

## Gahnite compositions compared

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**ABSTRACT.** Blue-coloured gem-quality spinel from Nigeria was analysed by wet chemical methods (using atomic absorption spectrophotometry) and investigated by X-ray diffraction. The results showed it to be gahnite (unit cell dimension  $a = 8.091 \pm 0.003 \text{ \AA}$ ) containing 36.7% ZnO, 3.58% FeO, and 0.12% MgO. The spinel has an RI of 1.79 and density between 4.4 and 4.59. Broadening of the  $n[111]$  XRD reflections indicates a measure of compositional heterogeneity. The gahnite analyses were compared with compositions of zinc spinels from other parts of the world. The analyses cluster into two distinct groups, Mg-rich spinels of metamorphic origin and Mg-poor spinels (including the Nigerian gahnite) with igneous affinities. Diadochy seems to operate within the zinc spinel structure between  $(Zn + Mn)$  and  $(Fe + Mg)$ .

GEM-QUALITY gahnite (zinc spinel) occurs as an accessory phase disseminated in pegmatites and quartz-sillimanite veins of late Pan-African age (450–500 Ma) in central Nigeria. The veins cross-cut metasedimentary sequences of mica schists and amphibolites. The pegmatites are in a zone extending from near Ife, in SW Nigeria, 400 km NE towards Jos in central Nigeria. Within the mineralized pegmatites, cassiterite is the dominant ore mineral, followed by minerals of the columbite-tantalite series. Pegmatites found within granitic bodies are invariably barren of ore minerals.

The Nigerian pegmatites have been correlated with similar Sn-Nb-Ta mineralized pegmatites of the Amapa Territory situated along the eastern margin of the Guyana craton in South America (Kloosterman, 1969). Sn- and Zn-bearing varieties of spinel have also been identified in these pegmatites (Kloosterman, 1970).

Jacobson and Webb (1946) subdivided the Nigerian pegmatites into three groups according to their mineralogy: (1) microcline-quartz pegmatites, which commonly occur within the calc-alkaline granitoids and are rarely mineralized; (2) microcline-quartz-mica pegmatites, found within metasedimentary sequences; (3) quartz-mica veins, which occur in schists and gneisses or marginal to group 2 pegmatites. Gahnite occurs in groups 2 and 3.

The pegmatite body from which the analysed gahnites were collected forms a heavily forested

ridge, 3.2 km north of Jemaa ( $9^{\circ} 29' \text{ N } 8^{\circ} 24' \text{ E}$ ), with a strike length of approximately 100 m. The pegmatite, which is 18 m wide, cuts dark streaky hornblende-biotite gneiss. Quartz and muscovite are the major minerals, with gahnite as the most common accessory, forming approximately 2% of the rock. Traces of albite and tantalite occur, and schorl tourmaline is abundant at the contact with the country rock.

*Mineral description.* The gem-quality gahnite varies in colour from greenish blue to deep blue. It occurs as euhedral octahedra from 2 to 5 mm in size, rarely reaching 1 cm. Dodecahedral faces occur occasionally as a slight bevelling between the octahedral faces. Twins are rare. The refractive index, determined on a Rayner Dialdex refractometer using sodium light, was 1.793–1.794, and the specific gravities, measured on a Berman density torsion balance, lay in the range 4.400 to 4.589 (Jackson, 1982). Specimens with a greener hue tended towards the lower specific gravity values.

The blue colour in gahnites has been ascribed to the  $\text{Fe}^{2+}$  cation by Anderson and Payne (1937). Jackson (1982) noted that on heating to  $1000^{\circ}\text{C}$  the blue Nigerian gahnite changed to a permanent blue-green colour, and at  $1400^{\circ}\text{C}$  the colour became olive green. He postulated that the colour change was due to iron oxidation. If ferrous iron causes the blue colour and ferric iron a yellow colour, a mixture of ferrous and ferric iron may give a green colour. Thus the colour of gahnite may be an indicator of crystallization temperatures and/or oxygen fugacity at the time of formation.

*Analytical procedure.* A number of unblemished transparent blue crystals were powdered to less than  $150 \times 10^{-6}$  m and four aliquots of 0.05 g were analysed. The analytical method involved fusion with lithium metaborate followed by atomic absorption spectrophotometry, based on Ingamells (1970), van Loon and Parissis (1969), and Boar and Ingram (1970). The solution was aspirated directly into a Varian Techtron AA4 spectrophotometer and the readings compared with artificial aqueous standards spiked with lanthanum, lithium metaborate, and nitric acid to match the sample solution matrix. For the determination of zinc a 1:50 dilution was prepared and spiked accordingly.

X-ray diffraction studies were performed using Cu-K $\alpha$  radiation (36 kV, 18 mA) on a Philips PW1540 goniometer system which incorporated a curved crystal monochromator.

**Results.** An X-ray powder diffractogram produced a subset of peaks which could not be attributed to gahnite. They coincided with  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (corundum) and a trace of low quartz. From the area under the  $I_{100}$  peaks for gahnite and corundum (333 and 6.5 units respectively) an estimate of 5 wt. % Al<sub>2</sub>O<sub>3</sub> was obtained which was used to correct the chemical analysis (Table I). The corrected

TABLE I. Chemical analysis of Nigerian gahnite

	Actual wt. %	Corr. wt. %	Std. dev.	Formula based on 32 O	
SiO <sub>2</sub>	0.72	0.77	—	Si	0.18
Al <sub>2</sub> O <sub>3</sub>	59.1	56.0	0.58	Al	15.87
FeO	3.58	3.85	0.13	Fe	0.77
MnO	0.08	0.09	—	Mn	0.08
MgO	0.12	0.13	—	Mg	0.05
ZnO	36.68	39.44	0.16	Zn	7.00
Total	100.28	100.28			23.95

The values and standard deviations for Al, Fe, and Zn are based on four determinations. The corrected values were obtained after removal of an estimated excess 5% Al<sub>2</sub>O<sub>3</sub>, ascertained from XRD data.

analysis is similar to that of a gahnite described by Simpson (1931) which occurred in an alkali feldspar granite from New Zealand (Table II, col. 4). The low MgO content of both (0.13 and 0.27% respectively) and the igneous association are notable.

Although an optical examination of this gahnite sample (Jackson, 1982) revealed no free corundum, the presence of corundum peaks on the X-ray diffractogram shows that the excess alumina in the structural formula must be ascribed, at least in part, to corundum, probably in cryptocrystalline form, though cation deficiency in the spinel lattice might account for some of the excess Al<sub>2</sub>O<sub>3</sub>. Artificial Mg-spinels have been produced containing excess Al<sub>2</sub>O<sub>3</sub> without changing the spinel structure (Deer *et al.*, 1962), and corundum can occur as a partial or complete pseudomorph after hercynite (Palache *et al.*, 1944).

The unit cell average for all the peaks is  $8.093 \pm 0.011$  Å. The large error results from peak broadening in the  $n[111]$  reflections. Discounting these broad peaks gives a unit cell dimension  $a = 8.091 \pm 0.003$  Å. This corresponds to a com-

position close to the zinc end-member of the spinel group (8.08 Å; Deer *et al.*, 1962).

The broadening of the  $n[111]$  reflections suggests compositional zonation within the mineral (Whittaker, 1981). An electron microprobe study of ferroan gahnite in granite from New Zealand (Tulloch, 1981) showed compositional zoning in iron and zinc from core to rim.

**Discussion.** In addition to the new Nigerian analyses, previously reported zinc-spinel compositions were plotted on a triangular variation diagram displaying the three major cations, Zn, Mg, Fe, expressed as molecular ratios (fig. 1). A bimodal

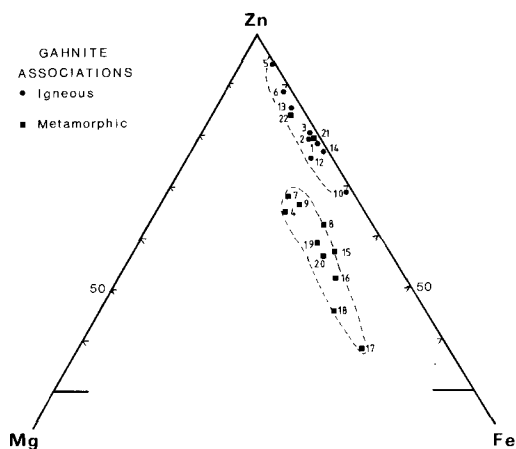


FIG. 1. Molecular ratios for Mg, Zn, and Fe. Sample points fall into two main fields, one an igneous association and the other a metamorphic association. Sample numbers as in Table II.

distribution is evident, with Mg acting as the discriminator. An investigation of the geological environment of each sample led to the conclusion that low-Mg gahnites are associated mainly with igneous pegmatites or highly differentiated granites, whereas high-Mg gahnites are invariably associated with schists or anatectic pegmatites. Exceptions to this come from old data (Shannon, 1923; Brush, 1871). The behaviour of Mg in igneous and metamorphic environments differs. Igneous pegmatite environments reflect the final stages of a crystal fractionation sequence, in which Mg, being associated with early crystallizing mafic phases, would be greatly depleted in the melt. During metamorphism, however, Mg could be re-mobilized into the fluid phase by the breakdown of biotite or amphibole and become available to a crystallizing spinel. Staurolite dehydration has been identified as

TABLE II Chemical analyses of zinc spinels.

Sample No.	1	2	3	4	5	6	7	8	9	10	12	13	14	15	16	17	18	19	20	21	22	
Wt %																						
SiO <sub>2</sub>	0.12	4.51	-	1.08	0.70	0.77	1.28	1.64	4.0	-	0.03	0.09	1.10	-	-	-	-	-	-	-	0.57	1.50
Al <sub>2</sub> O <sub>3</sub>	55.91	53.25	53.77	57.72	53.73	56.0	56.96	55.74	56.9	54.90	57.71	56.99	57.86	56.3	56.2	56.7	56.7	55.4	56.3	49.78	54.50	-
Fe <sub>2</sub> O <sub>3</sub>	-	-	-	0.39	2.53	-	-	0.95	+	-	-	-	-	1.34	1.76	2.77	2.42	2.42	2.04	+	-	-
FeO	7.90	6.57	6.88	8.88	1.72	3.85	8.43	11.73	7.92	10.15	7.85	4.86	7.79	13.7	15.0	20.0	16.4	12.1	13.1	7.12	4.86	-
ZnO	35.85	34.31	35.93	29.46	41.66	39.44	30.98	27.98	25.3	29.40	34.06	37.79	32.5	26.3	24.0	18.0	21.3	26.9	26.2	39.62	34.48	-
MnO	0.42	0.91	0.95	0.02	0.50	0.09	0.10	0.22	0.0	0.84	0.65	0.41	0.5	0.02	0.02	0.04	0.02	0.22	0.19	1.13	0.26	-
MgO	0.12	0.18	0.19	2.79	0.0	0.13	2.35	1.55	1.8	0.0	0.61	0.27	-	1.87	2.36	2.96	3.27	2.25	2.33	0.13	0.42	-
CaO	-	-	-	-	-	<0.1	-	0.0	0.8	-	-	-	-	-	-	-	-	-	-	-	-	*
Total	100.32	99.77	99.76	99.95	100.83	100.28	100.20	99.99	98.3	95.29	100.91	100.41	99.75	99.53	99.34	100.47	100.11	99.29	100.16	99.81	96.02	-
R.I.	1.795	1.810	-	1.818	1.794	1.794	1.782	-	1.940	1.790	1.80	-	-	-	-	-	-	-	-	-	1.790	-
S.G.	4.55	4.788	-	4.38	4.57	4.800-	4.34	4.465	4.365	4.47	-	4.50	-	-	-	-	-	-	-	-	4.89-	4.91
Unit cell	8.10	-	-	8.091	-	8.091	-	8.116	8.112	8.102	8.102	-	-	-	-	-	-	-	-	-	-	-
mol Zn/Fe	4.0	4.6	4.6	3.3	25.5	9.1	3.2	2.1	2.8	2.5	3.4	6.9	3.7	1.6	1.4	0.8	1.1	1.9	1.7	4.5	6.3	-

\* Includes 1.48% CoO, 1.50% insoluble  
 + Total iron reported as Fe<sub>2</sub>O<sub>3</sub>. Recalculated as FeO for calculations.

Sources: 1. von Knorring and Bearnley (1960); 2,3. Pehman (1948); 4. Simpson (1937); 5. Simpson (1931); 6. This work, Table 1. Analysis, R.A. Batchelor;  
 7. Simpson (1930); 8. Eskola (1914); 9. Alvarez-Peres et al. (1974); 10. Lisitsyn and Yurkina (1974); 12,13. Tulloch (1981); 14. Gandhi (1971);  
 15-20. Frost (1973); 21. Brush (1871); 22. Shannon (1923).

the mechanism for the production of zinc-rich hercynite in metapelitic gneisses in the Adirondacks (Stoddard, 1979). These metamorphic spinels contain 1.59 to 9.9% MgO.

To investigate the behaviour of Zn, Fe, and Mg within the spinel structure, molecular ratios of these major cations were plotted against a common structural element, aluminium. This diagram, proposed by Pearce (1968), highlights the extent of diadochy substitutions within a structure. Perfect diadochy produces a straight line plot with slope  $-1$ . The relationship between zinc and iron was examined. The plot gave a good linear correlation but the slope  $-1.4$  meant that these two elements alone do not explain the element variations in gahnite. A plot of mol Zn/Al versus mol (Fe + Mg)/Al gave a slope of  $-0.87$  which leaves zinc sites deficient. Mol (Zn + Mn)/Al versus mol (Fe + Mg)/Al were then plotted (fig. 2) and yielded a

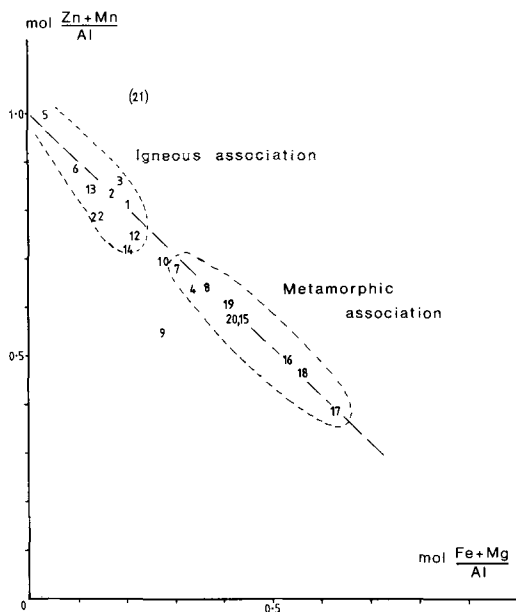


FIG. 2. Bivariate plot of the molecular ratio (Zn + Mn)/Al against the molecular ratio (Fe + Mg)/Al. (Diagram after Pearce, 1968.) The slope of the best-fit line is  $-0.97$ . Sample numbers as in Table II.

good straight line of slope  $-0.97$ . This suggests that diadochy exists between (Zn + Mn) and (Fe + Mg) within the gahnite structure.

An arbitrary division drawn between the igneous and metamorphic gahnites occurs at mol Zn/Fe =

3.8. Zinc tends to concentrate (within a fractionating regime) in later iron minerals and therefore Zn/Fe ratios will tend to increase with differentiation (Taylor, 1965). This observation is borne out in zoned gahnites (Tulloch, 1981) in which the core (sample 12) has a mol Zn/Fe ratio of 3.9, compared with the rim (sample 13) with a mol Zn/Fe ratio of 6.9. The samples formed in highly fractionated magmas will have the highest ratio, e.g. sample 5 from alkali feldspar granite has a mol Zn/Fe ratio of 25.5.

Sample 10 originates from a skarn deposit in which alteration of feldspar under oxidizing conditions in the presence of zinc-rich solutions is proposed for its formation (Lisitsyn and Yurkina, 1974). It plots in the transition zone between inferred zones of igneous and metamorphic origin.

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