

Crystal chemistry and radiation-induced amorphization of P-coffinite from the natural fission reactor at Bangombé, Gabon

ARTUR P. DEDITIUS,^{1,*} SATOSHI UTSUNOMIYA,² MATTHEW A. WALL,¹ VÉRONIQUE POINTEAU,³ AND RODNEY C. EWING¹

¹Department of Geological Sciences, University of Michigan, Ann Arbor, Michigan 48109-1005, U.S.A.

²Department of Chemistry, Kyushu University, Ropponmatsu, 4-2-1, Chuou-ku, Fukuoka-shi, 810-8560, Japan

³CEA Saclay, DPC/SECR, F-91191 Gif-Sur-Yvette cedex, France

ABSTRACT

Phosphorous-rich coffinite, $\text{U}(\text{Si,P})\text{O}_4 \cdot \text{H}_2\text{O}$, from the natural nuclear reactor at Bangombé, Gabon (depth 12.25 m), has been examined as an important primary mineral and alteration product of uraninite under reducing conditions. Based on electron microprobe analyses (EMPA) and textural relationships, two distinct types of coffinite have been identified: (1) P-coffinite-(i) [with P_2O_5 and $(\text{REE}+\text{Y})_2\text{O}_3$ as high as 9.84 and 8.66 wt%, respectively] replaces uraninite and has a chemical formula of $(\text{U}_{0.84 \pm 0.05} \text{Y}_{0.12 \pm 0.02} \text{REE}_{0.10 \pm 0.02} \text{Ca}_{0.003 \pm 0.002} \text{Th}_{0.007 \pm 0.006} \text{Si}_{0.41 \pm 0.07} \text{P}_{0.34 \pm 0.03} \text{S}_{0.08 \pm 0.05}) \Sigma 0.84 \pm 0.05 \text{O}_4$ and; (2) coffinite-(ii), lacks uraninite inclusions [with P_2O_5 and $(\text{Y}+\text{REE})_2\text{O}_3$ up to 1.45 and 1.79 wt%, respectively] and has a chemical formula of $(\text{U}_{0.78 \pm 0.02} \text{Ca}_{0.05 \pm 0.003} \text{Y}_{0.03 \pm 0.01} \text{REE}_{0.002 \pm 0.001} \text{Th}_{0.002 \pm 0.001} \text{Si}_{1.02 \pm 0.02} \text{P}_{0.06 \pm 0.01} \text{S}_{1.08 \pm 0.01}) \Sigma 1.08 \pm 0.01 \text{O}_4$. The EMPA elemental maps reveal a homogeneous distribution of P, Si, Nd, and U in P-coffinite-(i). Charge-balance calculations indicate that S substitution for Si in the coffinite structure results in the enhancement of the incorporation of P and REEs. High EMPA totals (95–100 wt%), suggest that water is not an essential component of the coffinite structure. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) reveal the decomposition of single crystals of uraninite into 50 nm grains during the alteration process to P-coffinite-(i). High-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) patterns confirm that P-coffinite-(i) has the coffinite structure. However, P-coffinite-(i) has a large amorphous fraction probably due to radiation damage caused by α -decay events. The calculated cumulative dose for both types of coffinite varies from $1.6\text{--}1.9 \times 10^{18}$ (α -decay events/mg), which is equivalent to 134.2–161.5 displacement per atom (dpa) that have accumulated most probably during the past 800 million years.

Keywords: Phosphatian coffinite, coffinite, uraninite, natural fission reactor, Bangombé

INTRODUCTION

Janeczek and Ewing (1996) first reported P-rich coffinite, $\text{U}(\text{Si,P})\text{O}_4$, at the natural fission reactor at Bangombé. The phosphatian coffinite was found below the “core” of the reactor zone, which experienced nuclear fission chain reactions approximately 2.0 billion years ago (e.g., Gauthier-Lafaye et al. 1996; Hidaka and Holliger 1998; Stille et al. 2003; Hidaka et al. 2005). The nuclear reactor experienced the first hydrothermal alteration during its operation or shortly after under the temperature conditions of 250–450 °C (Gauthier-Lafaye et al. 1989). Subsequently, the reactor was altered by hydrothermal fluids, probably associated with the intrusion of a dolerite dike ~800 Ma ago (e.g., Hidaka et al. 2005). The temperatures of the hydrothermal fluids associated with the dolerite dike range from 110 to 260 °C (Janeczek 1999). The precise age of the P-coffinite precipitation remains unknown. However, it is likely that the hydrothermal alteration

resulted in redistribution of U and REE and was also responsible for their subsequent precipitation in the form of P-coffinite and REE-phosphates. A series of isotopic studies have shown that P-rich coffinite is depleted in $^{235}\text{U}/^{238}\text{U} \sim 0.00623$ and contains fission product elements, such as Ru and REEs (e.g., Hidaka et al. 1994, 2005; Stille et al. 2003; Kikuchi et al. 2007). P-coffinite is of particular interest because of its potential for incorporating actinides and fissiogenic REEs, thus reducing their mobility. However, there are no data confirming the structure and stoichiometry of P-coffinite. Its identification is based primarily on electron microprobe analysis (EMPA). P-coffinite is associated with françoisite-(Nd), $\text{REE}[(\text{UO}_2)\text{O}(\text{OH})(\text{PO}_4)_2] (\text{H}_2\text{O})_6$ (e.g., Janeczek and Ewing 1996).

Coffinite is an orthosilicate with the general formula ABO_4 , and is isostructural with zircon (ZrSiO_4), thorite (ThSiO_4), xenotime (YPO_4), and various AcSiO_4 (where, $\text{Ac} = \text{Np}, \text{Pu}, \text{Am}, \text{and Cm}$) (Spear 1982). The variable chemical composition of coffinite has led previous investigators to propose many iso- and heterovalent substitutions that have been reviewed extensively in the literature (e.g., Janeczek and Ewing 1992, 1996;

* Present address: CSIRO Exploration and Mining, 26 Dick Perry Ave., Kensington, Perth, WA 6151, Australia. E-mail: artur.deditius@csiro.au; deditius@umich.edu

Förster 2006). For example, it has been demonstrated that Y+REE can substitute for U as P replaces Si (so called “xenotime type” of substitution, $\text{REE}^{3+} + \text{P}^{5+} \leftrightarrow \text{U}^{4+} + \text{Si}^{4+}$) (e.g., Finch and Hanchar 2003; and references therein). P-coffinite from drill core BAX03 has been observed to have as much as 47% of P substituting for Si. Due to this high concentration of P and the lack of charge balance from trivalent Y+REE, Janeczek and Ewing (1996) suggested the presence of a solid solution between coffinite and ningyosite, $(\text{U,Ca,Ce})_2(\text{PO}_4)_2 \cdot 1-2 \text{H}_2\text{O}$.

Here we present, for the first time, a structural model for the crystallochemical relations in P-coffinite, supported by a large set of electron microprobe analyses. A nano-scale investigation using transmission electron microscopy (TEM) provides important information about the amorphization process in P-coffinite.

EXPERIMENTAL METHODS

The coffinite-bearing samples were first examined in polished thin section and polished bulk samples by optical and scanning electron microscopy (SEM, Hitachi S3200N equipped with energy dispersive X-ray spectrometry, EDS). The chemical composition of coffinite was quantitatively determined by EMPA (Cameca SX100). The instruments are housed in Electron Microbeam Analysis Laboratory (EMAL) at University of Michigan. Operating conditions for analyses included an accelerating voltage of 20 kV, beam current of 40 nA, and a beam diameter of $\sim 1 \mu\text{m}$. Decomposition of coffinite and uraninite were not noticed under the specified conditions of the electron beam. Analyses were calculated using the PAP correction procedure. Count times on the peak and a half of that time on both sides of the peak were: 30 s for Al; 60 s for Si, P, S, Ca, Ti, Fe, As, Zr, and U; 100 s for Y, La, Ce, Pr, Nd, Sm, Gd, Dy, Er, and Th. The standards used for calibration and detection limits (in ppm) are listed as follows: albite for $\text{AlK}\alpha$ (84); CaTiO_3 for $\text{CaK}\alpha$ (185) and $\text{TiK}\alpha$ (194); YPO_4 for $\text{YL}\alpha$ (439); ErPO_4 for $\text{PK}\alpha$ (174) and $\text{ErL}\beta$ (767); andradite for $\text{SiK}\alpha$ (134) and $\text{FeK}\alpha$ (172); arsenopyrite for $\text{AsL}\alpha$ (176); BaSO_4 for $\text{SK}\alpha$ (144); cerussite for $\text{PbM}\beta$ (893); zircon (ZrSiO_4) for $\text{ZrL}\alpha$ (142); synthetic UO_2 for $\text{UM}\beta$ (924); ThSiO_4 for $\text{ThM}\alpha$ (755); LaPO_4 for $\text{LaL}\alpha$ (457); CePO_4 for $\text{CeL}\alpha$ (442); PrPO_4 for $\text{PrL}\beta$ (644); NdPO_4 for $\text{NdL}\alpha$ (314); SmPO_4 for $\text{SmL}\beta$ (508); GdPO_4 for $\text{GdL}\beta$ (571); DyPO_4 for $\text{DyL}\beta$ (592).

High-resolution transmission electron microscopy (HRTEM), analytical elec-

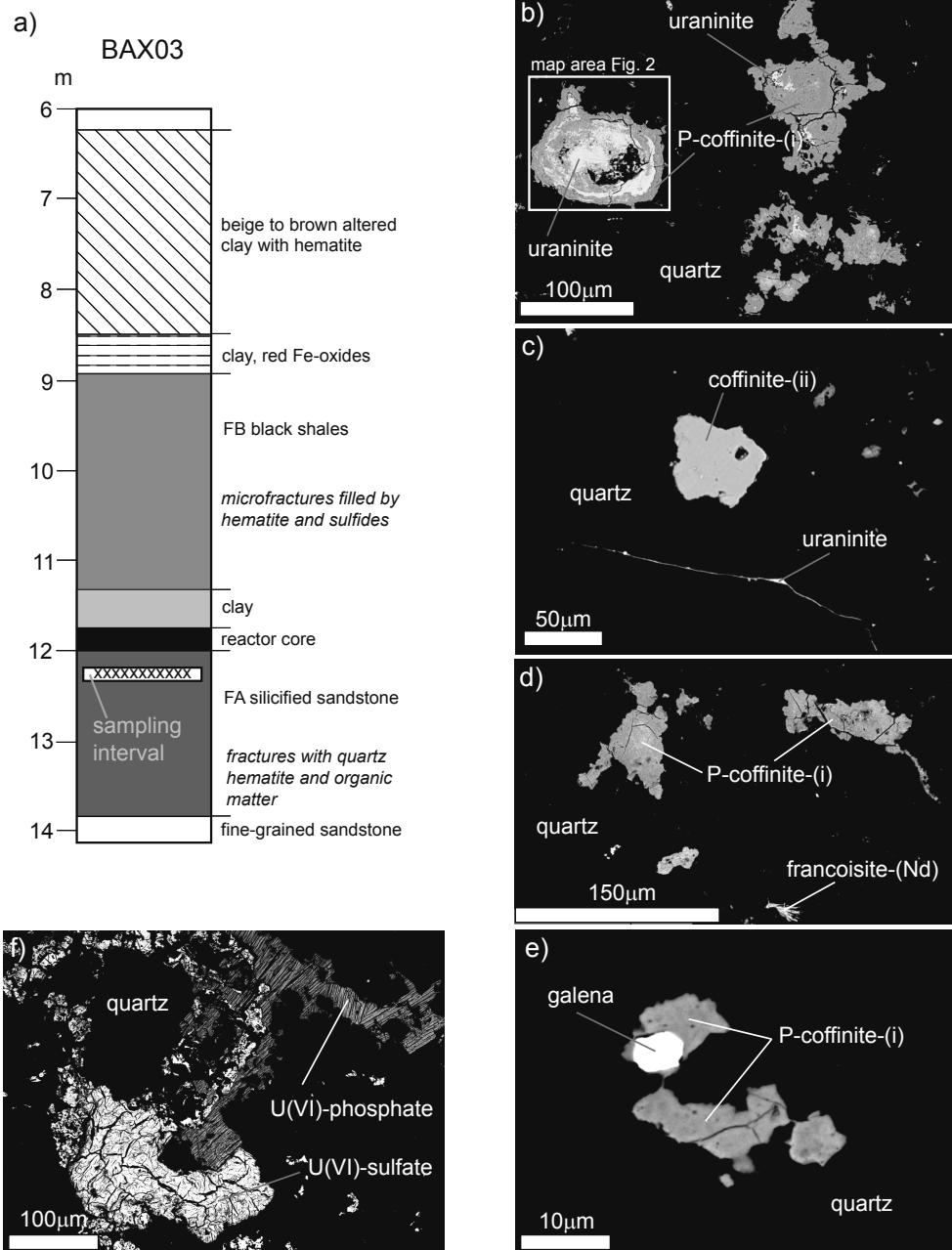


FIGURE 1. (a) Stratigraphic section of the BAX03 drill core with sample horizons marked; (b–f) BSE images of the various U minerals observed in samples from BAX03; (b) grains of uraninite replaced by P-coffinite-(i); (c) coffinite-(ii) and secondary uraninite filling a fracture; (d) P-coffinite-(i) associated with françoisite-(Nd); (e) P-coffinite-(i) with an inclusion of galena; (f) association of the secondary uranyl phosphates and sulfates.

tron microscopy (AEM), and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) were conducted using a JEOL JEM2010F (at Kyushu University). The spherical coefficient C_s is 1.0 mm. In STEM mode, the probe size was 1.0 nm and the collection angle of the HAADF detector was 50–110 mrad. The size of the condenser aperture was 20 μm .

RESULTS

Occurrence of coffinite

The geological setting and mineralogy of the natural fission reactors in Gabon have been described in detail (e.g., Gauthier-Lafaye et al. 1996; Janeczek 1999; Jensen and Ewing 2001);

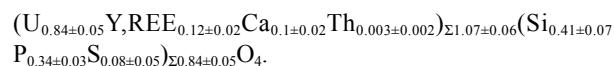
TABLE 1. Representative analyses of P-coffinite-(i)

Oxides	1	2	3	4	5	6	7	8	9	10
Al ₂ O ₃	0.32	0.36	0.23	0.43	0.24	0.21	0.27	0.43	0.33	0.27
SiO ₂	9.65	8.10	9.63	9.08	10.92	8.12	6.22	8.70	7.32	8.03
P ₂ O ₅	6.67	6.49	8.06	8.17	8.72	9.84	8.50	8.36	6.44	9.29
SO ₃	0.88	1.43	0.43	0.43	0.37	1.47	1.28	0.92	1.48	0.85
CaO	1.48	1.17	1.64	1.79	1.67	2.06	1.50	1.88	1.05	1.91
FeO	0.40	0.53	0.25	0.30	0.25	0.24	0.34	0.41	0.45	0.37
As ₂ O ₅	0.03	0.06	bdl	0.05	bdl	0.41	0.04	0.03	0.08	0.03
Y ₂ O ₃	1.22	1.10	1.82	1.80	1.77	1.93	2.02	2.52	1.26	2.78
La ₂ O ₃	0.16	0.16	0.13	0.20	0.19	0.20	0.17	0.19	0.09	0.20
Ce ₂ O ₃	0.67	0.68	0.88	0.84	0.82	0.90	0.81	0.94	0.55	0.95
Pr ₂ O ₃	0.18	0.14	0.16	0.22	0.24	0.23	0.21	0.30	0.10	0.31
Nd ₂ O ₃	1.42	1.33	1.87	1.90	1.89	2.03	1.83	2.45	1.20	2.47
Sm ₂ O ₃	0.40	0.34	0.55	0.63	0.54	0.62	0.63	0.90	0.47	0.88
Gd ₂ O ₃	0.28	0.32	0.63	0.56	0.53	0.56	0.63	0.77	0.43	0.82
Dy ₂ O ₃	0.04	0.07	0.04	0.14	0.06	0.08	0.15	0.15	0.11	0.15
Er ₂ O ₃	0.06	bdl	0.08	bdl	0.09	0.10	0.07	0.11	0.08	0.10
PbO	0.68	0.74	0.37	0.48	0.43	0.35	1.00	0.65	1.63	0.77
ThO ₂	0.10	0.20	0.14	0.16	0.09	0.19	0.20	0.29	1.24	0.21
UO ₂	73.44	73.51	69.42	69.48	66.97	67.30	71.41	67.71	72.60	68.02
ZrO ₂	bdl	bdl	bdl	bdl	bdl	bdl	0.05	0.11	1.02	bdl
TiO ₂	0.13	0.16	0.14	0.14	0.14	0.18	0.26	0.15	0.55	0.17
Total	98.21	96.89	96.47	96.80	95.93	97.01	97.59	97.97	98.48	98.58
Al ³⁺	0.020	0.023	0.014	0.027	0.014	0.012	0.017	0.026	0.021	0.016
Si ⁴⁺	0.510	0.435	0.509	0.481	0.558	0.399	0.331	0.445	0.391	0.409
P ⁵⁺	0.298	0.295	0.361	0.366	0.377	0.409	0.383	0.362	0.291	0.401
S ⁶⁺	0.070	0.115	0.034	0.034	0.029	0.108	0.102	0.070	0.119	0.065
Ca ²⁺	0.084	0.067	0.093	0.101	0.091	0.108	0.085	0.103	0.060	0.104
Fe ²⁺	0.017	0.024	0.011	0.013	0.011	0.009	0.015	0.017	0.020	0.016
As ⁵⁺	0.001	0.002	bdl	0.001	bdl	0.010	0.001	0.001	0.002	0.001
Y ³⁺	0.034	0.031	0.051	0.050	0.048	0.050	0.057	0.068	0.036	0.075
La ³⁺	0.003	0.003	0.003	0.004	0.004	0.004	0.003	0.004	0.002	0.004
Ce ³⁺	0.013	0.013	0.017	0.016	0.015	0.016	0.016	0.018	0.011	0.018
Pr ³⁺	0.004	0.003	0.003	0.004	0.004	0.004	0.004	0.006	0.002	0.006
Nd ³⁺	0.027	0.025	0.035	0.036	0.034	0.036	0.035	0.045	0.023	0.045
Sm ³⁺	0.007	0.006	0.010	0.012	0.009	0.010	0.012	0.016	0.009	0.016
Gd ³⁺	0.005	0.006	0.011	0.010	0.009	0.009	0.011	0.013	0.008	0.014
Dy ³⁺	0.001	0.001	0.001	0.002	0.001	0.001	0.003	0.003	0.002	0.002
Er ³⁺	0.001	bdl	0.001	bdl	0.001	0.002	0.001	0.002	0.001	0.002
Pb ²⁺	0.010	0.011	0.005	0.007	0.006	0.005	0.014	0.009	0.023	0.010
Th ⁴⁺	0.001	0.002	0.002	0.002	0.001	0.002	0.002	0.003	0.015	0.002
U ⁴⁺	0.863	0.878	0.817	0.819	0.761	0.736	0.845	0.771	0.863	0.771
Zr ⁴⁺	bdl	bdl	bdl	bdl	bdl	bdl	0.001	0.003	0.027	bdl
Ti ⁴⁺	0.005	0.006	0.006	0.005	0.005	0.007	0.010	0.006	0.022	0.006
Total	1.974	1.947	1.984	1.992	1.981	1.938	1.950	1.989	1.947	1.981
A ^{tot}	1.043	1.037	1.044	1.057	0.980	0.978	1.075	1.053	1.057	1.057
B ^{tot}	0.879	0.847	0.904	0.883	0.964	0.926	0.817	0.878	0.804	0.875

therefore, only the features related to the formation of coffinite are reported here. The core of the reactor at Bangombé is located at the uppermost part of the silicified sandstone, and it is mantled on the top by clay and the black pelite of the Franceville formation (Fig. 1a). The specimens were selected from drill core BAX03 at a depth of 12.20–12.30 m, which is below the core of the reactor zone. Texturally, two types of coffinite have been observed: (1) abundant phosphorous-rich coffinite that may contain relicts of uraninite; identified as P-coffinite-(i); and (2) very rare coffinite, without “visible” inclusions of uraninite, hereafter identified as coffinite-(ii). Both P-coffinite-(i) and coffinite-(ii) occur as ~100 µm inclusions in quartz (Figs. 1b–1e). Some crystals of uraninite, with brighter contrast in the back-scattered electron (BSE) images, are surrounded by atoll-like structures of P-coffinite-(i) (Fig. 1b). Long platy crystals (~10 µm) of françoisite-(Nd) are present 100–150 µm from P-coffinite-(i) (Fig. 1d). Some grains of P-coffinite-(i) contain 1–5 µm large inclusions of galena (Fig. 1e). The sandstone is cut by fractures filled with secondary uranyl phosphates and sulfates (Fig. 1f). The other minerals noted are chlorite and K-feldspar.

Chemical composition of coffinite

Phosphorous-rich coffinite-(i) with uraninite inclusions and relatively “pure” inclusion-free coffinite-(ii) are characterized by different chemical compositions (Tables 1 and 2). The main constituents of P-coffinite-(i) are UO₂ (66.97–73.51 wt%) and SiO₂ (6.22–10.92 wt%). P-coffinite-(i) is characterized by the general formula (with standard deviation):



A characteristic feature of P-coffinite-(i) is the elevated concentration of P₂O₅ (6.44–9.84 wt%) and (Y,REE)₂O₃ (3.22–8.66 wt%). Neodymium and Y attain the highest concentrations among total Y+REE in P-coffinite-(i) (to 2.47 wt% Nd₂O₃ and 2.78 wt% of Y₂O₃). SO₃ content ranges from 0.37–1.48 wt%, and CaO varies from 1.05–2.06 wt%. The amounts of Al₂O₃, As₂O₅, ThO₂, ZrO₂, PbO, and TiO₂ are below 2 wt%. Analytical totals range from 95.93 to 98.58 wt%.

The chemical composition of the coffinite-(ii) varies over a

TABLE 2. Representative analyses of coffinite-(ii)

Oxides	1	2	3	4	5	6	7	8
Al ₂ O ₃	0.74	0.80	1.43	1.71	0.83	0.77	0.81	0.94
SiO ₂	19.24	20.01	21.37	20.75	19.72	20.02	19.67	20.57
P ₂ O ₅	1.46	1.34	0.92	1.35	1.43	1.38	1.39	1.33
SO ₃	0.03	bdl	bdl	bdl	0.05	bdl	0.03	0.03
CaO	0.81	0.79	0.76	0.93	0.84	0.82	0.81	0.91
FeO	0.27	0.26	0.05	0.07	0.25	0.26	0.26	0.27
Y ₂ O ₃	0.44	0.44	0.26	0.32	0.45	0.41	0.41	0.43
La ₂ O ₃	0.11	0.10	0.12	0.11	0.10	0.12	0.12	0.11
Ce ₂ O ₃	0.38	0.40	0.34	0.32	0.40	0.37	0.39	0.39
Nd ₂ O ₃	0.53	0.55	0.39	0.43	0.53	0.54	0.54	0.55
Sm ₂ O ₃	0.15	0.15	0.10	0.09	0.13	0.14	0.16	0.13
Gd ₂ O ₃	0.15	0.15	bdl	bdl	0.11	0.14	0.13	0.14
PbO	1.36	1.27	0.74	0.62	1.23	1.32	1.26	1.24
ThO ₂	0.13	0.14	0.36	0.22	0.10	0.10	0.14	0.14
UO ₂	69.57	69.32	68.74	68.13	70.01	69.67	70.24	69.47
ZrO ₂	0.03	0.06	0.78	0.64	0.11	0.06	0.06	0.07
TiO ₂	0.21	0.22	0.24	0.20	0.21	0.24	0.18	0.19
Total	95.61	96.00	96.60	95.89	96.50	96.36	96.60	96.91
Al ³⁺	0.046	0.048	0.083	0.100	0.050	0.046	0.049	0.055
Si ⁴⁺	1.000	1.025	1.057	1.027	1.007	1.022	1.008	1.033
P ⁵⁺	0.064	0.058	0.038	0.057	0.062	0.059	0.060	0.057
S ⁶⁺	0.002	bdl	bdl	bdl	0.004	bdl	0.002	0.002
Ca ²⁺	0.045	0.043	0.040	0.049	0.046	0.045	0.045	0.049
Fe ²⁺	0.012	0.011	0.002	0.003	0.011	0.011	0.011	0.011
Y ³⁺	0.012	0.012	0.007	0.008	0.012	0.011	0.011	0.011
La ³⁺	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002
Ce ³⁺	0.007	0.007	0.006	0.006	0.007	0.007	0.007	0.007
Pr ³⁺	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Nd ³⁺	0.010	0.010	0.007	0.008	0.010	0.010	0.010	0.010
Sm ³⁺	0.003	0.003	0.002	0.001	0.002	0.002	0.003	0.002
Gd ³⁺	0.003	0.003	bdl	bdl	0.002	0.002	0.002	0.002
Pb ²⁺	0.019	0.018	0.010	0.008	0.017	0.018	0.017	0.017
Th ⁴⁺	0.002	0.002	0.004	0.002	0.001	0.001	0.002	0.002
U ⁴⁺	0.805	0.790	0.756	0.750	0.796	0.792	0.801	0.776
Zr ⁴⁺	0.001	0.001	0.019	0.015	0.003	0.002	0.002	0.002
Ti ⁴⁺	0.008	0.008	0.009	0.007	0.008	0.009	0.007	0.007
Total	2.041	2.043	2.043	2.047	2.041	2.042	2.042	2.046
A ^{tot}	0.889	0.874	0.844	0.843	0.883	0.874	0.887	0.864
B ^{tot}	1.068	1.083	1.095	1.085	1.073	1.083	1.071	1.092

Note: As₂O₃, Pr₂O₃, Dy₂O₃, Er₂O₃ = below detection limits.

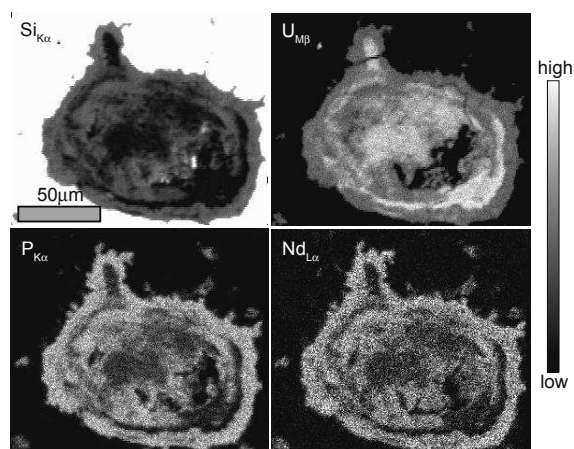
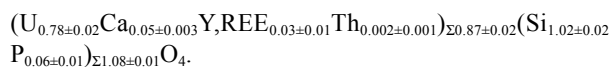


FIGURE 2. EMPA elemental maps of Si, U, P, and Nd in the area of uraninite and P-coffinite-(i) association.

much narrower range than that of P-coffinite-(i). Representative data for coffinite-(ii) are given in Table 2. The UO₂ and SiO₂ range from 68.13–70.24 wt% and from 19.24–21.37 wt%, respectively. The average chemical composition with standard deviation of the coffinite-(ii) is:



A comparison of this formula with that of P-coffinite-(i), illustrates that coffinite-(ii) contains fewer cations in the A-site than in the B-site, whereas the opposite is true for P-coffinite-(i). The concentrations of P₂O₅ and (Y,REE)₂O₃ are significantly lower in coffinite-(ii), ranging from 0.92–1.46 and 1.27–1.79 wt%, respectively. Coffinite-(ii) Al₂O₃ is up to 1.71 wt%, however, no clay minerals, which often account for elevated concentrations of Al, were found with respect to the resolution of EMPA and SEM. The amounts of SO₃, CaO, FeO, As₂O₃, ThO₂, ZrO₂, and TiO₂ are below 1 wt%. Coffinite-(ii) contains lower CaO (~0.76–0.93) and higher PbO (0.62–1.36 wt%) than P-coffinite-(i). The analytical totals of coffinite-(ii) range from 95.61 to 96.91 wt%. Concentrations of As₂O₃, Pr₂O₃, Dy₂O₃, and Er₂O₃ are below detection limits.

Elemental maps show the relative abundance of U, P, Si, and Nd in a U-rich grain composed of uraninite in the center, surrounded by atoll-like P-coffinite-(i) along the rim (Fig. 2). The distribution of Nd and P are correlative, and regions of high Si concentration within the coffinite match that of P, suggesting that

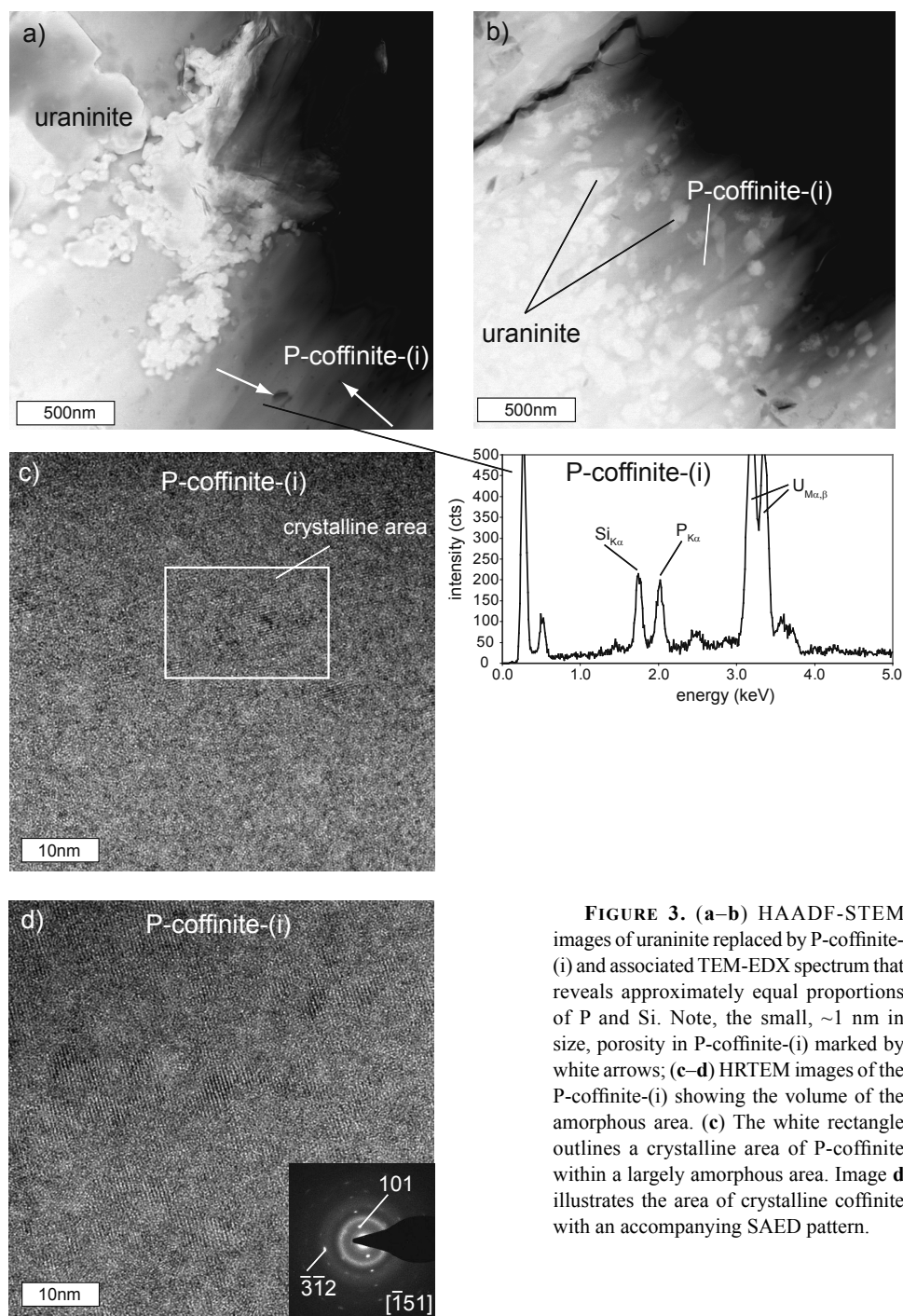


FIGURE 3. (a–b) HAADF-STEM images of uraninite replaced by P-coffinite-(i) and associated TEM-EDX spectrum that reveals approximately equal proportions of P and Si. Note, the small, ~1 nm in size, porosity in P-coffinite-(i) marked by white arrows; (c–d) HRTEM images of the P-coffinite-(i) showing the volume of the amorphous area. (c) The white rectangle outlines a crystalline area of P-coffinite within a largely amorphous area. Image d illustrates the area of crystalline coffinite with an accompanying SAED pattern.

Si, P, and Nd precipitated in a single phase. Thus, the substitution of P for Si allows for an increased incorporation of Y+REE into the coffinite structure.

Structure of P-coffinite and calculated cumulative dose

A TEM study of P-coffinite-(i) was performed on grains that would provide the best opportunity to investigate its relation to uraninite. The HAADF-STEM images show that P-coffinite-(i) replaces uraninite (Figs. 3a–3b). Single crystals of uraninite are decomposed to aggregates of small rounded grains, ~50

nm in size, which are embedded within P-coffinite-(i). The AEM of P-coffinite-(i) confirms the ~50/50 ratio of silicon to phosphorous (Fig. 3a). The HAADF-STEM image shows ~1–2 nm sized pores in P-coffinite-(i), which may be due to differences in the volume between uraninite and coffinite as a result of the replacement reaction (Fig. 3a). HRTEM images reveal that P-coffinite-(i) contains a heterogeneous distribution of amorphous domains (Figs. 3c–3d). Some areas have nanocrystalline islands of P-coffinite-(i) up to 10 nm across in a largely amorphous matrix (Fig. 3c), while in other areas a larger

fraction of crystalline P-coffinite remains (Fig. 3d). In some cases, the relatively large amorphous fraction was confirmed by observing the selected area electron diffraction pattern (SAED), which shows a diffuse ring pattern in addition to the diffraction maxima characteristic of crystalline coffinite (Fig. 3d). The HRTEM images reveal that areas resembling crystalline islands of P-coffinite-(i) have the same orientation (Figs. 3c–3d). This suggests that the P-coffinite-(i) precipitated as a larger, most probably a few micrometers in size, single crystal, which was subsequently subjected to radiation damage.

The large amorphous fraction of the P-coffinite-(i) is a result of damage via α -decay events. One can calculate the cumulative dose from the U and Th content of the P-coffinite-(i) and the estimated age using the formula (Ewing et al. 2000):

$$D\alpha = 8N_1[\exp(\lambda_1 t) - 1] + 7N_2[\exp(\lambda_2 t) - 1] + 6N_3[\exp(\lambda_3 t) - 1]$$

where N_1 , N_2 , and N_3 are the present values of ^{238}U , ^{235}U , and ^{232}Th , respectively in atoms/mg; λ_1 , λ_2 , and λ_3 are the decay constants for ^{238}U , ^{235}U , and ^{232}Th , respectively, in years $^{-1}$; and t is the estimated age of coffinite.

Note that the precise age of P-coffinite from Bangombé is unknown, which is one of the most important parameters for dose calculations. However, it is known that coffinite precipitates under low-temperature conditions, 100–140 °C (Janeczek and Ewing 1992 and references therein), which correlates relatively well with the second hydrothermal alteration ($T = 110$ – 260 °C) in the Franceville Basin that occurred during intrusion of the ~800 Ma dolerite dike (Gauthier-Lafaye et al. 1996). Although a younger age cannot be ruled out, it is assumed that the TEM results in the present study were performed on coffinite that is ~800 Ma.

The final dose expressed in dpa units is calculated according to the equation:

$$\text{Dose (dpa)} = 9.40 \times 10^5 \times D\alpha \times M / (N_A \times 6),$$

where M is the molar mass of coffinite and N_A is Avogadro's number. These calculations were corrected for ^{235}U depletion after Hidaka et al. (2005) who reported an isotopic ratio of $^{235}\text{U}/^{238}\text{U}$ for P-coffinite ranging from 0.00609–0.00619. The cumulative dose in coffinite at Bangombé varies between 1.6 and 1.9×10^{18} (α -decay events/mg), which are equivalent to 137.2 and 161.5 dpa. The range of the calculated cumulative dose is a result of various uranium concentrations. There is no correlation between the cumulative dose and the amounts of other elements in coffinite. The estimated age (~800 Ma) of the coffinite may explain the high cumulative dose as compared with other orthosilicates; cumulative doses vary from 0.3 dpa for zircon to 0.16 dpa for thorite (e.g., Meldrum et al. 1997, 1998, 2000).

DISCUSSION

Phosphatian coffinite

Several heterovalent substitutions in coffinite have been proposed by Janeczek and Ewing (1996) and Förster (2006) to explain the high concentrations of P and Y+REE including: (1) $(\text{Y,REE})^{3+} + \text{P}^{5+} \leftrightarrow \text{U}^{4+} + \text{Si}^{4+}$; (2) $2\text{Ca}^{2+} + 0.8\text{P}^{5+} + 0.2(\square)^{\text{IV}} \leftrightarrow \text{U}^{4+}$

+ Si^{4+} ; (3) $2\text{Ca}^{2+} + \text{P}^{5+} + (\text{OH})^- \leftrightarrow \text{U}^{4+} + \text{Si}^{4+}$; and (4) $2(\text{Y,REE})^{3+} + (\text{Ca,Fe})^{2+} \leftrightarrow 2(\text{Th,U,Zr})^{4+}$. Jensen and Ewing (1998) reported that S most probably substitutes for Si in P-coffinite from Bangombé. However, no mechanism of coupled substitution was proposed. It is suggested that S can be incorporated via the coupled substitution (5) $\text{Ca}^{2+} + \text{S}^{6+} \leftrightarrow \text{U}^{4+} + \text{Si}^{4+}$.

The EMPA analyses reveal that P-coffinite-(i) contains the highest concentrations of P and Y+REE ever measured; up to 9.84 and 8.66 wt% as oxides, respectively. These values are greater by about 1 wt% than those reported for coffinite from Bangombé and Witwatersrand by Smits (1989) and Janeczek and Ewing (1996). The measured concentrations of P account for 58% of Si substituted by P along the coffinite-xenotime solid-solution join. Consequently, some analyses indicate the composition of a Si-rich xenotime (Fig. 4a). However, concentrations of Y+REE in the A-site suggest substitution for only 20% of the U (Fig. 4a). This results in a large charge imbalance in the phosphatian coffinite, which is further enhanced by the incorporation of divalent Ca (Fig. 4a). This suggests the ningyosite type of substitution (2) proposed by Janeczek and Ewing (1996). However, the charge-balance calculations for P-coffinite-(i) reveal that S also substitutes for Si and definitely balances the needed charge (Figs. 4b and 4c), which agrees with data of Jensen and Ewing (1998). From this point of view, S reduces the number of vacancies that would have to be created during the substitutions of various non-formula elements into the coffinite structure. Furthermore, the incorporation of S into the coffinite structure causes the B-site to be fully occupied, and no vacancy is required to balance the charge deficiency (Table 1), which was often reported in previous studies of coffinite (e.g., Janeczek and Ewing 1996 and references therein). Another possibility for balancing the observed charge deficiency is that a portion of U is oxidized to U^{6+} . Based on charge-balance calculations, Deditius et al. (2008) estimated that the maximum amount of U^{6+} would be <0.2 apfu. Using the same method, including S in the B-site, the possible amount of U^{6+} in P-coffinite-(i) is <0.15 apfu. This calculation implies that the compositional variations for P-coffinite-(i) from Bangombé are best considered by examining two ternary systems: Si-P-S and U-Y+REE-Ca. Note that the P-coffinite-(i) analyzed in this study contains various heterogeneously distributed fractions of an amorphous area (Figs. 3c and 3d), which may also be responsible for the calculated charge imbalance and deficiency in the occupation of B-sites (Table 1).

Figure 5 summarizes the chemical compositions of coffinite from Bangombé and all other published coffinite data. There are two groups of analytical points for coffinite on the diagram illustrating B-site cations Si-P-S (Fig. 5a). One group of analyses cluster in the Si-rich corner, while the Bangombé P-coffinite-(i) analyses are concentrated along the boundary between coffinite and xenotime. In addition, there is a trend toward the S-corner marked by analyses of coffinite from the Grants uranium region (Fig. 5a, inset) (Deditius et al. 2008). All analyses for the A-site cations plot in the U-rich portion of the U-Y+REE-Ca ternary diagram (Fig. 5b). Two trends are recognized: (1) substitution of Ca for U, which is characteristic for low-REE coffinite from the Grants uranium region [(Y+REE)/Ca ratio ~0.17], and (2) a trend of P-coffinite from Bangombé, for which the (Y+REE)/Ca ratio is ~1.2. The distribution of the analytical points shown on Figure 5a

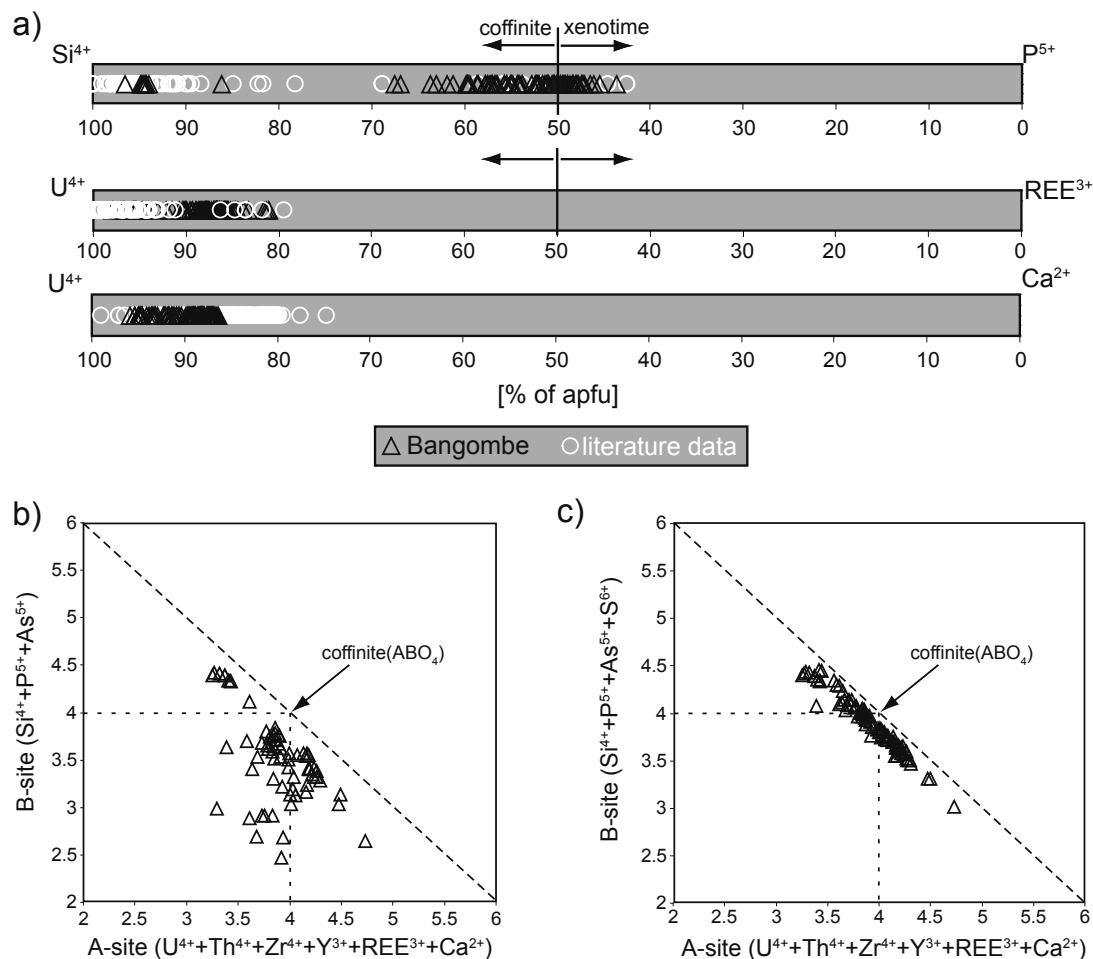


FIGURE 4. (a) Diagrams showing the bimodal distribution of cations in the A- and B-sites with respect to the ideal compositions of coffinite and xenotime. Literature data after: Janeczke (1991, 1999); Hansley and Fitzpatrick (1986); Smits (1989); Janeczke and Ewing (1996); Jensen and Ewing (1998, 2001); Jensen and Sinha (2003); Fayek et al. (2003); Förster (2006); Deditius et al. (2008). (b–c) Diagrams illustrating the distribution of the analytical points of P-coffinite-(i) with respect to the calculated total charge; without (b) and with (c) S⁶⁺ incorporated into calculations.

suggest that there is a limited solid solution between coffinite and xenotime from 0 to 10% and from 40 to 55%, with a miscibility gap from around 10–40 mol% of xenotime (based on Deditius et al. 2008 and references therein; and analyses presented in this paper). Figure 5c shows that the amount of S in coffinite is generally not higher than 0.25 apfu, with a large number of analyses clustering below 0.15 apfu. The TEM studies of P-coffinite-(i) confirm (Fig. 3) that coffinite is the sole mineral phase, and, based on the above arguments, one can assume extensive solid solution between coffinite and xenotime. The homogeneous distribution of P between the amorphous and crystalline areas precludes the possibility of other preexisting phases, such as ningyoite, which was proposed by Belova et al. (1980).

Although S⁶⁺ may substitute for tetrahedral Si⁴⁺ in orthosilicates (Spear 1982), the role of S in the coffinite-xenotime solid solution is not well constrained. Figures 5a and 5c suggest that the small S⁶⁺ (0.012 nm for tetrahedral coordination; after Shannon 1976) enhances the miscibility between coffinite and xenotime. The small size and high charge of S⁶⁺ might allow for the accommodation of the larger and lower charge Ca²⁺ and Y,REE³⁺. However, these relations are more complex because the amount

of Ca²⁺ can decrease in P-coffinite-(i) due to its competition for U positions with smaller Y³⁺ (ionic radius 0.1019 nm) or Nd³⁺ (ionic radius 0.1109 nm).

An additional important point of the analyses of the present study is the significantly improved analytical totals, 95–100 wt%, when compared with previously published analyses (Fig. 6; Table 1 and 2). Two molecules of H₂O or (OH)-groups have been suggested as a reason for low analytical totals (e.g., Janeczke and Ewing 1992) in coffinite analyses. However, simple calculations of possible analytical totals with respect to various amounts of H₂O or (OH)-groups suggest that coffinite contains a maximum of one molecule of H₂O or one OH-group (Fig. 6). The analytical totals do not change with respect to coffinite crystallinity. The analytical totals of the heavily damaged P-coffinite-(i) from Bangombé and very crystalline coffinite from Grants vary within the same range (Fig. 6). In addition, the relatively large variation in analytical totals (to 5 wt%), suggests that “water” in coffinite has a non-stoichiometric character. There are few analyses that correspond to a coffinite composition accommodating four OH-groups, as postulated by the first investigators (Stieff et al. 1956).

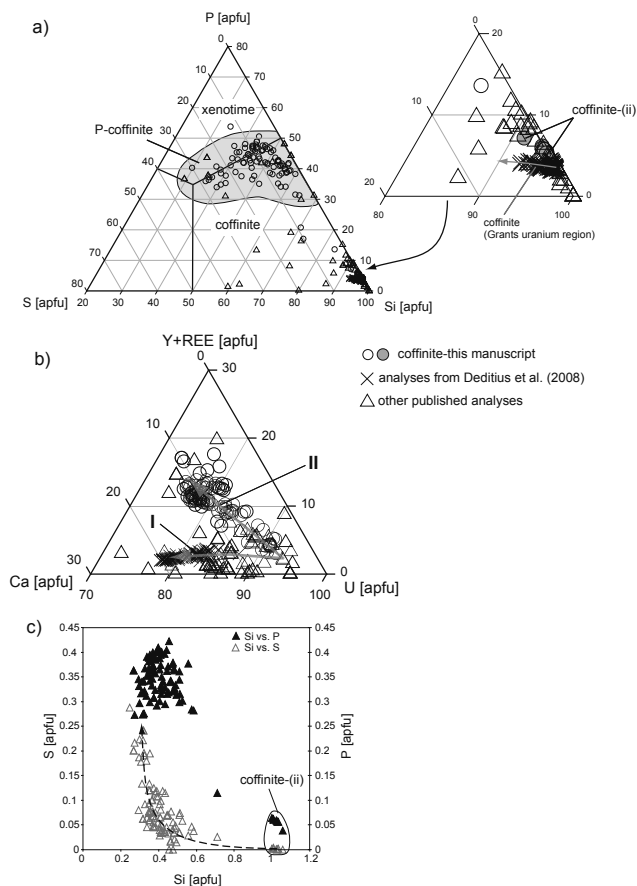


FIGURE 5. (a) Analyses of coffinite plotted on the Si-P-S ternary diagram. Note the bimodal distribution of the analytical points including: (1) a group of analyses closer to the Si-rich apex and reflecting the composition of coffinite, and (2) the shaded area that indicates the chemical composition of P-coffinite. Note that some of the analyses fall into the field of xenotime, and that these analyses deviate significantly toward the S-rich composition; (b) Analyses of coffinite on the diagram U-Y+REE-Ca. Note the two analytical trends shown by the arrows: (1) one indicating a low (Y+REE)/Ca ratio, characteristic for coffinite from the Grants uranium region, and (2) the other indicating a high (Y+REE)/Ca ratio characteristic for P-coffinite from Bangombé. References are identical to those in Figure 4; (c) Si vs. S and Si vs. P apfu. Note the negative correlation between Si and S (dashed curve) and the sharp boundary between concentrations of S and P in coffinite ~ 0.25 apfu. This suggests S enhances the incorporation of P into the coffinite structure.

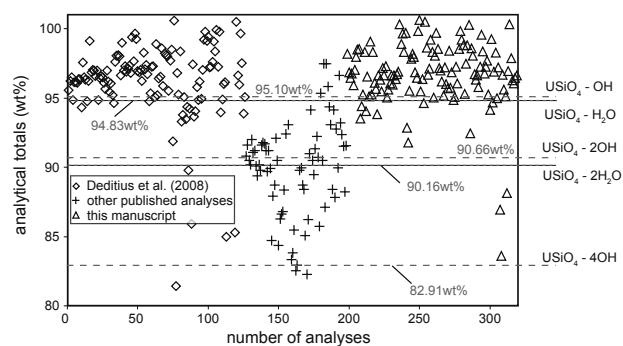


FIGURE 6. Diagram showing analytical totals of coffinite plotted against different calculated amounts of H₂O and (OH). References are identical to those in Figure 4.

Amorphization of P-coffinite

The amorphization observed in the present study is a result of radiation damage from α -decay events due to high concentrations of uranium and the assumed old age of the P-coffinite, ~ 800 Ma (e.g., Hidaka et al. 2005). The calculated doses for P-coffinite from Bangombé vary from $1.6\text{--}1.9 \times 10^{18}$ α -decay events/mg, which is equal 137.2–161.5 dpa. These doses are much higher than the most recent amorphization doses reported for nanocrystalline synthetic coffinite (0.27 dpa) (Lian, personal communication) and other orthosilicates such as: (1) zircon, 0.3 dpa (room temperature), 0.5 dpa ($\sim 400\text{--}800$ K); (2) hafnon, 0.4 dpa (room temperature), 0.6 dpa (400–900 K); (3) thorite, 0.16 dpa (room temperature–500 K); and (4) xenotime, 0.2 dpa (room temperature) (e.g., Meldrum et al. 1997, 1998). The calculated doses for P-coffinite-(i) from Bangombé are comparable to the doses accumulated in Pu-doped zircon. Begg et al. (2000) reported that ^{239}Pu -substituted zircon remained crystalline after the dose of 1.2×10^{20} α -decays/mg, but was highly amorphous after a dose of 1.2×10^{22} α -decays/mg. Similar results are shown in the TEM studies (Fig. 3c) where crystalline islands (~ 10 nm across) of P-coffinite-(i) are surrounded by an amorphous matrix. P-coffinite-(i) likely precipitated under the low-temperature conditions of the surrounding geological environment of the natural reactor at Bangombé ($\sim 130\text{--}140$ °C) as reported for coffinite from other localities (Janeczek and Ewing 1992). It is likely that the coffinite experienced some annealing since the time of precipitation. This agrees with the relatively low activation energy (0.28 eV) reported for dynamic defect annealing and recovery for synthetic coffinite. On the other hand, amorphous USiO_4 decomposes to UO_2 and SiO_2 at a temperature of 200 °C (Lian, personal communication). No amorphization was observed in the relatively young ($\sim 20\text{--}30$ Ma), single crystals of coffinite from the Grants uranium region (Deditius et al. 2008), in which the calculated α -decay dose is $4.3\text{--}8.5 \times 10^{16}$ /mg, which is equivalent to 3.68–7.36 dpa. Published HRTEM images of natural zircon grains subjected to various doses of damage revealed that crystalline fragments rotate and form low-angle grain boundaries during the crystalline-to-amorphous transition (e.g., Murakami et al. 1991). The same results have been observed in heavy ion-irradiation experiments on zircon (Wang 1998). However, P-coffinite from Bangombé does not reveal low-angle grain boundary formation between separated fragments of the crystalline areas (Fig. 3d). The large volume of the amorphous fraction in P-coffinite decreases its stability and makes it more susceptible to alteration and, perhaps, to the incorporation of impurities (Utsunomiya et al. 2007 and references therein).

Phosphatian coffinite and evolution of the natural fission reactor at Bangombé

The precipitation of the P-coffinite took place during the remobilization of U and fission products from the ~ 2.0 Ga old natural fission reactor due to the intrusion of a dolerite dike and associated hydrothermal activity in the Franceville basin (e.g., Gauthier-Lafaye 1996; Hidaka et al. 2005). Precipitation of phosphatian coffinite is one of the main processes responsible for the sequestration of migrating actinides and a large fraction of the fissionogenic LREE (e.g., Janeczek and Ewing 1996; Jensen et al. 2002; Hidaka et al. 2005). The present study has

revealed that two different types of coffinite occur below the reactor core in Bangombé based on their relation to uraninite and their varying concentrations of P, S, and Y+REE. P-coffinite-(i) replaces uraninite (Fig. 1b). A range of S contents suggest that the concentration of sulfur resulted from variations in fluid composition, while the very small range of P contents suggest that P was supplied almost at the same concentration as Si (P/Si ratio = 1.05 ± 0.19). This value is slightly lower than the P/Si ratio of 1.33 reported by Jensen and Ewing (1998). The variation in the S content is most likely related to alteration of sulfides under oxidizing conditions above the reactor horizon (Jensen and Ewing 1998).

The second type, “pure” coffinite-(ii), does not contain “visible” inclusions of uraninite but the occurrence of nano-inclusions of uraninite in coffinite-(ii) cannot be ruled out. Jensen and Ewing (1998) also reported P-depleted coffinite from Bangombé, but it replaced uraninite. To the best of our knowledge, coffinite with chemical signature of coffinite-(ii) (Table 2) in this study has never been reported from this part of the reactor in drill hole BAX03. However, its chemical composition is similar to the coffinite from the Oklo natural reactor, RZ10, in Gabon (Janeczek 1999). The lack of a textural relationship between coffinite-(ii) and uraninite makes it difficult to estimate the age of coffinite-(ii). The very low stable P/Si ratio (~ 0.066) in coffinite-(ii) indicates a very low concentration of P in the migrating and mineralizing fluids, and S is mostly below the detection limit (Table 2), which may suggest that the coffinite-(ii) precipitated before P-coffinite-(i). Such a scenario is in good agreement with the results of Jensen and Ewing (1998) who reported that S was introduced into the system later and also distinguished between two types of P-bearing coffinite based on the S content.

The close association of françoisite-(Nd) with P-coffinite-(i) (within ~ 100 – $150 \mu\text{m}$) observed in this study suggests precipitation of coffinite-(ii) and P-coffinite-(i) under reducing conditions, which subsequently evolved to oxidizing conditions. The very rare occurrence of françoisite-(Nd) and of the observation of minor corrosion of P-coffinite-(i) suggests limited leaching of U, P, and REE from coffinite, which was postulated by Janeczek and Ewing (1996) to be the source for constituent elements for the uranyl phosphate. Precipitation of the other more recent uranyl minerals records U mobilization by oxidizing groundwater (e.g., Jensen et al. 2002).

In summary, the HRTEM observations and accompanying SAED pattern prove that 800 Ma old phosphatian coffinite from Bangombé is a single mineral phase. It contains a variable, but significant amorphous fraction. The amorphous areas contain fairly large nano-crystalline islands of P-coffinite or form an interconnected network within the crystalline P-coffinite. Calculated doses (1.6 – 1.9×10^{18} α -decay events/mg, 137.2–161.5 dpa), are much higher than required for the amorphization of other orthosilicates, such as zircon, thorite, and xenotime. The damage was most likely preserved due to the rather low-temperature conditions following coffinite formation.

EMPA and HRTEM analyses suggest that there is a very limited solid solution between coffinite and xenotime: (1) from 0–10 mol% of xenotime end-member, and (2) 40–55 mol% of xenotime. However in the second case, significant S substitution enables the incorporation of P and Y+REE. Sulfur plays a

significant role in balancing the charge deficiency created during the substitution of Ca^{2+} and $\text{Y}+\text{REE}^{3+}$ into the coffinite structure. Structural data combined with electron microprobe analyses show that P-coffinite can sequester high levels of actinides and fission products, up to 76.4 and 8.6 wt%, respectively (Table 1). The lack of evidence for significant corrosion and alteration suggests that coffinite remains relatively stable even in heavily damaged areas, as long as conditions are reducing. Isotopic data will be required before the relation of coffinite-(ii) to the natural reactor at Bangombé can be fully elucidated.

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