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(U,Th)-BEARING SILICATES IN REEFS OF THE WITWATERSRAND, SOUTH AFRICA

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ABSTRACT

(U,Th)-silicates are extremely rare in most ore-bearing conglomerates in the Witwatersrand. However, authigenic coffinite is fairly common in the Dominion Reef, the oldest conglomerate in the Witwatersrand Basin, and on the West Rand Goldfield, in reefs in the uppermost part of the Witwatersrand Supergroup. The coffinite was formed *in situ* from detrital uraninite through the uptake of silica. Thorite and thorogummite of detrital origin also are present in the Dominion Reef. Chemical data indicate that (U,Th)-silicates form two complete series of anhydrous and hydrated species, for which the general formulae are $(U,Th)SiO_4$ and $(U,Th)SiO_4 \cdot nH_2O$ ($n<4$), respectively. On the basis of existing names, the end members of the anhydrous series are anhydrous coffinite and thorite, and those of the hydrated series are coffinite and thorogummite.

Keywords: (U,Th)-silicate, coffinite, thorite, thorogummite, (Zr,Th)-silicates, Witwatersrand, South Africa.

SOMMAIRE

Les silicates d'uranium et de thorium sont rarissimes dans la plupart des conglomérats minéralisés du bassin de Witwatersrand (Afrique du Sud). Toutefois, la coffinite authigène est relativement répandue dans le niveau du Dominion Reef, le conglomérat le plus ancien du bassin, ainsi que dans le camp aurifère de West Rand, dans les bancs de la partie supérieure du supergroupe de Witwatersrand. La coffinite s'est formée *in situ* à partir de l'uraninite détritique, suite à un apport de silice. Thorite et thorogummite d'origine détritique sont aussi présentes dans le Dominion Reef. Les données chimiques montrent que les silicates de (U,Th) appartiennent à une de deux solutions solides complètes, $(U,Th)SiO_4$ et $(U,Th)SiO_4 \cdot nH_2O$ ($n<4$). D'après la nomenclature déjà établie, les termes sont coffinite anhydre et thorite dans le premier cas, et coffinite et thorogummite pour la série hydratée.

(Traduit par la Rédaction)

Mots-clés: silicate de (U,Th), coffinite, thorite, thorogummite, silicates de (Zr,Th), Witwatersrand, Afrique du Sud.

INTRODUCTION

Tetragonal thorite was first described by Berzelius (1829), thorogummite by Hidden & Mackintosh (1889), and the monoclinic polymorph huttonite by Hutton (1950). However, the uranium-bearing silicates have been overlooked in many deposits because their optical properties are identical to those of the thorium-bearing species. Thorium-free coffinite was first recognized by Stieff *et al.* (1955, 1956) in the uranium deposits of sandstone type, of Phanerozoic age, on the Colorado Plateau, where it occurs in association with uraninite.

In recent years, coffinite also has been recognized in fossil placers of the quartz-pebble conglomerate type of Proterozoic and Archean age (Hiemstra 1968, Robinson & Spooner 1982, Oberthur 1983, Smits 1984).

MINERALOGICAL AND CHEMICAL ASPECTS OF (U,Th)-SILICATES

Except for thorite and thorogummite, the (U,Th)-silicates are black. In hand specimen, thorite can be yellowish grey, light olive to olive grey, or moderate light brown to light brown (*cf.* Rock Color Chart distributed by the *Geol. Soc. Am.* in 1963) (Frondel 1958). The variation in color is due mainly to the presence of trace amounts of ferrous and ferric iron. Synthetic thorite is white, and synthetic coffinite is blue (Fuchs & Hoekstra 1959). Thorogummite occurs as fine-grained aggregates that are moderate reddish brown to very pale orange, and is loosely referred to as orangite (Glatthaar & Feather 1985). Huttonite is colorless to very pale cream (Frondel 1958).

The reflectance of the (U,Th)-silicates in air ranges from 7 to 10% (Uytenbogaardt & Burke 1971), but is less than 1.5% in oil (Ramdohr 1961). The variation in the composition of the silicates does not affect their optical appearance, which is identical for all anhydrous and hydrated species.

The (U,Th)-silicates are microcrystalline and are, as a rule, intimately admixed with a number of impurities such as sulfides, gold, carbonaceous matter, clay minerals, and silica. For this reason, it is difficult to obtain a pure sample for the determination of its correct chemical composition and physical properties. Even with the electron microprobe (EMP), it is almost impossible to single out the microcrystallites, and to avoid contamination by neighboring minerals.

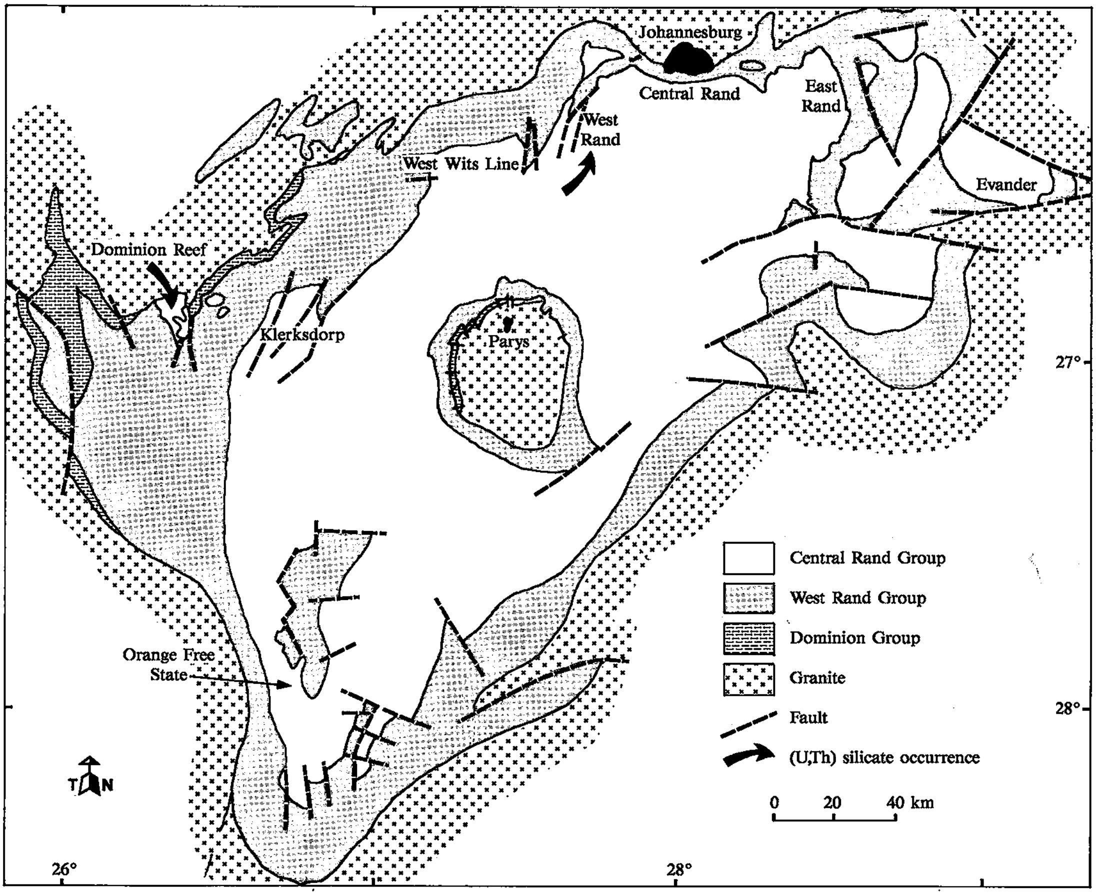

FIG. 1. Geological map of the Witwatersrand Basin after the removal of overlying rocks and the location of goldfields (modified from Borchers 1961).

The hydrated and anhydrous (U,Th)-silicates possess similar X-ray-diffraction (XRD) patterns. However, with the substitution of uranium by thorium, the *d*-values shift, and the cell parameters increase (Speer 1980). In the Witwatersrand reefs, XRD patterns are readily obtained from coffinite and thorogummite, but the hydrated uranoan thorite is metamict.

Frondel (1953) studied hydrated zircon species and thorogummite from various parts of the world, and proposed the following formula for thorogummite: $Th(SiO_4)_{1-x}(OH)_{4x}$. On the basis of infrared absorption spectral data, Stieff *et al.* (1955, 1956) introduced a similar formula for coffinite: $U(SiO_4)_{1-x}(OH)_4$.

Thorite also forms a complete series with zircon (Frondel & Colette 1957). Caruba *et al.* (1985) proposed the following general formula for these species: $(Zr,Th,U,REE)(SiO_4)_{1-x}(OH)_{4x}\bullet nH_2O$, in which x varies from 0.2 to 0.8. Thorian zircon occurs as a detrital component in the Dominion Reef, whereas the metamict, radioactive zones in the zoned zircon of the Witwatersrand conglomerates belong to the same series.

All (U,Th)-silicates crystallize in the space group D^{19}_{4h}-$I4_1/amd$ in the tetragonal system (Fuchs & Gebert 1958). They are isostructural with zircon, including the hydroxylated species, and xenotime.

(U,Th)-Silicates in the Witwatersrand Reefs

(U,Th)-silicates are rare in most of the ore-bearing reefs in the Witwatersrand, except for those that are mined on the West Rand Goldfield (G.F.), which belong to the uppermost sediments of the Witwatersrand Supergroup, and those mined in the Dominion Reef west of the Klerksdorp G.F. (Fig. 1), which is the oldest reef, located at the base of the sedimentary succession. An estimated 25% and 30% of the uranium that is held in detrital uraninite has been

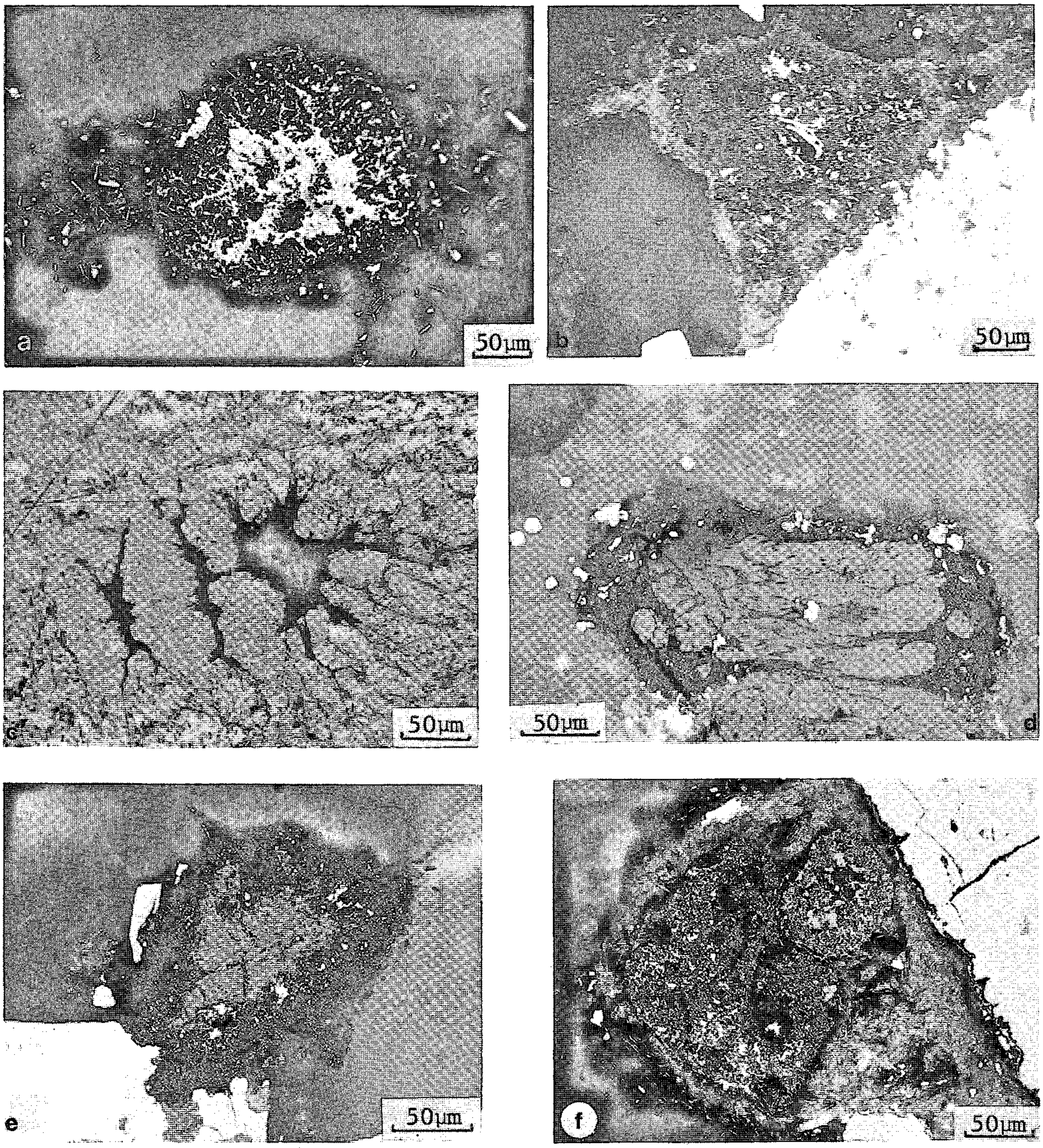

FIG. 2. Photomicrographs of thorian coffinite from the West Rand G.F. (incident light in oil). a. Well-rounded (black) grain with specks of galena (white), and minute laths of pyrrhotite (white). b. Amoeboid grain on pyrite (white), composed of coffinite (dark grey), gold (white), galena (white spots), phyllosilicates (black), and pyrrhotite laths (white), enveloped by a film of uraniferous leucoxene (pale grey) mixed with quartz and phyllosilicates. c. Coffinite (black) pigmented by galena (white) in kerogen. d. Kerogen (grey) enveloped by coffinite (black) enclosing minute specks of galena (white), and larger pyrrhotite grains (white). e. Uraninite (grey) grain partly transformed to coffinite (black), both pigmented by galena (white). f. Cluster of uraninite grains (dark grey) partly altered to coffinite (black) spotted by galena (white), and enveloped by a film (paler grey) of mixed uraniferous leucoxene, phyllosilicates, and quartz.

transformed *in situ* to (U,Th)-silicates in the West Rand G.F. and the Dominion Reef, respectively, as a result of geochemical interaction between detrital uraninite and silica from silica-saturated solutions.

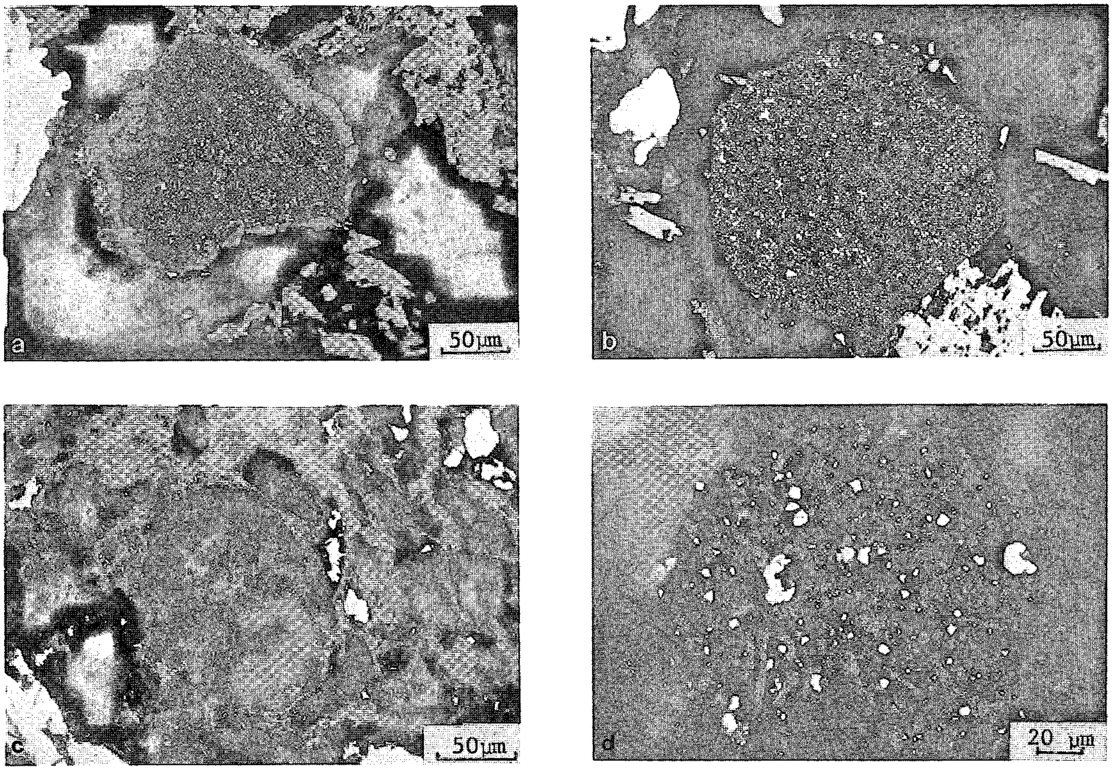

FIG. 3. Photomicrographs of (U,Th)-silicates in the Dominion Reef (incident light in oil). a. Uraninite (grey) grain altered to (U,Th)-silicates (black), covered by (U,Ti)-bearing authigenic mineral (grey). b. Subhedral thorite grain, spotted by galena (white) and intergrown with gangue (black). c. Well-rounded grain of cheralite (grey), enclosing thorian zircon and thorite (black) spotted by galena (white). d. Detrital grain of chlorite (black) intergrown with lens-shaped crystals and rectangular cross-sections of thorite (dark grey), dusted with galena (white). The larger white spots are other sulfides.

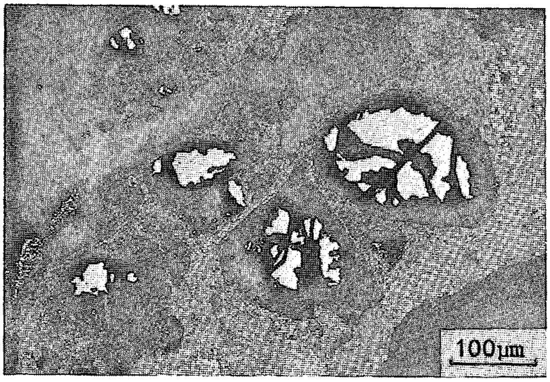

FIG. 4. Partly chloritized (black) grains of pyrite (white) cemented by a mushy mixture (pale grey) of anatase, uraniferous leucoxene, coffinite, phyllosilicates, and quartz (incident light in oil).

Microscopic description

On the West Rand G.F., thorian coffinite occurs: (1) as rounded (Fig. 2a), irregularly shaped or amoeboid (Fig. 2b) particles, (2) enclosed in kerogen (Fig. 2c), or surrounding it (Fig. 2d), and 3) in partly altered uraninite grains (Fig. 2e).

The coffinite is invariably pigmented by galena that is smaller than 5 μm in size (Fig. 2c), or by larger grains that formed through the coalescence of the small specks (Fig. 2a). The lead sulfide formed from radiogenic lead, was partly inherited from precursor uraninite, and was partly formed after the transformation.

The round shape of some of the grains of coffinite indicates that they were subjected to reworking. On the other hand, the amoeboid particles must have formed after burial. The latter variety is made up of several phases, *i.e.*, thorian coffinite, uraninite, uraniferous leucoxene, gold, phyllosilicates, quartz, and sulfides, and the admixture is enveloped by a 20-μm-wide film of mixed uraniferous leucoxene, phyllosilicates, and quartz. The (U,Ti)-bearing minerals found in the Witwatersrand are essentially uranous titanates of the general formula

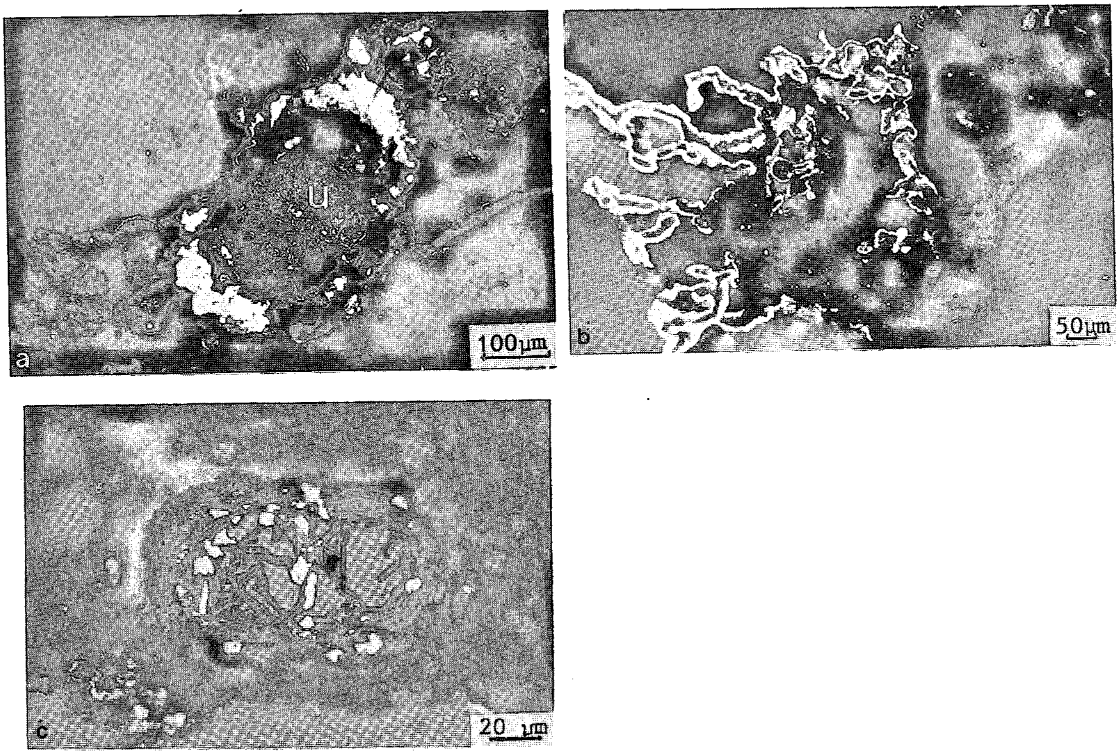

FIG. 5. Photomicrographs of secondary uranium-bearing minerals on the West Rand G.F. (incident light in oil) a. Colloform, secondary uraninite (smooth, grey) and coffinite (black) around a remnant of primary uraninite (u, grey). Galena (white) coalesced to larger grains. b. Colloform coffinite (black) onto which colloform pyrite (white) precipitated. c. Replacement *in situ* of primary uraninite by secondary uraninite (smooth, grey) and coffinite along cracks (dark grey), enveloped by a film of uraniferous leucoxene. Galena (white) coalesced to larger particles.

$U_{1-x}Ti_{2+x}O_6$. Two groups can be distinguished, according to their UO_2/TiO_2 ratio and optical properties. The species with a ratio below unity are referred to as *uraniferous leucoxene*, whereas those above unity are called *brannerite* (Smits 1984). Many of the coffinite grains seem to have formed *in situ* from small groups of detrital uraninite, of which the original shape may be retained (Fig. 2f).

In the Dominion Reef, hydrated (U,Th)-silicates of variable thorium and uranium concentrations commonly formed at the expense of detrital uraninite, the replacement starting at the grain boundaries and along crystal planes and cracks (Fig. 3a). Detrital thorogummite, thorite (Fig. 3b) and metamict detrital grains of hydrated thorian zircon, as large as 3 mm, which are optically identical to thorite, also have been identified. Like thorite, the hydrated thorian zircon is probably of pegmatitic origin. Well-rounded, pale-olive detrital grains of the thorium phosphate *cheralite* (Fig. 3c), which enclose remnants of thorite and thorian zircon, also have been found in the Dominion Reef, but are uncommon.

In a reef on the Orange Free State G.F., spindle-shaped thorite crystals enclosed in a detrital chlorite particle (Fig. 3d) were observed once. On the same goldfield, the partial alteration of uraninite that is enclosed by kerogen to hydrated thorian coffinite or hydrated uranoan thorite also has been noticed in the margin of well-developed, uraninite-rich seams of kerogen present at the base of the Beisa Reef (Smits 1984).

Coffinite has been positively identified by XRD as a component of a uraniferous, leucoxenic substance (Fig. 4) found in most of the reefs, but not in the Dominion Reef, to cement heavy minerals locally within the reef. The substance is of earthy habit and indefinite outline, and is referred to as 'mushy anatase', because the XRD patterns indicate that anatase mixed with quartz and phyllosilicates is the major constituent. The presence of radioactive material is confirmed by the presence of submicroscopic particles of radiogenic galena.

Secondary coffinite and uraninite of colloform habit (Fig. 5a), commonly covered by a film of secondary pyrite (Fig. 5b), have been recognized in reefs in the northern part of the West Rand G.F. The texture and optical appearance of these minerals differ distinctly from those of detrital uraninite and the coffinite that formed *in situ* from the uranium oxide (*cf.* Figs. 2e, 5c) and, like the absence of radiogenic galena in the uraninite, is indicative of their recent origin in a supergene environment. In contrast to the coffinite pseudomorphs after uraninite, the supergene minerals lack porosity and are homogeneous. The reflectance of the secondary uraninite is lower than that of the detrital grains, whereas the reflectance from the secondary coffinite is slightly higher than that of the much older coffinite in the reefs.

Composition of Witwatersrand (U,Th)-silicates

Compositions of (U,Th)-silicates and values of the ratio of UO_2 or (UO_2+ThO_2) to SiO_2 from the Witwatersrand and other deposits in the world are listed in Tables 1 to 3. The values above that for pure coffinite suggest the presence of uraninite, whereas lower values indicate excess silica.

TABLE 1. COMPOSITIONS OF COFFINITE FROM DEPOSITS OTHER THAN THE WITWATERSRAND

	Ideal coffinite										
Constituent	Anhydrous	Hydrated*	1	2	3	4	5	6	7	8†	9
UO_2	81.80	73.75	46.37	25.05		67.49	73.50	77.90	63.14	81.50	69.80
UO_3				17.63							
U_3O_8					45.50						
SiO_2	18.20	6.41	7.40	26.92	24.09	15.24	15.80	17.42	14.60	14.20	15.40
P_2O_5			2.69		2.10	2.18			0.09		
CaO				1.91	3.72	2.34	3.00	1.18	1.58	0.26	2.03
PbS						0.38				0.37	
PbO			0.52								
S			0.80	3.00	5.82				0.39		
Fe_2O_3			1.57	2.51	8.29	0.30			0.33		
As_2O_5			1.44								
V_2O_5			18.90		1.61	0.79					
MgO				1.34	0.95			0.17		0.85	0.15
Al_2O_3			6.80	12.88							
H_2O		9.84		7.86	6.52	10.65					
C									4.05		
LOI			10.04								
Total	100.00	100.00	96.53	99.10	98.60	99.37	92.30	96.67	84.18	97.18	87.38
UO_2/SiO_2	4.50	4.49	6.27	1.55	1.82	4.43	4.65	4.47	4.32	5.74	4.53

* $USiO_4 \cdot 2H_2O$

† Remainder: ThO_2, 0.2%; TiO_2, 0.18%; BaO, 0.59%; K_2O, 1.28%

LOI Loss on ignition

1 Colorado Plateau, USA (Stieff *et al.* 1956)
2 USSR (Filipenko 1958)
3 Spain (Arribas 1966)
4 Average of 10 samples from New Mexico (Kim 1978)
5 Average of 7 samples from Colorado Plateau, USA (Ludwig & Grauch 1980)
6 Average of 2 samples from Yugoslavia (Simova 1981)
7 Karoo, South Africa (Smits & Uiterwijk 1983)
8 Austria } (Kurat *et al.* 1977)
9 Yugoslavia } (Kurat *et al.* 1977)

The analyses represent coffinite from deposits of the sandstone-type and from hydrothermal veins, which do not contain thorium

TABLE 2. COMPOSITIONS OF THORIUM SILICATES FROM THE WITWATERSRAND AND ELSEWHERE IN THE WORLD

Constituent	1	2	3	4	5	6	7	8
ThO_2	81.46	67.33	45.30	57.79	62.60	56.80	30.31	44.59
UO_2			22.40	2.81	11.50	25.40	21.59	30.51
SiO_2	18.54	15.32	13.90	15.77	19.50	17.30	12.80	17.62
PbO			3.74	1.25	0.51		8.94	2.86
REE_2O_3*			1.86	0.97	1.10		1.64	2.06
Fe_2O_3					2.30		1.42	0.57
CaO			0.59	1.65	0.30		1.12	1.21
P_2O_5			0.67	1.33			3.28	1.22
H_2O		17.35	4.81	15.18	1.93			
LOI				1.50				
Others			5.48	1.48	0.30		4.01	1.80
Total	100.00	100.00	98.75	99.73	100.04	99.50	85.11	102.44
$(UO_2+ThO_2)/SiO_2$	4.39	4.39	4.87	3.84	3.80	4.75	4.06	4.26
Relative density	6.7	3.2 to 5.4	5.4		6.25	4.4 to 4.8		

* Mainly yttrium and cerium

LOI Loss on ignition

1 Ideal thorite
2 Ideal hydrated thorite
3 Baringer Hill, Texas (Hidden & Mackintosh 1893)
4 Wodgina, W. Australia (Simpson 1930)
5 New Zealand (Hutton 1950)
6 Utah, USA (Foord *et al.* 1985)
7 Hydrated uranoan thorite, Orange Free State G.F., Witwatersrand
8 Hydrated uranoan thorite, Dominion Reef, Witwatersrand (high total due to inhomogeneity of the sample)

TABLE 3. ELECTRON-MICROPROBE ANALYSES OF COFFINITES FROM THE WITWATERSRAND

Sample reference	UO_2	ThO_2	SiO_2	PbO	SO_3	Y_2O_3	P_2O_5	CaO	FeO	TiO_2	ZrO_2	Total	$(UO_2 + ThO_2)/SiO_2$
Rf 602-1	45.89	n.d.	14.33	5.92	1.77	5.02	4.73	0.51	0.40	-	n.d.	78.57	
2	62.58	n.d.	12.87	5.50	2.16	1.14	1.68	0.83	0.96	1.77	n.d.	89.49	
4	39.60	n.d.	9.45	14.78	3.63	7.95	7.90	1.41	0.60	-	n.d.	85.32	
1306-1	56.02	15.94	11.20	3.57	0.49	4.67	6.01	1.87	0.20	0.26	n.d.	100.23	6.43
1308-1	32.70	25.43	22.58	5.06	0.54	1.23	2.50	0.69	0.19	1.34	n.d.	92.36*	
WA 1216-2	62.80	9.98	14.85	6.02	0.63	1.97	2.02	1.03	-	0.06	n.d.	99.36	4.90
1211/2-2	54.43	8.00	18.61	2.77	0.39	1.38	0.90	0.59	0.13	0.01	0.18	87.39	3.36
3-1a	54.33	11.82	16.24	6.89	1.39	0.80	0.50	0.35	0.14	0.20	0.31	92.98	4.07
PB 833/1b edge	57.72	3.03	12.48	0.11	0.06	1.58	1.07	0.89	0.33	14.52†	0.17	91.95	4.87
1b-2	60.17	12.33	12.52	0.85	0.20	1.81	1.48	1.15	0.03	0.12	-	91.67	5.79
2a-3	67.03	5.62	10.99	1.60	0.27	1.47	1.23	1.15	0.09	0.35	0.66	90.54	6.61
Vir 705/1-1†	21.58	30.31	12.80	8.94	3.51	1.64	3.28	1.12	1.28	0.07	0.43	84.97	4.05
Beisa 1020-1	63.56	8.67	14.27	0.83	0.09	1.97	2.00	2.15	-	0.97	n.d.	94.51	5.06
GV 1345-2	62.06	5.36	11.28	8.27	1.15	1.22	2.99	1.51	-	0.30	n.d.	95.04	5.97
DR 1446/1a-1	46.26	14.90	13.91	13.94	2.31	0.34	0.03	0.75	0.47	0.78	0.48	94.16	4.40
1b-1	48.33	1.60	11.33	19.91	5.01	1.98	0.31	0.11	0.37	0.25	0.67	89.88	4.40
3a-2	46.39	8.91	8.36	12.40	3.20	0.98	0.34	0.30	0.51	0.40	0.37	82.16	6.61
3b-2†	30.51	44.59	15.62	2.86	0.86	2.06	1.22	1.21	0.51	0.14	0.80	100.38	4.81

Rf, WA—West Rand G.F.; PB, Vir, Beisa—Orange Free State G.F.; GV—Evander G.F.; DR—Dominion Reef

* All coffinites contain Al_2O_3 below 1.5%, except for sample Rf 1308-1, which contains 5.57%. The alumina is present in phyllosilicates

† Coffinite grains are often coated by titania, which causes the high titania content in the edge analysis of PB 833/1b

n.d. Not determined

\- Not detected

Because of the microcrystalline and porous character of the (U,Th)-silicates, the spots for quantitative analysis on the EMP were selected with care by the combination of back-scattered electron (BSE) imagery and energy-dispersion analysis, to ensure that single phases were being analyzed. EMP analyses of the (U,Th)-silicates from the West Rand G.F. (Table 3) indicate that these consist of anhydrous thorian coffinite of negligible water content.

The compositions of (U,Th)–silicates that are avail-able from the Witwatersrand and other deposits in the world are plotted in triangular (U + Th)–Si–H_2O and U–Th–Si diagrams (Figs. 6 and 7, respectively). In most cases, the water for the silicates from deposits elsewhere was determined chemically. However, the composition of the silicates from the Witwatersrand was determined on the EMP and, in these cases, it was assumed that water could account for the difference between 100% and the recorded totals.

The composition of the detrital thorian zircon in the Dominion Reef (Table 4) is similar to the 'cyrtolite' of Ellsworth (1928), a name that has since been discredited. The hydrated (Zr,Th)-species contain significant amounts of yttrium and phosphorus. Yttrium could have substituted for zirconium, and phosphorus for silicon, but xenotime, which is isostructural with zircon, also could be present. The moderate reddish brown patches in the core of this mineral appear to be enriched in iron (analysis 6). When the black thorian zircon was heated to approximately 1000°C, it turned to a greyish pink, translucent zircon.

The secondary uraninite and coffinite from the West Rand G.F. differ distinctly in composition from the detrital uraninite and the coffinite that formed *in situ* from the uranium oxide. The secondary minerals show low analytical totals, and the familiar specks of radiogenic galena are absent, whereas those inherited from the detrital uraninite coalesced to larger grains (Figs. 5a, c). The uraninite contains only trace amounts of thorium, and is therefore pitchblende, whereas the thorium content of secondary coffinite is similar to that of the original uraninite (Table 5).

The compositions of secondary pitchblende are given in Table 5, and are compared with the composition of detrital uraninite in well-packed (Fig. 8a) clusters of a diameter up to 5 mm, which consist entirely of grains of uraninite. Some of the uraninite has been transformed to coffinite (Fig. 8b). This type of agglomeration occurs in reefs in the north of the West Rand G.F., where the concentration of uranium in the reefs is particularly high, and gold is virtually absent.

EMP analyses of the mushy anatase recorded the presence of substantial amounts of uranium, titanium, and silicon (Table 6). The BSE image of the mushy anatase (Fig. 9) indicates that it is composed of a submicroscopic intergrowth of various phases. Even at high magnification, the extremely fine intergrowth cannot be resolved, and differentiation between discrete phases is difficult. Galena stands out because of the high atomic number of lead, but the BSE intensities of the uranium–silicon and uranium–titanium phases of varying composition overlap, so that the individual particles cannot be distinguished by their grey tone.

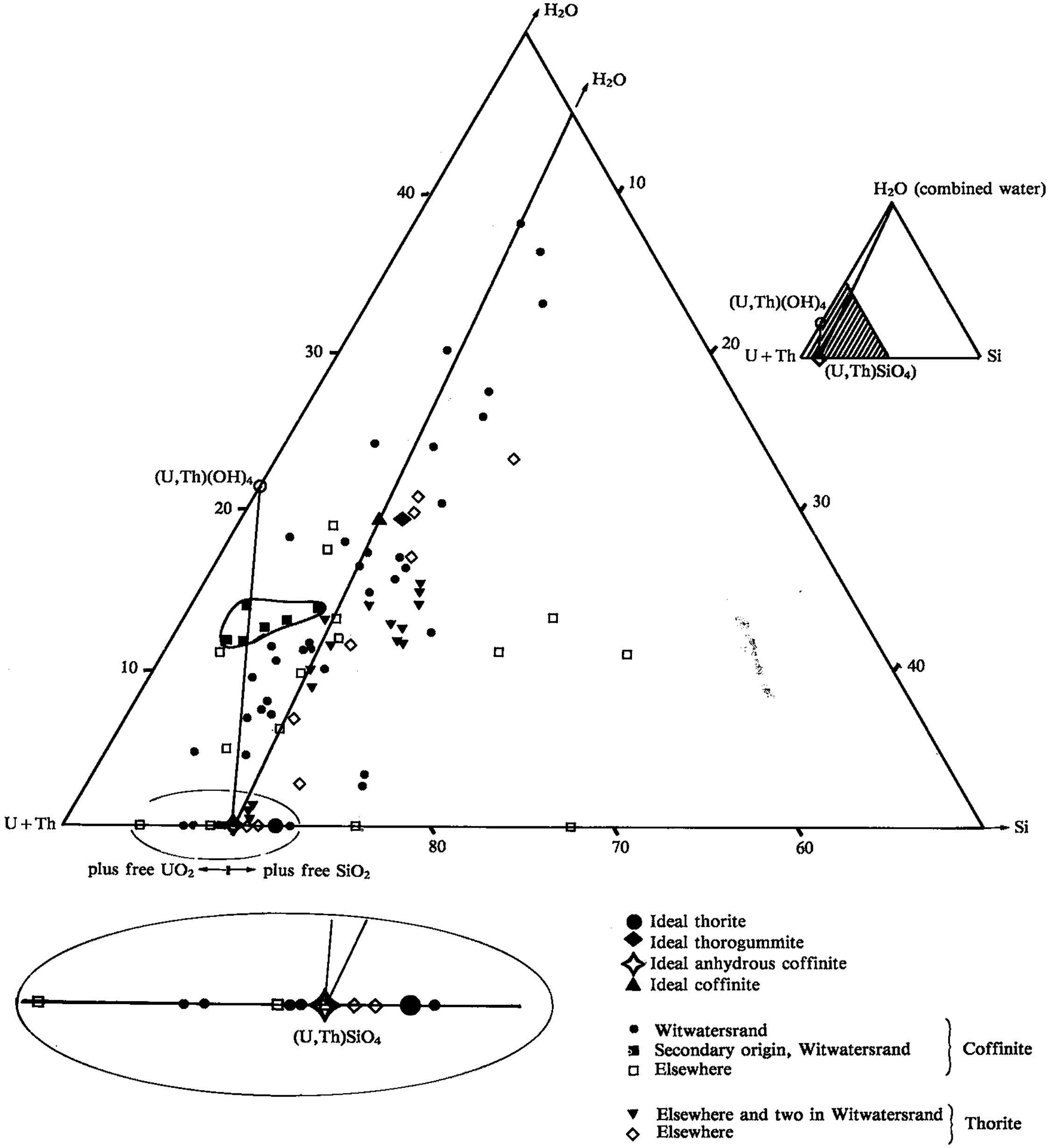

FIG. 6. Compositions of (U,Th)-silicates plotted on the basis of at.% in the (U+Th)–Si–H_2O system. The compositions lie on either side of the tie line between $(U,Th)SiO_4$ and H_2O, and there is no specific spread along the join between $(U,Th)(OH)_4$ and $(U,Th)SiO_4$. Hence water is present as absorbed water, and the correct formula is $(U,Th)SiO_4 \cdot nH_2O$ ($n < 4$).

For the above-mentioned reasons, the number of phases that are represented in the bulk compositions (Table 6) is uncertain. As indicated by XRD, the bulk of the titanium is present as anatase, some of which could occur as metamict uraniferous leucoxene. The presence of coffinite, which is positively indicated by XRD and supported by the presence of submicroscopic specks of radiogenic galena, could not be confirmed optically. Except for the first composition (Table 6), the ratio of ($UO_2 + ThO_2$) to SiO_2 is lower than that in ideal coffinite, which points to the presence of free silica.

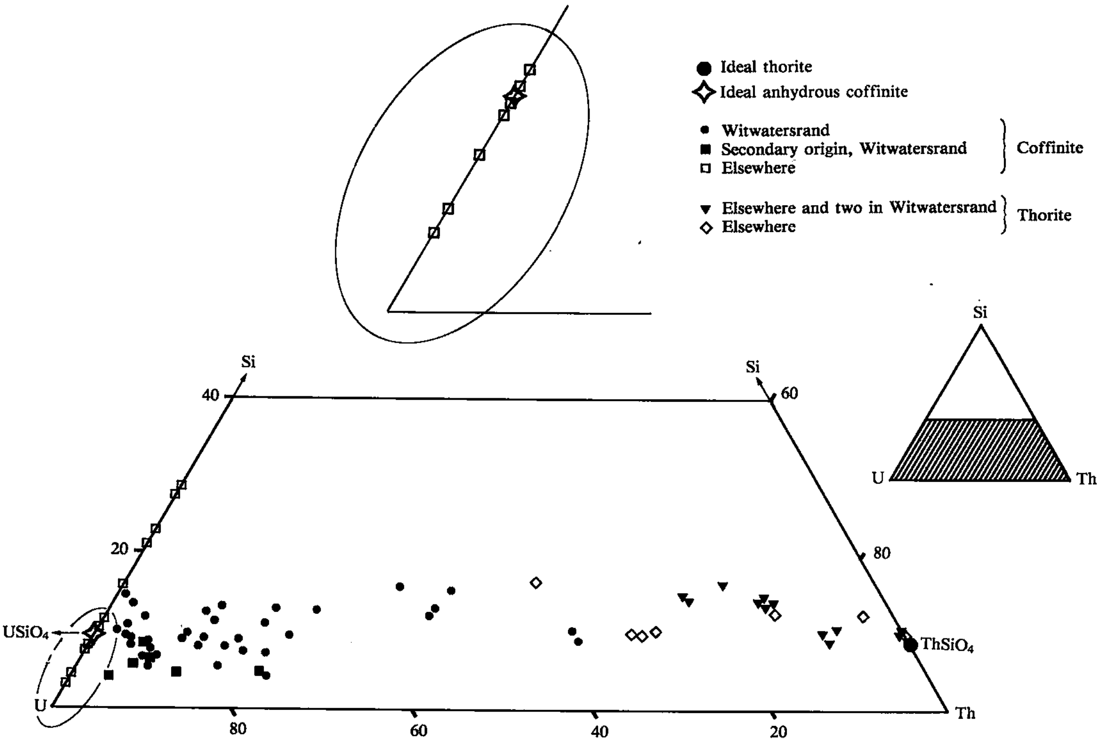

FIG. 7. Compositions of (U,Th)-silicates plotted on the basis of at.% in the U–Th–Si system. The distribution of the silicates suggests that a continuous series exists between the end members, as was established for the synthetic products (Fuchs & Gebert 1958).

TABLE 4. COMPOSITIONS OF MINERALS OF THE THORITE-ZIRCON GROUP

		Hydrated	Metamict zircon*			Dominion Reef		
	Zircon	zircon			Cyrtolite†	Orange	Black	Black
Constituent	1	2	3	4	5	6	7	8
ZrO_2	67.20	50.79	38.72	56.33	43.03	30.44	35.72	21.02
SiO_2	32.80	23.08	22.13	30.16	22.86	19.53	22.57	13.83
UO_2			1.63	0.12	1.40	2.37	1.16	11.31
ThO_2			0.46	-	0.66	4.63	4.22	5.99
PbO			0.75	0.26	n.d.	1.37	2.75	7.76
SO_3			0.41	0.12	n.d.	0.56	0.85	8.58
Y_2O_3			8.11	0.01	6.76	6.13	7.37	5.31
Other REE			n.d.	n.d.	0.34	n.d.	n.d.	n.d.
FeO			0.30	0.51	4.62	14.03	2.26	3.87
MnO			n.d.	n.d.	3.12	n.d.	n.d.	n.d.
CaO			1.50	0.27	1.58	0.62	1.22	1.12
P_2O_5			5.66	0.19	3.53	1.20	1.52	1.36
LOI		26.13	n.d.	n.d.	12.54	n.d.	n.d.	n.d.
Total	100.00	100.00	79.67	87.97	100.44	80.88	79.64	80.15
Elements not accounted for	-	-	20.33	12.03	-	19.12	20.36	19.85

* Analyses from the Witwatersrand
† Analysis from Ellsworth (1928)
LOI Loss on ignition
n.d. Not determined
\- Not detected
REE Rare-earth elements

DISCUSSION

Chemical data indicate that (U,Th)-silicates occur as anhydrous and hydrated species, and that they form two continuous series. Fuchs & Gebert (1958) established experimentally that a continuous series exists between the anhydrous members, whereas, for the hydrated species, the compositional data (Fig.

TABLE 5. ELECTRON-MICROPROBE ANALYSES OF URANINITE AND COFFINITE OF PRIMARY AND SECONDARY ORIGIN FROM THE WEST RAND G.F. ON THE WITWATERSRAND

Sample reference	UO_2	ThO_2	SiO_2	PbO	SO_3	Y_2O_3	P_2O_5	CaO	FeO	TiO_2	ZrO_2	Total
Uraninite concentrate	71.40	3.30	1.30	14.20	2.00	0.60	n.d.	0.80	2.30	n.d.	n.d.	95.90
Primary uraninite clusters												
WRC 1456/1-1	63.83	7.89	2.45	22.33	2.31	-	0.86	0.18	0.15	0.27	0.13	100.40
1-2	74,20	2.60	1.14	15.64	1.25	1.21	0.01	2.27	0.62	0.02	0.01	98.97
Alteration product of clustered uraninite												
WRC 1456/1-3	38.00	10.63	5.02	29.65	5.58	0.57	2.22	0.45	0.38	0.18	0.91	93.59
1-4	47.22	6.42	4.25	25.00	4.63	0.63	1.18	0.64	0.64	0.27	0.52	91.40
Secondary colloform pitchblende												
ECh 1457/1-1	67.66	0.24	1.81	0.05	0.32	0.09	0.56	0.70	0.81	0.69	0.56	73.49
1-3	71.35	0.26	2.00	0.61	0.69	0.16	0.45	0.50	1.34	0.47	0.50	78.33
1-3a	74.00	0.28	0.82	0.65	0.02	0.47	0.36	0.70	1.23	0.55	0.21	79.29
Remnant of primary uraninite												
ECh 1457/1-2	60.65	2.96	1.48	7.83	1.01	0.17	0.46	0.43	0.47	0.53	0.25	76.24
Secondary colloform coffinite												
Rf 1452/1-1	65.09	4.52	13.54	0.25	0.17	1.44	2.04	0.97	0.17	0.19	0.36	88.74
1-2	63.88	5.88	10.95	1.63	2.38	0.96	1.78	0.81	0.71	0.33	0.45	89.76
1-3	67.86	4.96	9.03	2.58	0.86	0.90	1.55	0.91	0.40	0.25	0.42	89.67
1-4	72.68	3.85	6.14	3.28	0.73	0.51	0.97	0.84	0.36	0.30	0.26	89.92

n.d. Not determined
- Not detected

WRC West Rand Consolidated G.M.
ECh East Champ d'Or G.M.
Rf Randfontein Estates G.M., Randfontein Section

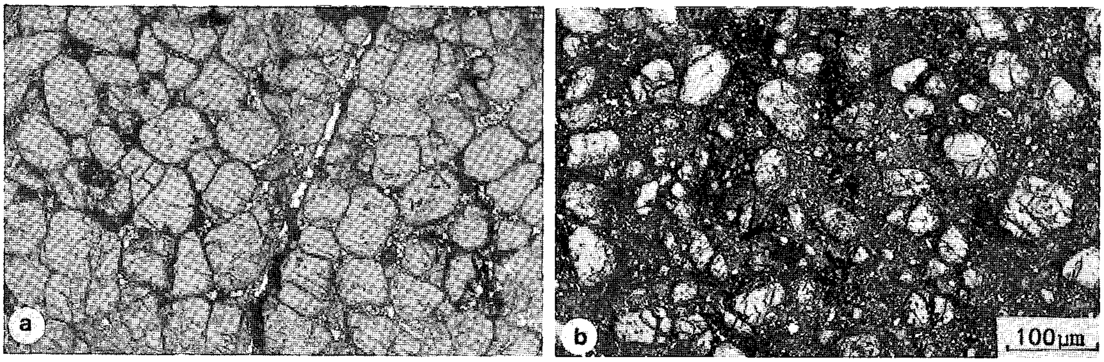

FIG. 8. Cluster of uraninite (incident light in oil). a. Well-packed uraninite (grey) grains pigmented by galena (white), some of which has been redistributed into a crack and interstitial voids. b. Similar cluster in which uraninite (pale grey) has been partly altered to coffinite (black).

7) indicate that it is a continuous series. The diagram also shows that the coffinite found in the Witwatersrand contains a significant thorite component.

On the basis of existing names, the end members of the two series are, respectively, anhydrous coffinite and thorite, and coffinite and thorogummite. Uranium-bearing thorite species should be referred to as *uranoan thorite* (Palache *et al.* 1944) and, analogous to this name, the thorium-bearing coffinite should be called *thorian coffinite* (Nickel & Mandarino 1987).

Anhydrous coffinite (Table 2, analysis 9) has been reported once from metamorphosed sandstones of Permian age (Kurat *et al.* 1977), and has since been identified in the Witwatersrand placers (Smits 1984). The Permian anhydrous coffinite is of hydrothermal origin and coexists with pitchblende. Both of these minerals are devoid of thorium, whereas the silicate in the West Rand G.F. is an anhydrous thorian coffinite.

Quantitative analysis on the EMP disclosed that the (U,Th)-silicates from the Dominion Reef are

TABLE 6. ELECTRON-MICROPROBE ANALYSES OF COFFINITE ASSOCIATED WITH MUSHY ANATASE

Sample reference	UO_2	ThO_2	SiO_2	PbO	SO_3	Y_2O_3	P_2O_5	CaO	FeO	TiO_2	ZrO_2	Total	$(UO_2+ThO_2)/SiO_2$
Bv 1415/2-1a	40.85	1.80	9.41	1.65	0.15	0.89	0.57	0.16	0.36	16.48	0.22	72.54	4.53
2-2	24.13	0.42	8.54	2.65	0.62	0.51	0.34	0.57	1.01	47.61	0.04	86.64	2.87
2-3	37.71	1.19	12.59	3.32	0.57	0.44	0.30	0.62	0.54	27.89	0.11	85.28	3.09
WR 824/1-1	48.48	1.98	12.95	1.04	0.20	1.08	1.07	0.68	0.52	22.00	0.66	90.66	3.90
1-2	38.43	2.18	11.69	0.56	0.17	1.12	0.99	0.64	0.83	33.86	0.62	91.09	3.47

Bv Blyvooruitzicht G.M.
WR Western Reefs G.M.

chiefly hydrated thorian coffinite, and those from the West Rand G.F. are anhydrous or hydrated thorian coffinite, whereas uranoan thorite is uncommon (Table 3). Metamorphism could be responsible for the dehydration of the (U,Th)-silicates, which could initially have been hydrated. In many of the coffinite grains, the thorium content was higher than that of the original uraninite, which suggests that some of the uranium was removed during the alteration process. The iron that was initially present in the uraninite was not taken up by the neoformed silicate, and now occurs in the form of minute laths of pyrrhotite (Fig. 2a), which could represent a product of the sulfidation of hematite. Furthermore, phosphorus and yttrium are usually present in quantities of less than 5%. These elements can be incorporated in the coffinite structure, or may occur as a discrete phosphate that is intergrown with the coffinite. Xenotime has been identified in some of the coffinite grains, but it should be noted that the uranium phosphate *ningyoite* has not been identified anywhere in the Witwatersrand.

Figure 6 shows that the (U,Th)-silicates are distributed on either side of the tie-line between H_2O and the ideal composition of anhydrous $(U,Th)SiO_4$, and that no specific concentration of species is found along the latter tie-line between $(U,Th)(OH)_4$ and $(U,Th)SiO_4$. The lack of compositions along this tie-line supports the conclusion drawn by Mumpton & Roy (1961) that the hydrated thorite and coffinite species contain molecular water rather than hydroxyl. In the same year Abdel-Gawad & Kerr (1961) established, on the basis of infrared-absorption spectra of coffinite that is free of organic matter, that the water is present as absorbed water. The correct formula for the hydrated (U,Th)-silicates is therefore: $(U,Th)SiO_4{\bullet}nH_2O$. Figure 6 indicates that generally, n does not exceed 4. The six coffinite species that show a water content of more than 25% could well contain phases that were not determined during the EMP analysis. The few silicates of very high silica content that are found elsewhere in the world probably represent species that are finely intergrown with free silica.

Genetic aspects

Because coffinite and uraninite coexist in the Colorado deposits, Langmuir (1978) assumed that the stability fields of uraninite and coffinite overlap, but that coffinite would be stable relative to uraninite at silica concentrations above those of the groundwater, which is, on average, 10^{-3} mol/L, but would be below the level of saturation with amorphous silica. Through the use of the transmission and scanning electron microscope and the EMP, Nord (1977) established that coffinite coexists in these deposits with amorphous silica and uraninite, which has compositions ranging from UO_2 to $UO_{2.08}$. From these data, Langmuir (1978) concluded that $UO_{2.08}$ is the upper limit of composition of the uraninite that coexists with coffinite and amorphous silica at low temperatures.

Hemingway (1982) proposed that coffinite precipitates from a uranium–silica gel when the conditions

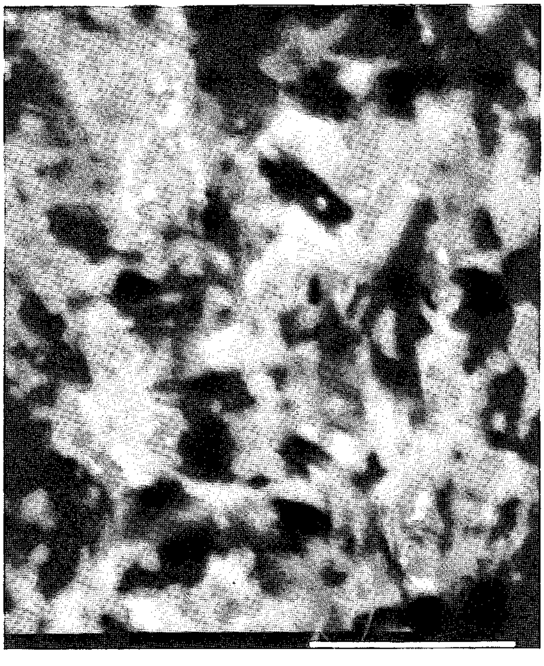

FIG. 9. BSE image of mushy anatase at high magnification. Galena specks (white) < 1μm indicate the presence of radioactive matter (pale grey). The black areas represent quartz or phyllosilicate. Bar scale: 5 μm.

are unfavorable for the rapid dehydration and alteration of the gel. Excess silica would crystallize as either quartz or another polymorph of silica, and excess uranium as uraninite. The secondary uraninite and coffinite found in reefs in the north of the West Rand G.F. (Fig. 5a, b), which are believed to result from supergene activity, could indeed have formed by this type of precipitation mechanism. The relationship between the two secondary products differs distinctly from that found between detrital uraninite and the portion that was converted to thorian coffinite in other reefs on the West Rand G.F. (*cf.* Figs. 2f, 3a, 5a). In this instance, the uraninite was converted *in situ* into coffinite through the direct uptake of silica from silica-saturated solutions, which started at the surface of the grain and along the cracks (Figs. 2a, 3a) and proceeded inward. As was proposed by Langmuir (1978), it is possible that uraninite was first altered to either a hydroxide or an oxide until the composition of $UO_{2.08}$ was reached, and was then altered to coffinite. Because of the uptake of silica, the conversion of uraninite to coffinite involved a considerable increase in volume. This process could therefore only have taken place soon after deposition, when the sediment was still porous enough to allow solutions to circulate freely and the grains to expand during their alteration.

The neoformed laths of pyrrhotite that are associated with the uraninite–coffinite transformation (Figs. 2a, b) suggest that alkaline and reducing

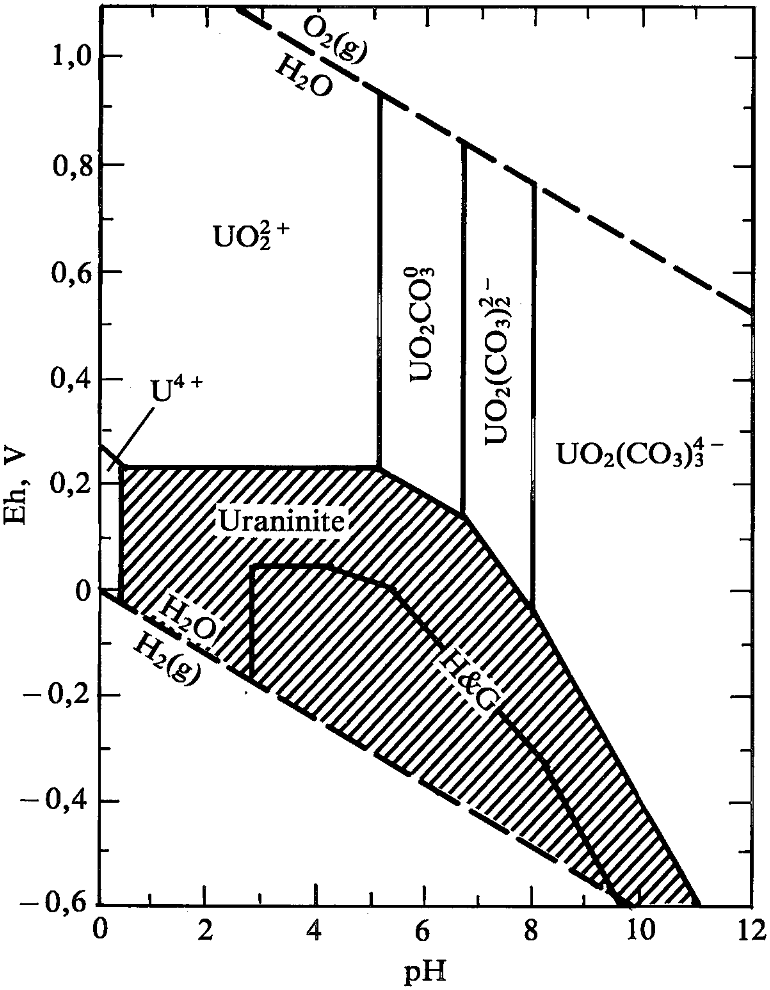

FIG. 10. Eh–pH diagram in the U–O_2–CO–$_2H_2O$ system at 25°C and 1 atm., a typical groundwater of $P(CO_2) = 10^{-2}$ atm. and a total dissolved-uranium concentration of 10^{-6} M. H & G outlines the boundary of the stability field as defined by Hostetler & Garrels in 1962 (after Langmuir 1978).

conditions (Fig. 10) prevailed during the conversion. The environment would have been less reducing had the pyrrhotite represented sulfidized hematite.

SUMMARY

Fuchs & Gebert (1958) established experimentally that a continuous series exists between the anhydrous end-members whereas, for the hydrated members, the chemical data for (U,Th)-silicates from the Witwatersrand and elsewhere in the world indicate that the series is continuous

On the basis of existing names, the end members are, respectively: anhydrous coffinite and thorite, and coffinite and thorogummite. Uranium-bearing thorite species are referred to as *uranoan thorite* and, analogous to this name, the thorium-bearing coffinite is called *thorian coffinite*.

Except for thorogummite and hydrated thorite of very low uranium content, the (U,Th)-silicates possess similar physical and optical properties. In the Witwatersrand, thorian coffinite and thorogummite can be identified by X-ray diffraction, but uranoan thorite is metamict.

Infrared spectral data indicate that the water in the hydrated coffinite is present as absorbed water (Abdel-Gawad & Kerr 1961), which is confirmed by the absence of a specific concentration of coffinite along the tie-line between anhydrous coffinite and (U,Th)-hydroxide. The correct formula for the hydrated (U,Th)-silicates is $(U,Th)SiO_4{\cdot}nH_2O$, where n lies between 1 and 4.

Textural relations indicate clearly that the coffinite in the reefs of the Witwatersrand is the product of the direct transformation of detrital grains of uraninite through the *in situ* uptake of silica.

The secondary coffinite and uraninite of relatively recent origin in the Witwatersrand precipitated from detrital uraninite in a supergene environment. The two minerals are readily distinguished from the older counterparts by their colloform habit, lack of porosity, and different reflectance, and by the absence of galena.

Both experimental and natural conditions indicate that, for the formation of (U,Th)-silicates, adequate amounts of dissolved silica and an alkaline and reducing environment are required.

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