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Compositional and crystallographic data on REE-bearing coffinite from the Grants uranium region, northwestern New Mexico

PAULA L. HANSLEY, JOAN J. FITZPATRICK
U.S. Geological Survey, Box 25046, M.S. 939, Denver Federal Center, Denver, Colorado 80225, U.S.A.

ABSTRACT

Paired substitution of Y and P in coarse-grained coffinite from the Upper Jurassic Morrison Formation in the Grants uranium region, northwestern New Mexico, indicates that coffinite forms an isomorphous series with xenotime, which is isostructural with thorite and zircon. Quantitative electron-microprobe analyses of coffinite crystals (>10 μm) demonstrate that significant amounts of Ca, Y, and rare-earth elements (REEs) proxy for U as P substitutes for Si, effectively maintaining the charge balance. The abundant rhyolitic volcanic ash present in the Morrison Formation at the time of deposition is believed to be the source for U, Y, and REEs.

Petrographic and stable-isotope data suggest that the coarse-grained, pore-filling coffinite analyzed in this study was formed at elevated temperatures (at least 100 °C) during maximum burial of the Morrison Formation in the mid-Tertiary. Supporting this relatively young age is the anisotropy and transparency of the coffinite crystals, indicating that they are not highly metamict. The coffinite owes its brownish color primarily to microscopic inclusions of carbonaceous material. The ubiquitous presence of carbonaceous inclusions in sedimentary coffinites suggests that organic C is critical to the formation of coffinite at low temperatures (<200 °C).

INTRODUCTION

Coffinite [$U(SiO_4)_{1-x}(OH)_{4x}$] was first described by Stieff et al. (1955) in an investigation of sedimentary uranium-vanadium deposits in the Upper Jurassic Morrison Formation from the Uravan mineral belt in southwestern Colorado and southeastern Utah. Coffinite was subsequently found to be the major ore mineral in unoxidized sandstone-hosted uranium-vanadium deposits in the Morrison Formation throughout the Colorado Plateau. It has also been identified in many other stratiform sedimentary uranium deposits and in hydrothermal vein deposits around the world (Ramdohr, 1980). The composition and crystal chemistry of coffinite in sedimentary deposits are poorly known, because it commonly forms submicrometer-sized crystals that are intimately mixed with amorphous organic matter and/or clay minerals. Coffinite is usually detected only from the presence of broad peaks on X-ray diffraction patterns. Peak broadening is due to the small size of coherent X-ray domains and to the tendency of older coffinites to be metamict (Ramdohr, 1961).

This report describes extraordinarily large and well-formed coffinite crystals in the Morrison Formation from three localities in the Grants uranium region of northwestern New Mexico, formerly the most productive uranium mining region in the United States (Chenoweth and Holen, 1980). Most coffinite samples were obtained from a U.S. Geological Survey drillhole (no. 7) located north of Crownpoint, New Mexico. This drillhole intersects a limb of the nearby Nose Rock uranium deposit, which also contains coarsely crystalline coffinite (Rhett, 1979, 1980). Coffinite-bearing samples from the Nose Rock deposit (provided by D. W. Rhett) and a polished thin section containing coffinite (provided by S. S. Adams, Colorado School of Mines) from a Homestake Mining Company drillhole (H26-22) located about 16 km southeast of Crownpoint were also studied. The large size (>10 μm) of crystals from these localities enabled determination of the unit-cell parameters and compositions of these coffinites.

Sedimentary coffinite crystals of large enough size and purity from which petrographic and crystallographic data can be gathered are rare, although hydrothermal vein deposits may contain masses of radiating coffinite crystals up to 5 mm long (Ramdohr, 1980). Most noted occurrences of coarsely crystalline coffinite from sedimentary deposits are from the Colorado Plateau and nearby areas. Colloform coffinite crystals (>20 μm in length) were found in the Woodrow pipe, a mineralized collapse feature in the Morrison Formation in the southeastern part of the Grants uranium region (Moench, 1962). Ludwig and Grauch (1980) described and analyzed coarse-grained colloform coffinite from Wyoming roll-front uranium deposits. Doubly terminated tetragonal prismatic crystals up to 5 μm in length are intergrown with vanadiferous chlorite in uranium-vanadium ore from the Morrison Formation in southeastern Utah (Goldhaber et al., 1987).

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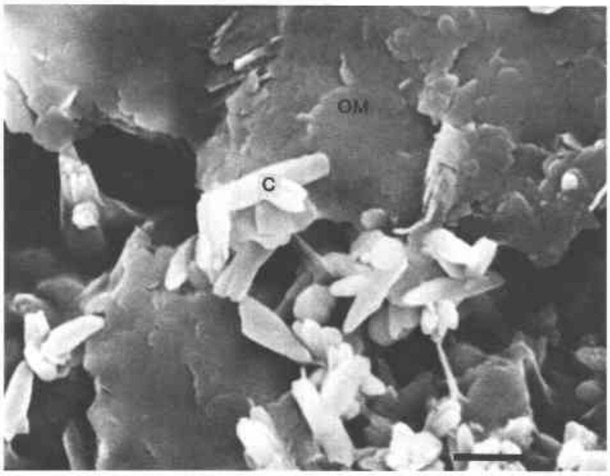

Fig. 1. Scanning electron micrograph of submicroscopic coffinite crystals in remnant primary ore. Note interpenetrating coffinite crystals (C). Matrix is a mixture of clay minerals and amorphous organic matter (OM). Sample 4-1933. Scale bar = 1 μm.

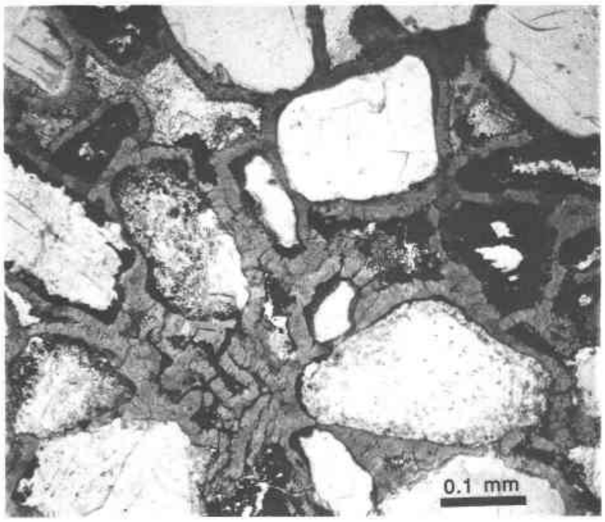

Fig. 2. Photomicrograph of colloform aggregates of coffinite crystals (gray) rimming framework grains. Black material is primary carbonaceous ore and pyrite. Plane-polarized light. Sample H26-22.

Table 1. X-ray powder-diffraction data for coffinite from the Grants uranium region, New Mexico

hkl	d_{calc}	d_{obs}	I_{rel}*	I_{calc}** (anhydrous)
101	4.654	4.661	S	56
200	3.473	3.472	S	100
211	2.783	2.779	MS	26
112	2.642	2.641	S	90
220	2.456	2.458	M	25
301	2.172	2.173	M	14
103	2.001	2.000	M	10
321	1.841	1.842	MW	15
312	1.799	1.800	S	74
400	1.737	1.735	M	21
213	1.734	—	—	9
411	1.627	1.626	MW	7
004	1.567	—	—	5
420	1.553	1.551	M	21
332	1.451	1.451	M	22
204	1.428	1.428	W	18
323	1.416	—	—	4
431	1.356	1.354	W	6
501	1.356	—	—	2
244	1.321	1.316	VW	17
413	1.311	—	—	5
521	1.263	—	—	3
512	1.249	1.250	W	22
105	1.234	—	—	1
440	1.228	1.228	W	6
404	1.163	—	—	9
215	1.163	—	—	4
600	1.158	1.158	VW(d)	6
433	1.157	—	—	3
503	1.157	—	—	2
611	1.123	—	—	3
532	1.114	1.113	W	17
424	1.103	1.103	W	18

* Intensities by visual estimate: S = strong; MS = medium strong; M = medium; MW = medium weak; W = weak; VW = very weak; (d) = diffuse.

** Intensities calculated using anhydrous formula with refined zircon oxygen positions and uranium scattering factors. Allowed reflections with zero intensity not shown.

PETROGRAPHY

Coffinite occurs primarily in fine- to medium-grained arkosic litharenites of the Morrison Formation. In hand specimens, coffinite-rich areas are black with a dull to adamantine luster. Crystals are less than 2 μm in length and are intimately mixed with organic matter and clay minerals so that definitive petrographic analysis is difficult (Fig. 1). In a few samples, however, coffinite crystals are large enough to be studied optically. These crystals commonly form colloform rinds on detrital grains, and the long axes of coffinite crystals are perpendicular to grain margins (Fig. 2). Detrital grains show no evidence of replacement where in contact with coffinite. In direct reflected light in oil, coffinite is brownish gray with a re-

Table 2. Comparison of unit-cell dimensions (Å) of selected coffinites

Reference	*a*	*c*	Occurrence
This report	6.946(1)	6.268(2)	Jm* sandstone
Dubinchuk et al. (1981)	6.98(3)	6.30(3)	hypergene
	6.93(3)	6.30(3)	hydrothermal
Dubinchuk et al. (1982)	6.98(1)	6.24(1)	sandstone
Belova et al. (1980)	6.90	6.21	sedimentary
Nord (1977)	6.938(1)	6.291(2)	Jm sandstone
Bayushkin and Il'menev (1969)	6.92	6.25	Mo-U ore
Taylor et al. (1966)	6.97(2)	6.22(3)	phyllite
Darnley et al. (1965)	6.95(2)	6.26(3)	hydrothermal
	6.98(2)	6.19(3)	hydrothermal
Dymkov and Nazarenko (1962)	7.01	6.26	hydrothermal
Simms et al. (1961)	6.93(5)	6.21(2)	hydrothermal
	6.97(1)	6.28(6)	hydrothermal
Fuchs and Gebert (1958)	6.981(4)	6.250(5)	synthetic
Stieff et al. (1955)	6.94	6.31	Jm sandstone
Gruner and Smith (1955)	6.92	6.22	Jm sandstone

* Jm = Upper Jurassic Morrison Formation on the Colorado Plateau.

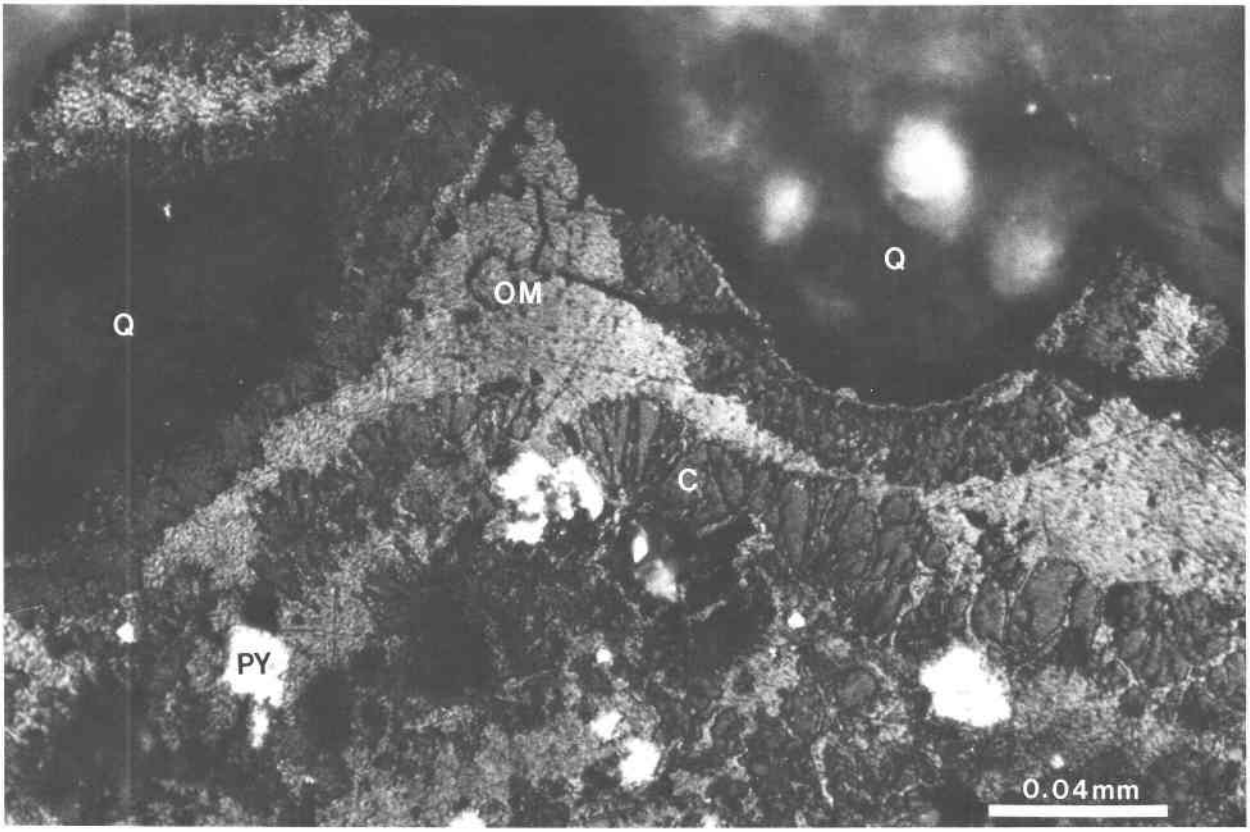

Fig. 3. Photomicrograph of coffinite (C) textures in Nose Rock ore. Q, quartz; PY, pyrite. Organic matter (OM) contains traces of U and other elements. Direct reflected light, oil immersion.

flectivity only slightly higher than associated quartz grains and much lower than nearby pyrite (Fig. 3). Coffinite is light to medium brown in transmitted light and light to medium green under crossed polarizers. Elongate coffinite crystals are length-slow with parallel extinction, and they exhibit a distinct anisotropy suggesting that they are not highly metamict (Ramdohr, 1980; Speer, 1982a). Crystal aggregates exhibit undulatory extinction, and the narrow bases of radiating crystal groups are opaque owing to numerous inclusions of titanium dioxides, pyrite, and carbonaceous material. Under the scanning electron microscope, the morphology of coffinite aggregates is clearly visible (Fig. 4).

CRYSTALLOGRAPHY

Coffinite is tetragonal (SG $I4_1/amd$) and is isostructural with zircon and thorite (Speer, 1982a). Coffinite crystals were handpicked from coffinite–organic matter mixtures for X-ray powder-diffraction analyses. An 8-h exposure in a Gandolfi camera using Cu radiation yielded a pattern of 21 well-defined X-ray diffraction lines, including several lines in the back-reflection region. Quartz was used as an internal standard. Unit-cell parameters calculated from measured 2-θ angles and corresponding d values (Table 1) were compared with published unit-cell data (Table 2). The unit-cell parameters were refined with a least-squares computer program (Appleman and Evans, 1973). The refined unit-cell parameters do not differ significantly from those reported for other coffinites.

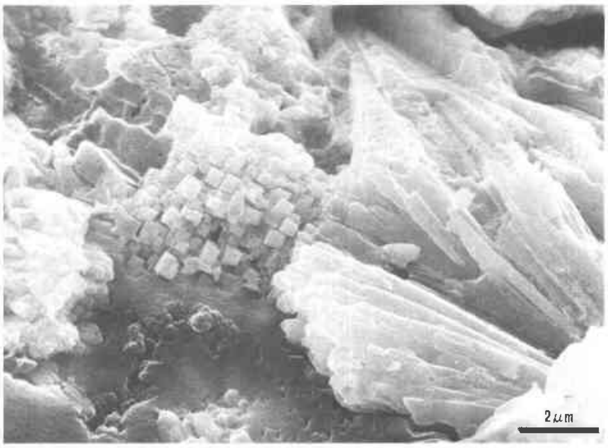

Fig. 4. Scanning electron micrograph of clusters of elongate coffinite crystals with square cross sections. Sample 7-3260.

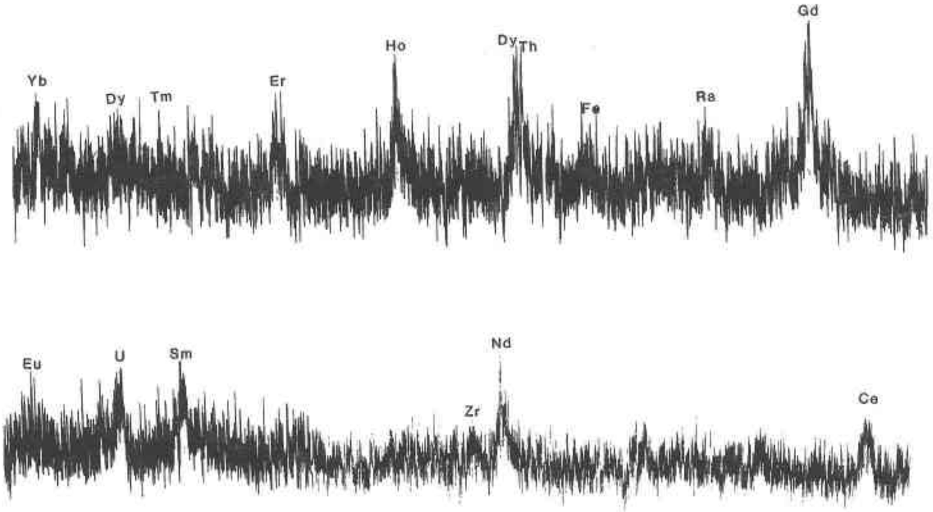

Fig. 5. Expanded wavelength-dispersive spectrum showing the *Lα* peaks of rare-earth elements in coffinite. Spectrum reads from upper left to lower right: Yb (7.41 keV) to Ce (4.84 keV). LiF spectrometer; 15 kV; sample current, 10 nA; time constant, 1.5 s. Sample 7-3185.

ELECTRON-MICROPROBE ANALYSES

Analytical methods

Because most coffinite crystals are submicroscopic and are commonly intergrown with other phases, electron-microprobe analysis is the most reliable method for determining the composition of coffinite. Electron-microprobe analyses were performed on polished thin sections of coffinite-bearing samples with the wavelength-dispersive system of an ARL-SEMQ electron microprobe. Both synthetic and natural standards were used: diopside for Ca and Si, apatite for P, and YAG garnet for Y (all prepared commercially by C. M. Taylor Corp.); natural uraninite (Smellie et al., 1978, Table 1) was used for U and Pb. Backgrounds were determined by offset on the high and low side of each peak. All analyzed spots were verified as being homogeneous and flat by viewing (at 5000×) the secondary electron image of the area to be analyzed. Each reported analysis is an average of 4–9 spot analyses within a small (<100 μm) area. U, Si, Ca, Y, P, and Pb (assumed to be radiogenic) were included in the analytical program; the energy-dispersive system was used during the analyses to check for the presence of other elements. Data were reduced using the MAGIC IV computer program (Colby, 1971).

Results

Quantitative electron-microprobe analyses revealed the presence of major Ca, Y, P, and minor Pb besides U and Si in the analyzed coffinites (Table 3). In addition, REEs were detected in all coffinites by energy-dispersive analysis. Due to their low individual abundances, however, the REEs were not included in the quantitative analysis scheme. Estimates of REE abundances based on relative peak heights in energy-dispersive spectra ranged from less than 1% to 4%. Because the *L* X-ray spectral lines of the REEs overlap those of the common elements Al and Mg, the presence of REEs was confirmed by plotting expanded wavelength-dispersive spectra of the REE region, which revealed REEs and traces of V, Fe, and Th(?). Sample 7-3185 contained the most REEs and Y with Gd > Dy

TABLE 3. Semiquantitative electron-microprobe analyses of coffinites from the Grants uranium region

	7-3185	7-3260-1	7-3260-2a	7-3260-b	7-3260-3	7-3260-4	H26-22-1	H26-22-2	H26-22-3	H26-22-4	H26-22-5	H26-22-6	H26-22-7	H26-22-8	H26-22-9
UO_2	63.8(5)	71.2(5)	70.3(5)	70.4(5)	68.7(5)	69.9(5)	68.9(5)	68.7(5)	69.0(5)	68.3(4)	68.2(5)	68.7(5)	69.0(5)	69.0(5)	68.3(5)
CaO	1.5(7)	1.9(8)	1.8(8)	1.8(8)	2.2(8)	1.8(7)	2.3(9)	2.0(1)	2.0(5)	2.0(8)	2.1(1)	2.5(9)	2.5(5)	2.4(9)	2.4(9)
Y_2O_3	6.0(3)	1.0(1)	1.0(1)	1.0(1)	0.4(1)	1.0(1)	0.4(2)	0.2(7)	0.2(1)	0.3(1)	0.2(1)	0.4(1)	0.4(1)	0.4(1)	0.4(1)
SiO_2	15.7(3)	15.8(3)	15.8(3)	15.2(3)	19.3(3)	16.6(3)	18.3(3)	18.5(3)	17.6(3)	18.1(3)	18.5(3)	18.6(3)	18.5(3)	18.6(3)	18.6(3)
P_2O_5	3.3(1)	1.4(1)	1.4(1)	1.4(1)	1.0(1)	1.5(1)	0.9(1)	0.7(1)	0.7(1)	0.8(1)	0.8(1)	1.1(1)	1.1(1)	1.0(1)	1.1(1)
PbO	0.4(1)	0.3(1)	0.3(1)	0.3(1)	0.3(1)	0.3(1)	0.4(1)	n.d.	n.d.	n.d.	n.d.	0.3(1)	0.3(1)	0.3(1)	0.3(1)
Total	90.8	91.6	90.5	90.2	92.0	91.1	91.2	90.1	89.4	90.2	89.8	91.6	91.8	91.7	91.2

Note: The numbers in parentheses represent 2 standard deviations in tenths of one percent; thus 63.8(5) indicates a standard deviation of 0.5; see text for discussion of other sources of error. Analyses (weight percent) are the averages of 4–9 spot analyses within an area of <100-μm diameter. Operating conditions were 15-kV accelerating potential and 10-nA current on brass. Spot size was 1 μm; counting time was 40 s on Y and Pb and 80 s on the other elements. n.d. = not detected.

= Ho > Er = Nd > Ce; traces of Yb, Tm, and Eu were also found (Fig. 5). The light rare-earth elements (LREEs) predominated in coffinites from sample 7-3260, which contained Ce > Nd > Gd, and in sample H26-22, which contained Sm > Ce = Nd > La. Apparently, no particular REE or groups of REEs are favored by the coffinite structure.

Discussion of results

Ca, which has commonly been detected in previous analyses of coffinite, and Y may proxy for U and P for Si because of similar ionic radii. Pb is considered to be a product of radioactive decay of U. Coffinite that contains no detectable Pb may have lost radiogenic Pb because of migration of Pb from the coffinite structure (Ramdohr, 1980) or the coffinite may be too young to contain detectable amounts of Pb. Qualitative electron-microprobe analyses of areas not containing coffinite in ore samples commonly detected small areas of clausthalite (PbSe).

Microprobe analyses of coffinite from roll-type uranium deposits in Wyoming detected U, Si, and Ca (Ludwig and Grauch, 1980). On the other hand, Kim (1978) found significant P (average P_2O_5, 2.18%) and trace amounts of Al, V, Ca, and Fe in coffinite from the Woodrow mine in the Grants uranium region. The inferred Al_2O_3 (0.79%) may actually be a composite of REE peaks because of the overlap between X-ray peaks of Al and REEs. Supporting this hypothesis, photomicrographs of the coffinite that Kim analyzed (Moench, 1962) show apparently pure coffinite crystals devoid of clay-mineral contamination. To our knowledge, the only other Y- and P-rich coffinite that has been reported in the literature is coffinite in organic-rich nodules from the Triassic Mercia Mudstone Group in England, which contained 21 wt% Y_2O_3 (analyses normalized to 100%; Harrison et al., 1983).

Most bulk chemical analyses of coffinite list elements that are unlikely to fit into the coffinite structure owing to incompatible ionic radii and/or ionic charge. Chemical analyses of the first described coffinite included As and Al (Stieff et al., 1956); Arribas (1966) listed Mg, Na, Al, S, and Fe as elements in coffinite; Belova et al. (1969) found Mg, Fe^{3+}, Al, and S in coffinite; Belova et al. (1980) noted Fe and P in coffinite pseudomorphs after ningyoite $[(U,Ca,Ce)_2(PO_4)_2 \cdot 1\text{–}2H_2O]$; Khalezov and Avalonin (1974) reported coffinite with Ti, Y, Fe^{3+}, Th, Ce, V, and Cr; and Bylinskaya (1980) found metamict coffinite that contained traces of Y and Ce. Coffinite that had replaced pitchblende in ore from Cornwall contained traces of La (Taylor and Harrison, 1958). Because of similar ionic radii and charges (see Shannon and Prewitt, 1969), As and P could proxy for Si whereas Y, Ce, La, and Th could substitute for U, but Al, Fe, Mg, S, Ti, Cr, and V were probably contained in admixed iron oxides, titanium dioxides, and clay minerals. These analyses undoubtedly reflect the impurity of the samples analyzed, because of the known difficulty in obtaining pure coffinite separates.

Accuracy of analyses

Our microprobe data are considered to be semiquantitative, because the oxide analyses do not total 100%. In general, the low analytical totals typical of microprobe analyses of coffinite may be attributed to a combination of the following factors: (1) substitution of hydroxyl for silica or absorption of nonstructural hydroxyl during metamictization; (2) the presence of U^{6+}; (3) angstrom-sized domains of C, titanium dioxides, and amorphous silica; (4) the additive effects of trace amounts of elements not in the analytical program, especially the REEs; (5) microcracks in coffinite crystals; (6) absorption and fluorescence not accounted for in the correction procedure; and finally (7) instrument and operator errors. These potential sources of errors are discussed below.

Hydroxyl was originally thought to be an essential component of coffinite, but anhydrous coffinite has been synthesized (Fuchs and Gebert, 1958; Fuchs and Hoekstra, 1959), and infrared and DTA studies have shown that hydroxyl is not an essential constituent of coffinite (Abdel-Gawad and Kerr, 1961; Belova et al., 1969). Smith (1984) suggested that the presence of organometallic complexes may account for deviation of the U:Si ratio from unity rather than the presence of $(OH)^-$. Nonetheless, $(OH)_4^{4-}$ may substitute for $(SiO_4)^{2-}$, or nonstructural hydroxyl may be absorbed during metamictization due to radioactive decay. Partial metamictization causes disordering of crystal domains and, finally, may lead to a complete breakdown of coffinite into amorphous silica and uraninite (Brodin et al., 1980). However, the analyses of this study show excess P and Si, suggesting that $(OH)^-$ has not substituted for silica. In addition, the anisotropy and transparency of the coarsely crystalline coffinite suggest that it is not highly metamict and, thus, probably does not contain significant hydroxyl.

The presence of U^{6+} has been confirmed in uraninite (Frondel, 1958) and in coffinite by X-ray photoelectron spectroscopy (Goldhaber, 1977). The uranyl ion, therefore, may partly account for low analytical totals and for apparent underpopulation of the uranium site, because the data reduction programs did not allow for the presence of U^{6+}. Even if all U were U^{6+}, however, only 3–4 wt% would be added to the analytical totals.

Visible inclusions of titanium dioxide, pyrite, and C in coffinite crystals suggest that submicrometer-sized inclusions may also be present. These phases, therefore, may constitute a significant portion of the missing percentage in analysis totals. In addition, secondary electron images of some ore samples at >40000 × revealed that botryoidal material containing varying proportions of U, Si, and C(?) was closely associated with the coarsely crystalline coffinite (Fig. 6). Although spots known to contain this amorphous material were avoided, small amounts may lie underneath analyzed areas.

As discussed under Results, the REEs may account for a significant portion of the missing percentage in the analytical totals. The isostructural minerals thorite and zir-

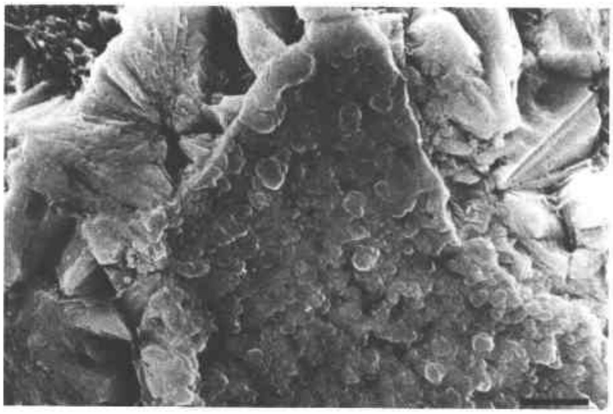

Fig. 6. Scanning electron micrograph of coffinite and associated siliceous microspheres containing major U, Ti, Si, and/or traces of other elements. Sample 7-3260. Scale bar = 5 μm.

con may also contain significant amounts of REEs. Up to 20 wt% Y and REEs have been detected in natural thorite (Staatz et al., 1976), and zircon can accommodate up to 25 wt% REEs and Y (Speer, 1982b). In a comprehensive geochemical study of the Morrison Formation in the Grants uranium region, Della Valle (1981) also found REE enrichment in ore zones, but he assumed that the REEs were adsorbed onto clay minerals.

Visible shrinkage(?) cracks in large crystals were avoided by checking the secondary electron image before each analysis; thus, error due to an uneven surface is thought to be minimal.

Absorption and fluorescence not corrected for by MAGIC IV may be significant owing to the presence of elements that were not included in the analytical program and to matrix effects arising from compositional differences between the unknown and standards. Elemental interferences were minimized by selecting background values using the expanded wavelength-dispersive spectra as guides.

Additional sources of error due to microprobe hardware (e.g., instrument drift), software (e.g., errors not accounted for by the data-reduction program), inhomogeneous standards (particularly uraninite), and operator error were kept to a minimum.

In summary, it is difficult to quantify the potential analytical sources of error discussed in this section; however, they may add as much as 5% error to the counting statistic errors listed on Table 3.

ISOMORPHISM

On the basis of experimental studies and the compositions of natural coffinites, substitution between coffinite and the isostructural minerals thorite and zircon is apparently limited. Mumpton and Roy (1961) were able to synthesize thorite hydrothermally (1350 °C) with up to 20 to 30 mol% $USiO_4$ substitution. Foord et al. (1985) described a uranoan thorite occurring in rhyolite with about 30 mol% $USiO_4$. On the other hand, only small amounts of $ThSiO_4$ have been found in coffinite (Speer, 1982a); a trace of Th was detected in only one coffinite analyzed in the present study. In synthesis experiments (1350 °C), Mumpton and Roy (1961) found that zircon can accommodate up to 6 mol% $USiO_4$, but only traces of $ZrSiO_4$ have been found in natural coffinite (Speer, 1982a; this study).

Isomorphism between coffinite and the isostructural phosphate xenotime is predicted by (1) isomorphism between zircon and xenotime evidenced by the intermediate varietal species "oyamalite," and (2) isomorphism between thorite and xenotime evidenced by the intermediate varietal species "auerlite" (Dymkov and Nazarenko, 1962). Zircon may exhibit coupled substitution of REEs plus Y and P for Zr and Si, respectively (Speer, 1982b). Similarly, substitution of Y and P for U and Si, respectively, strongly indicates that isomorphism between coffinite and xenotime exists.

Y^{3+} and the REEs (2+ and 3+) can proxy for U^{4+}, Th^{4+}, and Zr^{4+}; and P^{5+} can substitute for Si^{4+} because of similar ionic radii. Coupled substitution occurs because the charge imbalance caused by the substitution of 3+ (e.g., Y) for 4+ elements (e.g., U) is compensated by substitution of a 5+ (e.g., P) element for Si. Whether a new mineral phase intermediate between coffinite and xenotime exists owing to paired substitution is unknown. The diffraction pattern of coffinite in sample 7-3185, which contains up to 6 wt% Y_2O_3 and 3.3 wt% P_2O_5, was distinctly different from that of the other coffinites of this study, but insufficient sample was available to establish whether a new mineral phase was present.

GENESIS OF COARSE-GRAINED SEDIMENTARY COFFINITE

The coarsely crystalline coffinite analyzed in the present study probably formed from recrystallization of earlier U-bearing phases during burial diagenesis (Hansley, 1988). Silica activity remained locally high throughout diagenesis because of the dissolution of unstable silicate framework grains, such as rock fragments and plagioclase. Thermodynamic studies have shown that a high silica activity ($10^{-3.5}$) favors the formation of coffinite (Hemingway, 1982, and Goldhaber et al., 1987). Stable-isotope data on authigenic clay minerals in coffinite-bearing sandstones suggest that warm (130 °C), deep-basin fluids moved updip through ore-bearing units in the Grants uranium region during maximum burial of the Morrison Formation in the mid-Tertiary (Northrop and Whitney, 1985). The presence of regularly interstratified illite-smectite (Whitney, 1986), ankerite, and albite in coffinite-bearing ore zones (Hansley, 1986a) also indicate that temperatures of at least 100 °C were attained during diagenesis (Perry and Hower, 1970; Boles, 1978, 1982). Warm fluids (>80 °C) would have accelerated the maturation of organic matter in ore zones, causing the release of organic acids, which promoted the dissolution of detrital grains and authigenic cements (Surdam et al., 1984). The precipitation and growth of large coffinite crystals in secondary pores were facilitated by warm fluids, for despite its common occurrence in low-temperature sedimentary deposits, coffinite has not yet been synthesized at temperatures less than 200 °C (Hemingway, 1982).

The ubiquitous association of coffinite with organic matter and the occurrence of inclusions of organic matter in many sedimentary coffinites (Fuchs and Hoekstra, 1959; Smith, 1984) imply that the presence of amorphous organic matter as a strong sorbant and reductant (or as a substrate for biogenic H_2S) may be critical to coffinite formation at temperatures less than 200 °C. The black color, characteristic of coffinite, may be due to the presence of C and/or U^{6+} (Smith, 1984). X-ray elemental mapping (U, Si, and C) of ore samples performed on the electron microprobe indicated that not all U is in coffinite. Some U may be adsorbed onto organic matter (Leventhal, 1980), whereas some may be present as uraninite.

Associated rhyolitic volcanic ash (Waters and Granger, 1953) may have been the source for REEs in coffinite as acidic volcanic rocks are enriched in REEs (Humphris, 1984). Phosphorus contained in the coffinite and associated authigenic euhedral apatite may have been derived from organic material during diagenesis, as fossil bones and plants are abundant locally in the Morrison Formation. Detrital apatite grains in ore zones were not a source of phosphorus for they are generally unaltered (Hansley, 1986b).

CONCLUSIONS

Semiquantitative electron-microprobe analyses of unusually large crystals of coffinite from sandstone-hosted uranium deposits in the Grants uranium region demonstrate that coffinite can accommodate significant amounts of Ca, Y, P, and REEs. The apparent paired substitution of Y and REEs for U and of P for Si suggests that coffinite, like zircon and thorite, is isomorphous with xenotime. The degree to which REEs and other elements substitute in the coffinite structure is probably related to the relative proportions of each element in interstitial solutions at the time of coffinite formation. In the case of the Morrison Formation, the REEs, Y, and U were readily available because of abundant rhyolitic volcanic ash.

The 8–10% lacking in the microprobe analyses is due mainly to the presence of REEs, organic C, and U^{6+} that were not included in the analytical scheme. Optical properties of the coarsely crystalline coffinite suggest that it contains an insignificant amount of hydroxyl. The inferred low hydroxyl content of the coffinite, reported stable-isotope values, and types of authigenic phases in coffinite-bearing ore zones suggest that the large coffinite crystals were formed near 100 °C and are no older than mid-Tertiary. Ubiquitous inclusions of carbonaceous material (probably remnants of primary ore) in the coffinites of this study and in other sedimentary coffinites suggest that organic C plays an important role in the formation of coffinite at low temperature.

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