Niobian K–Ba–V titanates from micaceous kimberlite, Star mine, Orange Free State, South Africa

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Abstract

Compositional data are presented for Nb–Ba–K–V titanates from micaceous kimberlite (Star mine, S. Africa). These data significantly extend the previously known range of solid solutions in naturally occurring members of the hollandite group. Two distinct suites of crystals occur. One is a suite of primary groundmass prismatic crystals that are Ba–K–V-rich and represent solid-solutions from the priderite series towards mannardite. The second suite consists of anhedral xenocrysts that are Ba-free. In this suite relatively Nb-rich varieties (>4.0% Nb_2O_5) represent solid-solution towards a niobian-bearing potassian analogue of mannardite, whereas relative Nb-poor (<3.0% Nb_2O_5) varieties are Nb-bearing vanadian priderites. These hollandite-group minerals have compositions that differ significantly from priderites found in lamproites.

KEYWORDS: K–V–Ba titanate, hollandite, priderite, kimberlite, lamproites, Star mine, South Africa.

Introduction

COMPLEX K–Ba–V titanates belonging to the hollandite (AB_8O_{16}) structural group have been recognized in the New Elands micaceous kimberlite, South Africa (Mitchell and Haggerty, 1986) and the Argyle lamproite, Western Australia (Jaques et al., 1989). Mitchell and Meyer (1989) noted that K–Ba titanates also occur in the Star kimberlites. This paper presents compositional data for niobium-bearing K–Ba–V titanates from the Star kimberlite that significantly extends the previously known range of solid-solutions in hollandite group minerals.

Occurrence

The Star kimberlite is located in the Winburg District of the Orange Free State about 15 km northeast of Theunisen. The kimberlite, occurring in four near vertical dykes, is a macrocrystal phlogopite kimberlite in terms of the petrographic classification of Skinner and Clement (1979). The macrocrysts of rounded olivine and distorted laths of phlogopite are set in a closely packed mosaic of tabular phlogopite microphenocrysts. Other primary groundmass minerals include spinels, perovskite, apatite, pyrite and calcite. Compositional data for phlogopite and spinels in this kimberlite are provided by Mitchell and Meyer (1989).

K–Ba–V titanates occur in two distinct physical and chemical suites. One suite is present as stellate clusters of subhedral prismatic crystals; the other consists of anhedral isolated grains. The stellate prisms are commonly enclosed within groundmass calcite. Most crystals are very small (<1 mm), but some of the prisms reach up to 20 μm in length and 10 mm in width. Back-scattered electron imagery demonstrates that the larger crystals are zoned towards margins of higher average atomic number than their cores (Fig. 1). This zonation reflects marginal Ba-enrichment (see below).

Analytical methods

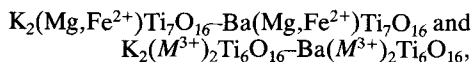The titanates were analysed by standard wavelength dispersive electron microprobe methods

FIG. 1. Back scattered electron image of prismatic titanate. Compositions 3 and 4 (Table 1) are of the core and mantle respectively.

(Table 1) and by a Hitachi 570 SEM equipped with a Tracor-Northern TN5500 energy dispersive system (Table 2). This latter instrument was used as the majority of the titanate crystals were very small ($<1\,\mu$m). Quantitative analyses for the SEM/EDS were obtained using the Tracor-Northern 'standardless' quantitative analysis package SQ. This program is based upon multiple least-squares fitting of the sample spectra to reference spectra as described by McMillan *et al.* (1985). Our experience with SQ has demonstrated that the technique is suitable for the analysis of elements with atomic numbers greater than fifteen in a heavy matrix. Light elements are not satisfactorily determined as the absorption correction is over emphasized. The suitability of the method was cross-checked by analysis of priderite and jeppeite samples that had been analysed by wavelength dispersion electron microprobe. Table 2 (compositions 11–14) provides comparative energy dispersive and microprobe data. Agreement between the two methods is excellent for priderite and satisfactory for jeppeite.

Nomenclature

Mitchell and Haggerty (1986) noted that K–Ba–V titanates of the hollandite group are members of the solid solution series between:

$$K_2(Mg,Fe^{2+})Ti_7O_{16}\text{–}Ba(Mg,Fe^{2+})Ti_7O_{16}\text{ and}$$
$$K_2(M^{3+})_2Ti_6O_{16}\text{–}Ba(M^{3+})_2Ti_6O_{16},$$

where M^{3+} = Cr,Al,V,Fe^{3+},Ce^{3+}. The existing nomenclature of these phases is unsatisfactory, as only three of the many possible end-member molecules have been described as mineral species.

These are $BaFe_2^{3+}Ti_6O_{16}$, termed barian priderite (Zhuravleva *et al.*, 1978), $BaV_2Ti_6O_{16}$, named mannardite (Scott and Peatfield, 1986) and $BaCr_2$-Ti_6O_{16}, named redledgeite (Gatehouse *et al.*, 1986). Only mannardite and redledgeite have been accepted by the International Mineralogical Association as valid names. Following current conventions of mineral nomenclature (Nickel and Mandarino, 1987) the potassian varieties of these minerals are referred to as the potassium analogues of mannardite and redledgeite, although there are precedents, i.e. lindsleyite–mathiasite (Haggerty *et al.*, 1983) and yimengite (Dong *et al.*, 1983)–hawthorneite (Haggerty *et al.*, 1989), which suggest that these potassium end-members could be given new mineral names.

Although priderite (Norrish, 1951) is accepted as a valid name, it is not actually an end-member composition. Most priderites are in fact intermediate members of the

$$K_2(Fe^{2+},Mg)Ti_7O_{16}\text{–}Ba(Fe^{2+},Mg)Ti_7O_{16}$$
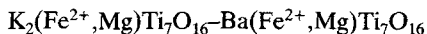
series, with some solid solution towards hollandites containing 6 Ti atoms/unit cell. The mineral $BaFe_2^{3+}Ti_6O_{16}$ is an end-member molecule for which a new name is desirable. If priderite is to be retained as valid mineral species then the term must be redefined as

$$K_2(Mg,Fe^{2+})Ti_7O_{16}\text{ or }Ba(Mg,Fe^{2+})Ti_7O_{16}.$$
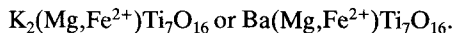
More logically, the solid-solution series of hollandites based upon 7 Ti atoms/unit cell (Dubeau and Edgar, 1985) might be named the priderite-series.

Titanium-based members of the hollandite group may be assigned the general formula $A_xB_yC_{8-z}O_{16}$, where

$A = K^+,Ba^{2+}$;
$B = V^{3+},Cr^{3+},Ce^{3+},Fe^{3+},Fe^{2+},Mg^{2+}$;
$C = Ti^{4+},Nb^{5+}$.
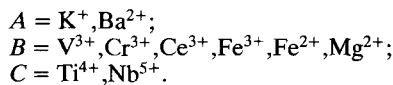
Ideally, x, y and z lie between unity and two. The A cations represent atoms situated in 8-fold sites lying at the centres of the tunnel structures formed by chains of MO_6 octahedra (where M = $B + C$ = 8). Determination of the structural formula is complicated by the common occurrence of non-stoichiometry and the presence of elements that occur in two valence states, e.g. Fe and Ti (Myhra *et al.*, 1988). All general formulae quoted are based upon 16 oxygens but it should be realized that this convention is followed only so that different hollandites may be compared on the same basis. The actual oxygen content and number of cation vacancies may vary substantially depending upon composition (Myhra *et al.*, 1988; Kesson and White, 1986).

Table 1. Representative compositions of prismatic K-Ba-V-Nb titanates in the Star kimberlite obtained by wavelength dispersive electron microprobe.

	1	2	3	4	5	6	7
SiO_2	0.02	0.31	0.00	0.18	0.05	0.20	0.17
TiO_2	71.3	67.1	72.9	66.2	65.9	66.9	70.3
Cr_2O_3	0.71	0.41	0.94	0.34	0.46	0.58	0.62
Fe_2O_3	6.62	6.49	6.87	4.12	4.46	4.19	5.41
MgO	0.21	0.21	0.23	0.10	0.12	0.10	0.12
V_2O_3	2.79	5.11	1.19	9.45	9.06	9.85	5.87
Nb_2O_5	4.57	1.87	3.78	0.53	0.89	0.87	1.34
K_2O	4.81	1.66	5.06	1.32	2.22	2.66	6.06
BaO	8.36	15.6	7.92	16.4	16.7	15.8	8.9
	99.4	98.8	98.9	98.6	100.3	101.0	98.8

Compositions 1-2, 3-4 and cores and mantles respectively of mantled prismatic titanate; 5-7 continuously zoned prismatic titanate mantle. Analyses 1-4, 5-7 by JEOL and CAMECA microprobes respectively.

Composition

Tables 1 and 2, and Figs 2 and 3 demonstrate that there is considerable variation in the composition of the hollandites analysed. Table 1 shows that the margins of crystals are enriched in BaO, V_2O_3 and depleted in K_2O and Nb_2O_5 relative to the cores. The small size of most of the prismatic crystals did not permit a detailed study of zoning and mantling patterns. Compositional data plotted in Figs 2 and 3 are representative of cores, margins or intermediate regions and are presented to illustrate the wide range of compositions occurring in the prismatic grains. Anhedral crystals were too small to allow detection of zoning although considerable inter-grain variation is demonstrably present (Figs 2 and 3).

The titanates analysed fall into two broad compositional groups:

(1) Ba–V-rich titanates (BaO = 5.9–16.7%; V_2O_3 = 2.5–9.85%) that are relatively poor in Nb_2O_5 (0.5–5.0%) and represent the stellate prismatic crystals. Cr_2O_3 contents range from not detectable to 2.39%. Fe_2O_3 contents (4.0–7.1%) are low relative to priderites from lamproites (8–11% Fe_2O_3; Mitchell, 1985). Fig. 2 illustrates the wide variation in $K/(K + Ba)$ and $Fe^{3+}/(Fe^{3+} + V)$ ratios. Compositions range from $A_{0.97}B_{0.97}C_{6.39}O_{16}(M = 7.73)$ to $A_{1.48}B_{1.47}C_{6.91}O_{16}(M = 7.87)$ and average (23 samples) $A_{1.10}B_{1.16}C_{6.59}O_{16}(M = 7.81)$. A positive correlation between decreasing C, decreasing $Fe^{3+}/(Fe^{3+} + V)$ and increasing Ba/K represent increasing amounts of solid solution towards the potassium analogue of mannardite–$(K, Ba)_{1-2}Fe_2^{3+}Ti_6O_{16}$ series and mannardite.

(2) Ba poor-to-free, V-poor titanates (BaO = 0–0.9%; V_2O_3 = 1.5–4.4%) that exhibit a wide range in Nb_2O_5 (0.8–6.5%) content and occur as anhedral crystals. Cr_2O_3 ranges from 0.1% to 1.4%. Fe_2O_3 contents (3.2–7.0%) are low relative to priderites from lamproites. The compositional variation is not as extensive as that shown by the group 1 prismatic titanates. Figs 2 and 3 suggest the existence of two subgroups, one relatively rich in Nb_2O_5 (>4.0%) and the other relatively poor in Nb_2O_5 (<3.0%).

The Nb-rich subgroup (4 samples) has an average composition of $A_{1.34}B_{0.97}C_{6.87}O_{16}(M = 7.85)$. Increasing Nb is coupled with increasing V and decreasing Ti suggesting solid-solution towards a niobian-bearing potassium analogue of mannardite.

The Nb-poor subgroup (12 samples) are all Ti7-based titanates closely related in composition to priderite, but being relatively richer in V_2O_3. They range in composition from $A_{1.22}B_{0.74}C_{6.93}O_{16}(M = 7.78)$ to $A_{1.38}B_{0.92}C_{7.09}O_{16}(M = 7.87)$ and average $A_{1.29}B_{0.79}C_{7.04}O_{16}(M = 7.82)$, and may be regarded as vanadian members of the Ba-free priderite series.

Discussion

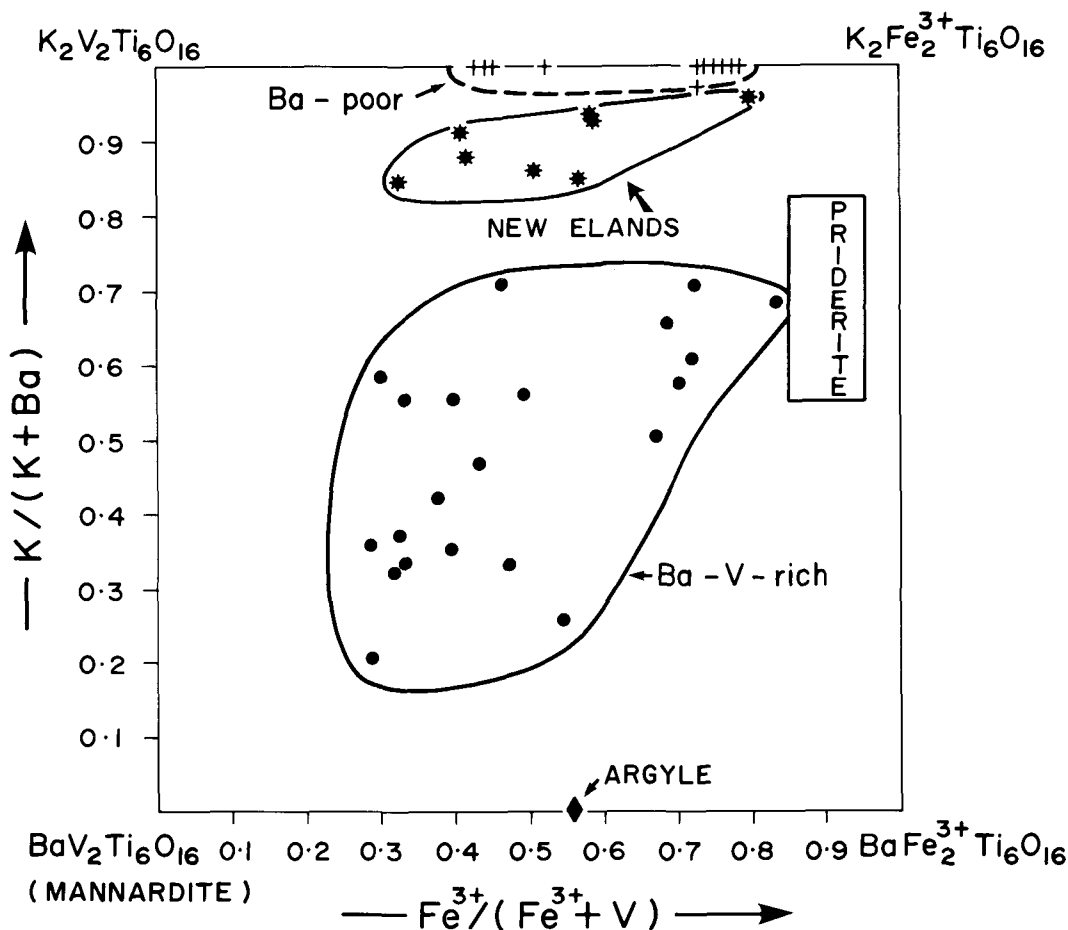Titanium-based members of the hollandite group of the compositions reported here have not

FIG. 2. Compositions of titanates from Star kimberlites plotted as K/(K + Ba) versus $Fe^{3+}/(Fe^{3+} + V)$ ratios. Field of lamproite priderite compositions from Mitchell (1985) and unpublished data. Argyle hollandite from Jaques *et al.* (1989). Field for New Elands K–Ba–V titanates from Mitchell and Haggerty (1986).

previously been recognized. They differ from the priderite series of titanates occurring in lamproites (Fig. 2) in being relatively poor in Fe and rich in V and/or Nb. Some examples are Ba-free in marked contrast to all priderites so far examined from lamproites (Mitchell, 1985; Jaques *et al.*, 1989). Hollandites from the Argyle lamproite (Jaques *et al.*, 1988) differ from those described here in being BaO (20.9%), Cr_2O_3 (6.0%) and Ce_2O_3 (4.0%)-rich and in being K_2O-free (Fig. 2).

K–Ba–V titanates from the New Elands kimberlite are similar in composition and paragenesis to the stellate prismatic crystals described here. Mitchell and Haggerty (1986) concluded that such crystals represent primary groundmass phases formed as a consequence of the concentration of incompatible elements during kimberlite crystallization. The New Elands titanates differ mainly in containing major amounts of Ce_2O_3 and not being as rich in Ba and V, i.e. do not show such extensive solid-solution towards mannardite. The cerium content of the New Elands titanate is real (Haggerty, pers. comm.) and not due to interference from Ba as suggested by Grey *et al.* (1987). Cerium was not detected in the Star material.

The anhedral habit of the Nb–K–V-titanates lacking Ba suggests that these are not late-stage groundmass phases. A xenocrystal origin would seem plausible and in keeping with the recognition of other exotic mantle-derived titanates in kimberlites (Haggerty, 1983). The high Nb-content of some of these samples supports the existence of Nb analogues of Ti-based hollandites.

Table 2. Representative compositions of K-Ba-V-Nb titanates obtained by SEM/EDS.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
SiO$_2$	0.3	0.3	0.3	0.6	0.4	0.1	0.5	0.3	0.2	0.4	0.2	n.d.	0.2	0.2
TiO$_2$	69.4	68.3	67.9	74.1	71.6	75.3	74.5	80.9	75.6	79.7	76.2	76.3	71.2	70.6
Fe$_2$O$_3$	4.5	5.2	5.8	7.1	7.1	3.8	3.9	7.0	3.3	5.7	10.4	10.6	5.0	4.8
Cr$_2$O$_3$	0.1	2.4	1.1	0.5	0.6	1.1	1.4	0.2	1.3	0.6	0.0	n.d.	0.0	n.d.
V$_2$O$_3$	8.2	6.4	6.1	2.6	2.8	4.4	3.1	1.4	4.1	1.6	0.7	n.d.	0.9	n.d.
Nb$_2$O$_5$	0.5	0.2	0.6	2.6	2.9	4.8	6.5	1.6	5.9	2.5	0.0	n.d.	0.2	n.d.
MgO	0.0	0.5	0.3	0.3	0.2	1.4	1.0	0.1	0.8	0.5	1.0	1.1	0.0	0.4
K$_2$O	2.2	3.5	2.4	4.1	4.3	9.1	9.1	8.5	8.9	9.1	6.7	7.1	8.9	10.5
BaO	14.8	13.3	15.6	8.4	10.3	0.0	0.0	0.0	0.0	0.0	5.0	5.0	13.7	14.0

Compositions 1-10 K-Ba-V-Nb-titanates, Star kimberlite; 11, 13 priderite and jeppeite respectively from the Wolgidee Hills, W. Australia analysed by SEM-EDS; 12, 14 priderite (11) and jeppeite (13) analysed by wavelength dispersive electron microprobe (ARL-SMQ). n.d.=not determined. Compositions 1-5 and 6-10 are prismatic and anhedral crystals respectively.

No totals given as Tracor-Northern quantitative program SQ automatically sums to 100%.

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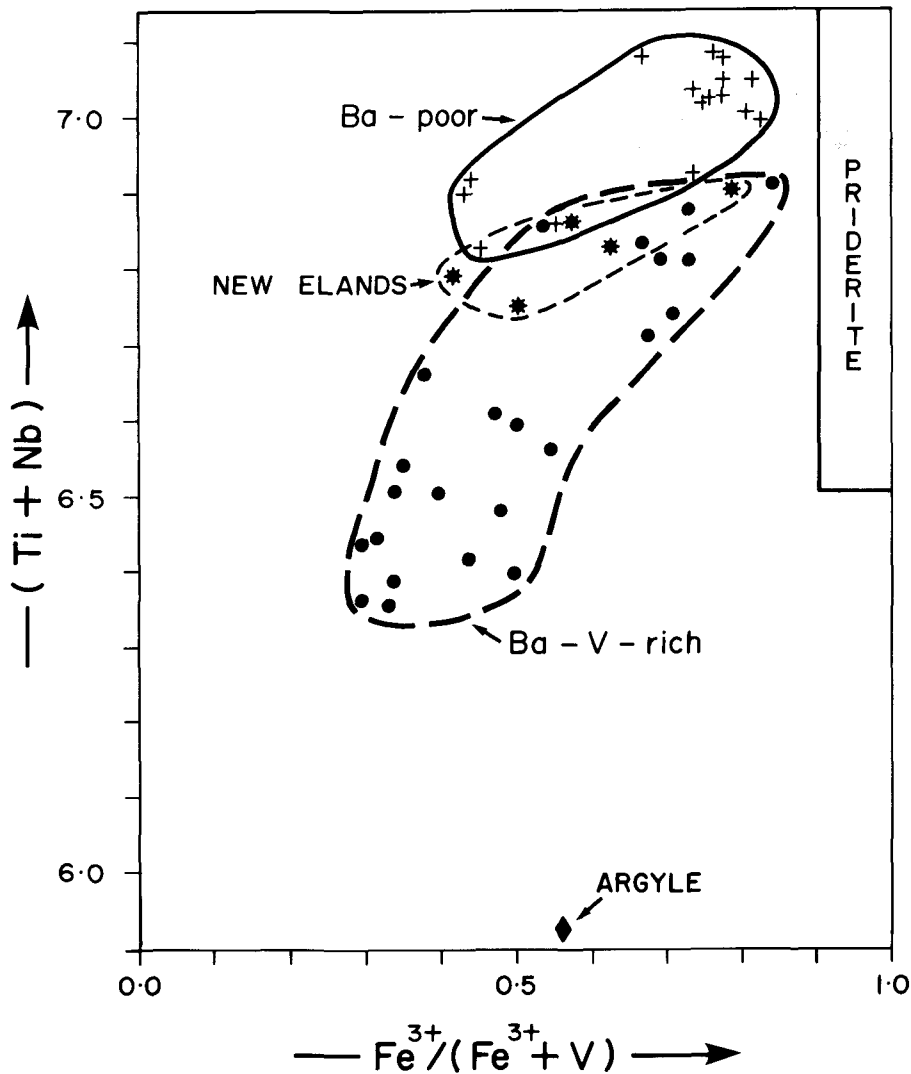
FIG. 3. Compositions of titanates from the Star kimberlite plotted as $Ti + Nb$ versus $Fe^{3+}/(Fe^{3+} + V)$ ratios. Data sources for lamproite and New Elands titanates given in Fig. 2.

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