being obtained, indicate the precipitation of vaterite and amorphous calcium carbonate at the same time. The latter has the main absorption (v_3) at 1492 cm^{-1}, in good agreement with Andersen and Brecevic (1991). The spectra, however, show other absorptions in the 1410–1470 cm^{-1} interval, where intensity and frequencies are strictly related to the synthesis followed (Fig. 2).

Further studies on this topic, and particularly, about the conditions of crystallization of vaterite in hydraulic mortars are in progress.

References

Andersen, F.A. and Brecevic, L. (1991) Infrared spectra of amorphous and crystalline calcium carbonate. *Acta Chem. Scand.*, **45**, 1018–24.

Cole, V.F. and Kroone, B. (1959) Carbonate minerals in hydrated portland cement. *Nature, Brit. Assoc.*, **B.A.**, 57

Davies, P., Dollimore, D. and Heal, G.R. (1978) Polymorph transition kinetics by DTA. *J. Thermal Anal.*, **13**, 473–87.

Deer, V.A., Howie, R.A. and Zussman, J. (1964) *Rock-forming Minerals – V. 5, Non-silicates.* London, Longman, Green and Co Ltd, 372 pp.

Ducloux, J., Dupuis, T. and Laouina, A. (1987) Influence de gels mineraux et d'argiles sur la cristallogenese du carbonate de calcium a partir des solutions bicarbonatees. *Catena*, **14**, 553–60.

Friedman, G.M. and Schultz, D.J. (1994) Precipitation of vaterite ($CaCO_3$) during oil field drilling. *Mineral. Mag.*, **58**, 401–8.

Kamhi, S.R. (1963) On the structure of vaterite, $CaCO_3$. *Acta Crystallogr.*, **16**, 770–2.

Sato, M. and Matsuda, S. (1969) Structure of vaterite and infrared spectra. *Z. Kristallogr.*, **129**, 405–10.

Weir, C.E. and Lippincott, E.R. (1961) Infrared studies of aragonite, calcite, and vaterite type structures in the borates, carbonates, and nitrates. *J. Res. NBS – A Physics and Chemistry*, **65A**, 3, 173–83.

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Phosphatian coffinite with rare earth elements and Ce-rich françoisite-(Nd) from sandstone beneath a natural fission reactor at Bangombé, Gabon

JANUSZ JANECZEK

Department of Earth Sciences,
University of Silesia,
ul. Bedzinska 60,
PL-41-200 Sosnowiec,
Poland

RODNEY EWING

Department of Earth and Planetary Sciences,
University of New Mexico,
Albuquerque,
NM 87131-1116,
USA

SPONTANEOUS fission reactions occurred in several uranium deposits in SE Gabon approximately two billion years ago. The reactor zones, between 10 to 50 cm thick, are found in Proterozoic sandstones and consist of high-grade uranium ore mantled by illite and/or chlorite (Gauthier-Lafaye *et al.*, 1989). During a mineralogical study of sandstones (quartz arenites) underlying a natural fission reactor at Bangombé (20 km south of the Oklo uranium deposit), we have found several grains of a uranous silicate, coffinite, with unusually high concentrations of phosphorous and enriched in light rare earth elements (*LREE*). The same specimen also contains an aggregate of bladed crystals with a chemical composition close to françoisite-(Nd), $RE(UO_2)_3O(OH)(PO_4)_2 \cdot 6H_2O$. To our knowledge, this is the second occurrence of françoisite, which was first described by Piret *et al.* (1988) from the copper-cobalt deposit at East-Kamoto, Zaïre. The specimen containing both minerals was collected by R. Bros and F. Gauthier-Lafaye from the drill core BAX 03 at a depth range of 12.20–12.30 m, some 20 cm outside the reactor's 'core'. The small quantity of the material precluded any other characterization of the minerals besides electron microprobe analyses (EPMA) and back scattered electron (BSE) imaging.

Experimental

Electron microprobe analyses were made using a JEOL 733 Superprobe operated at an excitation voltage of 15 kV, a specimen current of 20 nA, and a beam diameter of 1–2 μm. Concentrations of P, Si, and U were measured by energy dispersive (EDS) analysis. Peak profiles for P, Si, and U were generated using data for apatite, diopside, and synthetic UO_2, respectively. The EDS calibration was performed on a Ni standard. Other elements were analysed in the wavelength-dispersive mode. Minerals (diopside for Ca, olivine for Fe, rutile for Ti, albite for Al, cerussite for Pb) and synthetic rare earth element phosphates were used as standards. Calcium was analysed by combined ED and WD methods because of the Ca-*K*α peak overlap with the U-Mγ peak.

Results

Phosphorus coffinite. Grains of coffinite occur in the secondary porosity of the quartz arenite. They are dark brown in thin section and weakly pleochroic. Some of the grains contain relics of uraninite (Fig. 1). Inclusions of a Ru- and As-bearing mineral were observed in one of the grains. This finding is particularly interesting, because Ru-bearing minerals which occur in uraninites in the 'core' of two natural reactors at Oklo are composed of Ru isotopes formed due to fission events (Hidaka *et al.*, 1994). Most probably, the Ru-As mineral in coffinite in sandstone beneath the Bangombé reactor also contains fissiogenic Ru.

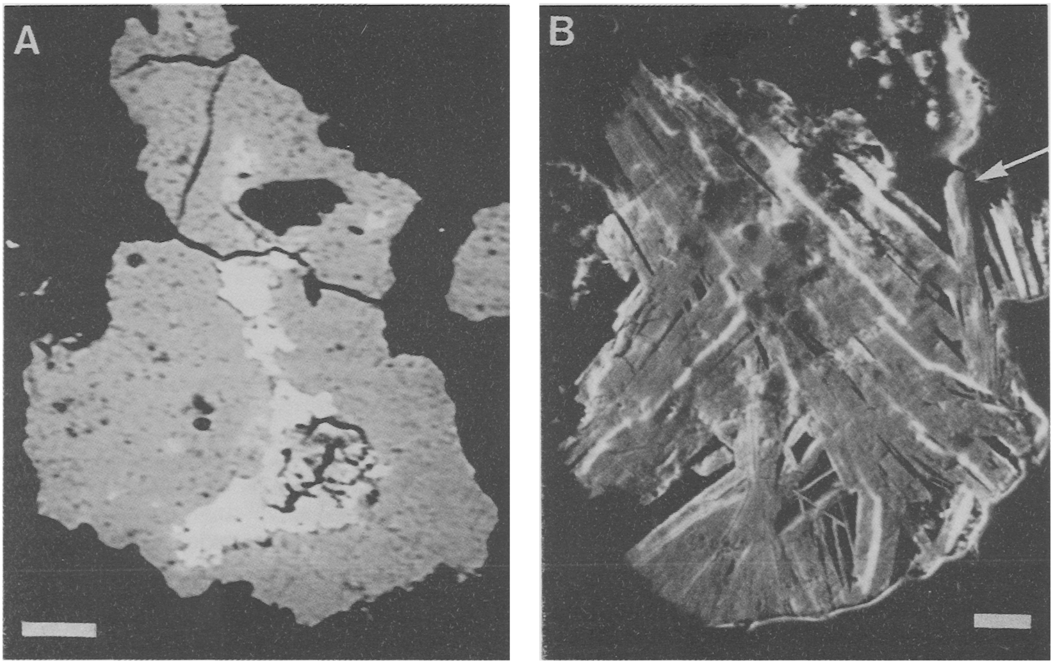

FIG. 1. Phosphatian coffinite and françoisite-(Nd) in quartz arenite from Bangombé, Gabon. (A) BSE image of a grain of coffinite with a relic of uraninite (white). Black background is quartz. Scale bar 10 μm. (B) Secondary electrons image of an aggregate of françoisite crystals. The termination of one of the crystals is indicated by the white arrow. Scale bar 10 μm.

Electron microprobe analyses of five coffinite grains show high concentrations of P and enrichments in Nd and Ca (Table 1). Neither Y nor *REE* other than those reported in Table 1 were detected by wavelength dispersive scans. Lanthanum occurs at concentrations lower than one standard deviation; thus, it is not reported in Table 1. Different grains of coffinite show different values of the P/Si ratio ranging from 0.89 to 0.98. All of them, however, have concentrations of P exceeding 6.5 wt.% P_2O_5 with the highest recorded value of 8.9 wt.% P_2O_5. To calculate the number of ions in the coffinite formula unit (Table 1), we used the general formula $USiO_4 \cdot nH_2O$ suggested by Smits (1989) and Janeczek (1991) rather than the formula $U(SiO_4)\cdot 1-x(OH)_{4x}$ proposed by the first investigators of coffinite (Stieff *et al.*, 1956). From these calculations it follows that between 43 and 47% of Si is substituted by P. Calcium, *REE* and Pb have partially replaced U. In all grains Nd predominates over Ce, and Ce/Nd ratio ranges from 0.5 to 0.6.

Françoisite-(Nd). A single aggregate of elongated, bladed crystals, up to 0.1 mm long, has been observed in the secondary porosity of the quartz arenite (Fig. 1*b*). The crystals are yellow in thin section. Their habit appears to be similar to the crystals of françoisite-(Nd) from Kamoto (Fig. 1 in Piret *et al.*, 1988). The quality of the surface polish of the aggregate is poor because of the large difference in hardness between the crystals and surrounding

TABLE 1. Electron microprobe analyses of coffinite from Bangombé

	1	2	3	4
UO_2	73.75	68.72 (67.4–69.3)	69.56 (68.8–69.9)	69.75 (69.7–69.9)
SiO_2	16.41	7.94 (7.64–8.38)	8.64 (8.56–8.75)	8.18 (8.08–8.28)
TiO_2		0.29 (0.26–0.55)	0.34 (0.27–0.39)	0.54 (0.52–0.56)
Al_2O_3		0.32 (0.27–0.35)	0.42 (0.34–0.49)	0.46 (0.44–0.48)
Ce_2O_3		0.74 (0.70–0.76)	0.68 (0.64–0.71)	0.60 (0.58–0.62)
Pr_2O_3		0.24 (0.21–0.29)	0.23 (0.18–0.27)	0.15 (0.12–0.17)
Nd_2O_3		1.24 (1.17–1.36)	1.03 (0.95–1.11)	0.87 (0.79–0.98)
Sm_2O_3		0.34 (0.24–0.40)	0.26 (0.23–0.30)	0.24 (0.20–0.28)
FeO		0.20 (0.14–0.26)	0.20 (0.12–0.33)	0.23 (0.13–0.25)
PbO		0.79 (0.63–0.85)	0.84 (0.73–0.86)	1.08 (0.98–1.18)
CaO		1.93 (1.78–2.03)	1.80 (1.77–1.86)	1.77 (1.73–1.80)
P_2O_5		8.68 (8.41–8.93)	8.02 (7.81–8.25)	7.67 (7.54–7.75)
Total	100.00*	90.69	92.02	91.54
Number of cations based on O = 4.000				
U^{4+}	1.000	0.878	0.885	0.904
Ti^{4+}		0.012	0.015	0.024
Ce^{3+}		0.016	0.014	0.013
Pr^{3+}		0.005	0.005	0.003
Nd^{3+}		0.025	0.021	0.018
Sm^{3+}		0.007	0.005	0.005
Fe^{2+}		0.010	0.010	0.011
Pb^{2+}		0.012	0.013	0.017
Ca^{2+}		0.119	0.110	0.110
Σ	1.000	1.084	1.078	1.088
Si^{4+}	1.000	0.456	0.494	0.477
P^{5+}		0.422	0.388	0.378
Al^{3+}		0.022	0.028	0.032
Σ	1.000	0.900	0.910	0.887

1. Ideal hydrated coffinite, $USiO_4 \cdot 2H_2O$; *including 9.84 wt.% H_2O.
2. Coffinite with relic of uraninite (Fig. 1). Average of 13 analyses.
3. Average of 5 analyses on another grain.
4. Coffinite with Ru-, As-bearing phase. Average of 3 analyses.

Compositional ranges are given in brackets.

quartz. Only the better polished areas were selected for EPMA. This is a significant factor, which affected the measurements of elemental concentrations, as evidenced by high values of standard deviation, especially for U (Table 2). There are two groups of electron microprobe analyses reported in Table 2, which were obtained on different areas of the aggregate. Electron microprobe analysis of the crystals revealed a composition similar, but not identical, to françoisite-(Nd). The most significant difference between françoisite-(Nd) from Kamoto and the mineral from Bangombé is the higher amount of U in the latter (Table 2). In some analyses the U/P ratio is closer to 4:2 rather than to 3:2 as in françoisite, leading to the general formula *RE*$(UO_2)_4O_2(OH)(PO_4)_2\cdot7H_2O$. The Ce/Nd ratio is equal to one in a sample from Bangombé, whereas, in françoisite from Kamoto, Nd is distinctly predominant (Ce/Nd = 0.22). Yttrium and heavy *REE* have not been detected in the sample from Bangombé, which is enriched in, most probably radiogenic, Pb and contains small amounts of Al. Both elements are absent in françoisite from Kamoto.

Discussion

Phosphorus is present in almost all chemical analyses of coffinites reported in the literature. However, the only other coffinite with similarly high concentrations of P (up to 7.9 wt.% P_2O_5 in a single analysis) is the Th- and Y-rich coffinite from Witwatersrand (Smits, 1989). The presence of P in coffinites has been attributed by some authors to the pseudomorphous replacement of ningyoite, (U, Ca, Ce)$(PO_4)_2\cdot1-2H_2O$, by coffinite. According to Belova *et al.* (1980) an amorphous material with a ningyoite composition occurs in the coffinite microcrystals (1 μm in size), apparently as relics of ningyoite replaced by coffinite. However, inspection of samples from Bangombé by BSE imaging and by EPMA did not show evidence for the presence of phosphates on the scale of 1 μm. Stoichiometric considerations clearly show that P replaced up to 47% of Si in the coffinite. A coupled substitution, $Si^{4+} + U^{4+} = P^{5+} + (Y, REE)^{3+}$, has been proposed to explain P- and Y-enriched compositions of coffinite from New Mexico (Hansley and Fitzpatrick, 1989). This coupled substitution is analogous to the substitution found in the *REE*-rich zircons with a relatively high phosphorus content (Speer, 1982). By analogy with zircon, with which coffinite is isostructural, a limited coffinite – xenotime solid solution is expected. However, in the Bangombé coffinite the amount of *REE* is too low and P concentration is too high to be explained solely by the above-mentioned mechanism. The presence of significant Ca in the Bangombé coffinite (Table 1) suggests a solid solution between coffinite and ningyoite. The possible substitution reactions include $2Ca^{2+} + 0.8P^{5+} + 0.2\square = U^{4+} + Si^{4+}$ and $2Ca^{2+} + P^{5+} + (OH)^- = U^{4+} + Si^{4+}$. The former reaction implies the presence of vacancies in the tetrahedral sites of the coffinite structure. Indeed, there is a deficiency of cations in the tetrahedral sites of the Bangombé coffinite (Table 1), and a deficiency in silica is commonly reported in chemical analyses

TABLE 2. Electron microprobe analyses (wt.%) of françoisite-(Nd) from Bangombé, Gabon (1–2) and Kamoto, Zaïre (3)

				Number of ions based on O = 15.5#		
	1	2	3	1	2	3
UO_3	68.96(1.05)	71.26(1.01)	67.30	3.111	3.120	3.120
Al_2O_3	0.21(07)	0.23(07)		0.053	0.056	–
Y_2O_3	n.d.	n.d.	1.53	–	–	0.180
La_2O_3	0.99(07)	0.95(10)	0.71	0.078	0.073	0.058
Ce_2O_3	3.52(19)	3.58(20)	1.00	0.277	0.273	0.081
Pr_2O_3	1.04(07)	1.11(09)	0.92	0.081	0.084	0.074
Nd_2O_3	3.61(23)	3.66(30)	4.60	0.277	0.273	0.362
Sm_2O_3	0.72(08)	0.76(08)	1.60	0.053	0.055	0.056
PbO	2.55(45)	1.91(33)		0.147	0.107	–
P_2O_5	10.54(29)	10.91(32)	10.15	1.916	1.925	1.896
Total	92.14	94.37	97.13*			

*including 0.79 wt.% Dy_2O_3 and 8.63 wt.% H_2O. # in the anhydrous formula unit.
Numbers in brackets refer to values of one standard deviation (%). Electron microprobe analysis of françoisite from Kamoto after Piret *et al.*, 1988. Number of ions calculated by the present authors.

of coffinites. The second mechanism involves hydroxylation of the coffinite structure. Low analytical totals in electron microprobe analyses of the Bangombé coffinites suggest the presence of water. Whether it occurs as molecular water or as structurally bonded OH groups, or both, could not be determined. Infrared studies found no evidence for essential OH in hydrated coffinite (see Janeczek and Ewing, 1992, for the discussion of the problem). Low analytical totals may also result from the presence of U^{6+} in coffinite. A substitution of the type $Ca^{2+} + U^{6+} = 2U^{4+}$ has been postulated in coffinite (Janeczek, 1991). The observation that 47% of Si in coffinite is substituted by P clearly demonstrates that coffinite compositions may vary widely because of substitutions for both U and Si. The first investigators of coffinite reported As in their chemical analysis of impure material (Stieff *et al.*, 1956). Arsenic may substitute for P; therefore, it is possible that As may also replace Si in coffinite.

Coffinite is considered to be thermodynamically unstable relative to uraninite plus quartz at temperatures greater than 25°C (Hemingway, 1982). This contrasts with the observations of the uraninite replacement by coffinite in the quartz arenite environment at Bangombé (Fig. 1*a*). Most probably, formation of coffinite is a kinetically controlled process, which also explains the wide variations of its chemical composition. While the coffinite replaced uraninite under reducing, or moderately reducing conditions, the françoisite must have formed under oxidizing conditions. Leaching of nearby phosphatian coffinites enriched in *REE* may have been a source of both P and *REE* in the françoisite. The rarity of the françoisite occurrence suggests that conditions favourable for its crystallization were localized. The same contents of Ce and Nd atoms in françoisite from Bangombé suggests that different *REE* can be predominant in this mineral.

Florencite-(La) with fissiogenic Nd and Sm has recently been observed by the authors in illite surrounding uraninite in the Bangombé reactor. The proximity of the coffinite and françoisite occurrences (some 20 cm) to the Bangombé reactor suggests that portions of *REE* in these minerals may be fissiogenic.

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References

Belova, L.N., Gorshkov, A.J., Ivanova, O.A. and Sivtsov, A.V. (1980) Nature of the so-called phosphorus-bearing coffinite. *Doklady Earth Science Sections*, **255**, 156–8 (translated from *Dokl. Akad. Nauk SSSR*, **255**, 428–30).

Gauthier-Lafaye, F., Weber, E. and Ohmoto, H. (1989) Natural fission reactors of Oklo. *Econ Geol.*, **84**, 2286–95.

Hansley, P.L. and Fitzpatrick, J.J. (1989) Compositional and crystallographic data on REE-bearing coffinite from the Grants Uranium region, northwestern New Mexico. *Amer. Mineral.*, **74**, 263–70.

Hemingway, B.S. (1982) Thermodynamic properties of selected uranium compounds and aqueous species at 298.15 K and 1 bar and at higher temperatures. Preliminary models for the origin of coffinite deposits. *U.S. Geol. Survey Open-File Report*, 82-619, 60 pp.

Hidaka, H., Takahashi, K. and Holliger, P. (1994) Migration of fission products into micro-minerals of the Oklo natural reactors. *Radiochim. Acta*, **66/67**, 463–8.

Janeczek, J. (1991) Composition and origin of coffinite from Jachymov, Czechoslovakia. *N. Jb. Miner. Mh.*, 9, 385–95.

Janeczek, J. and Ewing, R.C. (1992) Coffinitization – a mechanism for the alteration of UO_2 under reducing conditions. *Mat. Res. Soc. Symp. Proc.*, **257**, 497–503.

Piret, P., Deliens, M., and Piret-Meunier, J. (1988) La françoisite-(Nd), nouveau phosphate d'uranyle et de terres rares; propriétés et structure cristalline. *Bull. Minéral.*, **111**, 443–9.

Smits, G. (1989) (U,Th)-bearing silicates in Reefs of the Witwatersrand, South Africa. *Canad. Mineral.*, **27**, 643–55.

Speer, J.A. (1982) Zircon. In: *Orthosilicates. Reviews in Mineralogy* (P.H. Ribbe, ed.), MSA, pp. 67–112.

Stieff, L.R., Stern, T.W. and Sherwood, A.M. (1956) Coffinite, a uranous silicate with hydroxyl substitution – a new mineral. *Amer. Mineral.*, **41**, 675–88.

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