

# Replacement phenomena in tantalum minerals from rare-metal pegmatites in South Africa and Namibia

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## Abstract

Manganotantalite replacement by (1) microlite and (2) ferrotantalite, and changes in composition of uranoan microlite from rare-metal pegmatites in South Africa and Namibia have been investigated with the electron microprobe. A uranomicrolite from Karibib, Namibia contained 14.35%  $\text{UO}_2$ , 1.03%  $\text{PbO}$ , 56.12%  $\text{Ta}_2\text{O}_5$ , 13.18%  $\text{Nb}_2\text{O}_5$ , 0.58%  $\text{Fe}_2\text{O}_3$ , 6.87%  $\text{CaO}$ , 0.54%  $\text{SrO}$ , 0.59%  $\text{MnO}$ , 0.86%  $\text{Na}_2\text{O}$  and 0.47%  $\text{F}$ . Analyses along traverses across a 1.3 mm uranoan microlite, Tantalite Valley, Namibia, revealed two essentially distinct compositions: a more hydrated rim area of 200  $\mu\text{m}$  radius containing 7% higher  $\text{Ta}_2\text{O}_5$ , 10% lower  $\text{CaO}$  and 1.3% lower  $\text{F}$  than a main central area of slightly variable composition. Back-scattered electron images reveal zoning and distinctive subspheroidal structures. New data and structural features are given for radioactive uranoan microlite from Namaqualand, South Africa. These crystals contain remnants of a bismuth phase and are in various stages of replacement. In the microlites replacing manganotantalite, the microlite reflects the composition of the replaced mineral. At Rubicon Mine, Karibib, a narrow marginal zone of manganotantalite is replaced by ferrotantalite along cleavages; a zone of intermediate composition is apparent. Detailed traverses have been completed across all of these crystals.

**KEYWORDS:** microlite, manganotantalite, ferrotantalite, South Africa, Namibia, replacement.

## Introduction

MICROLITE minerals of the pyrochlore-group have been analysed with the electron microprobe, initially because of their rare occurrence and unusual and varied composition, and also because of their association with and replacement of other tantalum minerals. On a preliminary investigation the microlites appeared to be inhomogeneous although all the microlite crystals are isotropic. Detailed traverses have been completed across several crystals to investigate zoning. This paper presents new data on uranomicrolite and detailed results on uranoan microlite; new data are given on secondary microlite, i.e. replacement of manganotantalite by microlite, and on zoning and replacement of manganotantalite by ferrotantalite from differentiated lithium pegmatites in (1) Namaqualand, South Africa, (2) Tantalite Valley, Namibia, and (3) the Karibib/Usakos area, Namibia.

The microlites have been confirmed by X-ray diffraction photographs at the Natural History Museum and by O. von Knorring with the excep-

tion of the uranomicrolite from Okongava, Karibib (due to insufficient material) and the uranoan microlite from Tantalite Valley.

## Geological setting of the pegmatites

The pegmatites containing tantalum are usually complex, well differentiated bodies, and microlite associated with tantalite is frequently found in the intermediate zone, marginal to the quartz core. Sometimes these minerals are developed in feldspar which has been albitized to 'sugary albite'. In addition microlite may also be found in replacement units consisting of cleavelandite and lithian mica, and also in albite-spodumene-lithian mica units.

(1) The Steinkopf area, Namaqualand, occupies the extreme west of a continuous belt of pegmatites which runs east-west for 450 km across the northern Cape Province of South Africa (Gevers, 1937). This prominent belt is 30–60 km wide and extends from Putsonderwater in the east to Richtersveld in the west. In the Steinkopf region of the belt, lithium minerals are widely

TABLE 1. *Microclites from South Africa and Namibia*

|                                  | 1      | 2      | 3a    | 3b    | 4a    | 4b    | 5     |
|----------------------------------|--------|--------|-------|-------|-------|-------|-------|
| Ta <sub>2</sub> O <sub>5</sub>   | 73.48  | 82.57  | 66.64 | 73.74 | 57.14 | 67.26 | 56.12 |
| Nb <sub>2</sub> O <sub>5</sub>   | 5.20   | 1.24   | 2.29  | 2.63  | 5.56  | 5.43  | 13.18 |
| TiO <sub>2</sub>                 | 1.11   | 0.16   | 0.04  | 0.07  | 6.96  | 3.00  | 0.00  |
| WO <sub>3</sub>                  | 0.77   | 0.62   | 0.68  | 0.99  | 0.39  | 0.45  | 0.00  |
| Al <sub>2</sub> O <sub>3</sub>   | tr.    | 0.00   | 0.24  | 0.24  | 0.12  | 0.41  | 0.00  |
| Fe <sub>2</sub> O <sub>3</sub> * | 0.26   | tr.    | 0.64  | 0.97  | 0.13  | 0.17  | 0.58  |
| UO <sub>2</sub> **               | 0.56   | 0.23   | 7.71  | 8.41  | 4.03  | 0.77  | 14.35 |
| Bi <sub>2</sub> O <sub>3</sub>   | -      | -      | -     | -     | 4.27  | 1.67  | -     |
| CaO                              | 13.77  | 10.60  | 15.29 | 4.61  | 16.21 | 14.62 | 6.87  |
| SrO                              | 0.13   | 0.00   | 0.26  | 1.13  | 0.00  | 0.00  | 0.54  |
| BaO                              | 0.00   | 0.00   | 0.21  | 0.37  | 0.00  | 0.00  | 0.00  |
| PbO                              | tr.    | 0.00   | 0.40  | 0.53  | 0.53  | 0.15  | 1.03  |
| MnO                              | 0.47   | tr.    | 1.66  | 1.38  | 0.85  | 0.81  | 0.59  |
| Na <sub>2</sub> O                | 2.44   | 5.23   | 0.43  | 0.25  | 0.91  | 1.90  | 0.86  |
| F                                | 2.17   | 1.20   | 1.62  | 0.33  | 1.78  | 2.27  | 0.47  |
| Total                            | 100.36 | 101.85 | 98.11 | 95.65 | 98.88 | 98.91 | 94.59 |
| -O=F                             | 0.91   | 0.50   | 0.68  | 0.14  | 0.75  | 0.95  | 0.19  |
|                                  | 99.45  | 101.35 | 97.43 | 95.51 | 98.13 | 97.96 | 94.40 |
| IONS per 2B                      |        |        |       |       |       |       |       |
| Ta                               | 1.696  | 1.928  | 1.801 | 1.777 | 1.316 | 1.540 | 1.409 |
| Nb                               | 0.199  | 0.048  | 0.103 | 0.105 | 0.213 | 0.207 | 0.550 |
| Ti                               | 0.071  | 0.010  | 0.003 | 0.005 | 0.443 | 0.190 | 0.000 |
| W                                | 0.017  | 0.014  | 0.017 | 0.023 | 0.009 | 0.010 | 0.000 |
| Al                               | 0.000  | 0.000  | 0.028 | 0.025 | 0.012 | 0.041 | 0.000 |
| Fe                               | 0.017  | 0.000  | 0.048 | 0.064 | 0.008 | 0.011 | 0.041 |
| Total B site                     | 2.     | 2.     | 2.    | 2.    | 2.    | 2.    | 2.    |
| Bi                               | -      | -      | -     | -     | 0.094 | 0.037 | -     |
| Ca                               | 1.251  | 0.975  | 1.627 | 0.438 | 1.470 | 1.320 | 0.679 |
| Sr                               | 0.007  | 0.000  | 0.015 | 0.058 | 0.000 | 0.000 | 0.029 |
| Ba                               | 0.000  | 0.000  | 0.008 | 0.013 | 0.000 | 0.000 | 0.000 |
| Pb                               | 0.000  | 0.000  | 0.011 | 0.013 | 0.012 | 0.004 | 0.026 |
| Mn                               | 0.034  | 0.000  | 0.140 | 0.104 | 0.061 | 0.058 | 0.046 |
| Na                               | 0.401  | 0.870  | 0.083 | 0.043 | 0.150 | 0.310 | 0.154 |
| U                                | 0.011  | 0.005  | 0.170 | 0.166 | 0.076 | 0.015 | 0.295 |
| Total A site                     | 1.704  | 1.85   | 2.054 | 0.835 | 1.863 | 1.744 | 1.229 |
| F                                | 0.58   | 0.33   | 0.50  | 0.09  | 0.47  | 0.61  | 0.14  |

1. Secondary microlite, Noumas pegmatite, Namaqualand, South Africa.
  2. Secondary microlite, Homestead pegmatite, Tantalite Valley, S.W. Africa.
  - 3a. Uraoan microlite (Ave. central area), Lepidolite pegmatite, Tantalite Valley, S.W. Africa.
  - 3b. Uraoan microlite (Ave. rim of crystal), Lepidolite pegmatite, Tantalite Valley, S.W. Africa.
  - 4a. Uraoan microlite (2) (central area), Kokerboomrand pegmatite, Namaqualand, South Africa.
  - 4b. Uraoan microlite (2) (Ave.intermediate area), Kokerboomrand pegmatite, Namaqualand, South Africa.
  5. Uranmicrolite, Okongava Ost, Karibib, S.W. Africa.
- \* Total iron as Fe<sub>2</sub>O<sub>3</sub>. \*\* Total U as UO<sub>2</sub>.

distributed, with spodumene of major significance. Two of the major pegmatites of the area are the Noumas pegmatite situated 40 km north of Steinkopf and the Kokerboomrand pegmatite.

(2) Tantalite Valley in the Karasburg district, Namibia, is a mountainous area of 50 square km, situated some 40 km south of Warmbad and 10 km north of the Orange River. The pegmatites in the area are up to 1000 m along strike and belong to the Namaqualand pegmatite province. Two of the largest prominently mineralized pegmatites in the Valley are the Homestead and Lepidolite pegmatites.

(3) Pegmatites occur at various levels within the Damara succession in Namibia. The pegmatites are associated with granites that are intrusive into the Damara sequence. In the area of Karibib, north west of Windhoek, there are numerous

mineralized rare-metal pegmatites which are an important source of Li, Cs, Rb, Be, Nb, Ta and Bi minerals. This pegmatite field is approximately 200 km long and 100 km wide and is one of the most extensive economic pegmatite fields in the world. The pegmatites have a typical geochemical pattern, where Li, Na and K phases are well developed and the minerals lepidolite, petalite, amblygonite, Li-Mn-Fe phosphates, microcline, albite (cleavelandite), muscovite, beryl and tourmaline are common.

#### Chemical composition of manganotantalites and microlites

Secondary microlites are formed by various alteration processes of hydration or replacement

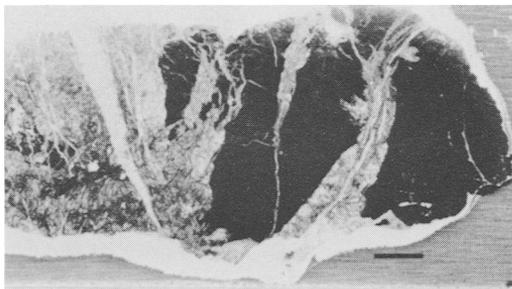


Fig. 1. Photomicrograph in transmitted light, of micro-lite veins (grey) replacing manganotantalite (black), Homestead pegmatite, Tantalite Valley, Namibia. Scale bar: 2 mm

of other tantalum minerals. Their chemistry frequently reflects the composition of the replaced minerals (von Knorring and Fadipe, 1981). Two examples of secondary microlites replacing manganotantalite have been investigated with the microprobe from (1) the Noumas pegmatite, Namaqualand, and from (2) the Homestead pegmatite in Tantalite Valley.

The microanalyser used was a Cambridge Instrument Microscan 5, with an accelerating potential of 20 kV and a beam current measured by a Faraday cage of 30 nA for crystal spectrometry. A full ZAF correction procedure as described by Sweatman and Long (1969) was used to calculate final concentrations. In WDS techniques the 95% confidence limit for Ta up to the 75% level is  $\pm 0.46$  wt. %; for Ca, Fe, Mn and U at the 15% level  $\pm 0.08$ ,  $\pm 0.09$ ,  $\pm 0.10$  and  $\pm 0.27$  wt. % respectively; with similar values for the minor elements. The standards used were tantalum metal (Ta), niobium metal (Nb), uranium metal (U), rutile (Ti), galena (Pb), celestite (Sr), jadeite (Na), wollastonite (Ca), manganese metal (Mn), iron metal (Fe), tungsten metal (W), bismuth metal (Bi) and magnesium fluoride (F).

Black tantalite from the Noumas pegmatite is replaced by brown microlite to a very small degree at certain edges of the crystal. The main mineral is manganotantalite which is opaque in transmitted light. Three specific areas of microlite were analysed with the microprobe and an average analysis contained 73.48% Ta<sub>2</sub>O<sub>5</sub> (range 72.99–75.92%) and 5.20% Nb<sub>2</sub>O<sub>5</sub> (4.32–6.11%) with CaO 13.77% (12.88–15.15%) and Na<sub>2</sub>O 2.44% (Table 1, anal. 1, ave 8 anal.). A traverse across the manganotantalite showed the mineral to be variable in composition with Ta<sub>2</sub>O<sub>5</sub> over the range 71.84–73.63% (ave. 72.34% in 5 anal.); Nb<sub>2</sub>O<sub>5</sub> 11.48–14.80%; MnO 13.46–14.14%; and FeO

0.50–1.11%. The minor elements in both the microlite and manganotantalite are similar in value.

Microlite forming pink veins in orange brown tantalite (Fig. 1) at the Homestead pegmatite, Tantalite Valley, is almost certainly a replacement feature. The replacement in this tantalite is more definite and complete than the previous example from Noumas. In certain areas the microlite is fibrous; in other areas the replacement of the tantalite is incomplete and the microlite is overlain by remnants of tantalite. A traverse across the tantalite showed this mineral to be manganotantalite with a relatively uniform composition containing 83.14% Ta<sub>2</sub>O<sub>5</sub> (ave. 13 anal. range 82.17–84.13%), 1.4% Nb<sub>2</sub>O<sub>5</sub> and 13.83% MnO (range 13.56–14.07). The microlite contained 82.57% Ta<sub>2</sub>O<sub>5</sub>, 1.24% Nb<sub>2</sub>O<sub>5</sub> and 0.23% UO<sub>2</sub> (Table 1, anal. 2), values similar to those in the tantalite.

#### Uranoan microlite

Two examples of uranoan microlite and a urano-microlite as defined by the IMA Pyrochlore Subcommittee (Hogarth, 1977) have been analysed by the electron microprobe.

(1) An isolated crystal of microlite, of maximum length 1.3 mm, occurs in lepidolite in the replacement unit of the Lepidolite pegmatite, Tantalite Valley. The crystal studied showed two different compositions when initially analysed (Table 1, anals. 3a, 3b). Traverses were made across the crystal at right angles to examine the composition in detail.

The variation in composition is represented diagrammatically for each element in Fig. 2. The dashed line represents the traverse across the crystal from south to north (Y microns) and the unbroken line the traverse from east to west (X microns). Analyses (13) were made at 100  $\mu$ m intervals across the first traverse Y and the results are presented in Table 2. Two essentially different compositions were obtained; a rim area approximately 130–200  $\mu$ m wide (Fig. 2, points 1, 11–13) and a central area (points 2–10). The contact area was investigated in detail at 25  $\mu$ m intervals and there is no transitional area between the two compositions: there is, however, some variation within each of the two different compositions (see Table 2). At the edges of the crystal, Ta, Sr and W increase. Ta increases from an average value of 66.64% as Ta<sub>2</sub>O<sub>5</sub> in the core to 72–78% in the outer zone. Pb, Ba and Fe, present in small amounts, also increase in the rim. Ca and F show a definite decrease in the rim, CaO decreasing from approximately 15% in the centre to values between 5 and 8%, and as low as 3% in the rim.

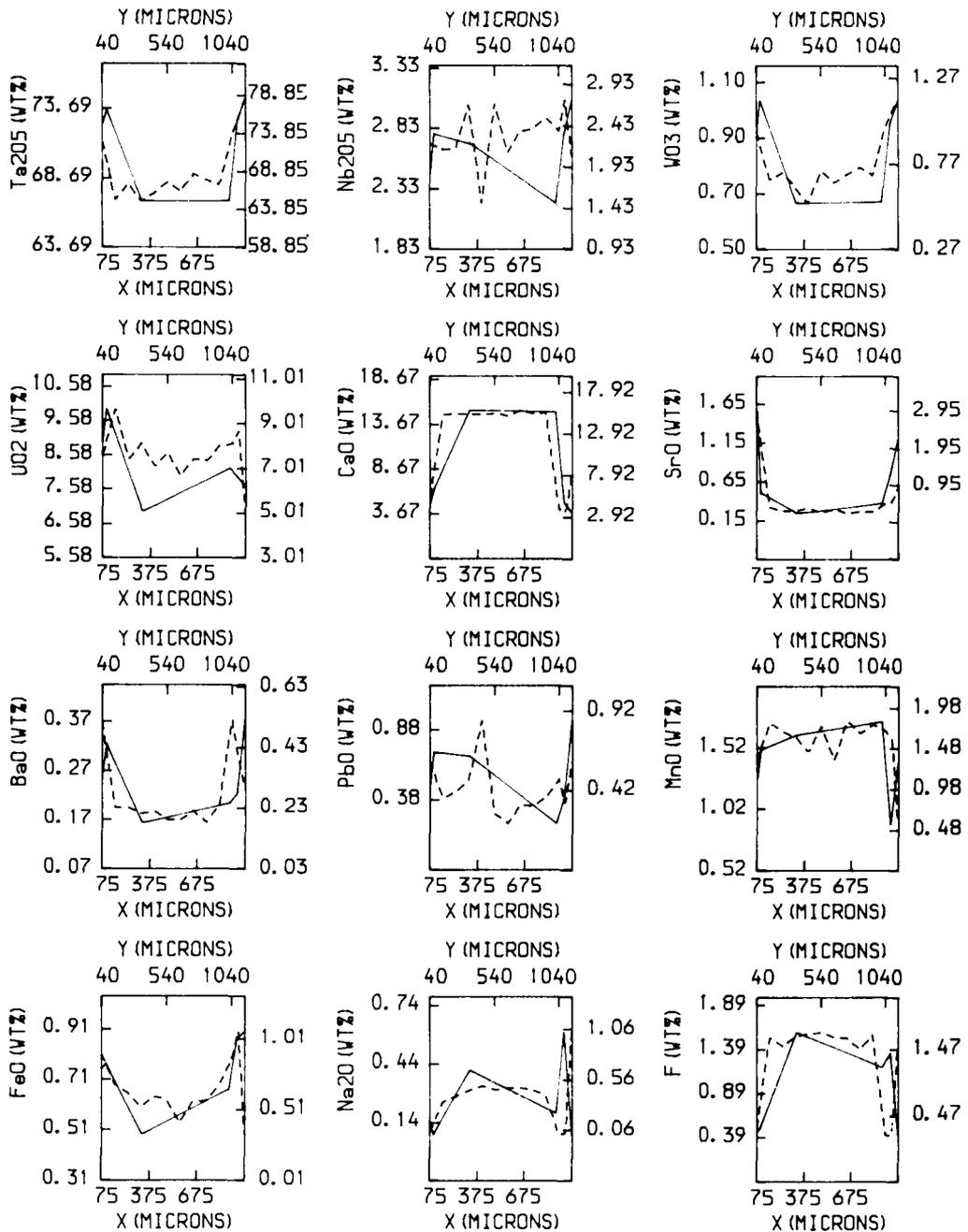


Fig. 2. Analyses along two traverses at right angles across a crystal of uranmicrolite, Lepidolite pegmatite, Tantalite Valley, Namibia. Traverse X 'continuous' (75  $\mu$ m represents distance from L.H. edge of crystal, 'X' wt. % on the L.H. axis of diagram) and traverse Y 'dashed'. Values of Y are given in Table 2. Anal. 6, traverse X taken at 100  $\mu$ m from edge of crystal.

TABLE 2. Traverse (Y) across uranoan microlite, Lepidolite Pegmatite, Namibia

|                                  | 1     | 2     | 3     | 4     | 5     | 6     | 7     | 8      | 9     | 10    | 11    | 12    | 13    |
|----------------------------------|-------|-------|-------|-------|-------|-------|-------|--------|-------|-------|-------|-------|-------|
| Ta <sub>2</sub> O <sub>5</sub>   | 72.56 | 65.05 | 67.19 | 64.85 | 66.04 | 67.38 | 66.19 | 68.42  | 67.61 | 67.04 | 73.68 | 76.07 | 78.34 |
| Nb <sub>2</sub> O <sub>5</sub>   | 2.22  | 2.14  | 2.17  | 2.69  | 1.49  | 2.70  | 2.10  | 2.37   | 2.40  | 2.53  | 2.37  | 2.74  | 2.07  |
| TiO <sub>2</sub>                 | 0.04  | 0.04  | 0.04  | 0.04  | 0.04  | 0.03  | 0.04  | 0.03   | 0.03  | 0.05  | 0.06  | 0.07  | 0.02  |
| WO <sub>3</sub>                  | 0.95  | 0.68  | 0.72  | 0.63  | 0.54  | 0.73  | 0.66  | 0.71   | 0.75  | 0.70  | 0.98  | 1.07  | 1.14  |
| Al <sub>2</sub> O <sub>3</sub>   | 1.59  | 0.15  | 0.40  | 0.19  | 0.11  | 0.10  | 0.40  | 0.28   | 0.42  | 0.11  | 0.27  | 0.18  | 0.08  |
| Fe <sub>2</sub> O <sub>3</sub> * | 0.99  | 0.76  | 0.69  | 0.58  | 0.67  | 0.63  | 0.46  | 0.62   | 0.63  | 0.74  | 0.96  | 1.18  | 0.37  |
| UO <sub>2</sub> **               | 7.61  | 9.64  | 7.42  | 8.13  | 7.08  | 7.70  | 6.65  | 7.41   | 7.33  | 8.01  | 8.10  | 8.67  | 5.05  |
| CaO                              | 5.32  | 15.12 | 15.31 | 15.25 | 15.10 | 15.42 | 14.98 | 15.69  | 15.28 | 15.43 | 3.81  | 3.39  | 7.99  |
| SrO                              | 2.95  | 0.33  | 0.24  | 0.28  | 0.32  | 0.19  | 0.30  | 0.18   | 0.25  | 0.23  | 0.45  | 0.49  | 0.87  |
| BaO                              | 0.51  | 0.23  | 0.23  | 0.21  | 0.22  | 0.19  | 0.19  | 0.22   | 0.18  | 0.24  | 0.52  | 0.39  | 0.30  |
| PbO                              | 0.60  | 0.37  | 0.41  | 0.49  | 0.86  | 0.27  | 0.21  | 0.33   | 0.32  | 0.38  | 0.49  | 0.34  | 0.60  |
| MnO                              | 1.33  | 1.79  | 1.68  | 1.61  | 1.43  | 1.75  | 1.33  | 1.81   | 1.66  | 1.77  | 1.69  | 1.60  | 0.54  |
| Ni <sub>2</sub> O                | 0.04  | 0.33  | 0.39  | 0.44  | 0.49  | 0.45  | 0.47  | 0.47   | 0.45  | 0.39  | 0.01  | 0.02  | 1.03  |
| F                                | 0.29  | 1.64  | 1.50  | 1.67  | 1.70  | 1.72  | 1.64  | 1.63   | 1.46  | 1.68  | 0.16  | 0.18  | 1.45  |
| Total                            | 97.00 | 98.27 | 98.39 | 97.06 | 96.09 | 99.26 | 95.62 | 100.17 | 98.77 | 99.30 | 93.55 | 96.39 | 99.85 |
| O=F                              | 0.12  | 0.68  | 0.63  | 0.70  | 0.71  | 0.72  | 0.69  | 0.68   | 0.61  | 0.71  | 0.07  | 0.08  | 0.61  |
|                                  | 96.88 | 97.59 | 97.76 | 96.36 | 95.38 | 98.54 | 94.93 | 99.49  | 98.16 | 98.59 | 93.48 | 96.31 | 99.24 |

Anal. 1-10 were made at 100 micron intervals, anal.11-13 at 50 micron intervals. Anal. 1 was made at 40 microns from the edge and anal.13 at 35 microns from the opposite edge of crystal. \* Total iron as Fe<sub>2</sub>O<sub>3</sub>. \*\* Total uranium as UO<sub>2</sub>

With the exception of anal. 13, F shows a definite decrease in the rim from 1.62% in the centre to 0.2-0.3%. U shows random variation across the traverse, values varying from 9.9 to 5.05% as UO<sub>2</sub>. However on average there is an increase in UO<sub>2</sub> of 0.7% core to rim. Nb shows random and minimal variation. Na, present in small amounts, decreases in the rim (see Table 1, anal. 3a, 3b).

The same general trend may be observed for the X traverse (unbroken line, Fig. 2). From the diagrams it may be clearly seen that at the edges of the crystal, Ta, W, Sr, Ba and Fe increase in content and Ca, F, Mn and Na decrease.

Uranoan microlite is commonly formed by the replacement of other niobium-tantalum minerals and therefore may be grouped with the secondary microlites (von Knorring and Fadipe, 1981). However uranoan microlite ('djalmite') from a Siberian pegmatite has also been reported as being first generation (Kornetova and Kazakova, 1964).

A back-scattered electron image of one section of the uranoan microlite from Tantalite Valley shows that the crystal has a fissured structure and is broken into subspheroidal areas, in some cases resembling octahedra (Fig. 3). Alteration, possibly initiated by lattice damage from radiation, appears to have developed along the very fine fissures and has proceeded to divide the crystal into areas, giving the effect of radiating septa. A similar fabric has been observed in barium pyrochlore ('pandaite') from Mrima Hill, Kenya, by Harris (1966).

A detailed examination (Fig. 3) shows that the subspheroidal areas are zoned, the lighter col-

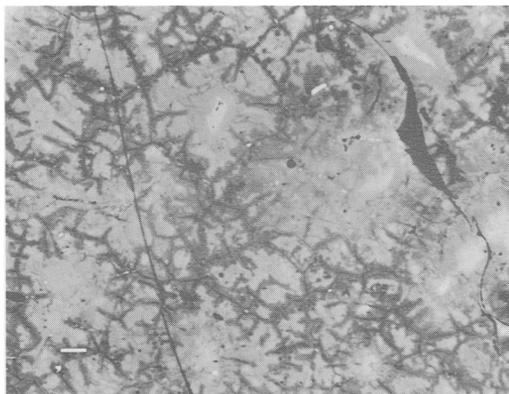


Fig. 3. Back-scattered electron images of part of a crystal of uranoan microlite, Lepidolite pegmatite, Tantalite Valley, Namibia, showing fissured structure and zoned subspheroidal areas: Scale bar: 20  $\mu$ m.

oured central areas representing elements with a high atomic number such as Ta (73) and U (91), contrasting with Nb (41) and Ca (20), thus accounting for the range in composition of these elements throughout the traverse of the centre of the crystal. For example Ta varies from 64.85 to 68.42% Ta<sub>2</sub>O<sub>5</sub> and U from 6.65 to 9.64% UO<sub>2</sub> (see Table 2, anal. 2-10). The edges of the crystal, from their lighter colour, are thought to contain more higher atomic-number elements than the centre of the crystal. This observation is consistent with the higher Ta content of approximately 10% Ta<sub>2</sub>O<sub>5</sub> in the rim of the crystal (see Table 1, anal. 3b).

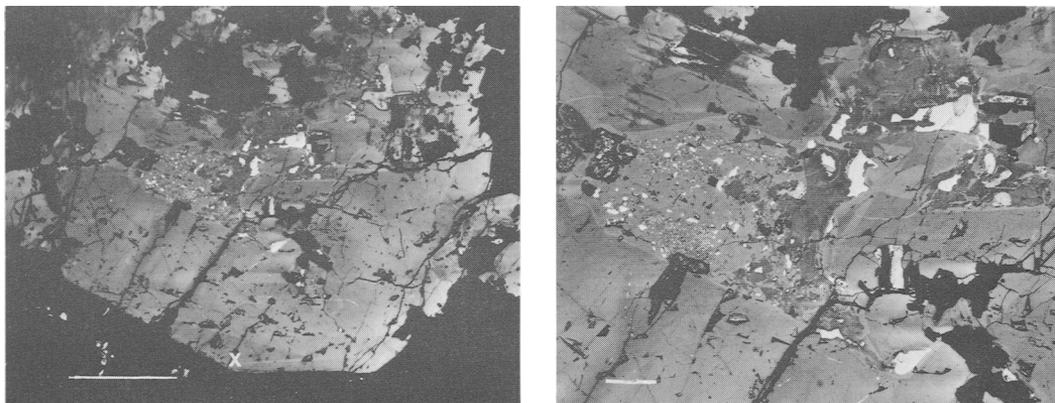


FIG. 4. (a, left) Back-scattered electron image of crystal 1, uranoan microlite, Kokerboomrand pegmatite, Namaqualand, South Africa, showing oscillatory zoning in the lower rim. The white areas represent remnants of a former bismuth phase. Scale bar: 500  $\mu\text{m}$ . Traverse taken from 'X' northwards across centre of crystal. (b, right) An enlargement of the central area of crystal 1, Kokerboomrand pegmatite, Namaqualand. Scale bar 100  $\mu\text{m}$ .

(2) The second example of uranoan microlite is from the Kokerboomrand pegmatite, Namaqualand. The radioactive crystals range from one to eight mm in diameter; they occur in greenish mica greisen as brownish-black octahedra intergrown with muscovite, and are in various stages of development, some skeletal in outline, less commonly anhedral. Electron-probe examination shows the crystals to be zoned. A traverse was completed and analyses made at 100  $\mu\text{m}$  intervals across two separate crystals. Crystal 1, a comparatively well-formed crystal, approximately 2 mm in diameter was chosen for analysis. Only four faces are partly developed, the other sides being incomplete. Complex zonation may be seen in the well-formed lower edge (Fig. 4a) and there is an area of different composition in the centre, possibly containing relics of a previous Ta mineral. Von Knorring and Fadipe (1981) state that corroded fragments of the original mineral may commonly be located in the matrix of the replaced microlite, indicating the composition of the primary mineral.

The profiles of the traverse across crystal 1 for each element are shown in Fig. 5. On average Ta, Na, W and F seem to increase towards the centre, while Nb, Ti, U and Bi decrease, with Ca, Mn and Fe showing no definite trend. Pb, with the exception of one point (6) at 550  $\mu\text{m}$ , appears to be constant. The very bright areas in the centre of the crystal (see Fig. 4b) contain a bismuth phase, suggesting that a former phase may have been composed of bismutotantalite. Von Knorring and Fadipe (1981) suggest that mic-

rolite can replace tapiolite, bismuto- and stibio-tantalite.

The results of the traverse across crystal 2, of diameter 1 mm, are illustrated in Fig. 6 which shows the crystal to have distinct changes from the intermediate areas to the core; Ta, W, Na, Mn and F decrease in the centre, whereas Bi, Ti, U, Ca, Pb and Fe increase. The element which is affected to a major extent is Ta, which decreases in the centre to 57% as  $\text{Ta}_2\text{O}_5$  from 67.86% in the intermediate areas (Table 1, anal. 4a, 4b). There is more U, Bi and Ti in crystal 2 than in crystal 1. A back-scattered electron image (Fig. 7) shows the crystal to have at least two distinct zones, with primary growth zoning in the outer rim. In addition, the tiny bright areas resemble the areas containing a bismuth phase in the centre of crystal 1.

(3) The third example is uranmicrolite from Jooste's pegmatite, Okongava Ost, Karibib (Table 1, anal. 5). The microlite is rather sparsely distributed in lepidolite. It is very similar to the crystal from the Lepidolite pegmatite, with very fine cracks and the development of subspheroidal areas. These areas, however, have no inner zoning. An average of 8 analyses contained 14.35%  $\text{UO}_2$  (range 11.31–15.77%); 56.12%  $\text{Ta}_2\text{O}_5$  (52.8–59.79%); 13.18%  $\text{Nb}_2\text{O}_5$  (10.97–13.9%) and CaO 6.87% (6.2–7.67%). The chemical content of this uranmicrolite varies across the crystal but, unlike the uranoan microlite from Tantalite Valley, is without any concentric pattern in the rim. A composition of this type has been referred to as 'djalmaite' in the literature (Guimaraes, 1939).

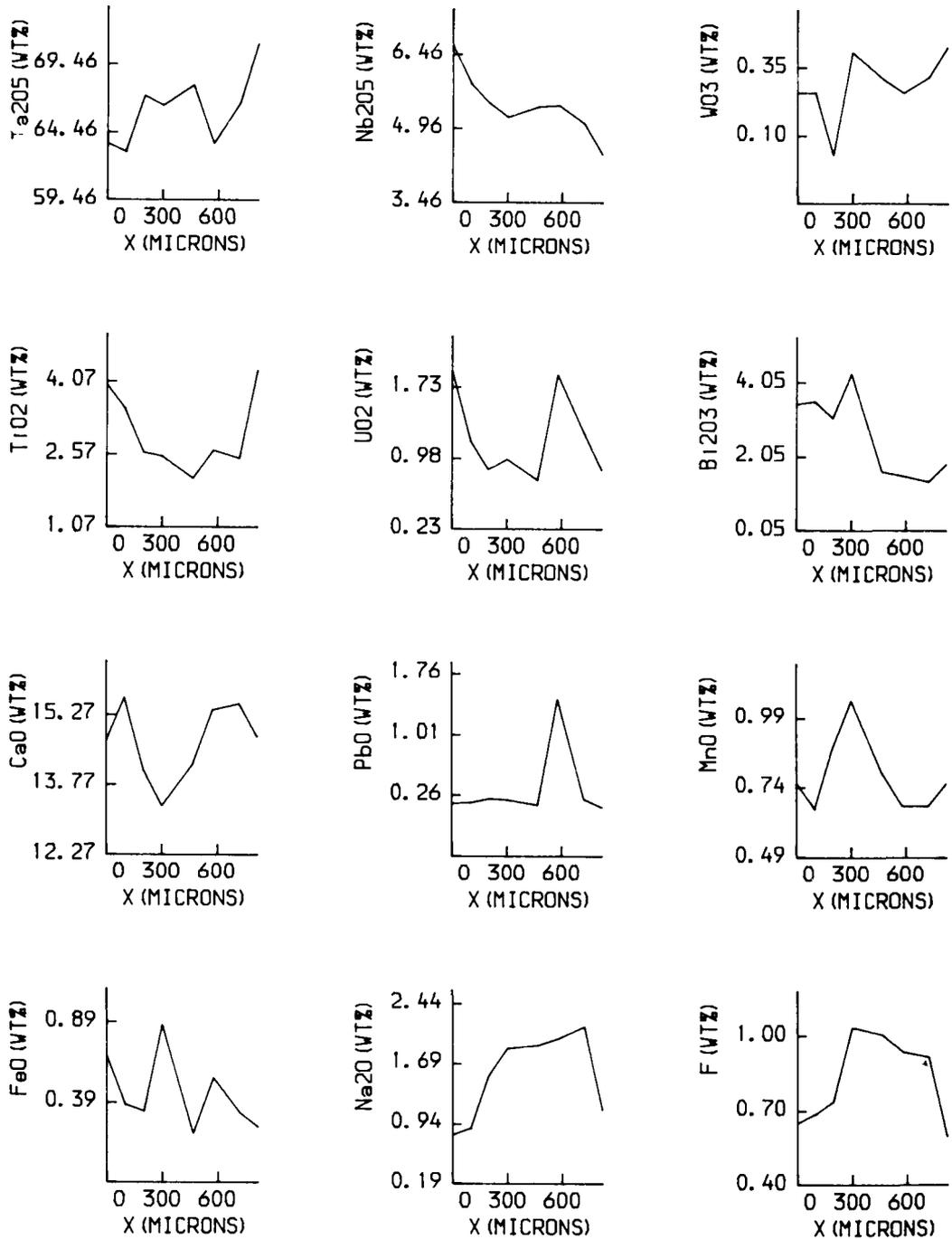


Fig. 5. Traverse across microlite crystal 1, Kokerboomrand pegmatite, Namaqualand, South Africa.

### Discussion

The composition of an ideal mineral of the pyrochlore group may be represented by the general formula  $A_2B_2X_7$  (Machatschki, 1932; Borodin and Nazarenko, 1957; but see also Von Gaertner, 1930; Brandenberger, 1931; Ginzburg and Gorzhenskaya, 1960; Hogarth, 1961; Van der Veen, 1963; and Hogarth, 1977).

In the uranoan microlites containing larger amounts of water and uranium there is a considerable deficiency of cations in the *A* site. This deficiency may be explained by reference to Borodin and Nazarenko (1957); in pyrochlore, because the substitution in both the *A* and *B* sites is heterovalent rather than isovalent,  $\text{Na}^+$  is replaced by the higher valence cation  $\text{U}^{4+}$  and to a lesser degree by  $\text{Ca}^{2+}$  in the *A* site. This may be compensated for by  $\text{Ti}^{4+}$  replacement of  $\text{Nb}^{5+}$  in the *B* site, and before hydration there is no deficiency in the *A* site. The univalent cation is mainly leached from the less hydrated varieties of pyrochlore; as the hydration process continues,  $\text{Ca}^{2+}$  is also leached out. The same principles apply to microlite except that  $\text{Ti}^{4+}$  is replaced by  $\text{Ta}^{5+}$ .

This may be illustrated in microlite by the crystal from the Lepidolite pegmatite. From anal. 3a and 3b (see Table 1), if the deficiency in wt. % totals may be considered as water, it can be inferred that a high water content (anal. 3b) is compatible with a low Ca content (4.61% CaO), and a less hydrated centre (anal. 3a) with a high Ca content (15.29% CaO). The rim of the microlite has a total of 0.8 cations in the *A* site, whereas the centre has a total of 2.05 cations (see Table 1). Consequently, there is a deficiency in the *A* site cations in the rim, with its high water and low Ca content.

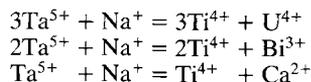
Eid (1976) observed that the deficiency of *A* cations is usually greater in altered microlite, which contains high water and low F. High water, low F and low Ca characterize the periphery of the microlite from the Lepidolite pegmatite (Table 1, anal. 3b).

The change in composition in the crystal from the Lepidolite pegmatite is quite distinct, with no intermediate phases. This is in agreement with Harris (1966) who found compositional changes in pyrochlore to be similarly distinct. However, this contrasts with microlite reported by Mihalik (1967) who found alteration from a deep brown to a clear green variety and a gradual change in composition. Mihalik found that the alteration was effected by the removal of Ca and Mn ions, hydration, and the introduction of Cu and Si; Ta, Nb and U remain unaffected.

The rim area of the microlite from the Lepido-

lite pegmatite and the uranmicrolite from Okongava (Table 1, anal. 5) have some similarities. Ca is low in both; however U is low in the former (averaging 8% as  $\text{UO}_2$ ) and high in the latter (14.35%). This difference is compensated by the combined Ta and Nb contents (Table 1, anal. 3b, 5) and corresponds to the suggestion (von Knorring and Fadipe, 1981) that high uranium in microlite is usually accompanied by low tantalum. Both of these microlites have low totals, suggesting high water, and both are deficient in *A* site cations (see Table 1, anal. 3b and 5).

Usually the lowest fluorine contents are found in the altered microlites and in Bi, Pb and U microlite (Eid, 1976). In the Kokerboomrand crystal (2) the lowest F content is found with the highest Bi-U-Pb values, in the centre of the crystal (Table 1, anal. 4a, 4b). In this crystal, compositional changes from the intermediate to the central area suggest major substitutions of the type:



The two crystals from the Kokerboomrand pegmatite show different characteristics in both fabric and composition. On average, crystal 1 has a low F content (0.8%, see Fig. 5) in comparison with crystal 2 containing 1.78–2.27% (Fig. 6 and Table 1, anal. 4a, 4b). Crystal 1 has also a higher water content (denoted by a low total). Does this denote a higher degree of alteration in crystal 1? It has been suggested (Eid, 1976) that the degree of alteration in microlite is characterized by the amount of hydration and the lowest F contents. Traverses across the two crystals show different trends (see Figs 5 and 6) and this may be substantiated by comparisons of the back-scattered electron images of the two crystals (Figs 4 and 7). Crystal 1 is simple; as well as having zoning in the rim, there are at least two phases of mineralization. Crystal 2 is complex; it has at least three distinct compositional zones.

### Manganotantalite and ferrotantalite

Manganotantalite occurs with cleavelandite in the intermediate zone of the Rubicon pegmatite, Karibib. A single zoned crystal of manganotantalite, approximately 2 cm by 1 cm, was investigated with the electron probe. The crystal shows three distinct areas, a main area and a marginal area consisting of two zones (see Fig. 8). A traverse across the crystal from left to right revealed the main area to be manganotantalite (Table 3, anal. 1–4, 6) with a  $\text{Ta}_2\text{O}_5$  content between 83.86 and 84.95% and a MnO content of 12.33–12.49%.

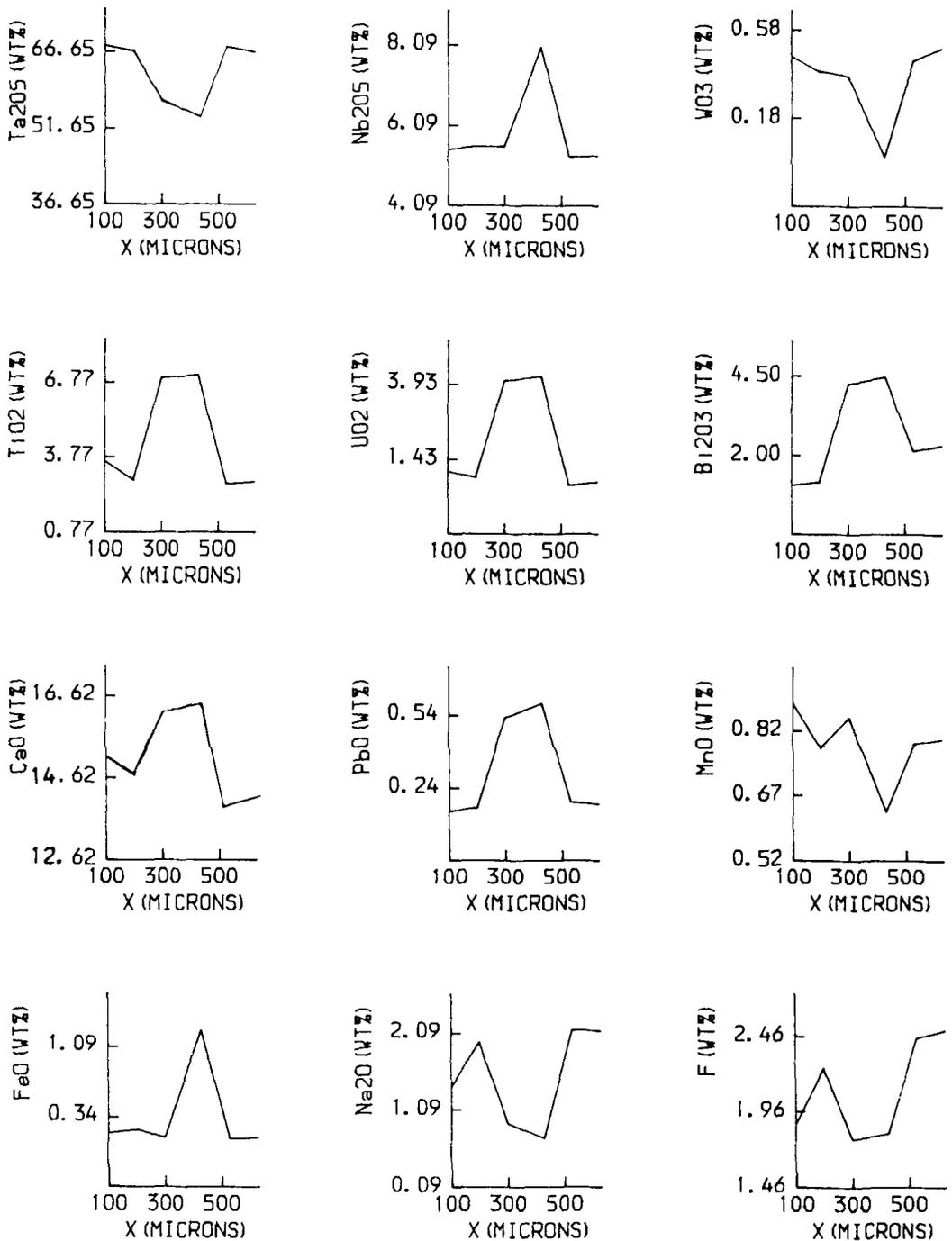


Fig. 6. Traverse across uranoan microlite crystal 2, Kokerboomrand pegmatite, Namaqualand pegmatite, South Africa.

TABLE 3. Traverse across a composite crystal of manganotantalite and ferrotantalite, Rubicon Mine, Namibia

|                                | 1      | 2      | 3      | 4      | 5      | 6      | 7      | 8      | 9      | 10     |
|--------------------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Ta <sub>2</sub> O <sub>5</sub> | 84.11  | 83.86  | 84.95  | 83.88  | 78.72  | 83.71  | 79.42  | 85.30  | 85.13  | 85.86  |
| Nb <sub>2</sub> O <sub>5</sub> | 3.06   | 3.03   | 3.02   | 3.15   | 7.68   | 3.14   | 7.02   | 1.70   | 1.78   | 1.38   |
| TiO <sub>2</sub>               | 0.01   | 0.02   | 0.03   | 0.02   | 0.01   | 0.02   | 0.01   | 0.04   | 0.04   | 0.01   |
| WO <sub>3</sub>                | 0.41   | 0.41   | 0.45   | 0.44   | 0.29   | 0.37   | 0.33   | 0.39   | 0.43   | 0.63   |
| UO <sub>2</sub>                | 0.07   | 0.10   | 0.04   | 0.13   | 0.12   | 0.07   | 0.57   | 0.04   | 0.10   | 0.07   |
| MnO                            | 12.38  | 12.33  | 12.49  | 12.35  | 9.91   | 12.37  | 10.00  | 2.41   | 2.43   | 2.46   |
| FeO                            | 1.19   | 1.17   | 1.16   | 1.20   | 4.23   | 1.19   | 3.98   | 11.37  | 11.24  | 11.18  |
| Total                          | 101.23 | 100.92 | 102.14 | 101.17 | 100.99 | 100.87 | 100.81 | 101.25 | 101.15 | 101.59 |

1-4,6. Manganotantalite (light area) see Fig. 8. Rubicon Mine, S. W. Africa.  
 5,7. Area of intermediate composition (dark grey area)  
 8-10. Ferrotantalite (Black areas)

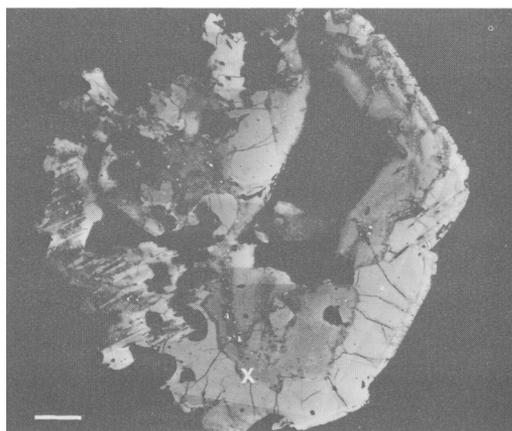


Fig. 7. Back-scattered electron image of crystal 2, Kokkerboomrand pegmatite, Namaqualand, South Africa. Traverse taken from 'X' northwards across centre of crystal. Scale bar: 100  $\mu$ m.

The right hand margin contrasts sharply with the main area (see Fig. 8). At the extreme margin the Ta<sub>2</sub>O<sub>5</sub> content lies between 85.13 and 85.86%; however in contrast to the main area, where the MnO ranges from 12.33 to 12.49%, the MnO value is only 2.44% with a FeO content of 11.25% (Table 3, anal. 8, 9, 10). This chemical composition corresponds to an iron-rich tantalite, and also to the mineral tapiolite; however the X-ray diffraction data so far indicated that only the orthorhombic tantalite phase is present (von Knorring pers. comm.).

It is interesting to note that in the intermediate rim area, represented by the dark grey colour in Fig. 8, the Ta:Nb ratio has changed, indicating enrichment of Nb relative to Ta (see Table 3, anal. 5, 7); at the extreme rim, however, the situation is reversed, and the Ta:Nb ratio is simi-

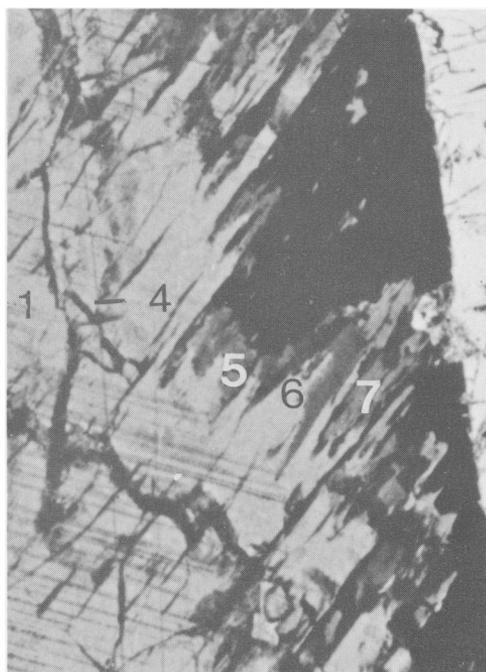


Fig. 8. Manganotantalite (main area, 1-4, 6) showing replacement by ferrotantalite (black area along R.H. edge), and area of intermediate composition (dark grey, 5, 7) Rubicon pegmatite, Karibib, Namibia. Scale  $\times 12$ .

lar to the interior of the crystal. The Mn:Fe ratio has also changed, but in this case indicating a progressive enrichment of Fe at the right hand margin (Fig. 8).

Von Knorring and Condliffe (1984) have pointed out that manganotantalites sometimes display a simple macrozoning visible to the naked eye: a light-coloured Ta-rich marginal zone representing Ta enrichment during the last stages of

pegmatitic crystallization. In the Rubicon crystal, although there is a slight Ta enrichment in the marginal right hand zone (see Table 3, anal. 8–10), the area is on the contrary darker, which in this case is controlled by Fe enrichment relative to Mn, rather than Ta enrichment relative to Nb (anal. 5, 7–10).

The compositional pattern at the margin of the Rubicon crystal (Fig. 8) could be due to growth zoning; the zones are quite sharply defined. However, contrary to the findings of von Knorring and Condliffe (1981) not only is there Nb enrichment in the margin, but Fig. 8 strongly suggests that the areas of different composition are rather a feature of replacement than of growth zoning, replacement taking effect along cleavages, initially at one margin.

### Conclusions

A uranmicrolite from Okongava, Karibib, contains 14.35% UO<sub>2</sub> and 56.12% Ta<sub>2</sub>O<sub>5</sub>. This appears to be the second occurrence of the species according to the IMA definition (Hogarth, 1977).

In general, the major changes in composition in uranoan microlite in this study are characterized by a loss in Ca and F, hydration and a gain in Ta. In uranoan microlite, containing Bi, the major changes involve U, Bi, Ca and Ti on the one hand and Ta and Na on the other. The role of water is unclear.

A traverse across a 1.3 mm crystal of uranoan microlite revealed two essentially different compositions; a rim, 200 μm wide and a central area. The transition zone between the two compositions is very distinct. Electron probe examination does not reveal any zoning, only that the rim probably contains more Ta than the central area. The central area has a fissured structure and alteration appears to have developed along very fine fissures and has proceeded by dividing the original crystal into subspheroidal areas. Both the uranoan microlite from the Lepidolite pegmatite and the uranmicrolite from Okongava appear similar in internal structure on preliminary examination. These textures characterize metamict varieties of the pyrochlore group.

The crystals from the Kokerboomrand pegmatite have completely different characteristics from the two previous crystals and are also different in replacement from each other. They are both distinctly zoned, showing both primary zoning and replacement features. Crystal 2 is complex; there is a central area of one composition and an intermediate zone of another and two outer zones. Crystal 1 is simpler, the very bright areas in the centre of Fig. 4 containing a bismuth phase,

and one suggestion is that microlite may have replaced bismutotantalite. However more of these crystals must be studied closely in relation to the back-scattered images and in relation to each other.

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