Nb-rich baotite in carbonatites and fenites at Haast River, New Zealand

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Abstract

Baotite occurs as an accessory mineral in carbonatites, fenites, and carbothermal veins associated with a lamprophyre dyke swarm in the Haast River area of south Westland, New Zealand. Carbonatites are petrogenetically evolved, with assemblages dominated by ankerite, siderite and Ba–Sr–*REE* carbonates. Microprobe analysis indicates baotite compositions more Nb-rich than previously recorded, with compositions close to $Ba_4[Ti_3(Nb,Fe)_5]Si_4O_{28}Cl$. Ti must be partially replaced in both crystallographically-independent octahedral sites. Compositional zoning, and stoichiometric considerations suggest that the dominant octahedral substitution is the same as that described in rutile, namely $3Ti^{4+} \rightleftharpoons 2Nb^{5+} + Fe^{2+}$. Contrary to previous suggestions, Fe in the octahedral site should, therefore, be dominated by Fe^{2+}.

The presence of baotite further documents the involvement of halogens in carbonatite magmas. In the New Zealand occurrences it is suggested that the chlorine originates from associated phonolitic magmas and is partitioned into carbonatite during liquid immiscibility.

KEYWORDS: baotite, carbonatite, fenite, niobium, New Zealand.

Introduction

BAOTITE is a rare, Ba–Nb–Ti chlorosilicate, first described in quartz veins associated with alkaline granites and syenites from Inner Mongolia by Peng (1959) and Semenov *et al.* (1961). Subsequently, baotite has been documented from a calcitic carbonatite at Ravalli County, Montana, where it occurs with aeschynite, ancylite, baryte, sodic amphibole and monazite (Heinrich *et al.*, 1962). Additional occurrences of baotite in Russia were described by Efimov and Es'kova (1973) and Shuriga *et al.* (1980), the former in alkaline rocks from the Urals, the latter in aegirine–albite–microcline fault-zone metasomatites associated with eastern Siberian syenites. Baotite occurs as a component of evolved microsyenite and microgranite dykes which form part of the alkaline minette series of minor intrusives in the southeast Bohemian Massif (Nemec, 1987). A similarly Nb-poor, but W-rich baotite occurs included in alstonite and celsian, in hydrothermal veins of sphalerite, galena, pyrite, siderite and calcite associated with a Zn-Pb ore body from the central Pyrenees (Johan *et al.*, 1991).

This paper describes a further seven occurrences of baotite associated with carbonatitic members of a lamprophyre dyke swarm in the Southern Alps of Westland, South Island, New Zealand.

Local geology

In northwest Otago and south Westland, New Zealand, the Haast Schists are intruded by a regional lamprophyre dyke swarm up to 25 km wide, that extends over 110 km southwards from the vicinity of the Alpine Fault. Dykes are predominantly campto-nites, monchiquites, and ouachitites, although in the Haast River area of south Westland, where intrusion is more intense than elsewhere, intrusive lithologies include tinguaites, trachytes and carbonatites (Cooper, 1971; 1979; 1986). All dykes, but particularly the carbonatites, show pronounced fenitization of the country rock. The pumpellyite–actinolite to amphibolite facies, peraluminous, quartzofeldspathic schist mineralogy is converted distally to a peralkaline aegirine–arfvedsonite–albite assemblage, and proximally to aegirine–albite fenites at dyke contacts, and along fluid access channels parallel to fractures and to the regional schistosity. Dyke intrusion of mantle-derived lamprophyric magmas (Barreiro and Cooper, 1987) is thought to relate to tensional forces related to the propagation of
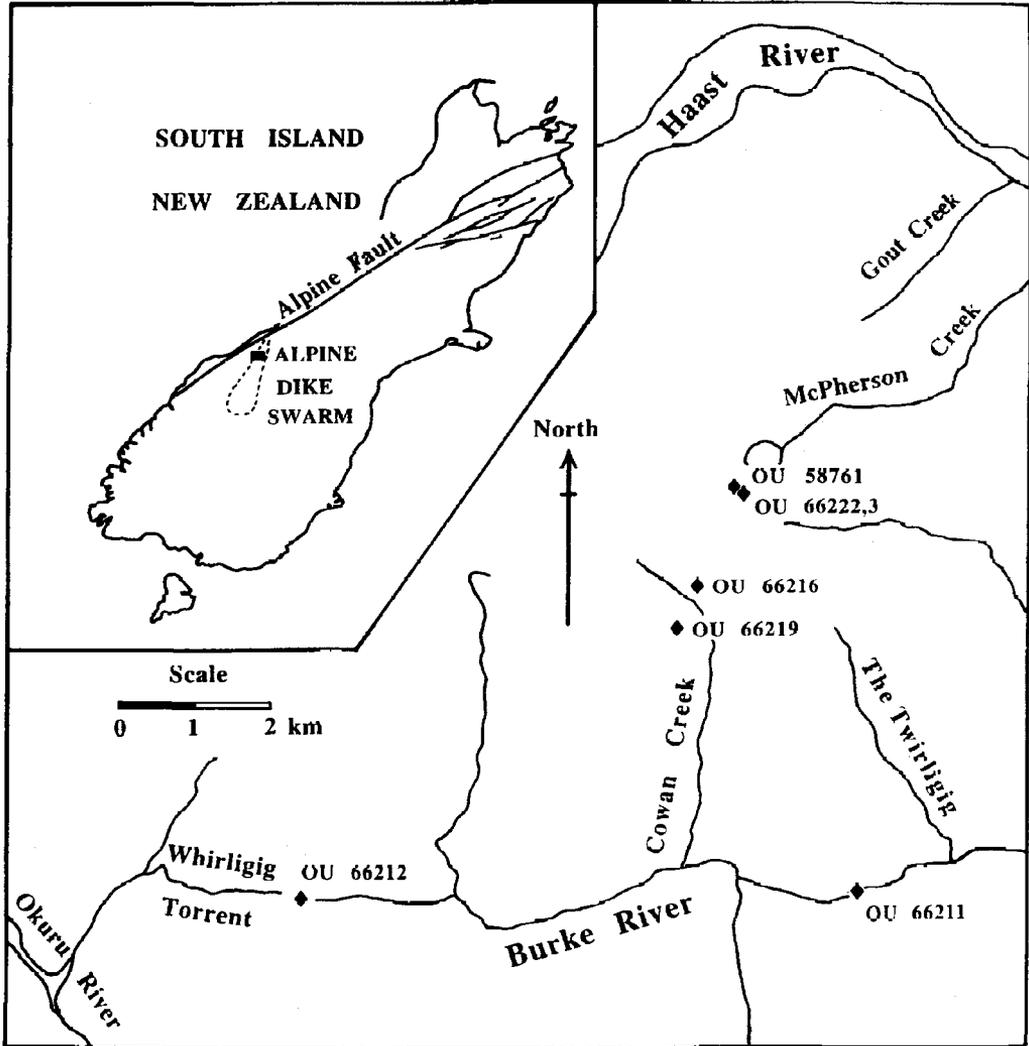
FIG. 1. Locality map showing distribution of the Alpine lamprophyre dyke swarm and baotite occurrences in Haast-Burke-Okuru Rivers area, south Westland, New Zealand.

the Alpine Fault plate boundary through the South Island, New Zealand, during the late Oligocene–early Miocene (Cooper *et al.*, 1987).

Carbonatites form a volumetrically minor (<1%) component of the Haast River dyke swarm, yet are mineralogically diverse, ranging from calcite-, through calcite–dolomite-, to ankerite- and siderite-dominated mineralogies (Cooper, 1986; Paterson, 1992). One of the most unusual of these evolved compositions is a norsethite-rich sill (Cooper, 1971;

1983) which occurs in a 2.5 km-long carbonatite intrusion zone. Five of the baotite records come from this zone, with occurrences in both carbonatites and their associated fenites. Baotite also occurs in thin veins of calcite–ankerite carbonatite exposed in the nearby Burke River, close to the Twirligig tributary, and in a magnesioriebeckite-rich vein from the vicinity of a large fault in a tributary of the Okuru River. Localities are indicated on Fig. 1 and details of mineral assemblages are listed in Table 1.

TABLE 1. Baotite occurrences, south Westland, New Zealand

Haast River area.
Mt Campbell.
OU58761: Norsethite-rich carbonatite
Norsethite-ankerite-Ca Ba carbonate–aegirine–arfvedsonite–albite–apatite–pyrite–pyrrhotite–ilmenite-baotite

OU66222: Ankerite carbonatite
Ankerite(Fe$_{0.482}$Mn$_{0.052}$Mg$_{0.452}$Ca$_{1.004}$ (CO$_3$)$_2$)-siderite (Fe$_{1.476}$Mn$_{0.104}$Mg$_{0.418}$Ca$_{0.016}$(CO$_3$)$_2$)-albite(Ab$_{99.5}$Or$_{0.5}$)-aegirine–quartz–riebeckite–rutile–apatite–pyrite–chalcopyrite–baotite

OU66223: Fenite adjacent to ankerite carbonatite
Albite(Ab$_{100}$)-aegirine-niobian rutile(up to 18.4 wt.% Nb$_2$O$_5$)-ilmenite-quartz-apatite-monazite-pyrite-pyrrhotite-baotite

Burke River area.
Cowan Creek
OU66216: Fenite adjacent to norsethite-rich carbonatite
Titanian aegirine-albite(Ab$_{99.5}$An$_{0.5}$)-niobian rutile–magnesio-arfvedsonite-siderite (Fe$_{1.172}$Mn$_{0.022}$Mg$_{0.802}$Ca$_{0.088}$ (CO$_3$)$_2$)-chalcopyrite-pyrite-sphalerite-pyrrhotite -Ba muscovite–biotite–ankerite (Fe$_{0.475}$Mn$_{0.041}$Mg$_{0.477}$Ca$_{0.989}$ (CO$_3$)$_2$)–ilmenite–baotite

OU66219: Siderite carbonatite
Siderite (Fe$_{1.292}$Mn$_{0.152}$Mg$_{0.564}$Ca$_{0.012}$ (CO$_3$)$_2$)-albite (Ab$_{100}$)-niobian rutile-ilmenite-apatite-ankerite (Fe$_{0.436}$Mn$_{0.030}$Mg$_{0.508}$Ca$_{1.024}$ (CO$_3$)$_2$)-pyrite-pyrrhotite-sphalerite-galena-chalcopyrite-monazite-baotite

Twirligig
OU66211: Calcite-ankerite carbonatite
Calcite (Fe$_{0.05}$Mn$_{0.05}$Mg$_{0.02}$Ca$_{2.01}$Sr$_{0.01}$ (CO$_3$)$_2$)-albite (Ab$_{99.3}$Or$_{0.5}$An$_{0.2}$)-ankerite (Fe$_{0.42}$Mn$_{0.10}$Mg$_{0.44}$Ca$_{0.96}$ (CO$_3$)$_2$)-titanian aegirine-calcian strontianite (Sr$_{1.23}$Ca$_{0.73}$Ba$_{0.04}$ (CO$_3$)$_2$)-Ba Ca Sr *LREE* carbonate (possibly burbankite)-pyrite-sphalerite-galena-chalcopyrite-baotite

Okuru River area.
Whirligig Torrent
OU66212: Magnesio-riebeckite vein
Magnesioriebeckite-ankerite(Fe$_{0.365}$Mn$_{0.009}$Mg$_{0.550}$Ca$_{0.960}$Sr$_{0.035}$ (CO$_3$)$_2$) -norsethite (Fe$_{0.140}$Mn$_{0.030}$Mg$_{0.855}$Ca$_{0.005}$ Ba$_{0.945}$(CO$_3$)$_2$)–barite-sphalerite-siderite (Fe$_{1.070}$Mn$_{0.030}$Mg$_{0.895}$(CO$_3$)$_2$)–apatite–magnetite–galena–baotite

Field and petrographic characteristics

In OU66211, a thin (4 cm) calcite–ankerite carbonatite dyke exposed in the Burke River, baotite occurs in trace or accessory amounts as equigranular to prismatic crystals, ranging in size up to 0.05 mm. Baotite is clearly a late-crystallizing phase associated with calcian strontianite and a Ba-Ca-Sr *LREE* carbonate (possibly burbankite), poikilitically enclosing needles of aegirine along calcite–ankerite grain boundaries.

The most Ba-rich carbonatite of the Haast River area is a 1.4 m thick sill, dominated by norsethite (Cooper, 1971; 1983; 1986), cropping out on the eastern cirque wall of Cowan Creek, Burke River. The 10 m wide fenite zone shows a mineralogical zonation from aegirine-albite-niobian rutile-norsethite schists adjacent to the carbonatite contact, through an intermediate zone characterized

by additional magnesioriebeckite/magnesio-arfvedsonite and barian muscovite, to a country rock, garnet zone quartzofeldspathic schist. An intermediate fenite, OU66216, occurring 2.13 m from the carbonatite contact, contains baotite intergrown with prisms of aegirine and magnesioriebeckite in thin, foliation-parallel segregations. The alkaline pyribole laminae represent quartzofeldspathic segregations from the parent schist, metasomatically replaced during fenitization.

On the western wall of Cowan Creek, a 22 m wide zone of carbonatite, fenite and altered lamprophyre is exposed, 1 km along strike from the norsethite-rich sill. A sulphide-rich, siderite carbonatite (OU66219) from this intrusion zone contains rare granules of baotite, up to 0.5 mm in diameter, generally associated with aggregates of niobian rutile, sphalerite and pyrite. Baotite has a blotchy appearance defined by irregular pale- and dark-brown coloured

patches. Contacts between adjacent colour zones are optically sharply defined.

The carbonatite intrusion zone can also be observed on the northern slopes of Mt Campbell, 1.5 km north of Cowan Creek, where baotite-bearing, ankerite carbonatite (OU66222) and adjacent fenite (OU66223) have been observed in situ. In the ankerite carbonatite, baotite occurs in association with sulphides as 0.6 mm granules and as more irregularly-shaped, isolated grains, that have grown along pre-existing albite grain boundaries. Adjacent to the ankerite-rich carbonatite, the country rock, quartzo-feldspathic schist, has been metasomatically altered to an albite aegirine schist, OU66223. In this fenite, baotite occurs as overgrowths on niobian rutile, or as intergranular, skeletal grains up to 0.2 mm in diameter. A norsethite-rich carbonatite, virtually identical mineralogically to the Cowan Creek sill, has been subsequently found as a loose scree block in the same area as the ankerite carbonatite (Paterson, 1992; OU58761). In the norsethite carbonatite, baotite occurs as rounded granules (up to 0.14 mm diameter) in one of many norsethite-dominated bands, which occur in a matrix of norsethite–ankerite–albite–aegirine–pyrite–ilmenite.

In Whirligig Torrent, a tributary of the Okuru River, an east–west fault surface has been miner-alized by carbonatitic fluids, forming a blue amphibole-rich vein (OU66212). Baotite forms isolated, rounded granules or stubby prisms in a felted matrix of magnesorioriebeckite. Other barian phases, baryte and norsethite, occur in thin inter-laminated foliae.

In all of the above occurrences, baotite is characterized by high to very high relief, intense pleochroism (ω = brown or pale brown, ε = dark red-brown to black) and an optically positive uniaxial character. Chemical zoning, determined in OU66211 and OU66219 by microprobe analysis, could be detected optically only in OU66219, where the high Nb-Fe, low Ti zones have the deeper brown absorption tints. In separated grains (OU66211 and OU66223), baotite has a vitreous to resinous lustre, occurring in stubby, striated prisms with prominent orthogonal cleavages parallel to the prism zone.

Mineral chemistry

Analyses of baotite have been determined by wavelength-dispersive microprobe analysis with results presented in Table 2. Analyses were determined in part at the University of Edinburgh using a Cambridge Microscan 5 with microprobe techniques following the methods of Sweatman and Long (1969). Analytical coverage was extended, and in part duplicated, at Otago using a JEOL JXA 8600. Accelerating voltage and probe current were

increased to 25 kV and 7×10^{-8} A respectively to increase count rates for Ba and Cl. Standards included oxides for Si, Al, Ti, Fe, Mn, albite (Na), K-feldspar (K), wollastonite (Ca), benitoite (Ba), scapolite (Cl), topaz (F) and Nb metal. All raw data were processed using a ZAF correction procedure.

The composition of baotite reported in the literature has been variously suggested as
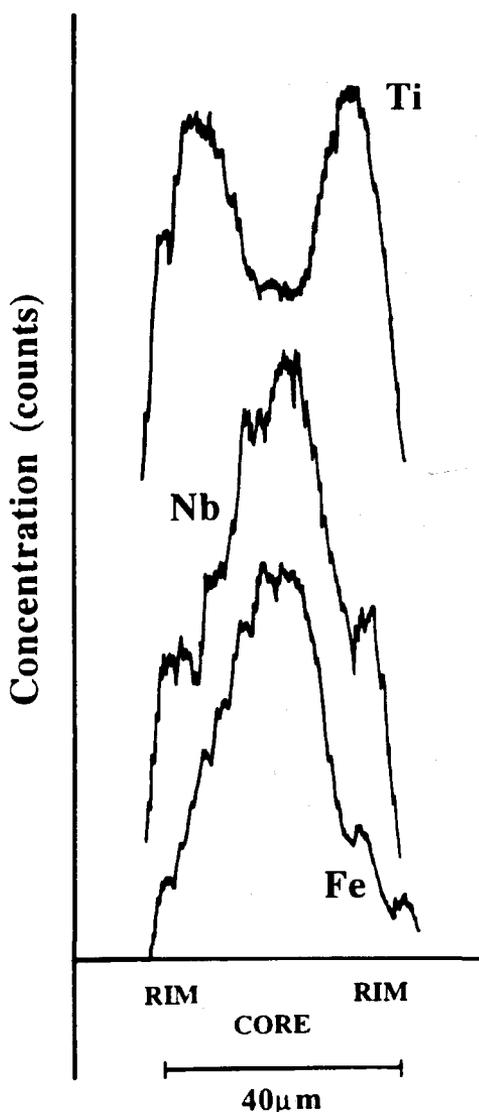
FIG. 2. Zoning profile determined by electron microp-robe of baotite grain in calcite-ankerite carbonatite, OU66211.

$Ba(Ti,Nb,Fe)_2SiO_7Cl$ (Peng, 1959), $Ba_4(Ti,Nb)_8$-$ClO_{16}Si_4O_{12}$ (Simonov, 1960), $Ba_4Ti_7NbSi_4O_{28}Cl$ (Semenov et al., 1961), $Ba_4Ti_4(Ti,Nb,Fe)_4ClO_{16}$-$Si_4O_{12}$ (Nekrasov et al., 1970), $Ba_6(Ti_4Nb)_2O_{22}$-$(Si_4O_{12})Cl$ (sic) (Shuriga et al., 1980) and finally, $Ba_4Ti_8Si_4O_{28}Cl_x$ (where $x = 0.6$ to 1.0) (Nemec, 1987). X-ray crystallographic analysis has shown that the baotite structure consists of $[Si_4O_{12}]$ rings (the first mineral to be shown to have this grouping), and square tubes or columns of Ti-Nb octahedra aligned parallel to the c-axis (Simonov, 1960; Nekrasov et al., 1970). A Cl atom occupies the large cavity between each pair of $[Si_4O_{12}]$ rings (Nekrasov et al., 1970, Fig. 2), while channels in the framework between metasilicate rings and Ti octahedral columns are filled by Ba cations. The structural refinement of Nekrasov et al. suggested that there are two crystallographically independent octahedral sites, Ti_1 and Ti_2. In the type material, from Inner Mongolia, Nb replaces Ti only in the Ti_2 site, although Nekrasov et al. (1970) acknowledge that there was a greater probability of Ti being replaced by Fe^{3+} in the Ti_1 site.

Haast River baotites have variable compositions with the octahedral site occupancies ranging from Ti-rich, Nb-Fe-poor (approximating to $Ti_{6.4}(Nb,Fe)_{1.6}$) to Ti-poor, Nb-Fe-rich (approximately $Ti_3(Nb,Fe)_5$). All analysed rocks contain baotites with higher combined Nb and Fe contents than any previously published analysis. The maximum Nb+Fe octahedral site occupancy exceeds the 4 cations needed to fill the Ti_2 octahedral site, with the surplus presumably accommodated in Ti_1.

Baotite exhibits a restricted range of compositions in all but two of the probed specimens. In OU66211 there are grains in which a (Nb,Fe)-rich baotite core is mantled by a Ti-rich overgrowth. Typical zoning profiles (Fig. 2) show a sharp transition between chemically homogeneous concentric zones. In OU66219 the zoning, although defining a very similar compositional transition, is more irregular and patchy. Zoning profiles and the analyses listed in Table 2 clearly indicate that there is a coupled substitution of Ti for Nb + Fe. In order to maintain charge balance and occupancy in the octahedral site the substitution mechanism could be:

$$2Ti^{4+} \rightleftharpoons Nb^{5+} + Fe^{3+}$$

or

$$3Ti^{4+} \rightleftharpoons 2Nb^{5+} + Fe^{2+}$$

or

$$5Ti^{4+} \rightleftharpoons 3Nb^{5+} + Fe^{3+} + Fe^{2+}$$
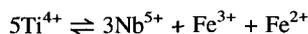
Other possible substitutions, where charge balance is maintained through the involvement of Cl^- (e.g. $Ti^{4+} \rightleftharpoons Nb^{5+} + Cl^-$, or $3Ti^{4+} \rightleftharpoons 2Nb^{5+} + Fe^{3+} + Cl^-$), are considered less likely since there is no systematic change in Cl content through the composition range observed,

and Nemec (1987; p 38) showed that essentially Nb-free baotites contain appreciable Cl and F.

If the substitution in natural baotites was $2Ti^{4+} \rightleftharpoons Nb^{5+} + Fe^{3+}$, as suggested by Nemec (1987; p. 37) and Johan et al. (1991; p. 23), and implied by Nekrasov et al. (1970), then the Nb:Fe ratio should theoretically be equal to 1.0. In New Zealand baotites the ratio varies between 1.86 and 3.14, with an average value (35 analyses) of 2.40. Similarly, the ratio of substituted Ti to Nb for all New Zealand baotites is close to 1.5 (average 1.471), requiring that the substitution mechanism should be of the form $3Ti^{4+} \rightleftharpoons 2Nb^{5+}$, rather than $2Ti^{4+} \rightleftharpoons Nb^{5+}$. The substitution mechanism in the octahedral site can be further assessed by plotting the Nb against Ti cation contents (Fig. 3). All Haast River baotites, together with analyses taken from the literature, cluster about the $3Ti^{4+} \rightleftharpoons 2Nb^{5+} + Fe^{2+}$ line and suggest that, as in rutile and tapiolite (Goldschmidt, 1954; Černý et al., 1964), this substitution dominates the octahedral Ti sites. The New Zealand baotites extend the range of compositions from essentially the Nb-free, Ti end member, $Ba_4Ti_8Si_4O_{28}Cl_x$ documented by Nemec (1987), through the type material of approximate composition $Ba_4Ti_4(Ti_{2.0}Nb_{1.4}Fe_{0.6})ClO_{16}Si_4O_{12}$ (Peng, 1959), to Nb-rich compositions close to $Ba_4[Ti_3(NbFe)_5]ClO_{16}Si_4O_{12}$. It is not clear whether $Ti_3(NbFe)_5$ represents the maximum extent of solid solution, or whether more extreme Nb substitution is possible. Irrespective of this question, which may only be answered as more baotites are analysed, the most niobian of the Haast River compositions has Nb>Ti, in contrast to the type material, in which Ti is dominant in both octahedral sites. If there are two crystallographically independent octahedral sites, as suggested by Nekrasov et al. (1970), and Nb is preferentially partitioned into one of them, then there is a strong possibility that many of the Haast River baotites have Nb>Ti in at least the Ti_2 site, even though Ti exceeds Nb in total octahedral site occupancy. It could be argued that dominance of Nb over Ti would warrant the recognition of a discrete mineral species.

Many analyses of baotite in Table 2 yield tetrahedral, octahedral, and Ba site occupancies significantly below those required to satisfy the ideal formula suggested by Nekrasov et al. (1971). All Haast River baotites were reanalysed under different analytical conditions, and using different standards, but the site deficiences remain. Johan et al. (1991) suggested that deficiences in the Ba site could be explained by coupled Ba site-tetrahedral site substitutions involving highly charged W^{6+} cations ($Ti^{4+} + Ba^{2+} \rightleftharpoons W^{6+} + \square$). However, given that in Haast River baotites the octahedral sites are free of more highly charged cations than Nb^{5+} and substitutions appear well characterized, the Ba and Si

TABLE 2. Baotite compositions

	66219 Dark	66219 Pale	66219 High Nb	66222 Avg. 2	58761 Avg.4	66211 Rim	66211 Core	66211 Low Nb	66216 Avg. 3	66212 Avg. 4	66223 Avg. 6	Peng 1959	Semenov et al. 1961
SiO_2	14.00	14.20	13.40	13.74	13.60	14.07	13.60	14.23	13.57	14.66	14.66	14.17	13.20
Al_2O_3	0.33	0.40	0.37	0.29	0.31	0.39	0.35	0.41	0.31	0.00	0.00	0.00	0.00
TiO_2	16.14	27.27	14.28	18.66	18.51	24.88	17.70	32.80	17.40	19.35	20.85	29.33	33.65
FeO^*	5.37	2.76	6.76	5.86	5.48	4.25	5.23	1.65	6.56	5.74	4.89	2.76	1.57
MnO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00
MgO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.05	0.01	0.00	0.00
CaO	0.00	0.07	0.03	0.00	0.00	0.05	0.03	0.03	0.01	0.00	0.00	0.00	0.00
BaO	36.79	37.07	35.73	35.99	36.42	37.41	35.55	38.45	35.99	36.33	37.29	37.55	38.60
Nb_2O_5	25.99	16.07	26.98	23.27	24.05	17.13	25.74	10.36	23.84	21.89	20.61	11.50	10.80
Cl	1.98	2.20	1.96	2.04	2.05	2.08	2.03	2.13	2.01	2.10	2.12	2.01	2.17
Total	100.60	100.04	99.51	99.85	100.42	100.26	100.23	100.06	99.69	100.13	100.44	97.32	99.99
Less O=Cl	0.45	0.50	0.44	0.46	0.46	0.47	0.46	0.48	0.45	0.47	0.48	0.45	0.49
Total	100.15	99.54	99.07	99.39	99.96	99.79	99.77	99.58	99.24	99.66	99.96	96.87	99.50

Structural formulae based on 28 oxygens

Si	3.812	3.714	3.723	3.732	3.684	3.729	3.676	3.672	3.721	3.944	3.928	3.808	3.438
Al	0.106	0.123	0.121	0.093	0.099	0.122	0.111	0.125	0.100	0.000	0.000	0.000	0.000
Σ^{IV}	3.918	3.837	3.844	3.824	3.783	3.851	3.787	3.796	3.821	3.944	3.928	3.808	3.438
Ti	3.306	5.364	2.984	3.812	3.771	4.960	3.598	6.366	3.589	3.916	4.202	5.929	6.592
Fe2+	1.223	0.604	1.571	1.331	1.241	0.942	1.182	0.356	1.504	1.292	1.096	0.620	0.342
Mn	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.002	0.002	0.000	0.000
Mg	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.020	0.004	0.000	0.000
Ca	0.000	0.020	0.009	0.000	0.000	0.014	0.009	0.008	0.003	0.000	0.000	0.000	0.000
Nb	3.200	1.900	3.389	2.857	2.945	2.052	3.145	1.208	2.955	2.663	2.496	1.397	1.272
Σ^{VI}	7.728	7.887	7.953	8.000	7.958	7.968	7.935	7.938	8.051	7.892	7.801	7.947	8.206
Ba	3.926	3.799	3.890	3.830	3.866	3.885	3.765	3.888	3.867	3.830	3.915	3.955	3.940
Cl	0.914	0.975	0.923	0.939	0.941	0.934	0.930	0.931	0.934	0.958	0.963	0.915	0.958
Total	15.573	15.523	15.687	15.655	15.607	15.705	15.487	15.622	15.740	15.667	15.644	15.709	15.583

* Total Fe as FeO
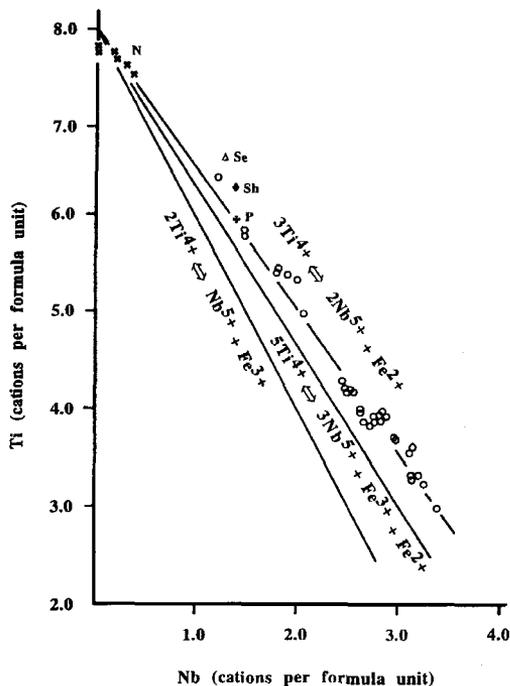
FIG. 3. Ti-Nb substitution in the octahedral site of baotite. All New Zealand baotites are represented by open circles, other symbols are analyses taken from the literature: P-Peng (1959), Se-Semenov et al. (1961), Sh-Shuriga et al. (1980), N-Nemec (1987). The baotite analyses of Johan et al. (1991) were not plotted since their octahedral substitutions are dominated by a Ti-W exchange.

analysis is not reported, so the discrepancy is difficult to resolve. If the Fe oxidation state is determined volumetrically (such as in the Wilson (1955) ammonium metavanadate method), a possible explanation might involve the presence in solution of the Nb^{5+} ion, which with its high Standard Electrode Potential, might be capable of oxidizing original Fe^{2+} to Fe^{3+}.

The large Cl atom occupies the cavities between the translationally identical $[Si_4O_{12}]$ rings (Simonov, 1960; Nekrasov et al., 1971). Semenov et al. (1961) suggested that the role of Cl was in the replacement $Nb^{5+} + Cl^- \rightleftharpoons Ti^{4+}$, but the presence of Cl in essentially Nb-free baotite (Nemec, 1987) suggests that this is inappropriate. The role of Cl is enigmatic in that a charged Cl anion is not required to balance the structure electrostatically. Low halogen contents have been reported for the Montana (0.45% Cl: Heinrich et al., 1962), Sebkovice (1.71% Cl) and Karlstein (1.43% Cl) baotites (Nemec, 1987), prompting the suggestion by Nemec that the baotite formula should be written as $Ba_4Ti_8Si_4O_{28}Cl_x$, where $x = 0.6-1.0$. However, Nemec (1987) cites an independent fluorine analysis for the Sebkovice baotite of 0.28 wt.% which, with the 1.71% Cl, yields a halogen occupancy of 0.94 atoms per formula unit. Contrary to the suggestion of Nemec (1987) the Cl + F content would appear to be constant, within the limits of analytical precision, and this is borne out by the constancy of Cl content over the extended range of Nb + Fe contents reported for Haast River baotites. Recent analyses by Johan et al. (1991) indicate chlorine contents of 1.2 atoms per formula unit, considerably in excess of that suggested for the ideal formula.

Crystallography

Baotite has attracted considerable attention from crystallographers, being the first silicate structure characterized by a quadruple (Si_4O_{12}) metasilicate ring (Simonov, 1960; Peng Chih-chung and Chang Kuang-jung, 1963; Nekrasov et al., 1970).

Two baotites, OU66223 and OU66211, were separated from their fenite and carbonatite hosts and X-rayed on a 114 mm diameter Debye-Sherrer powder camera. The resulting patterns show excellent agreement with X-ray diffraction data published by Heinrich et al. (1962), Nemec (1987) and Semenov et al. (1961). Using unambiguously indexed reflections, the unit cell parameters of the Haast River baotites were determined by least squares refinement using the programme of Benoit (1987). Despite the chemical zoning determined by microprobe in some grains of OU66211, no broadening of X-ray lines compared with those of OU66223 was observed on the powder photograph.

anomalies remain unexplained. The Si site deficiencies decrease with entry of Al^{3+}, but Al contents are generally low, often below detection limits, and reach a maximum content of only 0.127 cations per formula unit. Previous analyses of baotite (Peng, 1959; Nekrasov et al., 1971; Shuriga et al., 1980) also yield similar site deficiencies, so conceivably these may be an intrinsic feature of baotite.

Irrespective of whether these deficiencies are the result of contamination of the mineral separate, inferior analytical techniques, or natural site vacancies in the mineral, all occupancies are increased if the mineral formula is recalculated assuming Fe is present as Fe^{2+} rather than Fe^{3+}. Collectively, the stoichiometric evidence suggests that the Fe in baotite should be present as Fe^{2+}. Fe in baotites has, however, invariably been reported as Fe^{3+} (Peng, 1959; Semenov et al., 1961) or in microprobe analyses, recalculated as Fe^{3+} (Nemec, 1987; Johan et al., 1991). Usually the gravimetric method of

Cell parameters obtained for OU66211 are: $a = b = 19.9735 \pm 0.0013$ Å, $c = 6.0294 \pm 0.0004$ Å, $V = 2405.39 \pm 0.28$ Å^3, and for OU66223: $a = b = 20.063 \pm 0.028$ Å, $c = 6.042 \pm 0.005$ Å, $V = 2431.86 \pm 6.55$ Å^3. Rim sectors of zoned grains in OU66211 have lower Nb and Fe contents than the homogeneous population of OU66223 baotites, and appear from microprobe scans to form the majority of the OU66211 baotite population in this rock. Baotites from OU66211 have shorter a and b unit cell dimensions and a correspondingly smaller unit cell volume than those of OU66223. It is possible that the greater substitution in OU66223 of the larger ionic radius Nb (0.72 Å) for Ti (0.69 Å) is responsible for the increased cell size compared to that of OU66211. Cell dimensions of the Haast River baotites are larger than most published values, which have been determined for baotites of lower Nb and Fe content. The only comparably high cell parameters ($a = b = 20.02 \pm 0.02$ Å, $c = 6.006 \pm 0.004$ Å) are for the Montana occurrence described by Heinrich *et al.* (1962) for which no chemical analysis is given, and for the W-bearing baotite ($a = b = 19.92$ Å, $c = 5.93$ Å) documented by Johan *et al.* (1991).

Significance of baotite

Baotite is a widespread, but accessory phase at Haast River. It occurs in what would be traditionally considered in carbonatite nomenclature as relatively evolved ferrocarbonatites, in their adjacent fenites, and in broadly related hydrothermal or carbothermal veins that form along fault zones and fractures.

Baotite testifies to the presence of a halogen component in carbonatite magmas. Halogens, in particular fluorine, have long been known as an essential ingredient of carbonatites, manifest generally in the ubiquitous appearance of fluorite, fluor-micas (e.g. Cooper *et al.*, 1995), pyrochlore (Hogarth, 1989) and fluor-carbonates of the bastnae-site group. Fluorite, in particular, attains the status of an essential rock-forming mineral, subordinate only to nyerereite and gregoryite, in the 1988 natrocarbon-atites of Oldoinyo Lengai (Keller and Krafft, 1989). Chlorine-bearing minerals are less widely reported, although sodalite and halite are listed by Hogarth (1989) as carbonatite minerals, and halite has been described subsequently, together with sylvite, as an essential phase in the F-Cl-rich groundmass of 1963 pahoehoe natrocarbonatite lavas of Oldoinyo Lengai (Peterson, 1990). Chlorine is also an integral component of fluids associated with carbonatites, with many authors proposing that the essential fenitizing agent is an alkali carbonate-chloride fluid or brine (Woolley, 1969; Currie and Ferguson, 1971; Gittins, 1989). Evidence here is in the composition of fluid inclusions in carbonatite minerals (Rankin,

1977; Andersen, 1986) and in the presence of daughter minerals of diverse character, but including carbonates, sulphates, and chlorides, which have precipitated from such fluids (Nesbitt and Kelly, 1977). Additional significance has recently been attached to halogens, in particular F, in depressing the liquidus of carbonatite magmas to geologically reasonable temperatures (Jago and Gittins, 1991) and in controlling the magmatic crystallization of pyrochlore, a characteristic early carbonatite mineral (Jago and Gittins, 1993).

The ultimate source of chlorine in the Haast River carbonatites is probably from the associated silicate magmas. On the basis of pyroxene composition, and their often intimate field association, I suggested that the carbonatites were derived by liquid immiscibility from carbonated phonolitic or tinguaitic parent magmas (Cooper, 1986). Tinguaites are composed essentially of alkali feldspar, nepheline, and aegirine-rich pyroxene, but the undersaturated and chlorine-rich nature of the magma is underlined by the abundance of sodalite. During liquid immiscibility, some of the chlorine will be partitioned into the carbonatite and associated fluid, some ultimately crystallizing as baotite. The distribution coefficient for chlorine between coexisting immiscible silicate and carbonatite melts has not been determined experimentally. However, if the phonolite and natrocarbonatite from Oldoinyo Lengai are indeed immiscible pairs (Freestone and Hamilton, 1980; Dawson *et al.*, 1994), then the whole-rock analyses summarized in Dawson (1989) would suggest that K_D is likely to be low, with Cl strongly partitioned into carbonatite.

Conclusions

(1) Baotite occurs as a widespread accessory constituent of petrogenetically evolved, Ba-Sr-rich, ankeritic and sideritic ferrocarbonatites, their associated fenites, and mineral veins derived from related carbothermal fluids.

(2) Baotite compositions are richer in Nb and Fe than any previously analysed examples, with the extreme composition approximating to $Ba_4Ti_3(Nb,Fe)_5Si_4O_{28}Cl$. The Nb and/or Fe content must be accommodated in both of the structurally independent octahedral sites proposed by Nekrasov *et al.* (1971). Mineral zoning, the range of baotite compositions and stoichiometry arguments suggest that the dominant substitution in the octahedral sites is $3Ti^{4+} \rightleftharpoons 2Nb^{5+} + Fe^{2+}$, similar to that proposed for structurally similar octahedral chains in rutile. In contrast, all previous analyses and mineralogical studies have determined, or assumed, that Fe in baotite is present as Fe^{3+}.

(3) The presence of baotite in carbonatites and fenites emphasizes the petrogenetic importance of halogens to the evolution of carbonatite magma–fluid systems. It is suggested that in the lamprophyre-tinguaite association occurring at Haast River, New Zealand, chlorine originates in the silicate magma stem, and is partitioned into carbonatite magma and associated fluid (capable of producing the observed fenitization) during liquid immiscibility.

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