*. The rim of the grains has a slightly higher concentration of *HREE* than the respective core (Figs. 5a–d), and the *LREE/HREE* value increases slightly. Also, the garnet grains have *LREE* concentrations (1–10 times chondrite values for Nd) higher than those of other samples of garnet from regional metamorphic terranes (Schwandt 1991, Hickmott *et al.* 1987).

The TEM investigation revealed that the grain-boundary material or intergranular film consists of: 1) an amorphous material that is not a glass, but a gel-like phase, of composition similar to the garnet, but containing S, Cu, and Zn, 2) chlorite, 3) potassium and sodium chlorides, and 4) a titanium-rich phase. Each phase is large enough (>500 Å in size) to obtain representative compositions by EDS analysis. Amorphous grain-boundary films that may be similar to those observed here have been inferred to exist in some peridotites (Suzuki 1987, Stosch & Seck 1980). Suzuki (1987) and

TABLE 1. CHEMICAL COMPOSITION (MAJOR AND TRACE ELEMENTS) OF GARNET FROM GARNETITE, BROKEN HILL

(wt%)	Sample 1		Sample 3		Sample 4		Sample 5	
SiO2	36.88		36.40		36.83		36.45	
Al2O3	20.19		20.52		21.02		20.51	
MgO	0.14		1.03		2.80		0.27	
FeO	9.73		12.19		36.47		9.18	
MnO	18.30		24.16		2.40		28.40	
CaO	13.09		4.02		0.87		4.10	
TiO2	0.10		0.09		0.02		0.10	
Na2O	0.00		0.00		0.00		0.00	
Total	98.42		98.42		100.41		99.02	
(ppm)	core 1	rim 1	core 3	rim 3	core 4	rim 4	core 5	rim 5
La	0.32	0.27		0.03			0.03	
Ce	3.83	3.48	0.31	0.23	0.03	0.20	0.19	
Nd	10.99	11.14	1.69	2.34	0.70	0.46	1.16	1.15
Sm	6.79	7.55	2.85	4.62	2.71	2.37	1.69	1.13
Eu	5.21	5.41	1.21	1.75	0.59	0.90	1.94	1.90
Dy	8.82	9.88	11.93	20.12	9.17	13.13	2.93	3.49
Er	5.45	8.17	7.03	11.68	5.33	8.02	2.04	2.34
Yb	6.93	8.55	7.74	12.58	5.63	8.28	2.38	2.51
Sum	48.34	54.45	32.75	53.35	24.16	33.35	12.37	12.52

Stosch & Seck (1980) proposed the presence of grain-boundary films because they were able to leach *LREE*-enriched material from the surfaces of their garnet separates with acid.

Qualitative SIMS analysis of the intergranular material shows it to have very high *LREE*/*HREE* values. An analysis of intergranular material is qualitative because a pyrope standard was used, and no calibration curve is available for the material. The relative intensities of the *REE* ions produce a pattern shape representative of the bulk intergranular material, rather than of individual phases. Therefore, the specific location of the *LREE* cannot be determined because of the fine grain-size (< 1 μm) of the material. The high *LREE*/*HREE* value of the intergranular material suggests that the *LREE* reside in the amorphous phase and perhaps the chloride phases. The structural sites of the other mineral phases are probably too small for the *LREE* (*cf.* Grauch 1989, Papike 1988).

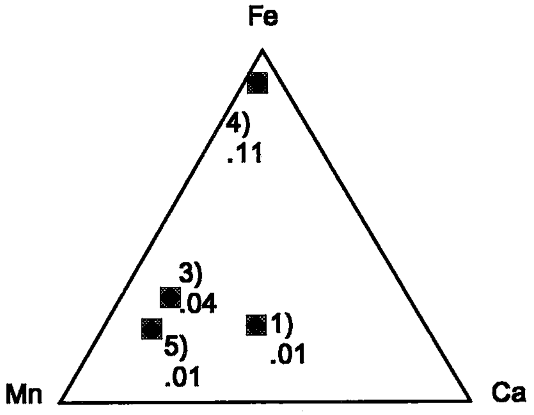

FIG. 4. Composition of garnet at Broken Hill, on the basis of dodecahedrally coordinated cations (mole fractions). Labels indicate sample number and mole fraction of Mg.

CRYSTAL-CHEMICAL CONSTRAINTS

After evaluation of his INAA data, Lottermoser (1988) suggested that the *REE* occur both in the

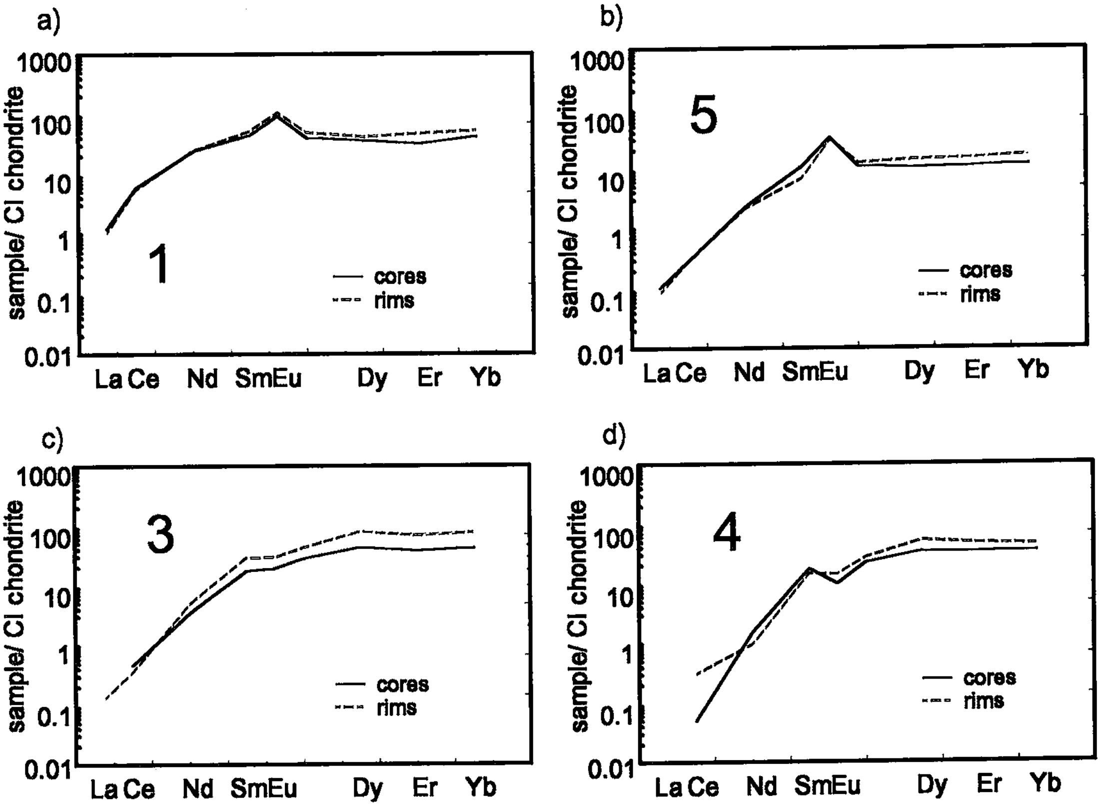

FIG. 5a–d. Chondrite-normalized abundances of the *REE* in garnet from Broken Hill, as determined by SIMS. Comparison of core and rim patterns reveals some enrichment of *HREE* in the rim relative to the core. Sample 4 (d) is farthest from the orebodies and poorest in manganese content. Note europium anomalies.

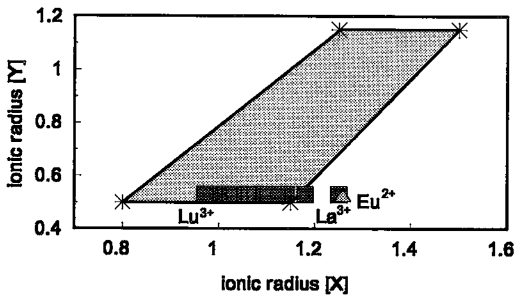

FIG. 6. Field of garnet stability, in terms of radius (Å) of dodecahedrally coordinated (*X*) and octahedrally coordinated (*Y*) cations (after Novak and Gibbs 1971). The ruled zone represents possible stable structures based on cation size. The plotted *REE* points refer to aluminum in the octahedrally coordinated site.

intergranular cement that holds the garnet grains together, and in crystallographic sites in the garnet. Nevertheless, based on his data, Lottermoser concluded that there is no correlation of *REE* concentrations with major-element chemistry, and therefore the crystal structure of garnet does not affect the incorporation of *REE*. The alternatives to structural incorporation of *REE* are site vacancies, and occupancy of defect and interstitial sites (Buseck & Veblen 1978, Harrison & Wood 1980). Lottermoser's (1988) data suggest either unique controls over *REE* incorporation in garnet, or a problem with contamination of the garnet separates.

The incorporation of minor and trace elements into a mineral structure is especially dependent on the composition of a mineral, as this modifies the crystal structure (Novak & Gibbs 1971). For example, in garnet, the dodecahedral site is larger in grossular than in pyrope. The increase in the size of the 8-coordinated triangular-dodecahedral *X* site with calcium content (Novak & Gibbs 1971) favors incorporation of the *REE* into the garnet structure. The importance of size of the dodecahedrally coordinated cation is demonstrated by using the ionic radii of Shannon & Prewitt (1969) for 8-coordinated *REE* and the "garnet stability field" of Novak & Gibbs (1971). Figure 6 is a plot of size of octahedrally coordinated cation against that of the dodecahedrally coordinated cation. The plot suggests limits, based on cation size, of possible stable compositions of garnet. The field only provides guidelines for stable compositions of garnet since there may be thermodynamic and kinetic reasons why combinations of dodecahedrally and octahedrally coordinated cations within the hypothetical field do not stably exist. Novak & Gibbs (1971) determined this stability field using X-ray-diffraction data for many natural and synthetic samples. Figure 6 illustrates that the *LREE* substituents do not form stable garnet compositions with Al in the *Y* site. Therefore, the very low *LREE*/*HREE* values of the garnet samples obtained with SIMS, as shown in Figures 5a–d, are consistent with structural predictions for garnet.

Empirical evidence also exists to show that the size of the dodecahedrally coordinated site and the size of the *REE* cations make the *HREE* more compatible in the garnet structure than the *LREE* (Shimizu 1975, Irving & Frey 1978, McKay 1989). The compatibility of elements can be predicted for coexisting minerals in view of partition coefficients (Matsui *et al.* 1977, Philpotts 1978). The partition coefficients of constituent elements are plotted against each respective element's ionic radius. The most compatible elements show the highest relative partition-coefficients. Distribution coefficients for the *HREE* are much larger than for the *LREE* in garnet; therefore, the *HREE* are more compatible (Irving & Frey 1978). The SIMS-generated patterns showing very low *LREE*/*HREE* values are consistent with this, and with the patterns for metamorphic garnet of Schwandt (1991), Hickmott *et al.* (1987), Hickmott & Shimizu (1990), and Seifert & Chadima (1989).

Multivariate analysis of the electron-microprobe and SIMS data suggest some correlation between major and trace elements in the garnet from Broken Hill. A correlation-coefficient matrix indicates that coefficients greater than 0.97 exist for La, Ce, Nd, and Eu with Ca. The apparent correlation of *LREE* with Ca at Broken Hill could also be due to differences in bulk composition of the garnetite samples. Our sampling is too limited to distinguish between the alternatives. The correlation of *REE* with Ca is well documented for pyroxenes (Papike *et al.* 1988, McKay 1989, Shearer *et al.* 1989). By analogy, we suggest that there is a correlation of *LREE* with Ca in garnet at Broken Hill.

As in the case of the *LREE*, the concentration of europium shows a correlation with calcium. Divalent Eu is larger than trivalent Eu (Shannon & Prewitt 1969, Bloss 1971), with an ionic radius similar to that of the *LREE*. The correlation of Eu with Ca suggests that the europium may have occurred in the divalent state prior to or during the formation of garnet. The larger size makes divalent Eu more incompatible in the garnet structure, as in the case of the *LREE*, but the divalent charge of Eu^{2+} may have favored incorporation into the dodecahedral site.

In summary, substitution of the *REE* in these samples of garnet is controlled by site characteristics. Although limited sampling is acknowledged, the extent of *REE* substitution appears to be dependent upon the amount of Ca in the dodecahedrally coordinated site. This type of control is observed in pyroxene-group minerals.

PETROGENETIC INTERPRETATIONS

The *REE* data discussed above provide insights into which petrogenetic hypotheses are most viable for the origin of garnet at Broken Hill. The models for the formation of garnet discussed above (Figs. 2a–d) are: 1) metamorphism of chemical sediments (an exhalative origin) (Lottermoser 1987, Plimer 1985, 1986), 2) metamorphism of hydrothermally enriched sediments (Hodgson 1975), 3) metasomatic formation of garnetites from sedimentary wallrock, during mineralization (Hodgson 1975), and 4) hydrothermal overprinting after granulite-grade metamorphism.

A metasomatic origin for the garnet seems less likely after evaluation of the SIMS *REE* data. The garnet samples do not have high *LREE/HREE* values that might be characteristic of a *LREE*-enriched hydrothermal fluid, as suggested by Hodgson (1975). Instead, the data are consistent with previously observed patterns of metamorphic garnet (Schwandt 1991, Hickmott *et al.* 1987) and agree with patterns predicted from crystal chemistry. Therefore, it seems that the garnet formed by the metamorphism of a unique chemical sediment or that a garnet-bearing metamorphic rock was altered by hydrothermal activity. The data do not allow us to choose among the models.

The intergranular material could represent a post-metamorphic hydrothermal overprint of the garnet-bearing rocks. A hydrothermal overprint could produce a *LREE*-enriched signature in the intergranular material without modifying the garnet pattern. This does not explain the nature or variation in the Eu anomaly with proximity to mineralization, as shown in Figures 5a–d. Alteration of the garnet patterns by a hydrothermal fluid and preferential mobilization of Eu are highly improbable. The introduction of Eu into the core zone of garnet would require extensive volume-diffusion. Extensive volume-diffusion is unlikely, considering the formation and presence of the intergranular chlorite and chlorides, which are stable at temperatures lower than that needed for diffusional homogenization (>600°C) to occur (Loomis 1983, Lasaga *et al.* 1977). Therefore, it seems most reasonable that the Eu anomalies in garnet represent premetamorphic *REE* signatures of the protolith.

Models 1, an exhalative origin (Fig. 2a), and 2, hydrothermal alteration of protolith sediments (Fig. 2b), are both consistent with the *REE* data acquired on the garnet. In both models, the positive Eu anomalies in garnet (Figs. 5a–d) may reflect conditions of low oxygen fugacity in the protolith of the proximal garnetite prior to garnet formation (*cf.* Lottermoser 1988, Plimer 1986, Stanton 1976). The lower the oxygen fugacity, the greater the tendency for europium to be divalent, and the greater its mobility (Michard 1989). The greater mobility of Eu^{2+} relative to the other *REE* may have caused it to be enriched in the protoliths of the proximal garnetite relative to that of the distal garnetite. Michard *et al.* (1983) and Michard (1989) have documented the presence of reduced hydrothermal fluids containing *REE* signatures with a positive Eu anomaly. The negative Eu anomalies observed in the *REE* signatures of garnet from the distal garnetite could result from a lower hydrothermal input or different conditions of oxygen fugacity in the distal protolithic sediments, prior to garnet formation. The negative anomalies also could represent the same fugacity conditions in the distal protolith, but with a decrease in Eu^{2+} relative to the other *REE* due to earlier deposition in the proximal protolith.

Though the Eu anomalies in garnet are most likely due to remnant protolith signatures, the decrease of *LREE/HREE* in the rim of garnet grains (Figs. 5a–d) probably represents changes in conditions that occurred during growth of the garnet. One explanation is that the *LREE* were partitioned into the intergranular material relative to the *HREE*. Subsequently, during the later stages of garnet growth, some other *HREE*-enriched phase may have broken down, providing for a higher concentration of *HREE* in the garnet rim. Alternatively, garnet could have partially broken down during retrograde metamorphism, with back-diffusion of *HREE* into the garnet, leaving the intergranular material enriched in the *LREE*. However, the euhedral boundaries of the grains and their homogeneous major-element chemistry do not support retrograde resorption of garnet. In addition, the decrease in *LREE/HREE* values of the garnet rim probably is too small to represent increased hydrothermal input, had it occurred during growth of the garnet.

CONCLUSIONS

This investigation demonstrates the importance of using microbeam techniques like SIMS in investigations of the trace-element chemistry of minerals, especially metamorphic minerals. Our SIMS analyses show that INAA analyses of bulk-mineral separates can lead to inappropriate conclusions. In the case of the garnet in garnetite from Broken Hill, the INAA data (Lottermoser 1988) do not represent the *REE* chemistry of the garnet, but in fact more closely represent the chemistry of the garnetites, as a rock type. Use of secondary ion mass spectrometry demonstrates that the garnet incorporates *HREE* more readily than *LREE*, in accord with theoretical predictions, and observations on other occurrences of garnet from metamorphic and igneous rocks. The *LREE* in the Broken Hill garnetite seem to be concentrated in an exotic amorphous material between garnet grains.

The SIMS data suggest that the rim of garnet grains is enriched in *HREE* relative to the core of the grains. The *REE* zoning indicates changing conditions during garnet growth. Possibilities include growth during retrograde metamorphism, changes in mineral assemblage, or possible hydrothermal input during growth. The number of samples is too limited to determine the mechanism more specifically. The *REE* signatures of the garnet at Broken Hill appear to primarily reflect protolith chemistries prior to garnet formation. It is, however, less clear whether the garnetite protolith was a chemical precipitate (exhalite) or a hydrothermally enriched sediment. Investigation of mineral assemblages of other "exhalites" with SIMS would surely help refine the petrogenetic history of the Broken Hill area.

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