Petscheckite and liandratite, two new pegmatite minerals from Madagascar

Arno Mücke and Hugo Strunz

Institut für Mineralogie und Kristallographie
Technische Universität Berlin
1000 Berlin 12, West Germany

Abstract

We discovered two new metamict minerals in the Antsakoa I pegmatite near Berere in Madagascar. They were recrystallized through heating and investigated with the following results:

(1) Petscheckite, idealized as $U^{4+}Fe^{2+}(Nb,Ta)_2O_8$, hexagonal, space group $P\bar{3}1m$, $a = 6.42$, $c = 4.02A$, $Z = 1$. It occurs as crystals up to 4 cm long and 2 cm thick, hardness ~ 5, specific gravity ~ 7. The color is black, streak brown-black, and fragments are opaque. Through oxidation and hydration, two intimately intergrown varieties occur: oxy-petscheckite, $U^{4+}(Fe^{3+}_{2/3}\square_{1/3})(Nb,Ta)_2O_8$ and hydroxy-petscheckite, $U^{4+}(Fe^{3+}_{1/3}\square_{2/3})(Nb,Ta)_2O_7(O,OH)$.

(2) Liandratite, $U^{6+}(Nb,Ta)_2O_8$, space group $P\bar{3}1m$, $a = 6.36$, $c = 4.01A$, $Z = 1$. It occurs as crusts up to 2 mm thick surrounding petscheckite. The color is yellow to brown, streak bright yellow, hardness $\sim 3\ 1/2$, specific gravity ~ 6.8, refractive index $n = 1.83$ for metamict material. The structure of liandratite is identical with that of synthetic $U^{6+}Ta_2O_8$. The empty position at $(00\frac{1}{2})$ for this species is occupied by Fe in petscheckite.

The names are for Mr. Eckehard Petsch of Idar Oberstein and Professor George Liandrat of Samoëns, France, who have performed noteworthy prospecting activities in Madagascar. Both species were accepted by the IMA Commission on New Minerals and New Mineral Names.
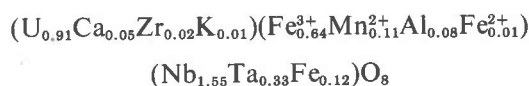
Occurrence

The pegmatites in the Berere region lie about 250 km north of Tananarive and approximately 40 km northeast of the town of Tsaratanana, in the inaccessible lowland of north Madagascar, near the boundary between basement and supracrustal rocks. Like nearly all Madagascar pegmatites they are linked to the "granite tardiff" of about 550 m.y. in age. According to Besairie (1964), they are intruded into amphibolites (group de Beforona, C5).

We focus attention on four pegmatites, Antsakoa I, Antsakoa II, Analila, and Ambany (Fig. 1). They are situated 0.5 to 2 km from the mining point of Berere, which has been abandoned since 1960. The pegmatities are distinctly zoned (Fig. 2). At the Antsakoa I pegmatite the outer zone is aplitic in the envelope (A) and beryl-bearing in the center (B). The feldspar of the quartz and feldspar core (Q + F) is extensively weathered. The nomenclature of the zones and the plan of the pegmatite follow Uebel (1977). The quartz of the core juts out as bleached rose quartz and extends 20–30 meters above the sur-

roundings. The mineralized zone (B) around the quartz and feldspar core was mined for beryl and Ta/Nb-bearing minerals during the years 1950–1960. The accessory minerals are found in this zone, including the new minerals petscheckite and liandratite. Associated minerals include strüverite, monazite, ilmenite, garnet, and tourmaline along with the major pegmatite minerals. Crystals of so-called "niobo-tantalite" from Berere/Tsaratanana, up to 4 cm long and 2 cm thick, weight 5–20 g, were secured during a research expedition to Madagascar in 1972. All examples are encased by a crust of varying thickness which is gray-brown, brown, yellow, or white in color.

Petscheckite: chemical analysis and formula contents

The analysis in Table 1 leads, on the basis of $\Sigma(Nb^{5+} + Ta^{5+} + Fe^{3+}) = 2.00$ at one site, to the formula unit

$$(U_{0.91}Ca_{0.05}Zr_{0.02}K_{0.01})(Fe^{3+}_{0.64}Mn^{2+}_{0.11}Al_{0.08}Fe^{2+}_{0.01})$$

$$(Nb_{1.55}Ta_{0.33}Fe_{0.12})O_8$$

After heating at 650°C, the pulverized mineral yields

Fig. 1. The pegmatite near Berere, Madagascar.

Fig. 2. The zoned Antsakoa I pegmatite in the province of Berere.
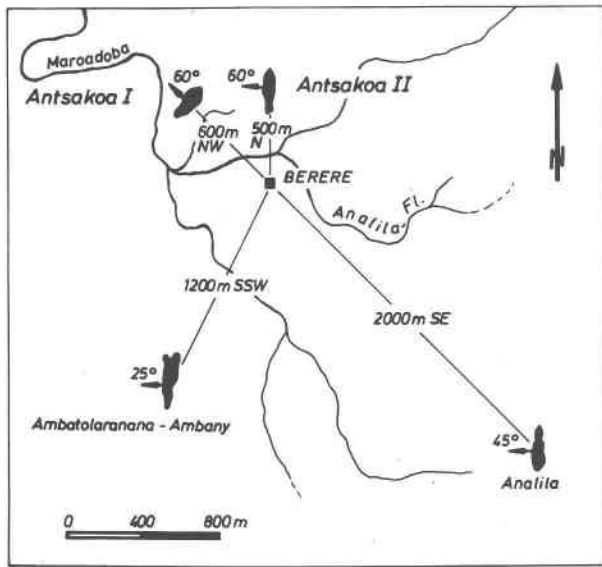
a powder pattern which corresponds to the hexagonal compound UTa_2O_8, synthesized by Gasparin (1960), in which the valency is U^{6+}. For the mineral described here, however, uranium is present as U^{4+}. For valence balance Fe^{2+} is built into the structure, assuring electrostatic neutrality. By metamictization and oxidation the original primary Fe^{2+} was oxidized. The original composition of petscheckite must have corresponded to the formula $U^{4+}Fe^{2+}(Nb,Ta)_2O_8$. In the course of subsequent reworking, two varieties were formed: (1) oxy-petscheckite, $U^{4+}(Fe^{3+},\square)$

Table 1. Analysis of the heated oxy- and hydroxy-petscheckites. Wet-chemical analysis by W. Napiontek

	Weight %	Molecular Contents	Cation Contents
UO_2	40.5	0.9087	3.68
Nb_2O_5	⎫ 45.99	1.5500	7.75
Ta_2O_5	⎭	0.3291	1.65
Fe_2O_3	10.01	0.7596	2.28
FeO	0.10	0.0084	0.02
MnO	1.32	0.1128	0.22
ZrO_2	0.42	0.0207	0.08
Al_2O_3	0.71	0.0843	0.24
CaO	0.49	0.0530	0.10
K_2O	0.05	0.0064	0.01
	99.59		16.03

$(Nb,Ta)_2O_8,\square = 1/3$ and (2) hydroxy-petscheckite, $U^{4+}(Fe^{3+}_{\leq 1/3},\square_{\geq 2/3})(Nb,Ta)_2O_{\leq 7}(OH)_{\geq 1}$. The general formula for petscheckite is therefore $U^{4+}(Fe,\square)(Nb,Ta)_2(O,OH)_8$.

Origin of the varieties

Through oxidation of primary $U^{4+}Fe^{2+}(Nb,Ta)_2O_8$, Fe^{2+} is changed to Fe^{3+}. In order to maintain valence balance and the structure type, a third of the total iron is removed according to the following scheme:

$$9U^{4+}Fe^{2+}(Nb,Ta)_2O_8 + 4O^{2-}$$
petscheckite

$$\rightarrow 3U^{4+}_3Fe^{3+}_2(Nb,Ta)_6O_{24} + Fe_3O_4 + 8e$$
oxy-petscheckite   magnetite
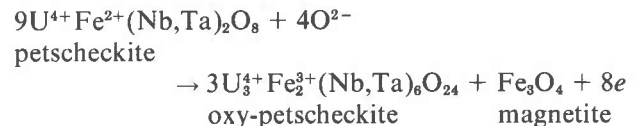
The solid phases on the right are products of the oxidative sequence. Through this reaction under intermediate temperature, oxy-petscheckite and magnetite are of the same age and are intergrown (Fig. 3). In addition we find another variety, called hydroxy-petscheckite. This hydroxylated phase is poorer in iron, and Mn occurs only in trace amounts, as established by microprobe scans. This implies that separation of iron and manganese occurs during the alteration process, so that the reaction occurred in an alkalic regime. The iron content varies significantly in hydroxy-petscheckite. Hydroxy-petscheckite is water-rich. The water content could only be approximately determined, since significant amounts of the varieties could not be separated. The limits are petscheckite < 3.2 weight percent H_2O, hydroxy-petscheckite > 3.2 weight percent H_2O.

On account of the significant difference in Fe-content, the formation of hydroxy-petscheckite proceeds step-wise (1) directly from petscheckite:
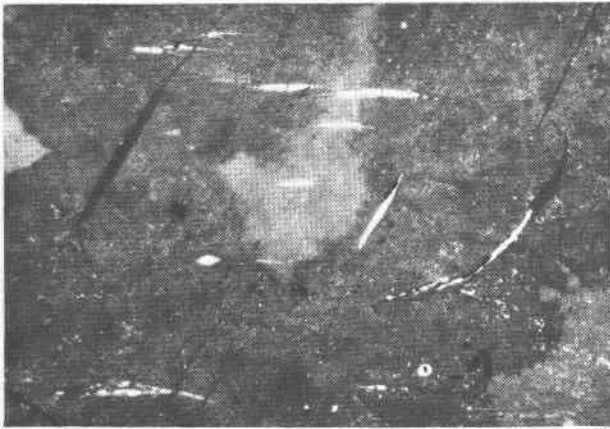
Fig. 3. Disklike magnetite inclusions oriented in hydroxy-petscheckite. The length of the disks is about 3 μ. Oil immersion.
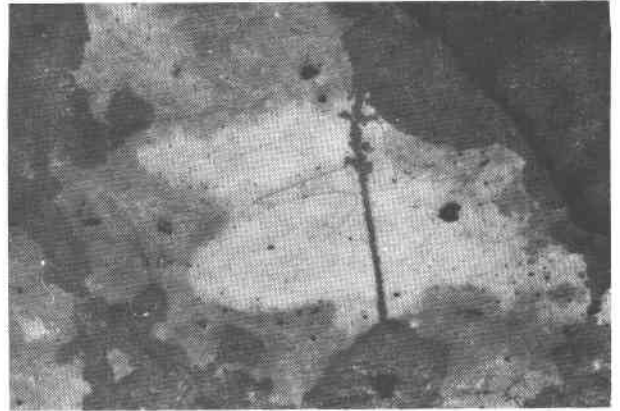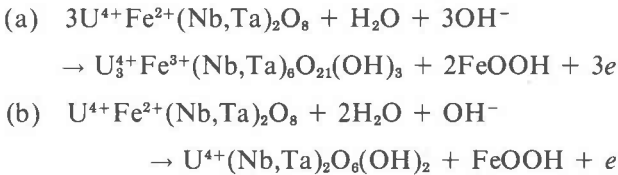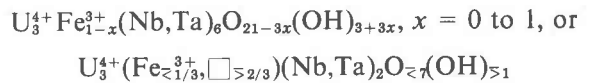

Fig. 4. Oxy-petscheckite (brightly reflecting) replaced by hydroxy-petscheckite. As a sign of progressive hydroxylation, the hydroxy-petscheckite extensively borders the oxy-petscheckite.

(a) $3U^{4+}Fe^{2+}(Nb,Ta)_2O_8 + H_2O + 3OH^-$

$\rightarrow U_3^{4+}Fe^{3+}(Nb,Ta)_6O_{21}(OH)_3 + 2FeOOH + 3e$

(b) $U^{4+}Fe^{2+}(Nb,Ta)_2O_8 + 2H_2O + OH^-$

$\rightarrow U^{4+}(Nb,Ta)_2O_6(OH)_2 + FeOOH + e$

It is also quite likely that hydroxy-petscheckite (2) forms indirectly from oxy-petscheckite. Analogous to reactions (a) and (b) the degree of hydroxylation can be distinguished although the same reaction products arise. For example, reaction (b) follows:

$U_3^{4+}Fe_2^{3+}(Nb,Ta)_6O_{24} + 4H_2O$
oxy-petscheckite

$\rightarrow 3U^{4+}(Nb,Ta)_2O_6(OH)_2 + 2FeOOH$
hydroxy-petscheckite
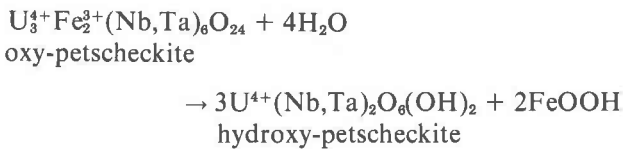
The hydroxy-phase occurs with limonite, which is recognizable in polished section, although it is transported away in part so that iron content and degree of hydroxylation is not constant in a sample. The amounts of both members, which reflect the degree of hydrolysis of the reaction, lead to variations of chemical contents between $U_3^{4+}Fe^{3+}(Nb,Ta)_6O_{21}(OH)_3$ and $U_3^{4+}(Nb,Ta)_6O_{18}(OH)_6$ (Fig. 4). The general formula of hydroxy-petscheckite is

$U_3^{4+}Fe_{1-x}^{3+}(Nb,Ta)_6O_{21-3x}(OH)_{3+3x}$, $x = 0$ to 1, or

$U_3^{4+}(Fe_{\lesssim 1/3}^{3+},\square_{\gtrsim 2/3})(Nb,Ta)_2O_{\lesssim 7}(OH)_{\gtrsim 1}$

Ore microscopic investigation

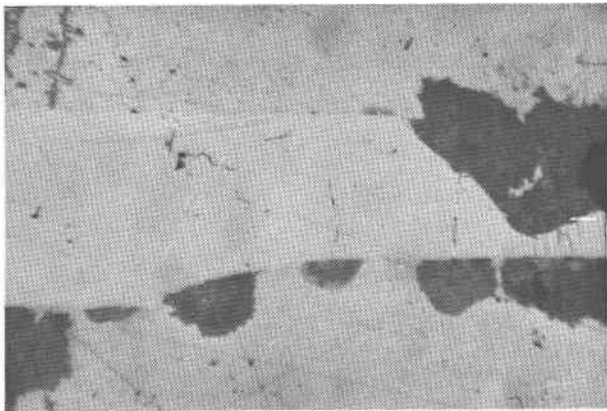In polished section, oxy-petscheckite and hydroxy-

Fig. 5. Columbite (most brightly reflecting) overgrown by oxy-petscheckite. The spherulitic boundaries are hydroxy-petscheckite. Oil immersion.

Fig. 6. Hydroxy-petscheckite with remains of oxy-petscheckite. Oil immersion.

Table 2. Microchemical analysis of liandratite

	I	II
UO_2	~ 50	48.73 (UO_3)
Nb_2O_5 }		36.22 }
	~ 50	} 51.27
Ta_2O_5 }		15.05 }
H_2O	~ 0.5	

Table 3. Lattice constants of the uranium minerals

	a(A)	c(A)	indexed d-value	remarks
Oxy-petscheckite	6.42	4.02	Table 4	
Hydroxy-petscheckite				decomposes by heating
Liandratite	6.36	4.01	Table 5	
UTa_2O_8	6.41	3.95	Table 5	
Uran-pyrochlore	10.36			by heating of hydroxy-petscheckite

petscheckite are clearly distinguishable (Fig. 5). Their proportions vary considerably, but the oxy-variety is always dominant. The results in Table 1 are based on an analysis of both varieties in about 1:1 proportion.

The color of oxy-petscheckite is white with a tinge of orange. Against columbite, the orange tint is absent. In oil, oxy-petscheckite is light brown and against columbite possesses a tint toward blue-gray. Reflectance in air is about 15 percent and in oil 6 percent, slightly below columbite (Fig. 5). Anisotropy under crossed nicols is absent, owing to the metamict character of the mineral. Also encountered are red-brown inner reflections which in oil are considerably augmented. Further properties are: metallic luster, color black, streak brown-black, hardness about 5 (on Mohs scale).

The reflectance of hydroxy-petscheckite is about 10–12 percent lower, and it is more strongly lowered in oil than oxy-petscheckite. The two varieties are thus easily distinguished from each other, and the "phase boundary" runs continuously (the reflectances alternate within the value of oxy-petscheckite on one side and hydroxy-petscheckite on the other side) and is a sign of progressive hydroxylation (Fig. 4).

The color is gray-brown, in oil dirty gray-brown and speckled; that is, it is in part a mixture of oxy- and hydroxy-petscheckite (Fig. 6). Some domains consist only of hydroxy-petscheckite with enclosures of limonite. Under crossed nicols, numerous red-brown to yellow-brown inner reflections can be discerned. Further properties are: luster semi-metallic, color dark brown, streak light brown, hardness 3 1/2.

Liandratite

Petscheckite is usually completely enclosed by a glassy translucent yellow to yellow-brown phase. The crust is within 1–2 mm in thickness and, like petscheckite, it is metamict. The mineral contains only the principal metals U, Nb, and Ta, and traces of Fe,

Table 4. d-values for oxy-petscheckite after a single heating at 650°C (Cu$K\alpha$ radiation, 57.3 mm camera diameter)

No.	Int.	$2\theta_{obs}$	d_{obs}	d_{calc}	hkil
1	10	22.10	4.02	4.02	0001
2	10	27.80	3.21	3.208	11$\bar{2}$0
3	8	35.75	2.51	2.507	11$\bar{2}$1
4	2	45.00	2.01	2.010	0002
5	2	48.95	1.861	1.861	21$\bar{3}$1
6	3	49.25	1.850	1.852	30$\bar{3}$0
7	4d	54.05	1.697	1.682	30$\bar{3}$1
				1.7032	11$\bar{2}$2
8	2	62.20	1.492	1.490	22$\bar{4}$1
9	2	64.90	1.437	1.439	31$\bar{4}$1
10	1	69.05	1.360	1.362	30$\bar{3}$2
11	1	72.30	1.307	1.312	40$\bar{4}$1
12	1	79.00	1.212	1.212	41$\bar{5}$0
13	1	83.20	1.161	1.161	41$\bar{5}$1

Table 5. d-values for liandratite (Cu$K\alpha$ radiation, 57.3 mm camera diameter) and for synthetic UTa_2O_8 (from Gasparin, 1960)

	Liandratite				UTa_2O_8		
No.	Int.	$2\theta_{obs}$	d_{obs}	d_{calc}	Int.	d	hkil
1	8	22.15	4.01	4.01	ai	3.94	0001
2	10	28.10	3.18	3.179	ti	3.20	11$\bar{2}$0
3	4	36.10	2.49	2.491	i	2.49	11$\bar{2}$1
4	1	45.35	2.00	2.005	ai	1.978	0002
5	3	49.60	1.838	1.835	ai	1.855	30$\bar{3}$0
6	2	54.20	1.692	1.696		–	11$\bar{2}$2
7	1	55.10	1.667	1.669	i	1.676	30$\bar{3}$1
8	1	58.00	1.590	1.590	ai	1.607	22$\bar{4}$0
9	1	62.85	1.479	1.478	ai	1.487	22$\bar{4}$1
10	1	69.45	1.353	1.354	af	1.351	30$\bar{3}$2
11	1	76.60	1.244	1.245	af	1.244	22$\bar{4}$2
12	2	79.95	1.200	1.201	ai	1.218	41$\bar{5}$0
13	1	84.20	1.150	1.151	ai	1.159	41$\bar{5}$1

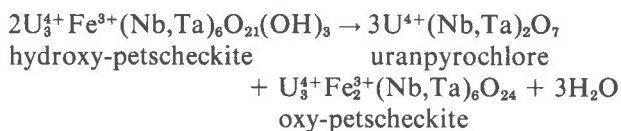Table 6. d-values for the pyrochlore (CuKα radiation, 57.3 mm camera diameter)

	U(Nb,Ta)$_2$O$_7$ after heating		U-bearing pyrochlore (crust mineral)		
No.	Int.	d	Int.	d	hkl
1		–	4	7.3	110
2	10	300	10	3.01	222
3	3	2.60	3	2.61	400
4	6	1.83	8	1.84	440
5		–	1	1.72	600
6	8	1.558	6	1.575	622
7		–	1	1.483	710
8	2	1.494	1	1.514	444
9	1	1.296	1	1.302	800
10	3	1.188	2	1.202	662
11	2	1.158	2	1.168	840
			1	1.070	844

Mn, Th, and Pb. The results from a microchemical analysis are in Table 2, column I. These contents correspond to a composition U(Nb,Ta)$_2$O$_8$ with a Nb:Ta content of about 5:1 (see column II in Table 2 for the theoretical composition). We name this mineral liandratite. Liandratite is yellow to brownish-yellow, streak yellow-white, translucent with glassy luster, fracture conchoidal, hardness 3 1/2, $n = 1.83$. U(Nb,Ta)$_2$O$_8$ arises through complete oxidation of uranium and iron, where nearly all Fe^{3+} ions have been removed. This process occurred *in situ* and only on the surface of petscheckite crystals, which are therefore epitaxially overgrown by liandratite.

X-ray studies

The petscheckite varieties and liandratite are recrystallized by rapid heating at red heat (~650°C). In hydroxy-petscheckite, shrinkage cracks appear. The results of the X-ray powder study are given in Tables 3 to 6. If both petscheckite varieties are heated for 24 hours at 1000°C, two distinct phases arise which appear to be homogeneous.

Liandratite remains a single phase by heating, but oxy-petscheckite forms a small amount and hydroxy-petscheckite principally converts to uranpyrochlore. The appearance of uranpyrochlore, especially from hydroxy-petscheckite, is supportive evidence for the afore-mentioned formulae. Through heating the following reaction is complete:

$$2U_3^{4+}Fe^{3+}(Nb,Ta)_6O_{21}(OH)_3 \rightarrow 3U^{4+}(Nb,Ta)_2O_7$$

hydroxy-petscheckite   uranpyrochlore

$$+ U_3^{4+}Fe_2^{3+}(Nb,Ta)_6O_{24} + 3H_2O$$

oxy-petscheckite

Starting with $U^{4+}(Nb,Ta)_2O_6(OH)_2$, only uran-pyrochlore arises by heating, so that collectively a quantity of preponderant uranpyrochlore and oxy-petscheckite remains behind. Hydroxy-petscheckite is therefore not fully transformed by heating from the metamict state to crystals, since during heating water is lost and a fraction of uranpyrochlore and oxy-petscheckite are decomposed. These transformations through heating conclusively demonstrate the afore-mentioned increase in the charge of uranium. If uranium in hydroxy-petscheckite was not 4-valent, it would not recrystallize as uranpyrochlore. In liandratite, where U^{6+} is present, lines corresponding to pyrochlore are missing in the powder diagram.

The specific gravity of unheated petscheckite is 5.0 and increases after heating to 5.5. Corresponding to Gasparin's (1960) structure cell with $Z = 1$, we get calculated values of 7.2 for oxy-petscheckite and 6.6 for hydroxy-petscheckite. The specific gravity of heated liandratite is 7.0. Computed specific gravity ranges between 6.523 for UNb_2O_8 and 8.604 for UTa_2O_8.

For petscheckite and liandratite the indices for the powder patterns are in accord with the results of Gasparin (1960) for UTa_2O_8 with space group $P\bar{3}1m$. In contrast with Fe-free liandratite which corresponds to synthetic UTa_2O_8, in petscheckite the atom positions at $00\frac{1}{2}$ (b) for this space group are occupied by Fe^{2+}. The U^{4+}–Fe^{2+} separation is 2A.
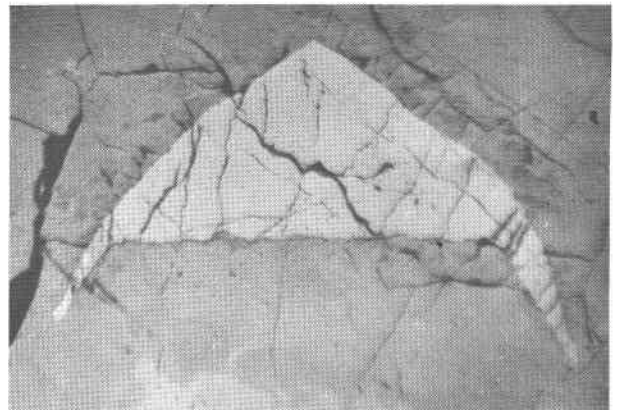
Fig. 7. Oriented inclosure of columbite (size about 1 mm) in hydroxy-petscheckite. Oil immersion.

Furthermore, the agreement between our data and those of Gasparin (1960) are quite good.

Inclusions in petscheckite

Both varieties of petscheckite have intergrowths of magnetite as elongated disks. The magnetite bodies are arranged parallel to each other and form an oriented intergrowth with petscheckite. As already discussed, magnetite is of the same age as oxy-petscheckite, and its presence suggests that during the formulated transformation of petscheckite into oxy-petscheckite, the formation of free Fe_3O_4 is quite probable. Furthermore, since a distinction in the frequency of magnetite could not be established in oxy-petscheckite and hydroxy-petscheckite, the indirect formation of hydroxy-petscheckite from oxy-petscheckite is more likely than the direct formation from petscheckite. The inclusions of magnetite in hydroxy-petscheckite are, in part, significantly more martitized than in oxy-petscheckite.

The characteristic appearance of the associated columbite, distinct in orientation from crystals which grew freely, is related to the petscheckite according to more than one law (Fig. 7). It forms with petscheckite, $U^{4+}Fe^{2+}(Nb,Ta)_2O_8$, a primary diataxial intergrowth. The columbite crystals appear to mimic the outline of an enclosed hexagonal crystal so that the primary petscheckite—analogous to the heated product—was in fact hexagonal.

Other products of reworking

In addition to the crust mineral liandratite, other locally concentrated minerals were encountered which are not metamict.

(1) Matted to ribbed thin examples of a dirty brown to yellow powder. The mineral belongs to the pyrochlore group. The powder photograph was indexed on $a = 10.44A$ (Table 6). From a crude estimate, the formula $(Ca,U,Pb)(Nb,Ta)_2O_7$ is proposed, and therefore it is a lead-bearing uranpyrochlore. In spite of its U-content the mineral is not metamict, suggesting late-stage younger crystallization. This implies that pyrochlore is not only an early high-temperature mineral but a phase which can also form under hypogene conditions.

(2) Next to liandratite, the most frequently encountered crust mineral is Nb- and U-bearing metahalloysite which is most frequently white and occasionally yellow-brown. Intimate mixtures of fine-grained pyrochlore and metahalloysite have also been encountered. Other crust materials exist in a similar association, but these minerals have not been investigated in greater detail.

References

Besairie, H. (1964) Madagascar, *Carte Géologique. Mise à jour au 1er Janvier 1964.* Editeur Service Geologique de Madagascar, Tananarive.

Gasparin, M. (1960) Contribution a l'ètude de quelques oxydes doubles que forme le tantale avec l'ètain, l'uranium et le calcium. *Bull. Soc. fr. Mineral. Cristallogr., 83,* 1–21

Uebel, P.-J. (1977) Internal structure of pegmatites, its origin and nomenclature. *Neues Jahrb. Mineral. Abh., 131,* 83–113.