

Ages of uraninite and coffinite from south-west England

By A. G. DARNLEY

Atomic Energy Division, Geological Survey of Great Britain

T. H. ENGLISH and Mrs. O. SPRAKE

National Chemical Laboratory, Teddington, Middlesex

and

E. R. PREECE and D. AVERY

Atomic Energy Research Establishment, Harwell, Berkshire

Summary. The mode of occurrence of uraninite, pitchblende and coffinite at five localities in south-west England is described. Chemical and isotopic analyses of concentrates containing these minerals provide the following $^{206}\text{Pb}/^{238}\text{U}$ ages (My.): uraninite, South Crofty, Cornwall, 277 ± 10 ; uraninite, Geevor, Cornwall, 223 ± 5 ; pitchblende-coffinite, King's Wood, Devon, 206 ± 5 ; pitchblende, Wheal Bray, Cornwall, 165 ± 4 ; pitchblende, South Terras, Cornwall, 47 ± 2 ; coffinite, Geevor, Cornwall, *c.* 45 (chemical analysis only). These results are compatible with geological and mineralogical evidence. Consideration of these and other results indicates that there were at least three periods of uranium mineralization in south-west England, at *c.* 290 My., *c.* 225 My., and *c.* 50 My. Other intermediate ages may also be valid but further work is required to substantiate these.

THE ages reported in this paper are on uranium minerals from five localities in south-west England spaced over a distance of about 90 miles from near Land's End to the south-eastern edge of Dartmoor. The specimens were taken from a variety of vein deposits, which include early E.-W. trending tin lodes and later N.-S. lodes with polymetallic mineralization.

Before describing the occurrences from which the analysed material was taken it is necessary to comment on the use of the terms uraninite and pitchblende. Uraninite is the name for the species as a whole, including all of its varieties (Fron del, 1958). Pitchblende is a variety of uraninite distinguished primarily by its appearance. In south-west England all detailed work to date shows that uraninite found there can be divided into two groups: a euhedral well-crystallized variety with a

significant thorium content and a cell size of $5.48 \pm 0.01 \text{ \AA}$; and a botryoidal poorly-crystallized variety of smaller cell size (in the range $5.45\text{--}5.40 \pm 0.01 \text{ \AA}$) and negligible thorium content. As these are found in different environments it is important to distinguish between them; therefore in this paper the name uraninite is restricted to the euhedral variety, and pitchblende to the other.

Geevor Mine. Geevor Mine at Pendeen near St. Just has been described in some detail by Dines (1956, pp. 83–90). Additional information is provided by Garnett (1963). The lodes are normal to the margin of the Land's End granite, and run approximately NW.–SE. entirely within granite. Recent work carried out by the Atomic Energy Division in conjunction with the mine geologist, Mr. R. Cox, although incomplete, has provided more detailed information than has been available hitherto on the occurrence of uranium within the mine. Three primary phases are present, uraninite, pitchblende, and coffinite; the last two commonly occurring together. Uraninite is associated with cassiterite in tabling concentrates and this has been the source of the material analysed to date. At the time the first age determination on uraninite from Geevor was published (Darnley, Smith, Chandler, Dance, and Preece, 1960) uraninite had not been found *in situ*, and in that publication the source of the mineral was wrongly attributed to the type of uraniferous occurrence described by Ostle in Dines (1956), where 'the uranium mineral occurs nearly everywhere in the sulphide-rich parts, close to the margins of the central quartz leaders'. Uraninite has since been isolated as a trace constituent in hand-specimens of tin ore taken from several lodes. The tin content of the specimens is between 1% and 4% SnO_2 , and the $e\text{U}_3\text{O}_8$ content between 30 and 200 ppm. The uraninite is identical in form, crystal size (20–40 microns) and cell size ($5.48 \pm 0.01 \text{ \AA}$) with that obtainable from tabling concentrates.

The uraniferous concentrations in the mine which can be detected radiometrically, such as those originally described by Ostle, are due to the presence of pitchblende with coffinite. Such occurrences have been found in Borehole Lode (Level 13), No. 3 Branch Lode (Level 12), Prospect No. 1E (Level 11), Pig Lode (Level 13), and Grenfell Lode (Level 11) (coffinite only). These identifications have been confirmed by X-ray powder photographs. Individual shoots of pitchblende–coffinite within particular lodes (e.g. on Grenfell Lode) have been traced by means of a Geiger counter for 300 ft vertically and 150 ft horizontally. Where the spatial relationships of the various stages of vein filling are apparent, pitchblende–coffinite is clearly associated with the final phase. Such an

example occurs in Coronation Lode on Level 10, where the paragenetic sequence following on reddening and kaolinization of the wall-rock granite is: (1) massive tourmaline (2 in.); (2) milky quartz cementing fragments of massive tourmaline and reddened granite (8 in.); (3) brownish milky quartz with scattered vughs (8 in.); (4) clearer milky quartz with sporadic pitchblende-coffinite mineralization along its margins and discontinuous vughy fissure at centre (4 in.); (5) earthy hematite along shear plane.

The age determinations in the present paper have been undertaken on material representing both types of uranium mineralization. The uraninite concentrate collected in January 1961, like the earlier concentrate collected in June 1957, could have been derived from a single point in the mine, or from several, depending upon the degree of mixing during transport and treatment of the ore. If different lodes, or different sections of lodes are of different ages, and if each contains uraninite then uraninite from the tables is likely to be a composite sample. However, concentrates collected after an interval of $3\frac{1}{2}$ years could not have been derived from the same location due to the steady progress of mining operations. The 1961 concentrate as collected assayed 0.68 % eU_3O_8 . This was upgraded by superpanning and electromagnetic separation, and provided a concentrate predominantly of uraninite with minor native bismuth and cassiterite. A qualitative X-ray fluorescence analysis of the final concentrate showed major U; subordinate Bi; minor Pb, Th; very minor Fe, Sn; trace Y and Ce group elements.

The coffinite-pitchblende concentrate which gave the chemical analysis shown in table VI was obtained from a 30 in. channel sample collected by Dr. R. H. T. Garnett assaying 3.1 % SnO_2 and 0.22 % eU_3O_8 taken on No. 3 Branch Lode, Level 12, 150 ft W. of cross-cut on North Pig Lode. Here much of the mineralized zone consists of highly-altered granite in which the original minerals and their textural relations have been almost completely replaced and obscured by chlorite, tourmaline, potassium feldspar, and minor cassiterite. The altered granite is cut by an irregular band of fractured pyrite, about an inch wide set in a calcite-dolomite gangue. Examination of a number of polished sections leads to the conclusion that there have been several stages of movement and mineral formation affecting this minor subdivision of the lode. The sequence appears to have been: (1) crystallization of pyrite; (2) movement and corrosion causing brecciation and rounding of pyrite; (3) sporadic growth of new faces on rounded pyrite cores (not found in all specimens); (4) development of coffinite, with minor chalcopyrite, mostly on pyrite

with crystalline overgrowths; (5) further fracturing of pyrite accompanied by displacement of coffinite where it coats the pyrite.

At this stage it appears that there was some minor replacement of pyrite by carbonate, but this is not prominent in most specimens examined. One specimen contains segments of broken botryoidal pitchblende within carbonate gangue. The carbonate also contains inclusions, sometimes blade-like, sometimes irregular, of chalcopyrite mantling bornite chalcocite and occasionally covellite. Some specimens contain coffinite surrounding such inclusions. The presence of unaltered carbonate points to the absence of supergene solutions.

The coffinite is unusually free from visible inclusions by comparison with most other Cornish examples of this mineral studied to date. It is colloform and in polished section is only distinguishable from pitchblende by its lower reflectivity. Diffraction lines attributable to pitchblende are just discernible in its X-ray powder photograph. At King's Wood it is quite clear that pitchblende has been substantially replaced by coffinite, but in this Geevor specimen, whilst the colloform appearance of the coffinite provides support for a replacement origin, co-precipitation of pitchblende and coffinite cannot be excluded. Mr. D. Atkin has indexed the diffraction lines of a powder photograph of the Geevor coffinite and determined the cell parameters as $a = 6.95 \pm 0.02 \text{ \AA}$, $c = 6.26 \pm 0.03 \text{ \AA}$.

Due to the similarity of density it proved impossible to obtain any significant separation of coffinite from the other metalliferous constituents by superpanning. Electromagnetic means were equally ineffective and consequently the channel sample could only be upgraded by a factor of about eight through removal of gangue constituents. A qualitative X-ray fluorescence analysis of the age determination concentrate showed major Sn; subordinate Fe, Cu; minor Ca, Ce group, Bi, U; trace Pb, Mn, Y, Zr, As.

South Crofty. South Crofty Mine is situated at Pool, between Camborne and Redruth, Cornwall, on the northern edge of the Carn Brea granite. The lodes described in detail in Dines (1956) are in granite and run approximately NE.-SW., parallel to the granite margin.

Uraninite has been identified by its diffraction pattern and cell size of $5.48 \pm 0.01 \text{ \AA}$ in grains isolated from a specimen of 8 % SnO_2 ore (taken from No. 12 Lode, 290 Fathom Level). The uranium content of this specimen is 20 ppm $e\text{U}_3\text{O}_8$. It thus appears that uraninite occurs at South Crofty in the same manner as at Geevor, as a trace constituent of the main tin mineralization.

Only a small amount of material was available to prepare the concentrate for analysis (results in table II) and, as at Geevor, this came from the highest density fraction produced in the mill circuit, and was probably derived from many tons of ore. The low grade of the starting material (0.8 % eU_3O_8) which was collected in June 1959 permitted it to be upgraded only to 15 % eU_3O_8 . Impurities in the concentrate submitted for analysis were principally cassiterite with lesser bismuth, pyrite, and a trace of galena.

Pitchblende with coffinite also occurs in South Crofty mine having been identified from No. 4 Lode, 260 Fathom Level, but an age determination has not yet been carried out on this material.

King's Wood. King's Wood Mine (Nat. Grid. Ref. SX/713665) is $1\frac{1}{2}$ miles ENE. of Buckfastleigh, South Devon, on the south-eastern side of Dartmoor. In 1918 a trial adit was driven at this locality to intersect a vein carrying copper minerals. In 1947 further excavations were carried out to ascertain the extent of the uranium mineralization which had been revealed by the original exploration.

According to Campbell (unpublished report) the vein which is in Upper Devonian slate, has a fairly constant NNW. strike, but in other respects it is very variable. Its dip varies from 20° to 90° depending on whether it is following a cleavage or a joint plane. Sometimes it cuts across both. Its width varies from a fraction of an inch to several inches, and it splits in places into two or three branches. Campbell remarks that the limits of the vein are always well defined, and there appears to be no dissemination of ore in the country rock. Mineralization is apparently restricted to those parts of the milky quartz lode that have suffered later brecciation, uranium being found where this brecciation is particularly prominent. The material for age determination was collected *in situ* in 1959, and was taken from the richest exposed part of the vein, on the south side of No. 2 Winze.

Both macroscopically and microscopically the mineralized zone shows marked variation. Polished sections show that vein quartz has been brecciated, and pitchblende with galena, chalcopyrite, cobaltiferous rammelsbergite, and native bismuth has been deposited in the fractures, with coffinite forming much of the matrix, and marginally replacing the pitchblende. Veinlets of pyrite appear to cut across the earlier formed minerals, and there is a later series of micro-veinlets filled with a yellow hydrated uranium mineral which structurally resembles *sabugalite*. At a magnification of 800 diameters no oxidation can be discerned beyond the margins of these veinlets, nor does chalcopyrite enclosed by them

TABLE I. Geevor uraninite (NCL1105)

Chem. anal. wt. %	Lead-isotope proportions in:				Isotopic ages	
	Uraninite	Common lead	Uraninite (corrected)	My.		
Pb 2.22 ± 0.03	²⁰⁴ Pb 94.1 ± 0.2	≥ 0.006 18.20	1 94.0	207/206	257 ± 120	
U 69.88 ± 0.14	²⁰⁶ Pb 4.90 ± 0.15	15.51	4.81	206/238	223 ± 5	
Th 1.34 ± 0.03	²⁰⁷ Pb 0.945 ± 0.005	37.97	0.717	207/235	226 ± 15	
	²⁰⁸ Pb			208/232	274 ± 125	

TABLE II. South Crofty Uraninite (NCL1013)

Chem. anal. wt. %	Lead-isotope proportions in:				Isotopic ages	
	Uraninite	Common lead	Uraninite (corrected)	My.		
Pb 0.52 ± 0.01	²⁰⁴ Pb 90.8 ± 0.1	≥ 0.074 18.20	1 89.45	207/206	309 ± 370	
U 12.51 ± 0.05	²⁰⁶ Pb 5.83 ± 0.09	15.51	4.68	206/238	277 ± 10	
Th 0.20 ± 0.005	²⁰⁷ Pb 3.35 ± 0.08	37.97	0.54	207/235	280 ± 50	
	²⁰⁸ Pb			208/232	321 ± 850	

TABLE III. King's Wood pitchblende-coffinite (NCL1030)

Chem. anal. wt. %	Lead-isotope proportions in:				Isotopic ages	
	Pitchblende- coffinite	Common lead	Concentrate (corrected)	in My.		
Pb 1.60 ± 0.03	²⁰⁴ Pb 66.6 ± 0.2	0.55 ± 0.01 0.4793	0.0263 56.4	207/206	268 ± 190	
U 32.725 ± 0.03	²⁰⁶ Pb 11.6 ± 0.1	0.4085	2.9	206/238	206 ± 5	
Th 0.003	²⁰⁷ Pb 21.2 ± 0.2	1	0	207/235	211 ± 20	
	²⁰⁸ Pb					

TABLE IV. Wheal Bray pitchblende (NCL1015)

Chem. anal. wt. %	Lead-isotope proportions in:				Isotopic ages	
	Pitchblende	Common lead	Pitchblende (corrected)	in My.		
Pb 0.876 ± 0.018	²⁰⁴ Pb 0.726 ± 0.014	0.0263	(-0.007)	207/206	91 ± 140	
U 18.04 ± 0.02	²⁰⁶ Pb 13.34 ± 0.04	0.4793 0.4085	45.5 2.17	206/238	165 ± 4	
Th 0.002	²⁰⁷ Pb 27.35 ± 0.07	1	0	207/235	160 ± 10	
	²⁰⁸ Pb					

TABLE V. South Terras pitchblende-coffinite (NCL1103)

Chem. anal. wt. %	Lead-isotope proportions in:				Isotopic ages in My.	
	Pitchblende- coffinite	Common lead	Concentrate (corrected)			
Pb 1.04 ± 0.02	²⁰⁴ Pb 0.949 ± 0.004	0.0263	(0.008)	207/206	411 ± 400	
U 49.34 ±	²⁰⁶ Pb 47.0 ± 0.1	0.4793	29.8	206/238	47 ± 2	
0.08	²⁰⁷ Pb 16.25 ± 0.04	0.4085	1.63	207/235	55 ± 9	
Th 0.0045	²⁰⁸ Pb 35.8 ± 0.4	1	0			

The method of calculation is based on Tables for the calculation of Lead Isotope Ages by Stieff, Stern, Oshiro, Senftle (1959).

The errors quoted with the lead-isotope analyses are twice the standard error of the mean.

All the common lead corrections are based on the average of South-West England galena analyses published by Moor bath (1962).

The accuracy given with each apparent age has been obtained by substituting the extreme values shown by the analytical results in the various stages of calculation so as to obtain maximum and minimum ages, and adding to these the uncertainty in the accepted values of the physical constants as given by Stieff *et al.*

show any signs of oxidation. One polished section shows particularly well-developed zonal growth structures, forming angular and colloform patterns in which rammelsbergite is interlayered with arsenolite (As_2O_3), in such an ordered manner as to suggest the arsenolite is of primary origin.

Galena occurs as a fine dissemination within areas of coffinite and pitchblende. Within pitchblende it is concentrated both in syneresis fractures and in zonal concentrations related to botryoidal textures. Chalcopyrite is similarly distributed. Larger areas of galena-chalcopyrite occur outside the pitchblende, and galena with lathlike inclusions of native bismuth is apparent at high magnifications. Galena was evidently co-precipitated with the other constituents.

The cell dimensions of the King's Wood coffinite are somewhat different to those of the coffinite from Geevor, referred to in a preceding section, being

$$a = 6.98 \pm 0.02 \text{ \AA}, \quad c = 6.19 \pm 0.03 \text{ \AA}$$

The cell size of pitchblende from the concentrate is $5.43 \pm 0.01 \text{ \AA}$.

The material for analysis was prepared from fragments selected from a sample weighing 45 lb. Fragments with any superficial coating of secondary minerals were rejected, and a concentrate was prepared from the remainder by repeated superpanning and electromagnetic separation. No secondary minerals were visible in the final concentrate, which

weighed 5 g and had the following heavy element composition: major U; subordinate Bi, Ni, Fe, As; minor Pb, Co, Cu; very minor Zr. An autoradiograph of the final concentrate shows that some migration of uranium decay products had taken place as indicated by the presence of point sources of intense alpha activity attributable to radium. The results of the analysis are given in table III.

Wheal Bray. Wheal Bray is an old copper mine, 2 miles WNW. of the village of Altarnun on the NE. side of Bodmin Moor (Nat. Grid Ref. SX 199823). The copper is confined to E.-W. lodes, whereas the uranium is associated with NNE. fractures, but it is best developed at the intersection of the two. The uranium occurrences are all in granite, within a few hundred yards of its contact with metamorphosed Upper Devonian sediments (Beer, unpublished report).

The concentrate prepared for analysis was obtained from a drill core at the intersection of the Middle Lode (E.-W.) with Rodd's crosscourse (N.-S.), at a vertical depth of 80 ft below surface. The same crosscourse was exposed by surface trenching, where it was examined in some detail. The main mineral developed is milky quartz, which is somewhat reddened where uranium is present. The central portion of the vein has a distinctive platy triangular boxwork structure, with cavities filled with smoky quartz. Microscopic examination shows that this texture results from the replacement of an earlier tabular mineral by quartz. The outlines of the original crystals are clearly marked by trains of dusty inclusions and the habit is similar to that exhibited by baryte. Support for the conclusion that quartz pseudomorphs baryte is provided by the presence of similar textures in uraniferous veins on the Kircudbrightshire coast, near Dalbeattie, where the replacement of baryte by quartz is only partial.

Within the platy portion of the Wheal Bray vein is a zone of very reddened vuggy quartz containing pitchblende. In the specimen used for analysis the pitchblende is distributed over a width of 2.5 cm, in small botryoidal aggregates averaging about 0.5 mm in diameter, occasionally being as large as 1.5 mm. These aggregates are rimmed by finely crystalline cobaltiferous rammelsbergite. Inclusions of rammelsbergite are present within the pitchblende. There is no visible galena. At high magnifications the pitchblende has a finely mottled appearance, but no coffinite¹ appears to be present. The mottling results from the presence of an unnamed and poorly characterized hydrated uranyl

¹ 'Coffinite' from 'Holmans Test Mine', Camborne, Cornwall (SW/657368; 2 miles SSE. of Camborne Station), has $a = 7.03 \pm 0.02 \text{ \AA}$, $c = 6.13 \pm 0.03 \text{ \AA}$.

arsenate, possibly an Al analogue of novacekite. This mineral fills fractures within pitchblende, and also a few microfractures cutting across the specimen. Autoradiographs of the vein material from the drill core show none of the radium concentrations commonly found in specimens where there has been migration of decay products. Vugs within the vein contain prismatic growths of the same novacekite-type mineral already referred to, and the walls of these vugs are lined with colloform cobaltian pyrite. Inclusions of pyrite have been noted within the prisms of the hydrated uranium mineral. These observations coupled with the absence of any signs of supergene alteration suggests that all the minerals present could be of hydrothermal origin.

The concentrate for analysis was prepared from a piece of core, cut so as to avoid all large vugs, and upgraded by repeated superpanning and electromagnetic separation. The amount of hydrated uranyl mineral present in the concentrate was not more than 2 % by volume. An optical spectrographic analysis of the vein material showed major Si; subordinate U, Ni, Co, As; minor Mg, Fe, Cu, Ca. The cell size of the analysed pitchblende is 5.42 ± 0.01 Å. The results of the age determination analysis are contained in table IV.

South Terras. South Terras Mine is 1 mile SW. of St. Stephen, Cornwall, and is notable as the only mine in Great Britain which was ever worked primarily for uranium. The workings, which were on a small scale by Cornish standards, have been flooded since 1928. An account of the mine is given in Dines (1956).

During 1952 and 1953 drilling was undertaken in the immediate vicinity of South Terras under the direction of the Atomic Energy Division to find if there was any extension of the known ore shoot in depth, or along the same strike. No economic extensions were found, but three drill holes intersected uraniumiferous mineralization, and material from one of these was used for the present age determination. The results of the exploration were given in an unpublished report by Ostle and Cosgrove. These showed that an identifiable N.-S. structure extends over a distance of at least 2300 ft, but that the main uranium mineralization only occupies the southernmost third of this length, the remainder of the structure being marked by predominantly barren comby quartz. At the southern end, the vein does not extend beyond an elvan (quartz porphyry) dyke, and in depth the vein narrows.

The uraniumiferous material which provided the analysis under discussion was obtained from borehole A4 between the (inclined) depths of 127 ft and 130 ft. This position is approximately 160 ft WSW. of the

main lode at its nearest point, at a depth of about 90 ft. The borehole log records 'slate with jasper lenses', 124 ft–129 ft; 'yellow altered greenstone', 129 ft–130 ft; 'slate with greenstone bands', 130 ft–137 ft. The core recovered from this length was all crushed for assay, and only one small piece taken at 128 ft was retained intact for detailed examination in polished section. The host rock consists of irregular aggregates of yellow chloritic material replaced in part by quartz. Larger areas of

TABLE VI. Geevor coffinite–pitchblende (NCL1104)

	1104 M	1104 H	1104 T
Pb	< 0.02 > 0.005	0.004	0.007
U	1.47	0.62	1.30
Th	0.012	n.d.	n.d.
Chemical age (My.)	> 25 < 100	45	40

Ages obtained from graphs published by Wickman (1944).

quartz contain euhedral crystals of pyrite. This early quartz–pyrite phase apparently formed the walls of an open fissure and was overlain by a thin coating of unzoned well-formed botryoidal pitchblende, followed by siderite. Isolated grains of botryoidal pitchblende are scattered through the siderite. Chalcopyrite mantles the pitchblende and appears to be later. Prismatic crystals of marcasite, blebs of irregular sphalerite, and some late pyrite are also present. Minor amounts of galena are associated with chalcopyrite, but not with the pitchblende. No coffinite is apparent in association with pitchblende in the carbonate gangue. However, there are separate areas of pitchblende–coffinite in quartz which could be a separate (and possibly older) generation within the specimen. The cell size of the pitchblende is 5.40 ± 0.01 Å. The unaltered nature of the carbonate points to the absence of supergene alteration.

The analysed concentrate (see table V) was prepared from the crushed core material which assayed 0.48 % eU_3O_8 . A hundredfold concentration was affected by repeated superpanning and electromagnetic separation. A qualitative X-ray fluorescence analysis of the concentrate indicated: major U, Fe; subordinate Pb; minor As, Cu, Mn; trace Zr, Ni, V, Sb, Co.

Discussion

The most notable feature of the results given above is the wide distribution of ages obtained from different localities, and in the case

of Geevor, from within the same mine. They range over about 250 My., from Upper Palaeozoic to Lower Tertiary. The results conflict with previously held concepts of the origin and age of mineralization in south-west England, so particular attention must be paid to their reliability and interpretation.

In the complementary paper on this subject presented by Pockley in another number of this Journal he has considered in some detail the analytical reliability of results which show a similar age range to those discussed here. He pays particular attention to the reproducibility of mass spectrometer analyses and the possibility of contamination and demonstrates that these could not explain the spread of results obtained.

In considering the apparent ages calculated from the different isotope ratios and comparing them one with another the $^{207}\text{Pb}/^{206}\text{Pb}$ results should be disregarded due to their unreliability in such comparatively young material. This is illustrated by the low accuracy quoted for the $^{207}\text{Pb}/^{206}\text{Pb}$ results. The $^{206}\text{Pb}/^{238}\text{U}$ age is preferred as the most reliable indicator of age because it is least sensitive to mass spectrometer errors and the uncertainty associated with the common lead correction. It is susceptible to radon loss, unlike the $^{207}\text{Pb}/^{235}\text{U}$ ratio which is not, but the close agreement of the two ratios in all the full analyses reported shows that radon loss is not appreciable. Pockley, for similar reasons, has also selected the $^{206}\text{Pb}/^{238}\text{U}$ ages as being most significant. It is the age derived from this ratio that is used throughout the subsequent discussion.

The chemical analysis of the Geevor coffinite concentrate (table VI) has been included in the absence of an isotopic analysis because of its special significance. The very low lead content has not yet permitted extraction of sufficient lead for isotopic analysis. The results are therefore only significant if it is assumed that the parent material has not been subjected to any leaching or enrichment of uranium or lead, and if no common lead is present. Specimen material, which has been described in an earlier section, is microscopically quite unaltered, and shows no visible galena. The fact that different concentrate fractions containing varying mineral proportions give comparable results suggests that no separate lead phase is present. This does not exclude the probability that some common lead is contained in the coffinite, which would tend to make the chemical ages maxima rather than minima; thus the inference of a Tertiary age seems justifiable.

In the case of the South Crofty uraninite concentrate it was only possible to assign an upper limit to the ^{204}Pb content, and in consequence this analysis shows the greatest uncertainty.

In recent years when age determinations carried out on uranium minerals from particular areas have provided a range of ages, there has been a tendency on the part of certain workers to rely upon a graphical construction to provide a solution. Wetherill (1956) showed that where uranium minerals of the same age have been subjected to chemical

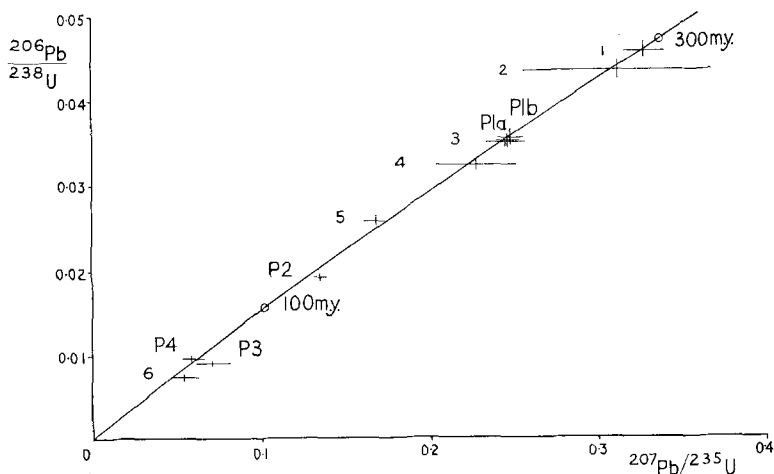


FIG. 1. A plot showing the relationship between the ratios $^{206}\text{Pb}/^{238}\text{U}$ and $^{207}\text{Pb}/^{235}\text{U}$ for all analysed uranium minerals from south-west England. For further explanation see text. The lengths of the horizontal and vertical lines indicate the analytical uncertainty of each measurement.

Analyses prefixed P are reported by Pockley (in press). 1, Uraninite, Geevor (Darnley *et al.*, 1960); 2, Uraninite, South Crofty; 3, Uraninite, Geevor; 4, Pitchblende-coffinite, King's Wood; 5, Pitchblende, Wheal Bray; 6, Pitchblende, South Terras; P1A, P1B, Pitchblende-coffinite, South Terras; P2, Pitchblende-coffinite, Redruth area; P3, Pitchblende-coffinite, South Terras; P4, Pitchblende-coffinite, Wheal Owles.

alteration involving a loss or gain of uranium or lead, the discordant ratios $^{206}\text{Pb}/^{238}\text{U}$ and $^{207}\text{Pb}/^{235}\text{U}$ when plotted against each other will fall on a straight line. This line cuts a concordia curve at two points, representing the original age and the time of alteration. The concordia curve is the line along which concordant ratios must fall. Unfortunately, the amount of curvature over the last 300 My. of the curve is so slight in relation to the accuracy of the determinations that this approach is of no assistance in explaining the present results. All the determinations from SW. England, including Pockley's, are plotted in fig. 1. Most of them fall on the concordia curve within the limits of accuracy of the

analyses, but equally within those limits most of them could fall on an indeterminate number of possible chords. Only when the analytical uncertainty in results can be greatly reduced, or when there are many more analyses of closely studied and localized material, is this method of interpretation likely to be of positive help over the time span considered here.

Therefore, it is necessary to rely on mineralogical and geochemical criteria to assess whether the present pattern of results is a consequence of supergene processes. The steps taken to avoid having any supergene mineral in the final concentrate have been described earlier. The consequences of including material that has been affected by supergene processes are apparent from considering the relative solubilities of uranium and lead under such conditions. In the zone of leaching where uranium is much more readily removed, primary uranium minerals are replaced *in situ* by hydrated uranyl minerals, resulting in a decrease in the uranium to lead ratio and hence an increase in the apparent age. In the zone of enrichment, reprecipitation of uranium is likely to take the form of fissure and cavity coatings of supergene minerals, so that the age of a bulk sample would show a decrease. In south-west England observation indicates that leaching and enrichment take place almost side by side. A comparison of the ages given by 'whole-vein' material and carefully separated pitchblende from an outcrop on the north shore of the Solway Firth, Scotland (Darnley, unpublished report) shows that weathered bulk-vein material gives excessive uranium-lead ages. The 'chemical age' of material from the outcrop of the Wheal Bray pitchblende vein described in this report is 750 My. (unpublished analysis), as compared with a 'chemical age' of 340 My. for the vein in depth. Thus the over-all conclusion is that supergene alteration cannot explain the pattern of results obtained.

The possibility must now be considered that the calculated ages have been given by concentrates that were mixtures of material of different ages, and that none of the results necessarily represents a single phase of mineralization. Arising from the way in which the uraninite was obtained, this possibility might apply to the concentrates from Geevor and South Crofty Mines. The figure of 290 My. originally obtained from Geevor (Darnley *et al.*, 1960), and the figure of 223 My. given here, may be mean ages of uraninite from different sections of the mine. In this case, the only firm conclusion about the uraninite mineralization at Geevor is that some of it must be older than 290 My. and some of it must be younger than 223 My. This problem will only be resolved by

further analyses now in progress. However, from consideration of other results from the region it is likely that the figure of 290 My. is not far below the maximum age at which mineralization could have occurred. Because of the results obtained from Geevor, it seems probable that there were also several ages of uraninite formation at South Crofty, in which case the 277 My. result cannot be accepted as providing certain evidence of primary mineralization at this time.

In contrast to the uraninite ages, the ages obtained from pitchblende and coffinite concentrates are derived from small volumes of vein material taken from selected places. In those instances where uranium appears to be of one generation there is little likelihood of the apparent age not being close to the true age, unless radiogenic lead has been incorporated in the single phase present at the time of its formation, in which case its age will be high rather than low. Instances where mineralization of this type is predominantly one phase are Wheal Bray (pitchblende), South Terras (pitchblende), and Geevor (coffinite). At King's Wood (also in several of Pockley's specimens) there are clear textural indications of coffinite replacing pitchblende. However, this is not necessarily an indication that a substantial time gap is involved.

If we include consideration of Pockley's results, there seems to be no reasonable grounds for not accepting the Tertiary ages obtained from South Terras, Geevor, and Wheal Owles as reliable indications of Tertiary mineralization. Pockley's duplicated analyses of older (*c.* 225 My.) pitchblende-coffinite from South Terras (which it should be noted differs considerably in appearance from the younger material described here) also have every justification for being regarded as the age of a real event. The fact that the analysis of two separate portions of an inhomogeneous specimen agree so well suggests that the phases present are contemporaneous.

Of the intermediate ages from King's Wood and Wheal Bray, the textural relations of the two phases in the former warrant some hesitation in accepting its age as that of a real event. The Wheal Bray age however, appears to be valid, though clearly it cannot be regarded as established until additional analyses have been carried out.

It should be noted that whereas the older uranium ages have been obtained on high-temperature minerals from veins of the main ENE. trend (at Geevor in the extreme west of Cornwall this becomes NW.-SE.) the younger ages come from lower temperature minerals in N.-S. structures. The only exceptions found so far are in the extreme west, at Geevor and Wheal Owles (Pockley, *in press*), where late in-filling of tin

lodes give Tertiary ages. The N.-S. lodes (sometimes called crosscourses) have long been recognized as almost everywhere later than the main ENE. lodes, and De la Beche (1839), Collins (1896), Hill (1901), and McAlister (1906) assigned a Tertiary Age to them. The recent results summarized in table VII suggest that they were subjected to mineralization at different times between Upper Permian and Upper Eocene. In the first part of this paper attention was drawn to the number of distinct

TABLE VII

Locality ¹	Lode ²	Mineral	Associated Metals ³	²⁰⁶ Pb/ ²³⁸ U age (My.)
Wheal Owles	E.-W. (late in- filling)	Pitchblende	Fe Pb Zn Bi	58 ± 3 ⁴
Geevor	E.-W.	Uraninite (mine ore 1957)	Sn	290 ± 7
	E.-W.	Uraninite (mine ore 1961)	Sn	223 ± 5
	E.-W. (late in- filling)	Coffinite-pitchblende	Fe Cu Bi	c. 45 (chemical age)
South Crofty	E.-W.	Uraninite (mine ore 1959)	Sn	277 ± 10
South Terras	N.-S.	Pitchblende-coffinite	Pb Fe As	225 ± 5 ⁵
	N.-S.	Pitchblende-coffinite	Fe Cu	47 ± 2
Wheal Bray	N.-S.	Pitchblende	Co Ni Cu Fe As	165 ± 4
King's Wood	N.-S.	Pitchblende-coffinite	Fe Co Ni Cu Bi Pb As	206 ± 5

¹ Localities are listed in geographic order, from west to east.

² Lode directions are generalized according to Dines (1956).

³ Only elements known to be present in more than trace amounts in the parent material are included.

⁴ Pockley (in press).

⁵ Mean of two analyses by Pockley (in press).

vein fillings that can be seen in the lodes at Geevor. It is well known that such repetition is characteristic of mineral veins in many parts of the world, but hitherto evidence has been lacking as to the time interval between the successive stages. The results from Geevor indicate that this may be of the order of tens or hundreds of millions of years.

Additional support for the reliability of the results presented can be obtained by considering some of the other ages obtained from south-west England. The mean age of biotite from Dartmoor granite is 285 ± 8 My. according to the Rb-Sr method (Lambert and Mills, 1961), and 265 ± 5 by K-Ar (Dodson, Miller, and York, 1961). By the same methods the age of biotite from Land's End granite is 270 ± 9 and 250 ±

15 respectively (Lambert and Mills). By either method the age of the Land's End biotite is clearly incompatible with the older uraninite age (290 ± 7 My.) obtained from Geevor, where all the mineralized lodes are younger than the granite. Since this Geevor analysis is satisfactorily concordant suspicion must fall on the biotite analyses. The discrepancies between the Rb–Sr and K–Ar results from these micas (which are greater than the discrepancies shown by micas in British Caledonian granites, for example) suggest that biotite may have been subjected to some alteration at a time appreciably later than its initial formation, giving rise to some loss of Sr and Ar. Such alteration could be connected with the extensive kaolinization of the south-west England granites. There is no evidence at present to show when kaolinization took place, or whether it took place in several stages, and there is nothing to exclude the possibility that it occurred tens of millions of years after the intrusion of the granites. At the time of writing the most reliable age for a Hercynian granite in the English Channel region may be that of the Huelgoat granite in Brittany; biotite has given a K–Ar age of 290 My. and Rb–Sr age of 293 My. (Deutsch and Chauris, 1960).

Recent results all serve to underline the fact that igneous activity in the region was not confined to the immediate aftermath of the Hercynian orogeny. Mesozoic ages have been obtained by Miller and Mohr by K–Ar analysis of whole-rock and sanidine from the Wolf Rock phonolite (*c.* 115 My.), and of whole rock from the Epson Shoal phonolite (*c.* 130 My.) (P. A. Mohr, personal communication). Tertiary igneous activity in south-west England has been firmly established by several analyses of the Lundy Island granite, which give results in the range 50–55 My. (Miller and Fitch (1962) and Dodson and Long (1962)). From other parts of England, Moorbath (1962) has obtained a considerable number of galena ages which fall in the range between 180 and 230 My.

A major question which arises from the ages now available is whether the later events are a consequence of those processes variously described as rejuvenation, regeneration, reworking or remobilization, or whether they represent fresh introductions of ore fluid from the same sources as provided the first mineralization in the area. It is fairly well known that the ages obtained by isotopic analysis of non-radioactive lead minerals such as galena do not date the same event as analyses of radioactive lead-bearing minerals. The former results date the time at which lead left its original source, deep within the crust, or within the upper mantle, whereas results of the latter date the time of crystallization of the radioactive mineral in its present site. A primary mineralization would only

seem to be well established where the ages provided by both radioactive and non-radioactive lead minerals are reasonably close together (say ± 10 My.). This would imply both the separation of ore material from its primary source, and its emplacement within the upper crust during the same period of activity.

Moorbath (1962) analysed seven galena specimens from south-west England and following from his choice of constants these give a mean model age of 280 My. Individual results range between 260 and 300 My. To establish that the uranium minerals of post-Hercynian age were emplaced by the same type of process as emplaced the 'Hercynian' (c. 290 My.) minerals it is necessary to find galena with a post-Hercynian model age. So far four such ages have been obtained, but they are not sufficiently well established to be accepted *without reserve*. It should be understood that the precision of galena ages is much lower than uranium-lead results. They are as follows:

Geevor Mine (Lode 33, Level 12)	220 My.
North Wheal Tamar, Devon	165 My.
Crow Hill, Cornwall	140 My.
South Terras, Cornwall	80 My.

These results have been calculated using Moorbath's constants, from the tables compiled by Pockley (1961). If these provisional results can be substantiated, then it would seem that a similar mineralization process has been operating throughout the period covered.

In conclusion, evidence at present available indicates that there were at least three periods in south-west England when uranium minerals were formed, c. 290 My., c. 225 My., and c. 50 My. There appears to be no analytical or other reason why the age of c. 165 My. obtained from Wheal Bray should not date a period of mineralization. A comparison of these results with others obtained in Western Europe, together with comments on the implication of these and other results in terms of mineralizing processes will be published elsewhere.

Acknowledgements. The co-operation of the management of Geevor Tin Mines Ltd. and South Crofty Ltd. is gratefully acknowledged, and in particular the assistance given by Dr. R. H. T. Garnett and Mr. R. Cox.

References

- BEER (K. E.), 1958. Investigations at Wheal Bray, Altarnun, Cornwall. Report No. 202, Atomic Energy Division, Geol. Surv. Gt. Brit. (unpublished).
 CAMPBELL (C. B.), 1947. Geological and radiometric report on King's Wood Mine. Report No. 20, Atomic Energy Division, Geol. Surv. Gt. Brit. (unpublished).
 COLLINS (J. H.), 1896. *J. roy. Instn. Cornwall*, vol. 13, p. 283.

- DARNLEY (A. G.), CHANDLER (T. R. D.), ENGLISH (T. H.), FIDLER (P. A.), JAMES (O.), PREECE (E. R.), and PROSSER (N. J. D.), 1962. Pitchblende from Sandy-hills, Kircudbrightshire. Age Determination Report No. 20. Atomic Energy Division, Geol. Surv. Gt. Brit. (unpublished).
- SMITH (G. H.), CHANDLER (T. R. D.), DANCE (D. F.), PREECE (E. R.), 1960. *Min. Mag.*, vol. 32, p. 654.
- DE LA BECHE (H. T.), 1839. Report on the geology of Cornwall, Devon, and West Somerset. *Mem. geol. Surv. Gt. Brit.*
- DEUTSCH (S.), and CHAURIS (L.), 1960. *C. R. Acad. Sci., Paris*, vol. 250, p. 1298.
- DINES (H. G.), 1956. Metalliferous Mining Region of South-West England. *Mem. geol. Surv. Gt. Brit.*
- DODSON (M. H.), MILLER (J. A.), and YORK (D.), 1961. *Nature, Lond.*, vol. 190, p. 800.
- , and LONG (L. E.), 1962. *Ibid.*, vol. 195, p. 975.
- FRONDEL (C.), 1958. Systematic Mineralogy of Uranium and Thorium. *Bull. U.S. geol. Surv.* 1064.
- GARNETT (R. H. T.), 1963. Polyascendent Zoning in the No. 3 Branch Lode of Geevor Tin Mine, Cornwall. Symposium Problems of Postmagmatic Ore Deposition, vol. 1, p. 97. Prague.
- HILL (J. B.), 1901. *Trans. R. geol. Soc., Cornwall.*, vol. 16, p. 279.
- LAMBERT (R. St. J.), and MILLS (A. A.), 1961. *Ann. N.Y. Acad. Sci.*, vol. 91, art. 2, p. 378.
- MCALISTER (D. A.), 1906. In Geology of Falmouth and Truro and of the Mining District of Camborne and Redruth. *Mem. geol. Surv. Gt. Brit.*
- MILLER (J. A.), and FITCH (F. J.), 1962. *Nature, Lond.*, vol. 195, p. 553.
- MOORBATH (S.), 1962. *Phil. Trans., Sec. A*, vol. 254, p. 295.
- OSTLE (D.), and COSGROVE (M. E.), 1953. The South Terras Uranium Mine, Cornwall. Report No. 138, Atomic Energy Division, Geol. Surv. Gt. Brit. (unpublished).
- POCKLEY (R. P. C.), 1961. Lead Model Age Tables. Dept. of Geology and Mineralogy, Oxford University (cyclostyled edition).
- , 1964. Four New Uranium-lead Ages from Cornwall. *Min. Mag.* (in press).
- STIEFF (L. R.), STERN (T. W.), OSHIRO (S.), and SENFLE (F. E.), 1959. *Prof. Pap. U.S. geol. Surv.* 334-A.
- WETHERILL (G. W.), 1956. *Trans. Amer. geophys. Un.*, vol. 37, p. 320.
- WICKMAN (F. E.), 1944. *Arsb. Sverig. geol. Unders.*, vol. 37 (1943), p. 3.
-