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Gahnite and columbite in an alkali-feldspar granite from New Zealand

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ABSTRACT. Gahnite and columbite with compositions $(Zn_{5.96}Fe_{1.55}Mg_{0.21}Mn_{0.13})_{\Sigma 7.85}Al_{16.09}O_{32}$ and $(Nb_{7.36}Ta_{0.60}Mn_{2.95}Fe_{0.98}Ti_{0.09})_{\Sigma 11.98}O_{24}$ occur as accessory phases in a highly evolved garnetiferous muscovite alkali-feldspar granite. Both phases have developed as a result of a concentration of Zn, Nb, and Ta during the final stages of the fractional crystallization which led to the formation of the pluton, and the lack of a major mafic mineral such as biotite, in which these elements are normally camouflaged in granitoid rocks.

GAHNITE and columbite occur as accessory phases in the Desolation Row alkali-feldspar granite, a 4 km^2 pluton in the Victoria Range, SE Nelson, New Zealand. The Desolation Row pluton is the most highly evolved of a suite of post-tectonic (Cretaceous?) granitoid rocks which intrude middle-upper Palaeozoic granitoid rocks in the Victoria Range segment (Tulloch, 1979) of the Karamea Batholith (Grindley, 1978). An average mode comprises: quartz 34.2%, microcline 21.6%, albite (An_{1-3}) 34.4%, muscovite 8.7%, garnet 1.2%. Albite and muscovite form tabular subhedral to euhedral crystals except where they are in contact with microcline (which is coarsely perthitic and generally interstitial). Euhedral garnet $(Spess_{63}\ Alm_{33}\ Py_3\ Gross_2)$ is interpreted as a primary magmatic phase. In addition to gahnite and columbite, magnetite, monazite, and zircon are also present in trace amounts (<0.01 modal %). This is believed to be the first record of columbite from New Zealand, and the first recorded occurrence of gahnite from a massive granite (as distinct from pegmatites) anywhere.

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Gahnite. The zinc spinel, gahnite, occurs as small (0.1-0.2 mm), subhedral crystals disseminated throughout the Desolation Row Granite. In thin section it is medium-deep green, and all grains observed were associated with muscovite (an association also noted by von Knorring and Dearnley, 1960). Octahedral and, less commonly, dodecahedral faces are developed on grains which were separated from crushed rock (fig. 1*a*, *b*). The development of the dodecahedral form shows every gradation from a slight bevelling of the octahedral edges, to faces which are as prominent as in the octahedral form. Fig. 1*a* also shows striations on the {110} faces which may be the {111} cleavage, and growth steps on the octahedral faces.

The refractive index is 1.80, and the cell edge, determined by least squares refinement of X-ray powder photograph data is 0.8102 nm. Line splitting

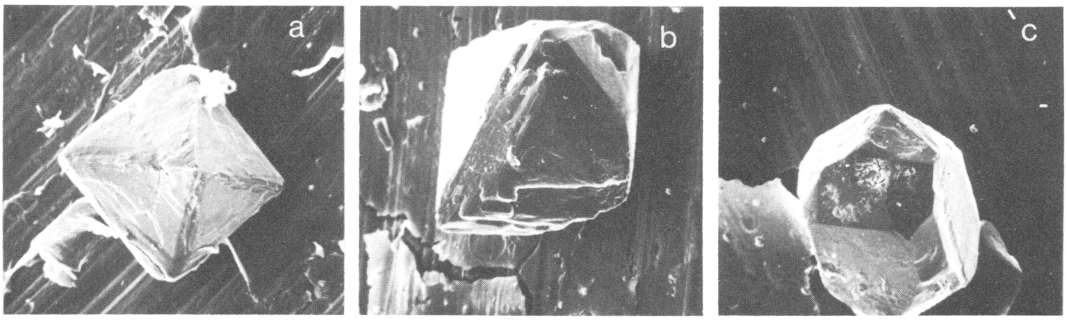

FIG. 1. SEM micrographs, field of view approximately 0.3 mm. (*a*) gahnite showing octahedral form, (*b*) gahnite displaying both octahedral and dodecahedral forms, (*c*) columbite.

suggested zoning which was later confirmed by microprobe analysis (Table I).

The composition of the ferroan gahnite described here is similar to most other published analyses of gahnite (Hutton, 1957*a*; Gandhi, 1971; von Knorring and Dearnley, 1960; Lisitsyn and Urkina, 1974; Frost, 1973) which generally include 5-15% FeO. The large Zn content appears to have stabilized the spinel in the presence of quartz (Richardson, 1968). The analyses show the rim to be enriched in Fe and depleted in Zn, and to a lesser extent Mg and Mn, relative to the core. Microprobe beam scans across an approximately (001) section (fig. 2) revealed regular normal zoning for Fe. The Zn profile is broadly antipathetic to the Fe profile but irregularities indicate that Mn and Mg are also somewhat irregularly distributed. Von Knorring and Dearnley (1960) have suggested that the Fe content of gahnite is a function of temperature, analogous to the increased substitution of Fe for Zn in sphalerite at higher temperatures, and the sense of zoning in the Victoria Range gahnite (crystallizing in a cooling body) supports this.

The octahedral site preference energy suggests that Mn^{2+} should be incorporated into the spinel lattice in preference to Zn^{2+} (Burns, 1970). Low Mn^{2+} in the observed spinel thus indicates that most available Mn had been taken by garnet before the spinel began to crystallize. This is consistent with the relatively late crystallization of spinel which is believed to have formed as a result of peraluminous conditions (possibly increasingly so, due to muscovite breakdown late in the crystallization sequence), and to the tendency for Zn to concentrate in late-stage aqueous solutions (Holland, 1972).

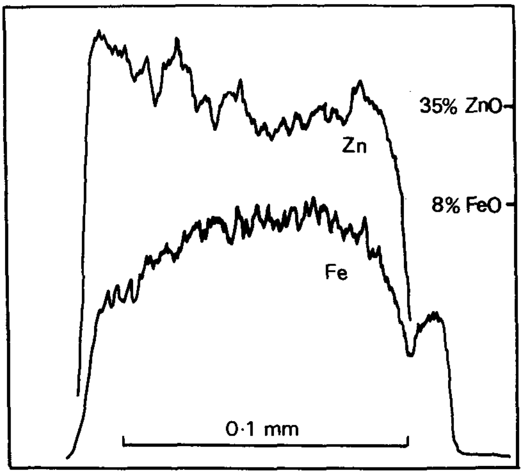

FIG. 2. Zn and Fe zoning in gahnite (microprobe scan). The FeO peak at approximately 4% on the right-hand side represents adjoining muscovite

Muscovite breakdown suggests emplacement of the pluton at pressures less than that of the intersection of the muscovite plus quartz breakdown curve with the wet granite solidus. The general association of gahnite with muscovite, and the inclusion of garent within muscovite support the crystallization sequence proposed above.

The whole-rock Zn content of the host Desolation Row Granite averages 66 ppm which is not greatly above the world-wide average 'granite' value of 50 ppm reported by Wedepohl (1970). Biotite is the chief carrier of Zn in granitoid rocks (Viswanathan, 1973; Rimsaite, 1967; Blaxland, 1971), and since the Desolation Row Granite contains no biotite or other major mineral with a suitable site for Zn, a separate phase has developed.

Columbite-pseudoixiolite. Small (0.1-0.2 mm), subhedral-euhedral grains of 'columbite' are also disseminated throughout the Desolation Row Granite. Grains separated from the crushed rock (fig. 1*c*) are black with a sub-metallic lustre; in thin-section these edges are translucent with a reddish-brown absorption tint. Relatively early crystallization within the Desolation Row pluton is indicated by intergrowth with garnet and inclusion within muscovite.

A microprobe analysis is presented in Table I. The Victoria Range 'columbite' is slightly rich in the $MnNb_2O_6$ component compared to many columbite-tantalite analyses (cf. Zelt, 1975, fig. 1). No Sn was detected (cf. Oftedahl, 1972) but the analysis does include significant Ti which is commonly 'admitted' to Nb, Ta sites in minerals due to their similar ionic radii [indeed, tantalite is isomorphous with brookite (Mason, 1963) and Nb-, Ta-rutiles are not uncommon (Deer *et al.*, 1966)].

Although columbite-tantalite group minerals comprise a continuous compositional series, they form a number of structural variants (Nickel, *et al.*, 1963*b*; Grice *et al.*, 1972). Neither heated nor unheated 'columbite' gave the low-angle X-ray diffraction peaks at 0.53 and 0.713 nm, indicating a disordered ixiolite structure (Nickel *et al.*, 1963*a*). However, the lack of Sn indicates the mineral may be best described as pseudo-ixiolite (Sn-poor ixiolite), or disordered columbite-tantalite. Indeed Giese (1975) points out that most natural columbites are disordered. Giese calculated energies for all 495 possible ways of distributing 8 Nb and 4 Mn atoms over 12 cation sites in the lattice. As there is only a small energy gap between the normal, and other possible ordered distributions, ions can occupy different sites with little penalty in terms of potential energy (cf. Barker and Graham, 1974). Nickel *et al.* (1963*a*) consider that there is complete gradation from fully ordered end-member columbite-tantalite

TABLE I. *Analyses of columbite, gahnite, and muscovite in alkali-feldspar granite from the Victoria Range*

	Columbite	Gahnite Core	Gahnite Rim	Muscovite
SiO_2	—	0.03	0.09	46.10
Al_2O_3	—	57.71	56.99	33.47
TiO_2	0.53	0.0	0.02	0.63
FeO^+	5.06	7.85	4.86	2.69
MgO	—	0.61	0.27	0.80
MnO	14.93	0.65	0.41	0.18
CaO	—	—	—	0.02
Na_2O	—	—	—	0.75
K_2O	—	—	—	10.12
Nb_2O_5	70.5	—	—	0.08
Ta_2O_5	9.52	—	—	—
U_2O_5	0.04	—	—	—
ZnO	—	34.06	37.79	0.08
Total	100.13	100.91	100.44	94.77
		Atomic proportions*		
Si	—	0.01	0.02	6.22
Al	—	16.09	16.07	5.32
Ti	0.09	0.00	0.01	0.06
Fe	0.98	1.55	0.98	0.30
Mg	—	0.21	0.10	0.16
Mn	2.95	0.13	0.09	0.02
Ca	—	—	—	0.00
Na	—	—	—	0.20
K	—	—	—	1.74
Nb	7.36	—	—	—
Ta	0.60	—	—	—
U	0.01	—	—	—
Zn	—	5.96	6.67	—
Total	11.99	23.95	23.94	14.03

* Columbite, gahnite, and muscovite atomic proportions on the basis of 24, 32, and 22 oxygens, respectively.
\+ Total Fe as FeO.
—Not determined.

to fully disordered pseudo-ixiolite. Donnay and Donnay (1960, in Nickel *et al.*, 1963*a*) suggest that a high Mn/Fe ratio may aid disorder in columbite-tantalite.

Thus the metal ions of columbite ($X_4Y_8O_{24}$) can be regarded as occupying equivalent positions in the disordered form, and the Victoria Range 'columbite' can be written 1/3 ($X_{12}O_{24}$), or 1/3 [$(Fe, Mn, Ti, Nb, Ta)_{11.98}O_{24}$].

Several other Nb, Ta multiple oxides have been reported from New Zealand, although none has been observed *in situ*. The fergusonite and samarskite reported from Canaan were probably derived from the nearby Separation Point Granite (Watters *et al.*, 1961) but the locations of kobeite and tapiolite described from South Westland by Hutton (1957*b*, 1958) suggest derivation from fenitized schist (Cooper, 1971) may be as viable as derivation from granitoid rocks. Ta-bearing cassiterite is common in Westland dredge concentrates (Hutton, 1950).

Niobium and tantalum abundances have not been analysed in Victoria Range rocks but approximately 0.005 modal vol. % columbite, at 70% Nb_2O_5 gives 40 ppm Nb, or twice the world-wide average granite value of Turekian and Wedepohl (1961). The behaviour of Nb and Ta is believed to have been broadly similar to that of Zn. Niobium and tantalum generally occupy Ti-sites in granitoid rocks, and are thus normally accepted by biotite (as is Zn) and sphene. Minerals of the columbite-tantalite group are common in granitic pegmatites, especially those containing Li, Sn, Be, and B-rich minerals (Berry and Mason, 1959).

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