Non-metamict uranoan pyrochlore and uranpyrochlore from tuff near Ndale, Fort Portal area, Uganda

D. D. HOGARTH

Department of Geology, University of Ottawa and Ottawa-Carleton Geoscience Centre, Ottawa, Canada K1N 6N5

AND

J. E. T. HORNE*

Formerly of the Atomic Energy Division, Geological Survey of Great Britain

Abstract

A thin (100 m) cover of flat-lying, Recent, calcite-rich tuff at Ndale near Fort Portal, Uganda, unconformably overlies steeply dipping Precambrian metamorphic rocks. It is locally radioactive owing to uranium-rich pyrochlore minerals and lesser amounts of zircon, monazite, titanite, and an unidentified thorium phosphate. In one concentrate, four grains of uranpyrochlore and one grain of uranoan pyrochlore showed a positive linear correlation of Ti with U, and negative linear correlations of Ti with Na, F and Sr. Ta remained high and relatively constant [11 anal., ave. 14.5 (0.6)% Ta_2O_5]. In the same concentrate the composition of a separate grain of uranoan pyrochlore did not plot on these lines and Ta was comparatively low [2 anal., ave. 4.5 (0.3)% Ta_2O_5]. The data suggest two separate paths of differentiation. However, zoned grains were not observed. Unit cells were cubic with $a = 10.351 \pm 0.002$ Å for a grain with 12.9% $UO_2^{tot.}$ and 10.333 ± 0.002 Å for a grain with 26.6% $UO_2^{tot.}$. On heating in air the cell size decreased, possibly due to oxidation of U^{4+}. The crystalline nature of these minerals can be attributed to a very young (4000–5000 yr) geological age.

KEYWORDS: Fort Portal, Ndale, Uganda, tuff, pyrochlore, uranpyrochlore, uranium, tantalum, titanium, non-metamict, radioactivity.

Introduction

A pyrochlore-group mineral from Ndale was tentatively identified as 'betafite' by Newman and Campbell (1952) and Campbell and Horne (1953). The mineral was of special interest because it was the first strongly radioactive pyrochlore-group mineral to be recorded as non-metamict (it was, in fact, shown to be highly crystalline) and it was the first example of the group to be described from tuff associated with volcanic carbonatite. During a recent review of the mineralogy of carbonatites by one of us (Hogarth, in press), the problem of the Ndale, non-metamict 'betafite' was reconsidered, and because its com-

position rested on semiquantitative optical spectrography and routine autoradiography, it was decided to analyse the mineral by microprobe. This paper presents new data and also summarizes the reports of Newman and Campbell (1952) and Campbell and Horne (1953) which are generally inaccessible to mineralogists.

Geological setting

The area lies within the Western Rift of Africa (Fig. 1). The lower ground of the Ndale area is characterized by steeply dipping metamorphic rocks of the Precambrian Toro System. The rocks are intruded by granite stocks and dolerite dykes of uncertain age.

Overlying the Toro System are Recent pyroclastics composed of horizontal to gently dipping

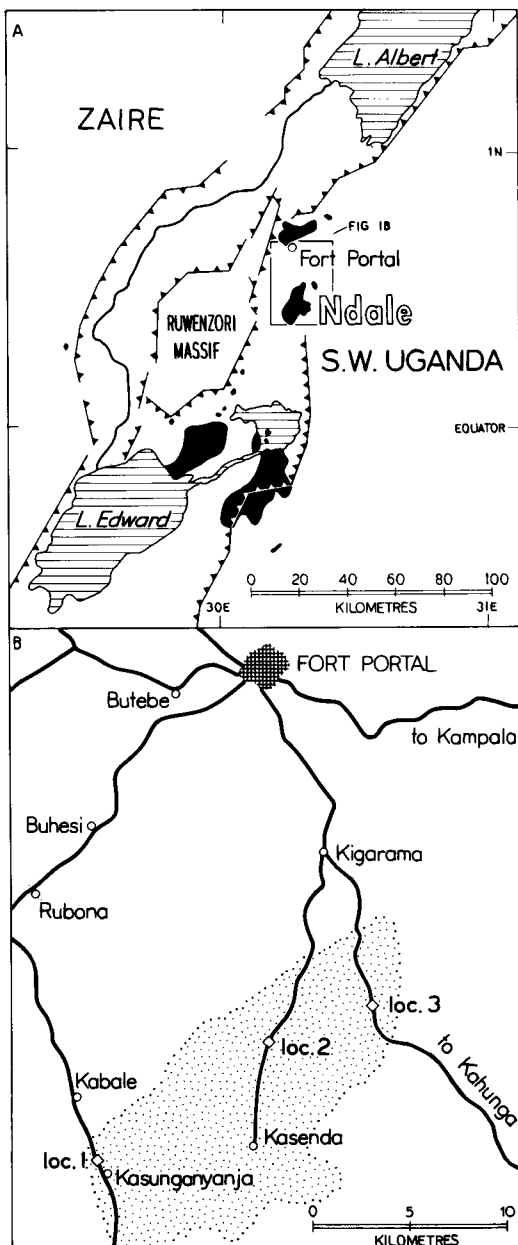* Present address: 58 Westend, Kemsing, nr Sevenoaks, Kent TN15 6QB

FIG. 1. Location maps of the Ndale region and radioactive localities. Regional map (*A*) modified from Holmes (1950), local map (*B*) redrawn from Campbell and Horne (1953). Area of map *B* has been outlined on map *A*. Black and stippled areas represent volcanic fields, shown in relation to the elements of the West African Rift.

ash beds, containing fragments of various sizes, that are commonly cemented by calcite. The land

surface is pitted by numerous volcanic vents, that are water-filled in the wet season, and vary from 45 to 800 metres in diameter. Lava flows have not been found at Ndale and are subordinate in neighbouring fields (Combe, 1938; Combe and Holmes, 1945; Holmes, 1956; von Knorring and Dubois, 1961; Nixon and Hornung, 1973; Kapustin and Polyakov, 1982; Barker and Nixon, 1983).

At Ndale, the thickness of pyroclastic cover probably does not exceed 100 metres. It attains a maximum in pre-existing valleys and depressions near the edges of steep-side cones. The main volcanic event in the Fort Portal area has been dated at 4000 to 5000 years b.p. by ^{14}C in included organic matter (Osmaston, 1965; Livingstone, 1967; Logachev, 1974).

Radioactivity was recognized in 1949 by the Geological Survey of Uganda and the region was examined by C. B. Campbell in 1951. Of the several volcanic fields in western Uganda, only Ndale was appreciably radioactive and three localities (1, 2 and 3 on Fig. 1) were examined in detail. Pits were excavated, some to 5 metres, radioactivity was measured and samples were collected. Chemical analyses range from 0.002 to 0.010% U_3O_8 and 0.007 to 0.040% ThO_2. An inclined borehole below occurrence 2 passed through the tuff at 36 metres depth and continued in gneiss to 43 metres. Only the tuff was noticeably radioactive.

Mineralogical composition of samples from Ndale

Cemented tuffs and unconsolidated ash beds from pits at the three localities contained the following:

(a) *Radioactive minerals*—minor pyrochlore and uranpyrochlore; rare zircon, titanite, monazite, and an unidentified Th phosphate.
(b) *Non-radioactive minerals*—major calcite, alkali feldspars (triclinic and monoclinic), quartz, magnetite and biotite; minor ilmenite, almandine, apatite, epidote, non-radioactive zircon and olivine (*c.* 45% Fe_2SiO_4); rare diopside (*c.* 40% $CaFeSi_2O_6$), hypersthene, pyrite, rutile and anatase. Kapustin and Polyakov (1982) also note minor baddeleyite and perovskite associated with pyrochlore from an unspecified occurrence in the Fort Portal area.

Chemical composition of pyrochlore-group minerals

A polished thin section was made from a few grains of concentrate U 2922–6 ('non-magnetic, heavy fraction'; locality 2) supplied by the British

Table 1. Representative compositions of pyrochlore from a heavy mineral concentrate of Ndale, Uganda tuff.

		1	2	3	4	5	6
	Nb_2O_5	32.30	34.25	36.93	38.24	40.01	56.36
	Ta_2O_5	15.76	14.52	14.58	14.37	14.36	4.35
	TiO_2	9.27	9.27	7.91	7.21	6.30	3.20
	ZrO_2	0.28	0.21	0.12	0.39	0.33	0.01
	$UO_{2\,T}$	26.44	26.63	24.32	23.22	22.49	13.23
	ThO_2	0.07	0.13	0.04	0.18	0.00	0.00
	$Fe_2O_{3\,T}$	0.64	0.57	0.64	0.81	0.73	0.23
	La_2O_3	0.12	0.05	0.08	0.08	0.02	0.05
	Ce_2O_3	0.21	0.11	0.11	0.16	0.20	0.21
	Nd_2O_3	0.00	0.00	0.00	0.00	0.00	0.00
	Y_2O_3	0.17	0.08	0.16	0.17	0.19	0.32
	SrO	0.16	0.22	0.17	0.28	0.21	0.66
	CaO	8.69	8.33	8.66	8.55	8.64	10.05
	Na_2O	5.29	5.21	5.46	5.58	5.76	7.56
	F	0.19	0.19	0.30	0.38	0.46	1.46
	Total	99.51	99.69	99.35	99.46	99.51	97.08
				Ions per 2B			
B	Nb	1.103	1.150	1.230	1.261	1.318	1.742
	Ta	0.324	0.293	0.292	0.285	0.285	0.081
	Ti	0.526	0.518	0.438	0.395	0.345	0.165
	Zr	0.010	0.008	0.004	0.014	0.012	0.000
	Fe	0.037	0.032	0.036	0.045	0.040	0.012
	Σ	2	2	2	2	2	2
A	U	0.444	0.440	0.399	0.377	0.365	0.201
	Th	0.001	0.002	0.001	0.003	0.000	0.000
	La	0.003	0.001	0.002	0.002	0.001	0.001
	Ce	0.006	0.003	0.003	0.004	0.005	0.005
	Nd	0.000	0.000	0.000	0.000	0.000	0.000
	Y	0.007	0.003	0.006	0.007	0.007	0.012
	Sr	0.007	0.009	0.007	0.012	0.009	0.026
	Ca	0.703	0.663	0.683	0.668	0.675	0.736
	Na	0.775	0.750	0.780	0.789	0.814	1.002
	Σ	1.95	1.87	1.88	1.86	1.88	1.98
	F	0.05	0.04	0.07	0.09	0.11	0.32
	Charge	13.415	13.30	13.72	13.22	13.20	13.20

Analyses by electron microprobe. Chemical formulae based on B ions in the general formula $A_{2-x}B_2O_6(OH, F)$. All Fe was assumed Fe^{3+} in B.

Geological Survey. Radioactive minerals were located by means of an oriented autoradiograph. The pyrochlore-group grains, numbered 1 to 6, were up to 0.4 mm long and averaged 0.15 mm long. In transmitted light they were deep red brown, except for one grain (No. 6) which was yellow brown. All pyrochlore grains were fragments, except No. 2 which was a well defined, spinel-twinned, octahedral pair.

Pyrochlore minerals were analysed by electron microprobe. Scans from 0 to 10 keV were made from grains 2 and 6 with EDS (Si detector interphased with multichannel analyser) followed by 13 WDS (Cambridge Geoscan Mk 5) analyses involving all 6 grains. Standards were $NaNbO_3$ (Na, Nb), tantalum metal (Ta), ilmenite (Fe, Ti), zircon (Zr), brannerite (U), thorianite (Th), REE–Ca glass (La, Ce, Nd, Y, Ca), celestite (Sr), and phlogopite (F). Data were reduced with an updated EMPADR program (Rucklidge and Gasparrini, 1969).

Pyrochlore-group minerals (Table 1) were high in Ta and U. Four grains (Nos. 1 to 4) were uranpyrochlore, one grain (No. 5) was just within the pyrochlore range, and one grain (No. 6), differing in many respects from the others, was well within the pyrochlore range, as defined by the IMA Pyrochlore Subcommittee (Hogarth, 1977). Although one grain differed appreciably from the next, there was no apparent zoning or chemical change within an individual grain.

The marked difference between grains 1 to 5 and grain 6 is especially evident in Fig. 2. On both Ta vs. U and Ta vs. Ca diagrams, the compositions of grains 1 to 5 tend to cluster but the composition of grain 6 plots well outside these clusters. Linear trends of the compositions of grains 1 to 5 are shown in diagrams involving Ti (Figs. 3 and 4). Slopes in Fig. 3 suggest major substitution of the type $3Nb^{5+} + Na^+ \rightarrow 3Ti^{4+} + U^{4+}$. The scheme is complicated by other substitutions involving Ca^{2+}, Sr^{2+}, REE^{3+}, vacant sites, and probably U^{6+}, Fe^{2+}, F^-, OH^- and O^{2-}. However, grain 6 does not lie on the linear trends of either Fig. 3 or 4.

If the compositions are plotted on a Ti–Nb–Ta diagram (Fig. 5), all grains lie within the domain of the pyrochlore subgroup (IMA classification)
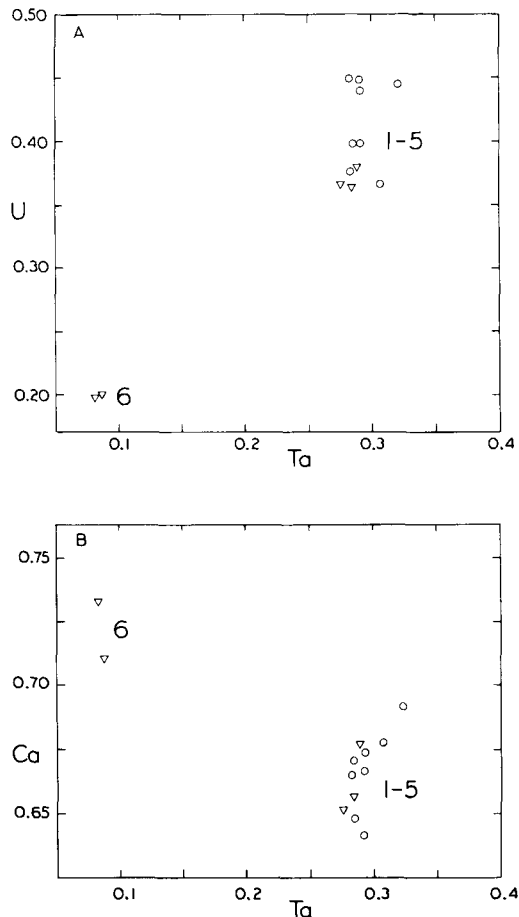
FIG. 2. (A) Ta vs. U diagram; (B) Ta vs. Ca diagram in atoms per standard formula unit $A_{2-x}B_2O_6$ (OH, F)$_{1-y}$ (s.f.u.). Numbers beside compositional plots represent grain nomenclature used in the text. Triangles represent uranoan pyrochlore compositions, circles uranpyrochlore compositions.

FIG. 3. (A) Ti vs. U diagram; (B) Ti vs. Na diagram in atoms per s.f.u. Symbols as in Fig. 2.

and grains 1 to 5 define a linear trend, by containing nearly constant Ta [ave. 14.5 (0.6)% Ta$_2$O$_5$ in 2 anal.]. Two trends were noted by Laplante (1980) for 281 pyrochlore-group compositions from the Crevier Complex, Quebec. They are plotted as broken lines in Fig. 5. The composition of grain 6 fits approximately on the low-U, low-Ta trend of pyrochlore from syenite at Crevier. The compositions of grains 1 to 5 fit approximately on the High-U, high-Ta trend of uranpyrochlore from carbonatite at Crevier.

The two trends are thought to represent compositional variation of pyrochlore minerals during differentiation in the magma chamber prior to eruption. However the direction of these paths
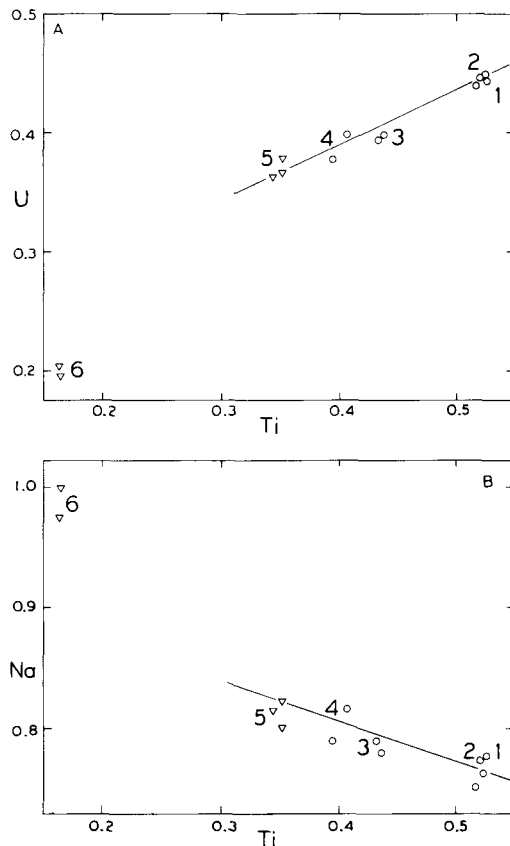
during carbonatite development cannot be interpreted unequivocally, as discussed by Hogarth (in press).

X-ray diffraction data of pyrochlore-group minerals from Ndale

Previous work (by J.E.T.H.). X-ray diffraction patterns of a deep-red, strongly radioactive pyrochlore phase were obtained by using a 90 mm camera with film in van Arkel mounting. Cell sizes were extrapolated to $2\theta = 180°$ and gave the following crystallographic data:

unheated— cubic, $a_0 = 10.357 \pm 0.002$ Å;
heated in air at 1200 °C for 36 hours—cubic, $a_0 = 10.335 \pm 0.002$ Å.

With the exception of a very weak line ($N = 10$), where $N = h^2 + k^2 + l^2$, all lines could be indexed on the basis of $Fd3m$ symmetry and the pyrochlore structure. The transition to the smaller

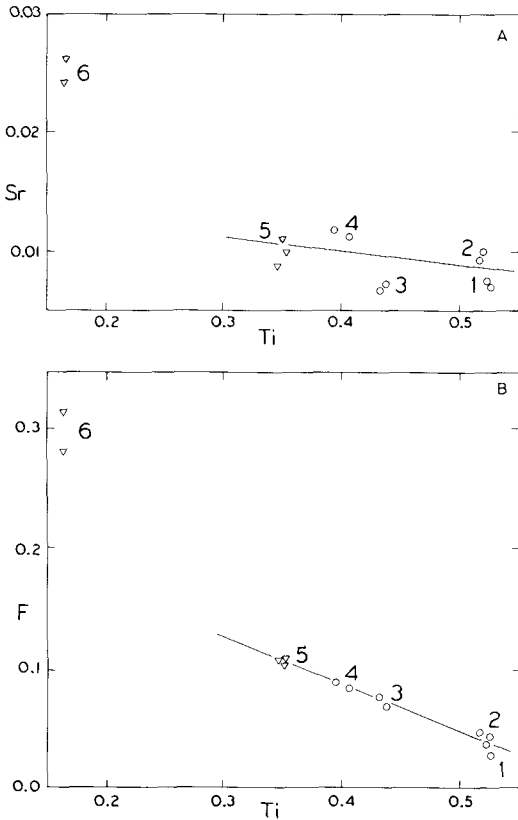FIG. 4. (A) Ti vs. Sr; (B) Ti vs. F diagram in atoms per s.f.u. Symbols as in Fig. 2.
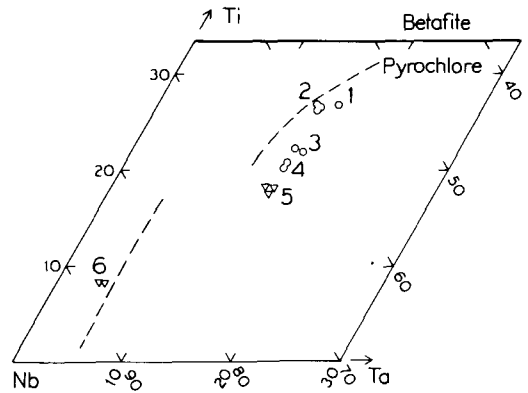

FIG. 5. Part of the Ti–Nb–Ta (atomic) diagram. Symbols as in Fig. 2. The broken line represents the compositional trend of 281 compositions of pyrochlore and uranpyrochlore from the Crevier Complex, taken from Laplante (1980).

cell was not instantaneous but involved an intermediate, two-cell stage. After heating in air at 1200° for $\frac{1}{2}$ hour the mineral showed *both* larger and smaller cells, but only that of the latter remained after heating for 36 hours. A similar transition was noted by H. Newman (in Newman and Campbell, 1952). The cell shrinkage of pyrochlore minerals on heating is best explained by oxidation of U^{4+} to U^{6+}, an explanation applied to the shrinkage of the uraninite cell after ignition by Brooker and Nuffield (1951). The intermediate, two-cell stage, may be an effect of incomplete oxidation.

New data (by D.D.H.). Grains characterized by extremes in chemical composition (Nos. 2 and 6) were extracted from the polished thin section and X-rayed in a 114.6 mm Gandolfi camera with filtered Cu radiation. All lines could be indexed on *Fd3m* symmetry and the pyrochlore structure. The non-pyrochlore line, $N = 10$, noted by Campbell and Horne (1953) was not evident, and significant intensity of odd-numbered planes (esp. *N*

= 3 and 11) agreed with uranpyrochlore rather than betafite (Hogarth, 1961).

After correction for film shrinkage, cell sizes were determined from the reflections $N = 140$, 144, 160, 172 and 176, where high-angle α_1 and α_2 doublets were clearly identifiable in the pattern of the unheated mineral. Values were extrapolated to $2\theta = 180°$ against $\sin^2\theta$. Cubic cell edges were 10.333 ± 0.002 Å for grain 2 (with 26.6% $UO_2^{tot.}$) and 10.351 ± 0.002 for grain 6 (with 12.9% $UO_2^{tot.}$). The smaller cell edge of No. 2 was probably due to the net effect of substitution of U^{4+} (and perhaps U^{6+}) for Na^+, substitution of Ti^{4+} for Nb^{5+} and a larger number of vacant positions in the structural site occupied by Na, Ca and U.

Conclusions

The pyrochlore minerals from Ndale are interesting because of the range of composition within a single sample. No doubt this represents one or more chemical trends during crystallization, but the full significance of this chemical variation must await correlation with new field or experimental data. The fact that individual grains are unzoned is also unusual because uranium-rich pyrochlore minerals are normally strongly zoned. Chemical equilibration within each grain is implied. However, the most striking feature is the high degree of crystallinity for pyrochlores of these compositions. This must be due to the very young age of the mineral (4000–5000 years), a feature that also explains the complete absence of Pb in EDS and WDS microprobe scans.

Acknowledgements

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