

Pandaite from the Mrima Hill niobium deposit (Kenya)

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Summary. A hydrated barium pyrochlore (pandaite) has been found at Mrima Hill (Kenya) in a residuum consisting mainly of goethite/limonite and gorceixite. The pandaite occurs as pale yellow or white octahedral crystals, which have a microcrystalline interior. It is isotropic, the refractive index varies from 2.07 to 2.11. The calculated specific gravity is 4.07, and the unit cell dimension is 10.59 Å. After deduction of impurities the following formula was obtained ($\text{Na}_{0.03} \text{K}_{0.02} \text{Mg}_{0.05} \text{Ca}_{0.09} \text{Ba}_{0.36} \text{Ln}_{0.05} \text{Th}_{0.01} \text{Pb}_{0.004} (\text{Ti}_{0.21} \text{Nb}_{1.78} \text{Ta}_{0.01}) (\text{H}_2\text{O})_{1.64} \text{O}_{5.52}$).

Comparison of the calculated formula, essentially $A_{0.614} B_2 (\text{H}_2\text{O})_{1.64} \text{O}_{5.52}$ with the ideal pyrochlore formula $A_2B_2O_6F$ indicates important deficiencies in the structure. Differential thermal analysis shows a large endothermic peak at 340° C and moderate exothermic peaks at 480 and 780° C. In its physical, chemical, X-ray, and thermal properties the Mrima pandaite is similar to pandaite described from other localities.

The nature of the alteration of primary pyrochlore to pandaite has been studied using an electron probe.

DURING the period 1960–2, Warren Spring Laboratory undertook a research programme on the beneficiation of niobium in the weathered residuum of the Mrima Hill (Kenya) carbonatite in association with Overseas Geological Survey. In the course of the mineral processing testwork, detailed mineralogical examinations were made of several samples that had been collected by the Kenya Mines and Geological Department. As a result it was shown that the major niobium-bearing mineral in many of the samples was a hydrated barium pyrochlore, subsequently identified as pandaite, which has previously been fully described from only two other localities, Panda Hill (Tanganyika) the type locality (Jäger *et al.*, 1959), and Araxa (Minas Gerais, Brazil) (Van der Veen, 1963).

The purpose of this paper is to describe the Mrima Hill pandaite and to compare it with the other reported pandaite. In addition, the probable alteration process by which the pandaite has been derived from the primary mineral is described.

Location and geology. Mrima Hill lies in SE. Kenya approximately 40 miles from Mombasa, close to the coast and to the Tanganyikan border. It forms a small elliptical hill approximately one to half a mile

in width that rises some 750 feet above the coastal plain. It forms one of the satellite centres of the nearby Jombo alkaline igneous complex and represents the carbonatite phase of this intrusive series. The carbonatite itself is intruded into Mesozoic sandstones, and except for isolated exposures it is covered by a ferruginous residual deposit, more than 100 feet thick in places, which is the result of much weathering *in situ*. A significant effect of the weathering has been the removal of calcite and other carbonates, which has reduced the volume of the residuum to approximately 20 % of the original carbonatite, and has led to a corresponding concentration of resistant minor minerals including pyrochlore. Economic interest, which is confined to the soils, is due to the high niobium content, which averages approximately 0.8 % Nb_2O_5 and rises to 2 or 3 % in high value areas.

The hill has been prospected for niobium by the Kenya Mines and Geological Department, and a comprehensive survey was carried out by the Anglo-American Prospecting Co. Ltd. in 1955-56. As a result, the general geology and mineralogy have been described by Coutzee and Edwards (1959) and the spatial distribution of niobium values in the residuum has been mapped.

Mineralogy. All the residual samples examined were broadly similar in mineral composition and had similar particle-size characteristics.

The residuum has the appearance and texture of a dark-brown flour containing a few gritty particles. In one fairly typical sample 52 % of the weight and 70 % of the niobium occur in the $-10\ \mu$ size fraction. This tendency for the niobium to concentrate in the very fine sizes has been the major cause of difficulties in developing a suitable method of beneficiating the niobium values and is due to the fact that the major niobium-bearing mineral is a very brittle altered pyrochlore that tends to disintegrate under the least pressure.

The major minerals in the residuum consist of hydrated iron oxides (goethite and limonite) and hematite together with a secondary hydrated aluminophosphate containing barium, strontium, and minor rare earths, which is referred to as gorceixite ($\text{BaAl}_3(\text{PO}_4)_2(\text{OH})_5 \cdot \text{H}_2\text{O}$) but in fact appears to vary in composition within the range defined by the species gorceixite-goyazite-florenceite. The gorceixite has a microcrystalline sponge-like texture and is usually light brown in colour due to intimate intergrowth with limonite.

Minor minerals include earthy cryptocrystalline monazite, psilomelane, ilmenite, rutile, ilmenorutile, anatase, brookite, perovskite, magnetite, baryte, quartz, feldspar, and pyrochlore.

Pyrochlore separation. In order to prepare a clean concentrate of the altered pyrochlore, it was necessary to confine treatment to the plus-300 mesh B.S.S. material as the final operation involved hand picking, which is impractical with fine material. Also due to the friable nature of the pyrochlore it was not possible to crush coarser size fractions to release locked grains as this caused complete disintegration of the pyrochlore to very fine sizes. Consequently recovery had to be confined to such naturally liberated pyrochlore as occurred in the coarser size fractions. Very little of the liberated coarse mineral is present in the average Mrima samples. However, a small 2-kg borehole sample was available in which the pyrochlore in the coarser size ranges was unusually well liberated and it was from this material, assaying 2.0 % Nb_2O_5 , that the analytical sample was derived. Even in this case most of the pyrochlore was either unliberated or too fine for convenient recovery and it was necessary to process the entire 2 kg of soil sample to make a final 1.6 g of pyrochlore concentrate available for further study.

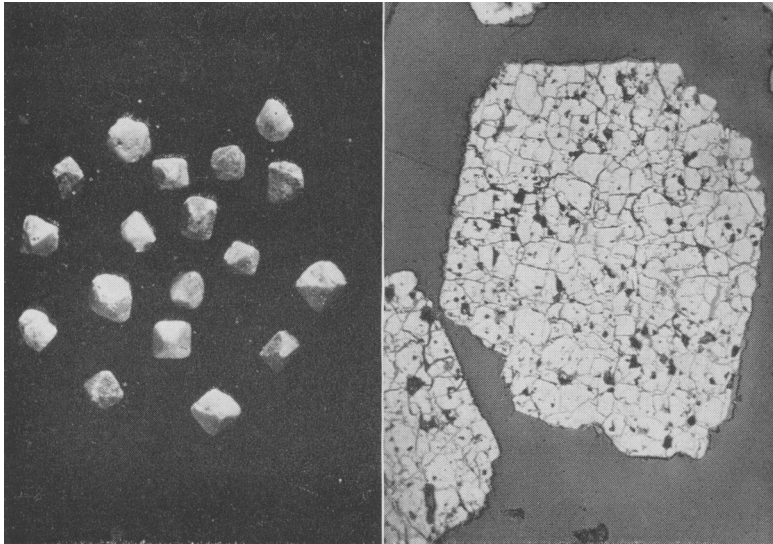
The separation process entailed mild scrubbing of the 2 kg sample with a suitable dispersant (sodium hexametaphosphate). This treatment effectively dispersed any flocculated particles and removed the limonitic coatings from the mineral grains. The resulting slurry was screened into size fractions, which were then dried and subjected to high intensity magnetic separation on the Franz Isodynamic Separator. By this means goethite, hematite, gorceixite/limonite intergrowths, and some trace minerals were removed, leaving a small non-magnetic concentrate mainly of altered pyrochlore together with some gorceixite, baryte, quartz, feldspar, zircon, perovskite, and a brown unaltered pyrochlore. The quartz, feldspar, and most of the gorceixite were removed by sink-float separations in methylene iodide. It was not possible to remove the baryte and zircon by using Clerici solution, as the altered pyrochlore tended to absorb thallium ions; the bulk of these minerals were therefore removed by means of a micropanner using tetrabromomethane as the wash liquid. Final cleaning of a pure pyrochlore concentrate for chemical analysis was effected by hand-picking from the coarser size fractions. The pyrochlore in the finer fractions was used for d.t.a. and other physical examinations.

Properties of the altered pyrochlore

The altered pyrochlore consisted of white to pale yellow octahedral crystals some of which had small cube face terminations. The crystal edges tended to be slightly rounded and the faces had an irregular sugary

appearance (fig. 1), while the interior was microcrystalline to such an extent that the grains were barely translucent.

On examining a polished section, the pyrochlore was found to possess a microgranular texture, with the original octahedra completely recrystallized into crystallites of approximately 2–30 μ diameter (fig. 2).



FIGS. 1 and 2: FIG. 1 (left). Grains of pandaite ($\times 40$) from the analysed sample. FIG. 2 (right). Polished section of pandaite ($\times 200$) showing fissured internal structure.

These were bounded by fine fissures or by minor inclusions of transparent phases (mainly silica and gorceixite); it is this texture that makes the mineral inherently friable.

In thin section the mineral is translucent and isotropic. The refractive index determined by immersion of grains in S/Se melts varied within the range 2.07–2.11 with most readings falling between 2.07 and 2.08.

The reflectivity of the pyrochlore could not be accurately measured as the fissures in the grains give rise to strong internal reflections and result in an abnormally high reflectivity. Reflectivity percentages varying between 14 and 19 % obtained; the true figure is probably close to 14 %.

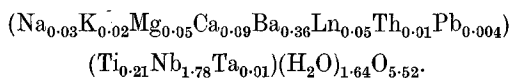
The peculiar physical condition of the pyrochlore has substantially reduced the accuracy with which many of its physical properties could

be determined. Thus in view of the presence of voids and inclusions the density could not be determined by the normal displacement methods, and it was necessary to allow several grains to sink through a graded density column of Clerici solution until they came to rest at the appropriate density level. In this way unusually light grains could be recognized and rejected. The majority of the grains formed a scattered band distributed over the density range 3.85–3.95. A density of 4.07 was calculated from chemical and X-ray data. After standing in the Clerici solution for several hours it was noted that the grains had become bright orange due to absorption of thallium ions.

An X-ray powder photograph was taken of the pyrochlore concentrate, from which a unit cell dimension of 10.59 Å was calculated (Pickup *et al.*, 1960). The mineral gave a clear pattern and there is no evidence of metamictization. The line positions and intensities gave an excellent match with the original Panda Hill pyrochlore (pandaite) reported by Jäger *et al.* (1959). The indexed powder pattern data are consistent with the cubic space group $Fd\bar{3}m-O_h^7$.

The *chemical analysis* of the pyrochlore is given in table I. In spite of the careful sample preparation, analyses and X-ray data indicated that approximately 10 % of the gorceixite remained in the concentrate. This was probably present as inclusions within the pyrochlore grains but, as insufficient material was available for further separation to be made, it was necessary to subtract constituents assigned to this and other minerals from the pyrochlore analysis. Other deductions included the total amount of Fe present in the sample as it is thought that this was due to limonitic material absorbed into the fissures of the grains rather than iron in the crystal lattice.

Infra-red examination of the pyrochlore suggests that H₂O molecules rather than hydroxyl ions are present in the crystal lattice; consequently all the hydrogen has been assigned to water in the calculation and the resulting formula of the altered pyrochlore is thus:



Comparison of the calculated formula, essentially $A_{0.614}B_2(\text{H}_2\text{O})_{1.64}\text{O}_{5.52}$ with the normal pyrochlore formula $A_2B_2\text{O}_6$ F indicates important deficiencies in the A, O, and F positions, although some of these positions are clearly occupied by H₂O molecules.

Jäger *et al.* (1959) proposed the name pandaite for the pyrochlore group mineral in which barium predominates over other elements in the

A position. The Panda Hill mineral, with an important Sr content, they characterized as strontian pandaite. The Mrima mineral, however, is a barium pyrochlore without strontium and is thus a true pandaite.

TABLE I. Chemical composition of altered pyrochlore from Mrima (pandaite), and comparison with other recorded pandaites

	1	2	3	A	B
Na ₂ O	0.2 %	0.23 %	Na 0.03	—	0.03
K ₂ O	0.2	0.23	K 0.02	—	0.01
MgO	0.5	0.57	Mg 0.05	0.001	—
CaO	1.4	1.37	Ca 0.09	0.004	0.05
SrO	tr.	—	Sr —	—	0.22
BaO	15.3	15.31	Ba 0.36	0.33	0.30
Ln ₂ O ₃	2.1	2.17	Ln 0.05	0.03	0.04
ThO ₂	0.8	0.92	Th 0.01	0.02	0.01
PbO	0.2	0.23	Pb 0.004	0.014	—
TiO ₂	4.1	4.63	Ti 0.21	0.21	0.17
Nb ₂ O ₅	57.4	65.60	Nb 1.78	1.73	1.83
Ta ₂ O ₅	0.5	0.57	Ta 0.01	—	0.004
H ₂ O ⁺	8.9*	8.17	H ₂ O 1.64	1.60	0.80
Sum	100.4	100.00	O 5.52	5.28	5.61
			<i>a</i> 10.59 Å	10.56 Å	10.56 Å
			Sp. gr. { calc. 4.07	3.90	4.01
			{ obs. 3.85-3.95	n.d.	4.00
			{ <i>n</i> 2.07-2.11	n.d.	2.07-2.10
			<i>D.t.a. peaks</i>		
			exothermic 340° C v.s.	300° C v.s.	330° C v.s.
			{ 480° C m.	500° C w.	540° C w.
			{ 780° C m.	800° C s.	800° C m.
			{ —	—	820° C m.

1. Analysis of concentrate; also total iron as Fe₂O₃ 1.3 %, Al₂O₃ 3.0, P₂O₅ 3.0, SO₃ 0.2, SiO₂ 1.1, and H₂O-0.2 %. Anal. R. Pickup, B.Sc., F.R.I.C.
2. Analysis recalculated after deduction of 9.8 % gorceixite, 0.6 % baryte, 1.1 % quartz, 1.0 % hematite, and 0.2 % Al₂O₃.
3. Atomic ratios to a basis of 2(Nb,Ta,Ti,Zr,Fe³⁺) in the general pyrochlore formula A₂B₂O₆(F, OH).

A. Pandaite from Araxa (Van der Veen, 1963).

B. Pandaite from Panda. (Jäger *et al.*, 1959).

* Loss on ignition at 1000° C; loss at 500° C 7.6 %.

† Includes 0.05 Fe³⁺ and 0.01 Zr.

‡ Includes 0.02 Fe²⁺.

Differential thermal analysis. A sample of the pandaite concentrate was subjected to differential thermal analysis using a Netzsch instrument. The main thermal features are a strong endothermic peak at approximately 340° C due to dehydration and two exothermic peaks at 480° and 780° C (fig. 3).

Some heating experiments were made to assist in interpretation of the d.t.a. data, and X-ray powder photographs were made of pandaite after heating in air at 400°, 580°, and 700° C and of the sample used for the differential thermal analysis (table II).

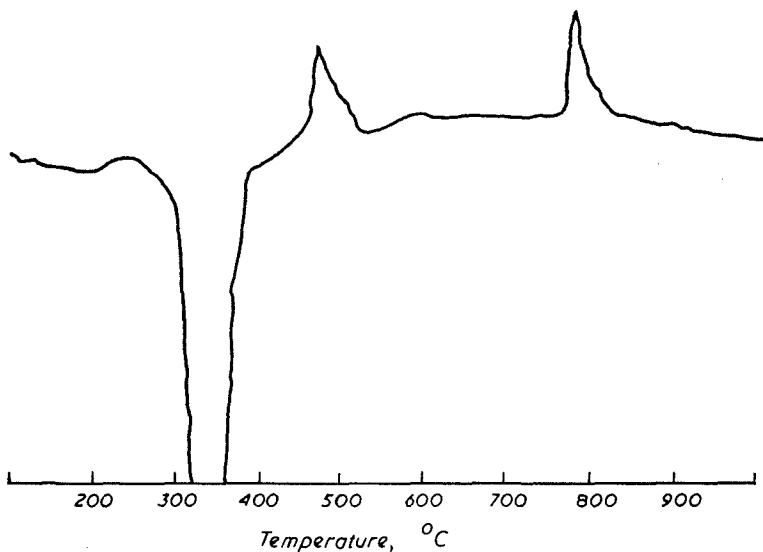


Fig. 3. D.t.a. diagram of pandaite.

TABLE II. Effect of heat treatment on Mrima pandaite

Treatment	Phase	Lattice parameter
Untreated	pyrochlore	10.59 Å
Heated at 400° C for 1 hour	pyrochlore	10.55
Heated at 580° C for 1 hour	pyrochlore	10.49
Heated at 700° C for 1 hour	pyrochlore	10.50
Heated to 1000° C at 10°/min	Barium niobate (3BaO.5Nb ₂ O ₆)	—

The d.t.a. and X-ray data show that heating results in a decrease of the lattice parameter up to a maximum temperature of 580° C. Consequently the exothermic peak at 480° C is probably a result of energy release connected with lattice shrinkage, which itself is perhaps caused by a structural reorganization necessary after the dehydration at 340° C. Above 580° C the lattice parameter remains approximately constant until decomposition of the pyrochlore structure takes place, which is represented by the exothermic peak at 780° C. The X-ray pattern of the

decomposition product corresponds to that given for the phase $3\text{BaO}\cdot 5\text{Nb}_2\text{O}_5$ (Roth and Waring, 1961). There was no evidence to suggest any decomposition or distortion of the pyrochlore structure at or below 700°C and there was no trace of pyrochlore structure in the sample heated to 1000°C .

Comparison of the Mrima, Araxa, and Panda Hill pandaïtes and other barium pyrochlores

The more important properties of the Mrima pandaïte are compared with those of the other reported pandaïtes from Araxa and Panda Hill (Pit 4 area) in table I. The Mrima and Araxa pandaïtes are clearly similar in terms of composition although the latter has a greater deficiency of *A* ions: both however, are more hydrated than the strontium rich type mineral. It is also of interest that the Araxa and Mrima eluvial deposits are broadly similar mineralogically.

The typical fissured, sugary texture of the Mrima pandaïte is referred to as 'cataclastic' by Van der Veen (1963) who describes similar textures in the Araxa and Panda pandaïtes.

The pandaïte d.t.a. patterns are similar and the relative size of the large endothermic peak appears to be approximately proportional to the degree of hydration.

Other reported pandaïtes include a barium pyrochlore, thought to be a true pandaïte, from the Mbale Zone of the Panda Hill carbonatite; however, difficulties in sample preparation due to intergrowth with a Ca-Na pyrochlore have prevented this mineral from being analysed. Other partially analysed Ba- and Ba-Sr-bearing pyrochlores, which do not qualify as pandaïtes, are also described from niobium deposits at Nkombwa, Nachomba, and Chasweta (N. Rhodesia), together with three Ba microlites from localities at São João Dei Rei (Minas Gerais) Brazil. As a result of his investigation on the above minerals, Van der Veen (1963) considers that all Ba and Ba-Sr pyrochlores and microlites, including pandaïtes, are distinguished from the more common Ca-Na pyrochlores by the following properties: cataclastic texture, a cell size greater than $10\cdot 50\text{ \AA}$, a high water content, a high deficiency in the *A* and *X* ions, and some ion exchange capacity, as shown by the absorption of Tl ions from Clerici solution.

Genesis of the Mrima pandaïte

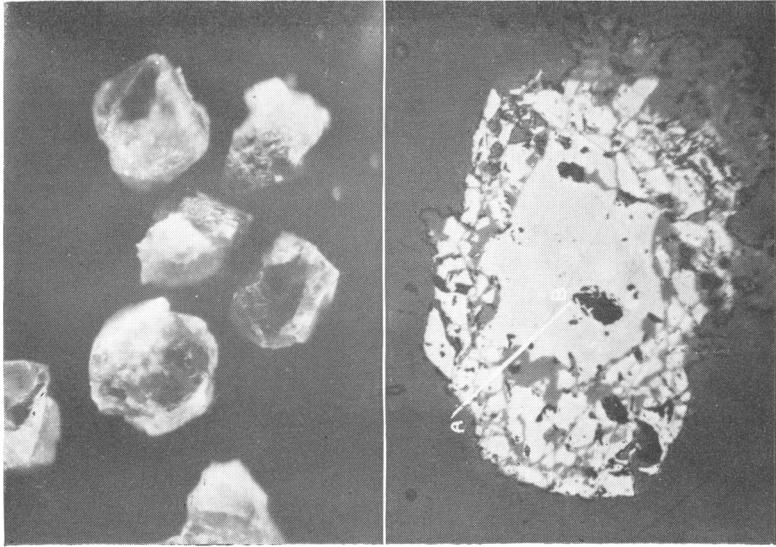
In an attempt to establish the origin of the Mrima pandaïte an examination was made of a weathered residuum sample taken from a

pit immediately overlying the carbonatite sub-outcrop. Most of the sample consisted of the typical residuum described earlier and contained both pandaite and some normal pyrochlore. However, approximately 2% of the pit sample was composed of a partly weathered but coherent chocolate-brown carbonatite, the texture of which was open and porous, indicating that part of the carbonate content had been removed by weathering. From its location and association with the overlying deposit this weathered carbonatite represents an intermediate breakdown product between the residuum and the original fresh carbonatite. The rock contained frequent lenses, and sometimes cubic crystals, of goethite and an altered iron-rich fibrous mineral, which suggested that pyrite and probably an iron-rich amphibole were among the original constituents. Several types of pyrochlore were present and these were recovered by careful leaching of the host rock in very dilute acid followed by heavy liquid separation in methylene iodide and hand picking.

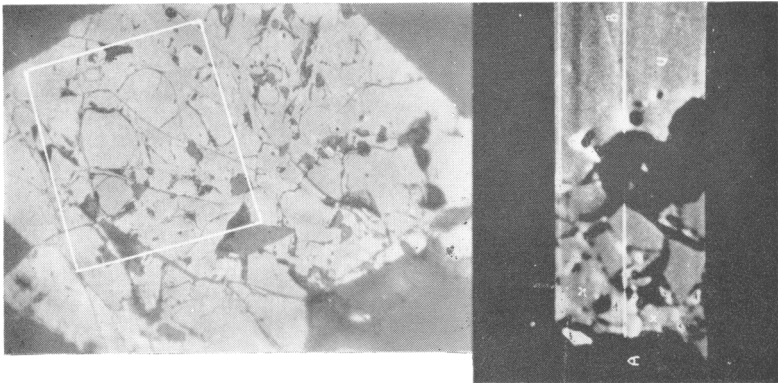
The pyrochlores occur mainly as octahedral crystals of approximately $130\ \mu$ diameter some of which appeared to be undergoing alteration from translucent crystals to a white microcrystalline material, which retained the octahedral form but had become very brittle. The unaltered pyrochlore comprised two types: the more abundant was translucent pale green or greenish-grey in colour, with a lattice parameter of $10.42 \pm 0.005\ \text{\AA}$; the other pyrochlore was usually clear and transparent, varied in colour from dark brown to honey-brown, and had a lattice parameter of $10.40 \pm 0.005\ \text{\AA}$.

X-ray powder patterns of pyrochlore grains containing altered and unaltered portions showed that the green primary mineral with a lattice parameter of $10.42\ \text{\AA}$ was associated with an alteration product of lattice parameter $10.55\ \text{\AA}$, and the brown pyrochlore of lattice parameter $10.40\ \text{\AA}$ had an alteration product of lattice parameter $10.48\ \text{\AA}$. In both cases the patterns were distinct and there was no evidence of intermediate phases.

The microscopic study was concentrated on the alteration of the brown pyrochlore since this variety presented a greater optical contrast with its alteration product than did the green-grey primary mineral. The relationship between the altered and unaltered pyrochlore is shown in photomicrographs (figs. 4-6). The physical nature of the alteration process is variable: sometimes it is accompanied by a complete shattering of the secondary mineral area followed by infilling of voids and cracks by a transparent mineral; more frequently the alteration develops in association with fissures and proceeds by dividing the original crystal



FIGS. 4 and 5: FIG. 4 (left). Brown pyrochlore grains ($\times 58$) showing peripheral alteration. FIG. 5 (right). Polished section of a pyrochlore grain ($\times 290$) shown in fig. 4. The unaltered central portion is surrounded by a fissured area of altered white pyrochlore with infillings of silica. The line *AB* indicates the location of electron probe traverse (figs. 7–10).



FIGS. 6 and 7: FIG. 6 (left). A partly altered pyrochlore ($\times 360$) with islands of primary pyrochlore, generally surrounded by fissures, in an altered matrix. The inset area has been analysed by the electron probe method (figs. 11–13). FIG. 7 (right). Electron image of the pyrochlore grain shown in fig. 5 adjacent to the line *AB*. Unaltered pyrochlore is marked *U*. The altered area is fissured and is marked *X*. Dark areas are pits in the section or inclusions of silica.



FIGS. 8 (top), 9 (middle), and 10 (bottom). X-ray traces showing the distribution of Ca, Sr, and Ba respectively across the traverse *AB* in fig. 7. The zero level of all three elements is given by the large trough corresponding to the siliceous inclusion. The unaltered pyrochlore contains approximately 10–15% Ca, a significant quantity of Sr and very little Ba. The altered portion is impoverished in Ca but shows considerable enrichment in Sr and Ba.

into generally rounded areas, which, in some cases, then appear to be altered by reduction from their periphery until all the primary mineral is converted. Complete alteration by the latter mechanism can be expected to result in a texture similar to the 'sugary' texture found in the Mrima pandaite (fig. 2).

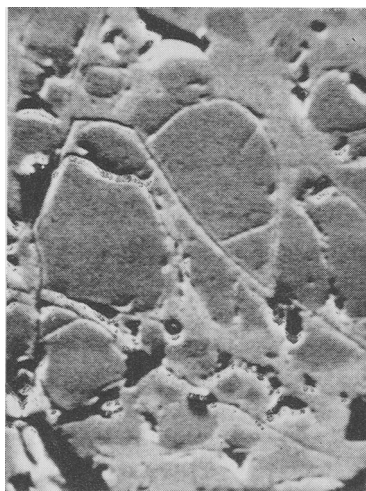


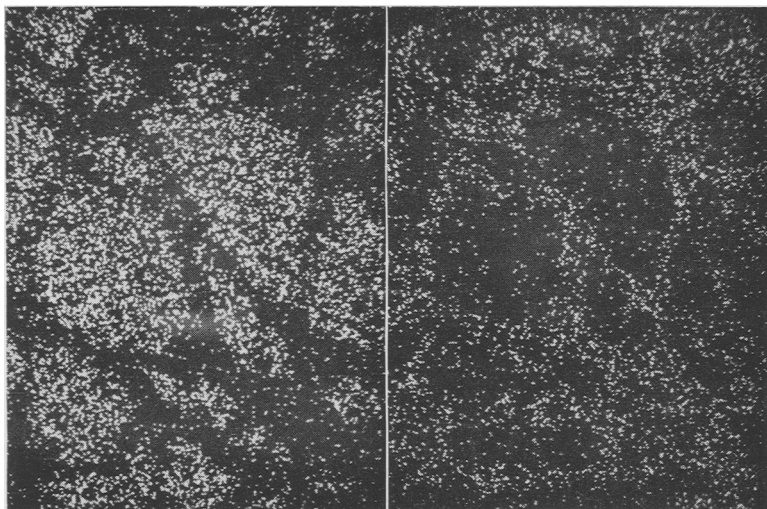
FIG. 11. Electron image of the inset area of fig. 6. The darker 'islands' are unaltered pyrochlore while the lighter matrix corresponds to altered material.

The chemical nature of the alteration process is demonstrated by an electron probe analysis carried out on the grains (figs. 5 and 6). The results of traverses across the alteration boundary (*A-B* of fig. 5) using a Cambridge Instrument Co. Microscan are shown in figs. 8–10 together with an electron image of the traverse (fig. 7). Further electron and X-ray images of partly altered pyrochlore crystals are given (figs. 11–13). These show that the unaltered mineral contains substantial Ca and a little Sr, while the altered pyrochlore contain much less Ca and is greatly enriched in Sr. It can also be shown that Ba has the same distribution as the Sr.

Unfortunately it was not possible to follow the distribution of Na between altered and unaltered pyrochlore as this element cannot be detected by the electron probe.

Since completely altered pandaite is found only in the residual soils, and partly altered pyrochlore occurs in the underlying severely weathered

carbonatite, it is logical to assume that the alteration process is connected with the normal weathering of the carbonatite. Essentially the process appears to involve expansion of the lattice parameter, the removal of virtually all the Ca, Na, and F ions from the pyrochlore structure, and partial reoccupation of the vacant sites by the less soluble Sr and Ba



Figs. 12 (left), and 13 (right). X-ray images showing the distribution of Ca and Sr respectively in the area covered by fig. 11. It is clear that the Ca is concentrated in the unaltered areas and the Sr in the altered matrix. It can similarly be shown that the distribution of Ba is identical with that of Sr.

cations and by water molecules. Presumably the excess charge remaining on the oxygen ions would be satisfied by hydration and the resulting water molecules either held in the structure or lost. The necessary Sr and Ba were probably derived from the minor amounts of these elements occurring in the carbonate minerals of the original carbonatite.

The role of Sr in the alteration process could not be fully established on the available material. Thus although the pandaite typical of the residual soils is Sr free, the alteration process described above involves the entry of Sr into the altered pyrochlore lattice. However, it is possible that the Sr that enters the lattice in the early stages of alteration is eventually removed and replaced or partly replaced by Ba, causing further expansion of the unit cell, as the leaching conditions become more intense. Alternatively, local conditions may eliminate Sr and allow the direct formation of pandaite from primary pyrochlore.

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