FACTORS INVOLVED IN DISCORDANT AGES OF EUXENITE FROM A GRENVILLE PEGMATITE[1]

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ABSTRACT

Metamict euxenite crystals from a pegmatite in Grenville rocks near St. Pierre de Wakefield, Quebec gave the following ages: Pb^{207}/Pb^{206} 1,000 m.y., Pb^{207}/U^{235} 710 m.y., Pb^{206}/U^{238} 620 m.y., and Pb^{208}/Th^{232} 550 m.y. Age of coeval microcline from this pegmatite by Rb/Sr is 1,050±50 m.y. Total Pb, U and Th analyses and Pb isotope analyses were made of different parts of the euxenite crystals and of the minerals enveloping them. Results of this work suggest that discordance in ages is due primarily to the following factors: 1. differential loss of uranium, relative to thorium from the outer zones of the euxenite, 2. Overall loss of lead from the euxenite with some evidence of greater loss of Pb^{208} than of Pb^{207} and Pb^{206}.

Experiments on driving off lead from metamict uranothorite and crystalline thorianite, both of Grenville age, by heating under vacuum, showed that lead from the metamict mineral is easily driven off but that from the crystalline mineral is much more difficult to move.

INTRODUCTION

Discordance in ages determined on a single mineral by the Pb^{206}/U^{238}, Pb^{207}/U^{235} and Pb^{208}/Th^{232} ratios is so common that it has been the subject of many papers (Kulp & Eckelman, 1957; Vinogradov *et al.*, 1960; Russell & Farquhar, 1960). In particular, the Pb^{208}/Th^{232} age is rarely concordant with the two lead/uranium ages, and in altered and metamict minerals it is usually anomalously low. For pitchblende in the Uranium City region of Saskatchewan, a great preponderance of results gave higher ages by the Pb^{207}/U^{235} ratio than by Pb^{206}/U^{238}. In 45 specimens of uraninite and thorianite from the Bancroft district, Ontario, however, there is no consistent difference in age as determined by these two Pb/U ratios.

These discordances in age have been resolved mathematically by assuming one or a combination of the following factors: (*a*) loss or gain of radiogenic lead as a continuous or intermittent process; (*b*) fractionation of radiogenic lead during its escape from the host mineral; and (*c*) differential loss or gain of uranium relative to thorium from the host mineral. A useful recent paper by Nielsen (1960) presents comment on this whole subject. A more direct approach taken by Tilton (1956) showed

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that proportions of elements leached from radioactive minerals by washing them in weak acids are consistent with discordances in their ages as determined by the different ratios.

The present paper records I, results of a preliminary investigation seeking direct evidence of postulated losses of parent and daughter elements and/or isotopes in a natural occurrence of euxenite; and II, results of experiments in driving off lead by heating metamict uranothorite and crystalline thorianite under vacuum. A brief description of the extractive and analytical methods used is given because possible errors inherent in them have not been fully assessed.

It is a pleasure to acknowledge the kindness of Mr. R. Lachaine who not only gave us the samples from his pit, but blasted out selected areas for us. Our thanks are tendered also to Bicroft Uranium Mines and their geologists, Messrs. H. Kozak and E. E. G. Heaslip, for specimens of uranothorite and analyses of them; and to our associate, Mr. G. R. Lachance who was particularly helpful in providing *x*-ray fluorescence analyses as the study progressed.

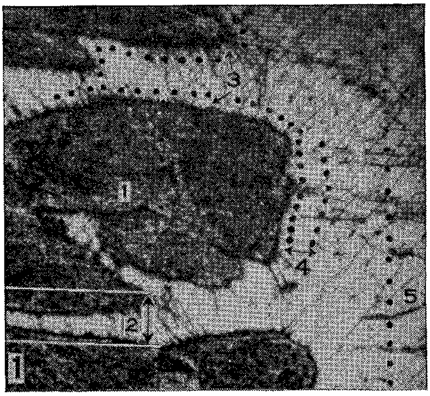
MINERALOGY

I. Metamict euxenite crystals and adjacent minerals in a pegmatite from near St. Pierre de Wakefield were collected for this study. Approximate ages of these crystals based on *x*-ray fluorescence analysis of U, Th and Pb and isotopic analysis of the lead are Pb^{207}/Pb^{206} 1,000 m.y., Pb^{207}/U^{235} 710 m.y., Pb^{206}/U^{238} 620 m.y., and Pb^{208}/Th^{232} 550 m.y. Age of microcline that occurs in large fresh crystals in this pegmatite, as determined by Rb/Sr is 1,050 m.y. ± 50 m.y. These results are typical of many from the Grenville Province of the Canadian Shield.

The pegmatite is exposed in a pit operated by Mr. R. Lachaine of St. Pierre de Wakefield. It is situated on the West side, and within 20 feet, of a road from St. Pierre de Wakefield to Ecluse Lake on lots 23 and 24 of range IX of Wakefield township, Quebec.

This pegmatite is being mined for its excellent pale green microcline that occurs in anhedral crystals up to 2′ in diameter and which, with quartz, forms a major part of the deposit. The euxenite crystals are restricted to a zone of pink albite with some interstitial microcline near the centre of the body, and are locally associated with deep purple fluorite. Although it is probable that zones in this pegmatite differ slightly in age, it is believed that these differences are less than can be measured by methods discussed here. For this paper therefore it is assumed that the euxenite and microcline are coeval.

Euxenite occurs in rounded subhedral crystals up to one inch in diameter. Around their margins, lath-like euxenite is intergrown with albite (Figs. 1 to 4). The euxenite is metamict and, as seen in polished section (Fig. 3), consists of light grey (a), medium grey (b), and dark grey (c) phases. In transmitted light phase (a) appears red, phase (b) is yellow and phase (c) is colourless. Phase (c) is always present along fractures and margins of the crystals and is thought to be a product of incipient supergene alteration. Powdery to partly colloform crusts of goethite and hematite (d) (Fig. 2) coat the euxenite crystals and are found in the wider fractures in them.



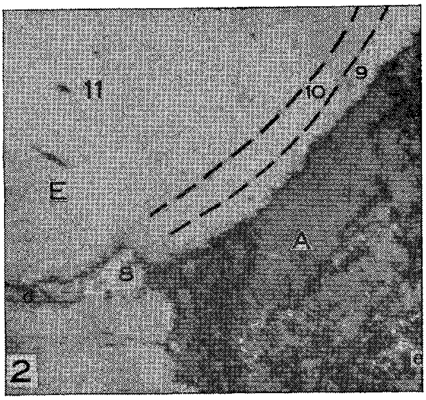
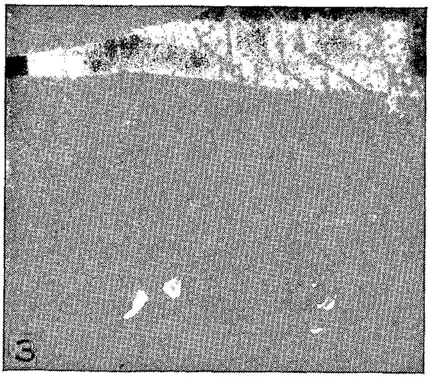


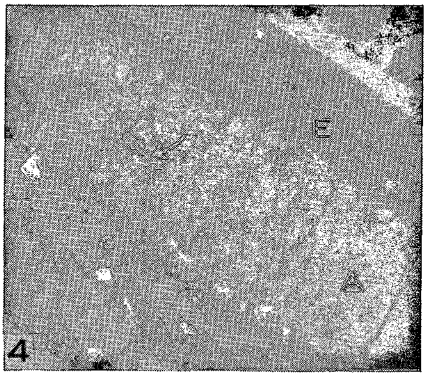
FIG. 1. (Transmitted light, ×37). Showing the relationship between euxenite (dark) and albite (light): (1) euxenite (Sample I-1); (2) euxenite-albite intergrowths (I-2); (3) powdery altered albite surrounding euxenite, rim 1 mm. in thickness (I-3); (4) Albite 1–10 mm. from euxenite (Sample I-4 is fine-grained material from fractures in compact albite, Sample I-5 is compact albite). (5) Albite 3 cm. from euxenite (Sample I-6).

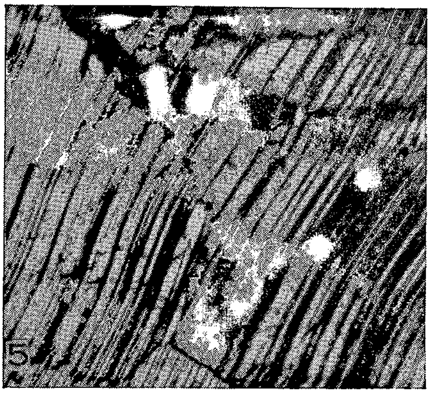
FIG. 2. (Reflected light, ×90). Showing a fracture with iron oxide coatings (d) and anisotropic columbite in the euxenite (E). Albite (A) adjacent to euxenite is altered and reddish due to admixed hematite (e). Following samples have been taken for XRF analyses: (8) iron-rich crusts and fracture fillings (Sample I-8); (9) outermost part of euxenite (I-9). (10) outer part of euxenite immediately inside where I-9 had been scraped off (Sample I-10); (11) core of euxenite crystal (I-11).

Albite immediately adjacent to the euxenite is usually altered to powdery clay minerals (e) (Fig. 2) and is reddish due to admixed hematite. Similar material occurs along fractures in unaltered albite (f) (Fig. 6) further away from the euxenite. Unaltered albite has a composition of An_8, CaO, 1.4%. It exhibits deformation of twin lamellae (Fig. 5) and in numerous fractures, hematite (g) (Fig. 6) and specks of a white metallic mineral that are thought to be galena, (Fig. 4, arrow) are present. Similar white specks are also seen in fractures in the euxenite.

The following samples were used in studies of euxenite and the minerals associated with it:







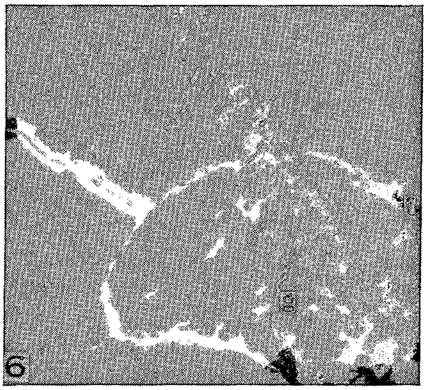


FIG. 3. (Reflected light, ×180). Showing intergrowths of euxenite and albite (upper field). Euxenite consists of light grey (a), medium grey (b) and dark grey (c) phases.

FIG. 4. (Reflected light, ×180). Euxenite (E)—albite (A) intergrowths. Euxenite phases (a), (b) and (c) exhibit different reflectivity. Fractures in albite are filled with hematite and very small white specks (galena?), $<1\mu$ in diameter (indicated by arrows).

FIG. 5. (Transmitted light, +N, ×90). Albite with deformed and ruptured twin lamellae.

FIG. 6. (Reflected light, ×180). Fractured albite with powdery material (f) in the fractures and films of hematite (g) along twin lamellae.

I-1. Euxenite, clean fragments, mainly light grey phase (a) (Zone 1 in Fig. 1).
I-2. Euxenite-albite intergrowths (Zone 2 in Fig. 1).
I-3. Altered albite immediately adjacent to the euxenite from a zone 1 mm. thick (Zone 3 in Fig. 1).
I-4. Altered albite from fractures in compact albite (Zone 4 in Fig. 1).
I-5. Compact albite (Zone 4 in Fig. 1).
I-6. Fresh albite 3 cm. from euxenite (Zone 5 in Fig. 1).
I-7. Fresh green microcline 2 m. from euxenite.

In order to obtain additional material for analysis, another crystal of euxenite was sampled. This crystal is from the same part of the pegmatite as samples I 1–6 but may not be identical in proportions of phases (a) to (c). Samples from this crystal were taken by scraping the outer parts of the crystal with a tungsten carbide chisel. A microphotograph of a polished surface of this crystal is reproduced as Figure 2.

I-8* is an iron-rich crust from fractures in the crystal (Zone 8, Fig. 2).

I-9* is the outermost part of the euxenite crystal (0.5 mm. thick) and probably consists of phase (c) with some admixed iron oxide (Zone 9, Fig. 2).

I-10* is composed mainly of phase (c) free from adhering iron oxide crust. It was taken immediately inside where I–9 had been scraped off. (Zone 10, Fig. 2).

I-11* is from the core of the crystal and like I–1 is composed primarily of phase (a) admixed with some phase (b) and possibly with some phase (c). (Zone 11, Fig. 2).

II. Uranothorite used in our experiments came from raise No. 8 G 3 of the Bicroft Mine near Bancroft, Ontario. The concentrate used contains 10.6% U_3O_8 and 35.0% ThO_2 as determined by chemical analysis in the mine's assay office. The uranothorite occurs with quartz, albite, minor microcline, traces of purple fluorite and, rarely, small zircon crystals. It is vitreous to porcelainic in lustre and is completely metamict. In the mass, it is jet black but at contacts with other minerals it has a 5 mm. selvage of reddish brown uranothorite. For more complete descriptions of uranothorite from this region, see Robinson & Abbey (1957).

The thorianite came from the property of Huddersfield Uranium Minerals Limited, lots 21 and 22 of Range V, Huddersfield township, Quebec. It contains 36.3% U_3O_8, 49.7% ThO_2 and 8.6% PbO (Robinson & Sabina, 1955, p. 631). It occurs typically as interpenetration twins of the cube that contain inclusions of calcite, diopside and phlogopite. These crystals occur in salmon-coloured calcite with euhedral diopside, subhedral phlogopite and traces of thorite and sphene. The sample used was crushed and free from inclusions.

Experimental Procedures

The methods used for lead separation prior to mass spectrometer analysis fall into two groups: (1) Chemical separation using an anion exchange resin. This procedure is based upon the work of Nelson & Kraus (1954) who demonstrated that the maximum adsorbtion of lead from the HCl upon a quaternary amine anion exchange resin occurs at 1 *N* HCl

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*No lead isotope analyses performed on these samples.

and decreases steadily with increase in acid normality. (2) Volatilization of the lead in a Vycor reaction tube. This method, with quartz reaction tubes of various designs, has been used to attempt a quantitative determination of Pb in rocks and minerals (Baskova, 1959 and Iordanov & Kocheva, 1956) and has been employed with success for the determination of the isotopic composition of lead in rocks (Starik & Soborovich) and in meteorites (Marshall & Hess, 1960).

The chemical (anion exchange) separation only was used for the euxenite and feldspar samples. The volatilization procedure was used for uranothorite and thorianite in addition to the separation of lead from the original minerals and from the residues by means of ion exchange.

Chemical Procedures

All reagents were purified with the exception of HF. These included HNO_3, $HClO_4$, 1 *N* HCl, 8–9 *N* HCl, NH_4OH, and KF. Distilled and de-ionized water was used throughout. Bio-Rad analytical grade anion exchange resin (AG 1–X8, 100–200 mesh) was used, with no purification being necessary.

Euxenite (approximately 900 m.g.) was fused with KF–HF in a platinum crucible and the fused cake then heated for three hours in a platinum dish with 5 mls. of $HClO_4$. The procedure then followed was essentially that of Catanzaro & Gast (1960). Separation of lead by anion exchange was carried out using standard pyrex tubing of 20 mm. O.D. and a resin bed height of 15 cm.; the flow rate was 1 ml./min. Separation of Pb from Ta and Nb (Huffman, Iddings, & Lilly, 1951) and Ti, Fe, U, and Th (Kraus & Nelson, 1954) was thus obtained.

The feldspar samples were treated in a similar way except that solution of 0.2 to 0.5 g. of the mineral was accomplished by heating in 10 mls. of HF and 10–15 mls. of $HClO_4$ at 100–150° C. for several hours in a platinum dish.

The thorianite and uranothorites were dissolved in HNO_3 and the lead separated by anion exchange as above. In preliminary experiments solutions of these minerals were obtained by heating with HF and $HClO_4$ in a platinum dish thus obviating the need for filtration of insoluble residues, but this proved to be prohibitively slow.

The lead from the thorianite and uranothorites was volatilized by heating the minerals at temperatures of 900–1100° C. *in vacuo* depending on the sample in question. From 0.8 to 2.5 g. of material was weighed into a previously ignited (1000° C. for 5 hours) ceramic combustion boat which was fitted into a horizontally mounted Vycor reaction tube 12 inches in length and closed at one end. The reaction tube was fitted into a small cylindrical furnace, a vacuum (5–10 mm.) applied for 10 minutes, and the tube heated. A cold finger was used but the lead mirror that formed did so on the sides of the reaction tube itself. The lead was washed from the sides of the tube with hot HNO_3, and the solution evaporated to dryness. The residue was fumed twice with 2–3 ml. of concentrated HNO_3 and 5–6 drops of $HClO_4$ and precipitated with H_2S at a *p*H of 5–6.

Mass Spectrometry

The isotopic analyses were carried out using a ninety degree, ten inch radius, Nier type solid source mass spectrometer having a resolving power of approximately one part in 300.

Five to twenty micrograms of lead sulphide in a few drops of de-ionized water and two drops of a saturated aqueous solution of boric acid (previously rendered lead free by passage through an ion exchange column) were placed on a single pre-baked rhenium filament.

The deposited sample was brought to dryness under a heat lamp. A blank run carried out on a pre-baked filament coated with purified boric acid indicated that the lead contamination level due to these sources was less than .005 microgram.

Isotopic abundances were calculated from the Pb^+ spectrum. Magnetically scanned ion currents were amplified by an electron multiplier, detected by a vibrating reed electrometer and displayed on a pen recorder. Isotopic abundance percentages were corrected for mass discrimination by applying a factor proportional to the inverse square root of the isotopic mass.

Vacuum X-ray Spectrography

Quantitative analysis of U, Th, Pb, Y, Fe, CaO, and K_2O were carried out by G. R. Lachance on a Philips *x*-ray vacuum spectrograph.

With the exception of the uranothorite concentrate from the Bicroft Mine, all analyses reported in this paper were made in the laboratories of the Geological Survey of Canada.

ANALYSES

I. Table 1 lists the elemental analyses for Y, U, Th, Pb, Fe, K_2O and CaO.

Table 2 contains analyses for Y, U, Th and Pb made by the late H. V. Ellsworth of three variably altered zones of a large mass (5–6 inches in diameter) of uraninite from the Villeneuve Mine, Papineau County, Quebec. The inner zone consisted of hard, metallic, virtually unaltered uraninite, the intermediate zone of pitch-black non-metallic uraninite

TABLE 1. RESULTS OF *X*-RAY SPECTROCHEMICAL ANALYSIS—SAMPLE I
(Analyst G. R. Lachance)

Sample	%Y	%U	%Th	%Pb	%Fe	% K_2O	% CaO
I-1 Pure Euxenite	13.4	9.8	3.8	0.96	1.4		
I-2 Euxenite-Albite intergr.	10.1	7.3	3.7	0.69	2.8		
I-3 Powdery Albite 0–1 mm. fr. Ex.	≅ 0.01 to 0.02	≅ 0.01	tr.	≅ 0.01	—	0.5	
I-4 Powdery Albite 1–10 mm. from Euxenite	≅ 0.01	tr.	tr.	≅ 0.01	—	0.5	
I-5 Compact Albite 1–10 mm. fr. Ex.	≅ 0.005	tr.	tr.	≅ 0.01	—	0.5	
I-6 Albite 30 mm. from Euxenite	—	Not detected	not detected	≅ 0.006	—	0.5	1.4
I-7 Fresh Microcline 2 m. from Ex.	not detected	not detected	not detected	≅ 0.01	—	11.0	Tr.*
I-8 Iron-rich crusts	1.0	0.6	0.5	0.6	23.0		
I-9 Outermost surface of Euxenite (0.5 mm.)	11.2	7.7	3.9	0.9	2.0		
I-10 Inner surface of Euxenite	11.5	8.0	3.3	0.7	1.8		
I-11 Central portion of Euxenite	13.1	8.8	3.7	0.8	1.5		

*(Rb_2O = 0.3%).

TABLE 2. ANALYSES FOR Y, U, Th AND Pb OF URANINITE FROM VILLENEUVE MINE, Extracted from Ellsworth 1932, p. 272

Sample	S.G.	Y_2O_3	%U	%Th	%Pb
Inner core	9.144	3.31	65.34	5.63	10.61
Intermediate zone	7.779	2.97	60.33	5.48	9.96
Outer zone	5.273	1.61	50.24	6.73	13.85

and the outer zone of flame-red alteration products. The description of this mass may be found in Ellsworth 1932, p. 242 and the complete analyses of the three zones on page 272.

Table 3 lists the isotope analyses of lead from samples I-1 to I-7 inclusive, the ratios of isotopes with Pb^{204} = 1.00, and the same ratios corrected for the lead from the microcline which is arbitrarily selected as being rock lead, free from contamination by radiogenic lead from the euxenite crystals. The 'corrected ratios' give some indication of the proportion of radiogenic lead in the feldspars surrounding the euxenite crystals. Although validity of this method of correction may be questioned, it will be noted that the total lead contents of the various feldspar fractions are all of the same order. Finally, the ratio of Pb^{206}/Pb^{208} in these 'corrected ratios' is given as a possible indicator of fractionation.

TABLE 3. LEAD ISOTOPIC RATIOS

Sample		%	Error ±	$Pb^{204} = 1.00$	$Pb^{204} = 1.00$ corrected for Pb of sample I-7	Pb^{206}/Pb^{208} after correction
I-1 Euxenite	208	10.41	.03	650.5	615.1	8.44
	207	6.19	.01	386.7	371.3	
	206	83.39	.03	5211.8	5189.8	
	204	0.016	.001	1.00		
I-2 Euxenite albite intergrowths	208	17.26	.06	120.7	85.3	5.91
	207	7.16	.03	50.1	34.7	
	206	75.44	.05	527.5	505.2	
	204	0.143	.005	1.00		
I-3 Albite adjacent to Euxenite crystals	208	50.56	.15	42.92	7.5	0.33
	207	18.97	.12	16.10	0.7	
	206	29.29	.17	24.86	2.5	
	204	1.178	.031	1.00		
I-4 Powdery albite 1–10 mm. from Euxenite	208	46.32	.07	36.72	1.3	2.9
	207	19.72	.04	15.74	0.3	
	206	32.71	.08	26.11	3.8	
	204	1.253	.012	1.00		
I-5 Massive albite 1–10 mm. from Euxenite	208	23.72	.08	38.64	3.20	24.3
	207	13.71	.09	22.33	6.9	
	206	61.96	.12	100.90	78.6	
	204	.614	.018	1.00		
I-6 Albite 30 mm. from Euxenite	208	40.45	.07	42.99	7.60	3.0
	207	16.26	.03	17.28	1.9	
	206	42.35	.07	45.01	22.7	
	204	.941	.006	1.00		
I-7 Fresh microcline 2 m. from Euxenite	208	47.74	.21	35.39		
	207	20.81	.16	15.43		
	206	30.10	.24	22.31		
	204	1.349	.036	1.00		

II. Table 4 contains the isotope ratios of lead extracted from uranothorite, and thorianite, by heating under vacuum and of lead extracted from the residues of these samples after heating and from the unheated sample.

TABLE 4. LEAD ISOTOPE RATIOS

Sample	Isotope	%	Error ±	Pb^{206} = 100.00	207/206	208/206
Uranothorite (vacuum extraction)	208	47.04	.07	95.80		
	207	3.84	.01	7.82	.0782	.958
	206	49.10	.07	100.00		
	204	0.02	.002	.041		
Uranothorite (chemical extraction from unheated sample)	208	46.66	.02	94.07		
	207	3.71	.01	7.48	.0748	.941
	206	49.60	.03	100.00		
	204	0.02	.001	.042		
Thorianite* (vacuum extraction)	208	27.99	.07	42.01		
	207	5.40	.03	8.11	.0811	.4201
	206	66.62	.08	100.00		
Thorianite* (chemical extraction from residue after vacuum extraction)	208	27.75	.04	41.23		
	207	4.95	.02	7.36	.0736	.4123
	206	67.30	.04	100.00		
Thorianite* (chemical extraction from unheated sample)	208	28.69	.09	43.26		
	207	5.00	.03	7.54	.0754	.4326
	206	66.32	.10	100.00		

*Pb^{204} in these leads was less than 0.002% and was therefore omitted.

TABLE 5. LEAD LOSS FROM URANOTHORITE AND THORIANITE UPON HEATING *in Vacuo*

Sample	%Pb	Pb/Th	% Lead lost
Uranothorite—before heating	1.5	0.05	
Uranothorite—after heating *in vacuo*	0.7	0.02	53
Thorianite—before heating	5.38	0.123	
Thorianite—after heating *in vacuo*	5.16	0.118	4

DISCUSSION OF RESULTS

Distribution of Elements

I. It is apparent from Table 1 that the thorium content of all zones in euxenite is essentially constant. Relative to thorium, there is a consistent diminution of uranium and yttrium from the cores of the euxenite crystals outward to their margins, (sample I-1, I-2 and I-11, I-10 and also I-9). Variation in lead content in euxenite samples I-9, 10 and 11 is almost exactly parallel to that of thorium.

In the iron oxide coating the euxenite, (sample I-8) the small amounts of Y, U and Th are probably attributable to admixed euxenite. The lead content of this sample is almost as great as in the euxenite and must represent selective accretion of lead.

The various samples of albite (I-3, 4, 5 and 6) were all purified in bromoform to remove traces of euxenite. Their content of yttrium, uranium and thorium is negligible. Their content of lead is also small but the ratio of lead to the above three elements in the albite is nearly 10 times as great as in the euxenite. In view of the poor sensitivity of the analytical method used in this range of concentration, this may not be significant.

Distribution of Lead Isotopes

In Table 2, the percentage of each of the 4 lead isotopes is given as determined by the mass spectrometer. From these, the ratios of the 4 isotopes were recalculated on the basis of $Pb^{204} = 1.00$. For rock leads formed 1000 m.y. ago, the average equivalent ratio is $Pb^{204} = 1.00$, $Pb^{206} = 17.00$, $Pb^{207} = 15.66$, $Pb^{208} = 37.00$. It is evident therefore, that all leads listed in Table 2 contain anomalous amounts of the three radiogenic isotopes. Because the lead from the microcline sample I-7 most closely approaches the 1000 m.y. average, and because this sample was most distant from the euxenite, it was arbitrarily decided to accept the lead in the microcline as representing the rock lead of the pegmatite at the time of its formation. The ratios of this lead were then subtracted from those of the other samples to yield a balance that could be interpreted as being due to accretion of radiogenic lead subsequent to crystallization of the pegmatite. Finally the ratio of Pb^{206}/Pb^{208} in the corrected radiogenic lead is listed. This final ratio indicates a wide disparity in the isotopic composition of the radiogenic lead in the feldspars. Correction using the average ratios for 1000 m.y. given above instead of the ratios for Pb in microcline changes these final Pb^{206}/Pb^{208} ratios considerably but does not diminish the disparity in values.

II. Very little difference was recorded in the isotopic composition of lead driven off by heating uranothorite under vacuum, and of lead extracted chemically from an unheated fraction of the original sample. Similarly there is little difference in the lead driven off by heating thorianite under vacuum and the lead extracted chemically from the residue after heating. Isotopic analysis of lead chemically extracted from a separate portion of thorianite is not intermediate between the other two fractions as would be expected. It will be necessary to confirm the validity of these results by further work. However, the differences in isotope ratios that were found do exceed experimental errors by significant factors and in both examples the lead driven off under vacuum is apparently slightly enriched in Pb^{208}.

CONCLUSIONS

(1) The accumulation of lead found in the minerals surrounding the euxenite crystals does not appear to be quantitatively sufficient to account for discordancies in age by the different ratios. It should be noted, however, that the powdery and fractured conditions of the albite would facilitate removal of lead by circulating ground water.

(2) Lead content in different layers of euxenite does not show a specific trend but nonetheless accumulation of lead in iron-rich crusts coating and veining the euxenite would appear to have come from the euxenite.

(3) Isotopic composition of lead in the albite surrounding the euxenite indicates an anomalously high content of the three radiogenic isotopes of lead and this presumably, must have come from the euxenite. In 3 out of 4 of these samples the Pb^{206}/Pb^{208} ratio is lower than in the euxenite which suggests greater relative loss of Pb^{208} than of Pb^{206}. This is in keeping with the discordance in age.

(4) There is clear evidence of progressive loss of uranium from the outer layers of the euxenite crystals, in marked contrast to retention of thorium. If no lead were lost, this would explain qualitatively the lower ages obtained from the Th^{232}/Pb^{208} ratios and would indicate that the uranium lead ages were too great. However, if loss of lead has occurred, the uranium lead ages are more likely to be correct and the thorium-lead ages would be too low. A parallel case is recorded for the uraninite in Table 2. In this case too there was progressive loss of uranium in the outer layers and retention of thorium.

Loss of uranium is probably due to its relatively greater solubility in the hexavalent state. Ellsworth (1932, pp. 88–93) has postulated that tetravalent uranium is automatically oxidized to the hexavalent condition as a result of its decay. Concomitant with this transformation he postulates an increase in volume that results in fracturing of the uranium mineral and the minerals surrounding it. This further facilitates leaching of uranium, yttrium, lead, etc. Thorium has no equivalent hexavalent state and is notably insoluble in the tetravalent state as indicated by the lack of supergene thorium minerals.

The apparent increase in thorium in the outermost layers of euxenite (I-9) and of the Villeneuve uraninite is roughly equivalent to the decrease in uranium and yttrium and therefore is consonant with no change of thorium in those layers.

(5) The net change in lead is difficult to assess because it was generated continuously since the formation of the pegmatite. Evidence of the lead in the iron-rich envelope of the euxenite and of an apparent increment in radiogenic isotopes in the adjacent albite together with the low ages obtained for the euxenite relative to the microcline, all point to extensive

loss of lead from the euxenite. Quantitatively our data do not suggest that lead found in adjacent minerals is enough to account for lead presumed lost from the euxenite. The apparent explanation is removal of lead by ground-water solutions. Presence of probable galena and pyrite in the outer part of the euxenite and in adjacent albite suggests that H_2S was able to enter the fractures in these minerals and that therefore, it would be possible for lead to be leached, particularly where it was relatively highly concentrated and not tightly bonded.

The increase in lead in the outer zone is greater than would be expected as a result of diminution of uranium. In the euxenite it is possible that some lead was fixed by precipitation as the sulphide because minute grains of galena were tentatively identified in every section. In studies of uranothorite (Robinson & Abbey, 1957), very thin black films in the uranothorite were found by x-ray to be galena. These films were too thin to yield recognizable surfaces in polished section; it is possible therefore that such films may account for some of the lead in altered zones of other minerals.

(6) The much higher retention of lead in well-crystallized thorianite when heated *in vacuo* compared with that in metamict uranothorite (Table 5), illustrates the readiness with which components of metamict minerals may be lost. In nature it is probable that these losses are due most commonly to circulating ground water but thermal metamorphism too would obviously have a much greater effect on metamict than on crystalline minerals.

(7) Although high temperatures normally inhibit fractionation of isotopes, slight fractionation was indicated in the lead driven off by heating uranothorite and thorianite under vacuum. The greater loss of Pb^{208} relative to Pb^{206} is in accord with the low age commonly given by the Pb^{208}/Th^{232} ratio.

(8) As a result of diminution of uranium in the outer parts of a crystal, the proportion of Pb^{208} generated there by radioactive decay will be greater than in the crystal as a whole. Obviously loss of lead from the outer parts may occur more readily from the margins than from the centre of a crystal. The net result would be a proportionately greater loss of Pb^{208} than of Pb^{207} and Pb^{206}. This secondary effect would further enhance the discordance between Pb/U ages and the Pb/Th age.

SUMMARY

This preliminary study indicates that preferential leaching of uranium does occur and that there is no equivalent leaching of thorium from two minerals containing these elements. Qualitatively this would result in lower ages from the Pb^{208}/Th^{232} ratio than from the Pb/U ratios, as was

found. There is also evidence of loss of lead. Depending on the amount of this loss, relative to that of uranium, it is probable that, because both uranium and lead are lost, the Pb/U ages are more accurate than the Th/U age. This is in accord with results for the euxenite and its coeval microcline. Evidence both from the natural occurrence and from heating experiments, indicates that fractionation of lead is possible during its escape from the host mineral. In both cases this fractionation favoured differential loss of Pb^{208} which is in accord with the low Pb^{208}/Th^{232} ages.

The fact that metamict minerals nearly always yield lower ages than coeval uraninites by the Pb^{208}/Th^{232}, Pb^{207}/U^{235} and Pb^{206}/U^{238} ratios suggests strongly that there is more ready loss of lead when the crystal structure has been wholly or largely disrupted. For those constructing mathematical models to establish when major loss of lead may have occurred, it is important that the effect of increasing disruption of the crystal lattice with time, be considered.

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