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THORIUM, URANIUM AND ZIRCONIUM CONCENTRATIONS IN BAUXITE ¹

J. A. S. ADAMS AND K. A. RICHARDSON

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ABSTRACT

Twenty-nine samples of bauxites from different locations were analyzed for thorium and uranium by gamma-ray spectrometric, alpha counting, and wet chemical methods. The thorium concentrations range from 5.0 to 131 ppm and average 48.9 ppm. The uranium concentrations range from 2.7 to 26.7 ppm and average 11.4 ppm. The thorium-touranium ratios range from 1.5 to 20.9, with an average value of 5.1. Zirconium determinations on some of the bauxites gave values ranging from 0.02 to 0.65 percent Zr, and averaging 0.09 percent Zr.

The thorium, uranium and zirconium contents of the bauxites are related to the type of source rock. Bauxites derived from nepheline syenites contain more thorium and uranium than bauxites derived from other rock types; bauxites derived from basic igneous rocks have the lowest thorium and uranium concentrations, and bauxites derived from carbonate rocks have the lowest thorium-to-uranium ratios. The greatest concentrations of Zr were found in bauxites derived from nepheline syenites, and bauxites derived from carbonates contained the lowest concentrations of Zr.

A study of samples from alumina plants treating Surinam and Arkansas bauxites shows that during the process, over 70 percent of the thorium and uranium in these two bauxites is concentrated into the red mud, and the alumina contains very small amounts of these elements.

t Based in part on a study conducted by K. A. Richardson as part of the requirements for the degree of Master of Arts at Rice Institute.

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This study also indicated that much of the thorium and uranium in bauxites occurs in either primary or secondary resistate minerals.

INTRODUCTION

FOR some time it has been known that certain bauxites contain greater amounts of thorium and uranium than the average crustal rocks. The primary purpose of this study was to make a general survey of bauxites to investigate the distribution of radioactive elements, and determine the significance of this distribution.

In addition to contributing to the geochemical knowledge of thorium and uranium, the results of this study may have some economic value. The possibility of by-product recovery of thorium is suggested, also the possible use of radiometry in prospecting for aluminum ore.

PREVIOUS WORK

Although no data regarding the absolute thorium and uranium contents of bauxites have been found in the literature, with the exception of recently published papers by Adams and others, there are a number of papers that give theoretical reasons to expect relatively high concentrations of these elements in bauxites, and a number of qualitative reports that support the theory.

The application of the concept of ionic potential to the behavior of elements during weathering has been discussed by Goldschmidt and, with particular reference to Arkansas bauxite, by Gordon and Murata. The latter paper verifies Goldschmidt's statement regarding the effect of bauxite formation on certain elements, showing beryllium, chromium, copper, gallium, lead, manganese, molybdenum, niobium, scandium, titanium, vanadium, yttrium and zirconium to be concentrated, and barium, calcium, lanthanum, magnesium and strontium to be depleted during the alteration of nepheline syenite to bauxite.

Figure 1 is a plot of the ionic radius against the ionic charge for a number of elements. Values for the ionic radii are taken from Ahrens. The diagonal lines on the figure are the lines of equal ionic potential used by Goldschmidt, and Gordon and Murata as the boundaries for the group of elements with intermediate ionic potential values that are precipitated in nature as hydrolyzates. Tetravalent thorium and uranium lie well within these boundaries; hexavalent uranium is near the field of elements which form soluble complex anions.

From consideration of the ionic potential alone, thorium should be concentrated in bauxites, whereas uranium might be oxidized and removed as the soluble uranyl ion, UO_2^{*+} . Measuring the radioactivity of Arkansas bauxite by beta counting, Frederickson found an equivalent radium content of 13.1×10^{-13} grams/gram of bauxite. This is larger by approximately one order of magnitude than the average value for acid igneous rocks. Frederickson believed that uranium was introduced into the deposit as uranyl ions and concentrated by adsorption on the aluminum minerals.

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Similarly, Lovering concludes from investigations of radioactive iron oxides that "colloidal ferric oxide hydrate" adsorbs uranyl ion, and thus removes uranium from solution. Most of the thorium minerals resist weathering and remain in their original form, but tetravalent thorium would also be removed from solution by ferric hydroxide. During crystallization of the ferric colloid adsorbed uranium is expelled and forms separate minerals. Heinrich discusses radioactive gossans and laterites briefly, agreeing with Lovering's conclusions.

Davidson states that some terra rossa deposits in Central Africa are significantly radioactive. The radioactive elements are again reportedly adsorbed on the iron hydroxides, but in contrast to the above authors. David-



Figure I. Grouping of certain elements according to ionic potential

son believes that the parent uranium is largely leached and the radioactivity is due to thorium series and uranium series daughter elements.

Kiss and Mehes have studied Hungarian bauxites and reported their radioactivity. Using nuclear emulsions, Kiss detected a small amount of radioactivity in tabular inclusions within zircon crystals. Mehes, measuring radioactivity in the field, found a relationship between radioactivity and ore grade, with increased radioactivity also along lines of faulting and folding in the bauxite.

Occurrences of bauxites with uranium have been found in Yugoslavia, according to Ristic, which "... will apparently also become a source for the obtaining of uranium, because in the processing of aluminum, the uranium concentrates itself in the so-called red mud."

SAMPLES STUDIED

Samples of 29 bauxites (Table I) from different countries were analyzed for this study. It is thought that they constitute a fairly representative collection. Among the samples are bauxites derived from both acid and basic igneous rocks, metamorphic, clastic and carbonate sediments. Parent rocks of Irish and Jamaican bauxites were also analyzed. Table I lists the samples, giving their geographic location, known or inferred parent rock, and literature references.

Table I. List of Bauxite Samples

Sample Location .		Parent Rock	Reference
KR-1	French Guines	nepheline syenite	Fermor (1915)
KN-2L	Gold Coast	volcanic ash	Cooper (1936)
KR-3 KR-3B	Dominican Republic	limestone	Goldich and Bergquist (1947)
KR-4 KR-4B KR-5L	Jamaica *	White limestone	Hartman (1955) Hill (1955)
KR-6L	Brazil	nepheline syenite	Teixeira (1942)
		Other parent rock types f (1955) bibliography, are: (Goodchild) and phyllite	or Brazilian bauxites, reported in Fischer's granite (Knecht), gneiss (Froes), schists (Guimarmes).
KR-7L	British Guiana	diabase	Kersen (1955) Harrison (1910)
KR-BL	India	basalt	Fox (1923)
KR-9L	Bintan, East Indies	hornfels	Bemmelen (1941, 1949)
XB-10	Falau Islands	tertiary volcanics	Bridge and Goldich (1948)
KR-11L	Istria, Yugoslavia	mesozoi: limestone	U.S. Bureau of Mines (1953)
KH-12L	Dalmatia. Yugoslavı -	mesozoic limestone	Franctovic (1955)
KR-13L	Italy		
KH-14L	France	manager and a second	Harder (1949)
KR-15L	Greece	mesozoic limestone	Lapparent'(1949)
KB-17L		mesozoic limestone	Frantovic (1955)
KR~18	Renry, Georgia Georgia	Amolinite	White and Benson (1952)
101-20L	Oregon	miocene besalt	Allen (1948); Libbey, Lowry and Mason (1946)
(R-22	Mississippi	Porters Creek shale	Burchard (1924); Morse and Hand (1923)
UR+23L	Missouri	palaeozoic linestone	Keller (1944)
CR-26 CR-31	Surinaa Surinaa	igneous and metamorphic	Kersen (1955) Meulen (1949)
08-27 28-38	Arkansas Arkansas	nepheline syenite	Mead (1915)
ж-во ж-вз	Jamaica Jamaica	White limestone	(see KH-4, above)
jk≁84	Antria, Northern Ireland	hasalt	Eyles (1952)

THORIUM, URANIUM AND ZIRCONIUM CONCENTRATIONS 1657 In addition to the individual bauxite samples, a suite collected on the

Aluminum Company of America property at Bauxite, Arkansas, illustrates some of the types of bauxite deposits and stages in the development of bauxite from the nepheline syenite parent rock. A section of drill core from the same area, extending through the bauxite into the top of the syenite, was

To trace the radioactive elements through the processing of bauxite to alumina, material balance samples from two treatment plants were studied.

These samples consisted of the feed bauxite, calcined alumina, red mud, and coarse sand, from plants operating on Surinam bauxite and on Arkansas

The alpha activities of a number of aluminum metal samples were also measured.

ANALYTICAL METHODS

Thorium and uranium analyses were made for this study by gamma ray spectrometry, alpha counting, and wet chemical methods. All of the bauxite samples were analyzed by the gamma ray spectral method; some were checked by the alpha activity-fluorometric uranium method. All of the samples were alpha counted. One chemical thorium and a number of chemical zirconium determinations were made. Determinations of aluminum, iron, titanium, and silicon oxides presented in this paper are the routine analyses made by the Aluminum Company of America.

Approximately half of the gamma ray results were obtained at the Shell Development Company laboratory, Houston, Texas; other thorium and uranium spectrometer results presented in the paper were obtained at the Rice Institute. A full discussion of the spectrometry procedure is found in papers by Hurley; Adams, Richardson and Templeton and Whitfield, Rogers and Adams. Thorium was determined by measuring the 2.62 Mev gammas from thallium-208, uranium by measuring the 1.76 Mev gammas from bismuth-214, and thorium and uranium concentrations were both calculated from counts made on a channel centered at 0.61 Mev. Potassium was determined for some samples, using the 1.47 Mev gammas given off by potassium-40. Potassium content of bauxite is low, but the measurements were conveniently obtained, and are therefore included (Table IX).

Individual limits of error for the gamma ray spectral values are not given. The number of events recorded for each measurement was sufficient to give a statistical error of less than ± 5 percent. Additional sources of inaccuracy are the "physical errors" inherent in this method, and the possible inhomogeneity of the samples. A result of the very high thorium concentration in bauxites is the smaller error in thorium measurements. Ninety percent of the chemical thorium analyses made by Pliler agree to within 10 percent with the gamma ray measurements. However, the accuracy of the uranium measurement suffers from the increased thorium contribution to counts made at 1.76 Mev. Uranium measurements are judged accurate to well within ± 20 percent, the greatest inaccuracy being in samples with high thoriumto-uranium (Th/U) ratios. Potassium measurements are considered to be accurate to within ± 5 percent of the amount present.

Calculation of thorium and uranium concentrations from thallium-208 and bismuth-214 gamma activity is based on the assumption that the thorium and uranium decay series are in secular radioactive equilibrium. Determinations of thorium and uranium by two independent methods showed samples of Arkansas and Surinam bauxites to be in equilibrium, but the fluorometric uranium procedure does not apply well to bauxites, due to (i) the difficulty in extracting all of the uranium from the sample, and (ii) interference of the high iron content of many bauxites with the fluorescence. However, a



few samples were analyzed by this method and the data obtained (Table II) are shown in Figure 2, a plot of (alpha counts per hour/fluorometric uranium) against the gamma ray thorium-to-uranium (Th/U) ratio.

Figure 2 contains too few data to lend itself to a definite interpretation, but it appears that the relationship

$$\frac{\text{alpha cph}}{U_{f}} = K_{1} + K_{2} \left(\frac{Th_{\gamma}}{U_{\gamma}} \right)$$

for bauxites may have a smaller K_z value than that determined by Adams, Richardson and Templeton for a group of sediments composed predominantly

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of limestones and shales. The diagonal line drawn on Figure 2 is taken and 7.57 for K_1 and K_2 , respectively.

The departure of the fluorometrically determined uranium values from the gamma ray values for samples KR-10, KR-38 and KR-80 might be attributed to lack of sample homogeneity, to absence of radioactive equilibrium, or, for samples KR-10 and KR-38, to incomplete extraction of the uranium in the chemical analysis. Because the thorium and uranium in a number of bauxites have been shown to be in equilibrium with their daughter elements, this paper continues on the assumption that this condition exists for all of the bauxites studied.

RESULTS AND DISCUSSION

Distribution of Thorium and Uranium in Bausites.—The thorium and uranium analyses of 29 bauxite samples are given in Table II. The bauxites are divided into four groups on the basis of the type of rock from which they were derived; the parent rock types are acid igneous, basic igneous, shale, and limestone. Average thorium and uranium contents for each of the bauxite groups are shown in Table III, with averages for the parent materials taken from the literature.

In some cases there is doubt regarding the exact type of rock from which the bauxite is derived. The location of the Brazilian sample, for instance, is known only by the country. This bauxite may be derived from any of a number of acidic or metamorphic rocks (Table I), depending on which specific deposit was its source. The parents of other South American samples are also questionable. Discussions by Goldich and Bergquist and Hill indicate some uncertainty regarding a purely limestone parent rock for the Caribbean ores.

In grouping the bauxite samples the following relationships were considered: (i) the Caribbean and European bauxites, and the Missouri diaspore clay have limestone parent rocks; (ii) the Georgia and Mississippi samples are derived from shales, and included with them is the Bintan sample whose parent is a low grade metamorphic hornfels; (iii) basic igneous rocks are the parents of the bauxite samples from the Gold Coast, British Guiana, India, Palau Islands, Oregon, U.S.A., and Antrim, Ireland; (iv) acid igneous rocks, mainly nepheline syenites, are parents of the samples from French Guinea, Brazil, Surinam and Arkansas, U.S.A.

It is evident from the data in Tables II and III, not only that the thorium and uranium contents of bauxites are generally much greater than the average for crustal rocks, but also that there is a definite relationship between the thorium and uranium contents of a bauxite and its parent rock type.

For the 29 bauxite samples the thorium concentration ranges from 5.0 to 131. ppm and has an average value of 48.9 ppm; the uranium ranges from 2.7 to 26.7 ppm and has an average value of 11.4 ppm. The Th/U ratio ranges from 1.5 to 20.9 with an average value of 5.1 (Fig. 3).

The higher concentration of thorium and uranium in acid igneous rocks

Arbonate			-	RA		and a	Rock Type			
1-10 1-10	5.25 5.25	2.0	1.3		100		Carbonata recisue	11 M2	n add	n/u
	1-1-1-	10.6	8°.3	11-5	906	2-74		IL	Fri	100
15-10	18.9 1	17.0	* 14		192		Neuxites derived from	(8.04)	(6.6)	(L'N)
		6.0	1.3		592		carbonates (13 samples)	14.0		
Sth-131	5115	8.9			243		Uruntum lewahed		6.21	4.4
747-19X	55.6	N.GT	1.5		202			-	(1691)	
151-90X	39.2	2.5	6.1		306		Intelegree	12.6	1.7	1:
20-00	1,51	250	24	1.722	361	14.4	Concentration factor	(3.7)	(2.8)	0.5
[Q-63	7.05	23.4	1.1		124		Sauxites derived from shales (k samples)		Interior	(1-3)
X08-9L	58.7	7.1	8.3	7.1	302	43.0	Uranitum leached	Trut	10.5 (238)	2.1
828-18	34.6	13.4	200		132		Basic Igneous*			1
22-53	36.3	6.5	6.2		179		Concentration factor	3.9 Ie -11	96.0	9''t
Masic Lepeous NR-2L	21.2	2.7	6.7	2.0	176	10.1	Bauxites derived from	15.6)	(4-4)	(1-3)
12-02	8.2	0.5	0.0	1	Tals	1	verse tgredus rocks (6 samples)	1.05	4.2	5.2
01-10	5.0	2.3	-	19.00			Urbailum lesched		(191)	
102-201 103-201	19.3	1.4 0			138	20.02	Acid Igneous*	12.4		
		1.4	211		-		Consistent and a set	A.C.	2.0	2:0
1-0	127.4	24.1	5.3		1253		Antonian and a station 180102	(6.9)	(2-3)	(1.6)
29-55 92-55	72.0	17.0	507		67 67 68 68		Appeols rocks (6 samples)	69.1	15.8	7.8
12-51	130.7	24.4	1.6		501		Urminium leached		(\$92)	
19-10 19-10	75.8	3.6 19.8	3.8	3.1	248	142.6 52.7				
Average (20 samples)	6.84	4.11	5.1				 Evans and Goodman (1941) Adams and Weaver (1953) 			

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as compared with basic igneous rocks is reflected by the bauxites derived from them. The bauxites with acidic parents are approximately four times richer in these elements than bauxites with basic parents. Bauxites derived from shales and carbonates are quite similar in both thorium and uranium content and are intermediate between the other two groups. The comparable radioactivities of the shale and limestone derivatives is not surprising if one considers, as Hartman suggested for Jamaican bauxite, that the source of the residual lateritic material is the clay impurity in the limestone.

It is noted from the data in Table II that the group of bauxites derived from carbonate rocks has the lowest Th/U ratio, and those derived from acid igneous rocks have the highest ratio. The low ratio for bauxites with limestone parent rocks is particularly well exhibited by the Caribbean samples, none of whose Th/U ratios is greater than 4.3.

Shown in Table III are average concentration factors for thorium and uranium during the formation of bauxite from the various types of source rock. The magnitude of these factors is dependent on two quantities: the fraction of the original rock mass removed in solution, and the amount of thorium and uranium leached. Assuming the thorium remains fixed, then the minimum concentration factor for this element depends only on the amount of parent rock removed. In the alteration of limestone to bauxite the thorium concentration is greatest, averaging 40-fold, while the alteration of shale results in less than 4-fold concentration of the thorium. As pointed out by Adams and Weaver, if all the thorium and uranium occurred in resistate minerals, lateritic weathering would concentrate both elements without changing the Th/U ratio. For each of the four groups of bauxites, the ratio is higher than the average for the parent rock type. Using the assumption that no thorium is lost, the concentration factor for this element multiplied by the uranium concentration of the parent rock gives the uranium concentration that the bauxite would have if no uranium were removed during bauxite formation. From such calculations it is estimated that approximately 20 percent of the uranium is leached from the igneous and shale parent rocks, and 75 percent from the carbonate rocks during lateritization. This is in close agreement with Adams and Weaver's report that an average of 80 percent of the uranium in a carbonate rock can be brought into solution by dissolving in weak acid.

From the foregoing considerations, and the rather general data in Table III, the following conclusions are drawn. In bauxites whose parent rocks are carbonates, the uranium retained is only the portion that occurred in the resistant minerals of the carbonate rock. Such a conclusion may also be valid for bauxites derived from shales and igneous rocks, in which case 70 to 80 percent of the uranium in shales and igneous rocks may occur either in primary or secondary resistate minerals. Because the Th/U ratio increases during bauxite formation, perhaps more of the thorium than of the uranium occurs in primary or secondary resistate minerals.

The reliability of the assumption that thorium is relatively immobile is demonstrated by the low Th/U ratio found in stream and occan waters. Adams, Osmond and Rogers give a value of less than 0.01 for this ratio.

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					Location.	Sample	-	A AND A A A A A A A A A A A A A A A A A	-	
alignet	Location	the rate	D mdd	Th/U	Section 14		Description		D mdd	Th/U
KG-55, Nepheline Syenite	Baucite, Arkensee	£-87	6.4	01	Gection 16	KR-54	Top of transported bauxite deposit	62.9	15.7	3.4
Average of 5 tauxites	(Drill Core Samples)	52.0	6.2	8.4			Fresh nepheline Syenite	19.3.	4.9	3.7
XB-81, limestone		(~ 0.2).	1.3	< 0.9		MI-56	Weathered Depheline Syenite	45.9	4.6	4.9
35-50, baurite	Jumenton					X0-59	Limonite band between KR-56 and XR-57	36.9	2.3	16.1
		1.95	9-5	3.4		12-57	Weathered, Maolinitic sympte	4.64	10.9	4.6
KR-00, basalt	Antrin,	(~0.5)* (<0.2)*	*(J.D.)	(0-+)		X8-60	Clay layer between weathered ayenite and bauxite	33.9	7.9	4.3
XB-84, baurite	R. Ireland	15.1	2.9	5.2		85-10X	Near bottom of bauxite (pisolitic)	51.8	3.5	14.6
						XR-62	10 ft. horizontally from NR-58	0.4E	10.3	3.3
· Error approaches	From approaches 100% for such low level measurements	measurements				KR-63	10 ft. horizontally from KR-62	1.72	6.5	8.8
	rrooste value (see Adams, Osmond, Rogers, 1959)	s, 1959)				XR-611	Near top of bauxite, 7 ft. above KR-58	50.5	3.9	13.0
						KR-612	Same horizon as KR-61 ₁	66.8	7.0	9.6
					Section 26	XR-64	Granitic textured	77.5	ph.o	

8.4

36.9

Clay veinlets in cauxite

Ma-65 Ga-66

bauxd te XR-64 THORIUM, URANIUM AND ZIRCONIUM CONCENTRATIONS 1663

Comparison of the Thorium and Uranium Contents of some Bauxites with their Parent Rocks.—Table IV gives thorium and uranium data for bauxite samples from Arkansas, Jamaica and Northern Ireland, and for samples of their parent rocks, nepheline syenite, limestone and basalt, respectively, taken from the same areas as the bauxite samples. The Arkansas syenite sample is somewhat kaolinized. The samples of Jamaican and Irish parent rocks are fresh.

Regarding the Arkansas samples in Table IV, the nepheline syenite is rather richer in thorium and uranium than the average acid igneous rocks; the bauxite contains less than the average amounts given in Table III for similar bauxites. The actual thorium and uranium concentrations of individual samples may not be highly significant, for it is shown later that the concentrations vary considerably within this deposit. Furthermore, the nepheline syenite, KR-55, is not quite fresh, and its thorium and uranium concentrations and the Th/U ratio may be greater than the unaltered rock.

The Jamaican parent rock contains an average amount of uranium for a limestone, but very little thorium. The typically low Th/U ratio of the limestone is reflected by the low ratio, 3.4, in the bauxite, KR-80. The thorium and uranium concentrations in KR-80 are close to the averages in Table III. Hartman estimated that 667 tons of the White limestone would be required to produce one ton of bauxite of 50 percent Al_2O_8 . Using this estimate, and assuming no thorium is lost during alteration, a thorium concentration of 0.048 ppm in the limestone would result in the observed concentration of 32.1 ppm in KR-80, the bauxite. The thorium content of the limestone sample, KR-81, determined by gamma ray spectrometry is 0.19 ppm. This concentration is close to the limit of sensitivity of the spectrometer and is subject to large error. It is reasonable to conclude from the thorium measurements that the White limestone could well be the parent rock of the Jamaican bauxite.

The sample of basalt from Ireland is extremely low in thorium and uranium. The thorium and uranium contents of the bauxite derived from the basalt are also low compared to the average in Table III. but the Th/U ratio for the bauxite sample, KR-84, is 5.2. This is the same as the average Th/U ratio for bauxites derived from basic rocks.

Thorium and Uranium in Arkansas Bauxite.—Thorium and uranium data for the weathering sequence and drill core samples from Arkansas are presented in Tables V and VI, respectively. All of these samples, with the exception of KR-54, are taken from residual deposits of bauxite that overlie the parent syenite. KR-54, like KR-26 in Table II, is from a plastic or colluvial type of deposit which overlies the Midway clays. KR-54 is taken from the top of a transported bauxite deposit, just below the contact with sediments of the Wilcox Group.

The two transported bauxite samples, KR-26 and KR-54, have very similar thorium, uranium and Th/U values, but these values are not distinctively different from the analyses of the many residual bauxite samples. It is thought (Shepard, pers. comm.) that as a result of transportation of

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					~	8e 7.4	5.4		R	TT	\$6			
		1	-		3.5	96 4.3	103.6%		p :	1.1	C 2			
		al pine	che	342	11	629		346 0.6	150 150	ł				
		f f			9	2								
		ar		3.1				0.0						
	ADCe Sampi	n/ti		20.9	34.5	п.9		2	2,8 11.0					
	sterial bal	n wid	1:	3.6 0.3	97IT	1.0L	8.61		39.8 6.4					
	ranium in je	# #	74.0	6.4	192	122	75.8		170 170		5 - 1 m			
and the second second	The state intorium and Urmanium in Material Palabice Samples	Surfame	bauxite	calcined slumina	fine red	classifier sand	Arkanaaa bauxi te	calcined alumina	fine red mud classifier sand		For sample surface of on a			
Table VIT.		Velght 1bs.	1.9	1.0	0.48	50.0	5.55		0.22		. For sam			
Lithology		carbonaceous clay carbonaceous clay Brown, carbonaceouâ clay.	And gray, fragmental, pisolitic bauxite	Fink and gray, fragmental, pisolitic bauxite	Red and grmy, fragmental, pisolitic taucite	Red and grey, pisolitic, fragmental, slightly sideritic bauxite	Red with some pink, pisolitic, fragmental, slightly sideritic bauxite	Red and gray, pisolitic, slightly sideritic bauxite	Gray with some red, pisolitic, slightly sideritic bauxite	Same as above	Same as above	Same as above, with occasional kaolicitic flecks	Gray bauxite and aider- itic clay with maclin fragmenta	Gray with some pink, kaolinitic, slightly sider- itic, vesthered sysmite
17#/n	1 4	6.0I		1.14	10.4	6.6	10.7	10.9	12.2	12.7	12.6	8.3	1.7	5.2
n mdd	5.4	6.6		8.3	8.4	ð.6	8.6	8.1	7.8	7.1	6.9	8.8	7.2	4.8
	24.5	71.8		94.6	87.5	85.3	91.8	88.1	7.46	4.06	87.3	13.6	51.6	7.45
rootage	136-138	011-951		140-14g	145-241	941-441	146-148	148-150	150-152	152-154	154-156	156-158	158-160	160-163
ardine	X3-67	89-EN		69-10	R-10	11-EX	KR-72	ka-73	12-14 1	XI3-75	XB-76	ха-тт к	KR-78	r 61-100

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the bauxite these samples have a smaller accessory mineral content. This hypothesized decrease of accessory minerals does not noticeably affect the amounts of thorium and uranium found in the bauxite. The radioactive elements must, then, be transported either in extremely fine grained primary resistate minerals or in resistate hydrolyzate minerals,

The Weathering Sequence samples were collected in Tp. 2 S., R. 14 W., Sect. 16 and 26, of Saline County, Arkansas. Figure 4 is a diagrammatic section showing the relative locations of the samples taken from the Section 16 mine. From the analyses of these samples the following observations are made:

i) The thorium and uranium concentrations increase by a factor of 2 to 3, in the distance of a foot or so from the relatively fresh nepheline syenite to the weathered, kaolinitic syenite.



Figure 4. Diagrammatic section showing relative locations of Arkansas samples.

ii) The thin limonite band in the kaolinitic rock and the clay material between the nepheline syenite and the overlying bauxite contain less thorium and uranium than the material immediately above or below. The hard limonite band, about 1 inch thick, is similar to that described by Goldman. If the uranium in bauxites occurred as ions adsorbed on the ferric hydroxide, the limonitic band that is represented by sample KR-59 might be expected to contain more than the measured 2.3 ppm uranium. The low radioactivity of the clay, sample KR-60, is in agreement with Frederickson's total activity measurements.

iii) The variations between samples KR-58, KR-62 and KR-63, and also between KR-61, and KR-61, illustrate large changes in thorium and uranium concentrations that occur in the distance of a few feet, with no apparent change in bauxite texture or vertical position in the deposit.

iv) Samples KR-64 and KR-66 from the Section 26 mine have higher

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radioactivity than the samples from Section 16 mine. The pisolitic bauxite (KR-66) contains more thorium than the underlying bauxite with granitic texture (KR-64), but the uranium contents of the two samples are approximately the same. The clay veinlets in these bauxites, as described by Goldman and Tracey, are much less radioactive than the bauxite, comparable to the clay layer of which KR-60 is a sample.

The Drill Core samples were taken from a hole drilled in the NE 1. SE 1, Sect. 26, Tp. 2 S., R. 14 W., Saline County. The 27-foot section of core includes 18 feet of pisolitic bauxite that grades into 4 feet of dark brown sandy and carbonaceous clay at the top of the section, and into 5 feet of kaolinitic clay and weathered nepheline syenite at the bottom. The lower



half of the bauxite is predominantly gray in color, the upper half predominantly red. Each sample listed in Table VI represents a 2-foot section of the core except KR-79 which represents the bottom 3 feet. Figure 5 illustrates results of the routine analyses for iron, aluminum, titanium and silica made by the Aluminum Company of America, as well as the thorium, uranium, and zirconium determinations on the drill core samples.

It is seen from Table VI that the thorium and uranium concentrations, as well as the Th/U ratio, increase rapidly from the nepheline syenite to the bottom of the bauxite, remain fairly constant through the bauxite section, and decrease in the top, carbonaceous part of the core.

From the nepheline syenite to the bauxite the uranium concentration does not quite double, but the thorium concentration is almost quadrupled. The

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drop in uranium concentration from KR-77 to KR-76, although it is close to the limits of error, is considered real. Figure 5 shows a similar drop in the Fe₂O₃ concentration from sample KR-78 to KR-77. It is suggested that the decrease in uranium content may be related to a change from a true residual deposit to overlying transported material. Another possibility is that corrosion of resistates, for example zircon, has permitted the leaching of more uranium from this level.

The nine samples representing the bauxite portion of the drill core contain an average of 88.2 ppm of thorium, 8.1 ppm of uranium, and have an average Th/U ratio of 11.0.

The histograms in Figure 5 indicate that concentrations and depletions. similar to those observed for uranium and thorium occur for alumina, ferric oxide and titania, whereas silica behaves inversely. Three analyses for zirconium show more than a 5-fold increase from the nepheline syenite to the bauxite with apparently little change in concentration through the bauxite.

For the decreased concentrations of aluminum and ferric hydroxides, and the increased concentration of silica, at the top of the drill core there are two possible explanations that suggest different modes of thorium and uranium occurrence in the bauxite. If the lateritic materials are leached from the top of the section by the influence of organic matter, the increased silica concentration in KR-67 and KR-68 should be accompanied by an increase of resistate accessory minerals. The decrease in thorium and uranium concentrations at the top of the drill core would then indicate that these elements had been held by the hydrolyzate minerals. On the other hand, if the composition of the top of the section is the result of dilution by quartzitic alluvial material, the radioactive elements may occur in resistate minerals. The approach of the Th/U ratio at the top of the section to a value typical of common crustal material is perhaps a factor favoring the latter explanation.

Concentration of Thorium and Uranium During the Processing of Bauxite. -Material balance samples from the St. Louis plant, which treats Surinam bauxite, and the Bauxite Alumina Works, which treats Arkansas ore, were studied. These samples, representing seven days' operation of each of the plants, are comprised of bauxite, calcined alumina, fine red mud. and classifier sand. The classifier sand is the coarser fraction of this mud, which is removed from the mud thickeners to reduce the load. The classification of the red mud and the coarse sand is not perfect; a fine sand fraction remains in the red mud. These samples were obtained through the courtesy of the Aluminum Company of America.

The analytical results of the material balance study are presented in Table VII. Column 1 gives the weight of bauxite required and the weights of mud and sand obtained in producing 1 lb, of calcined alumina. Gamma ray data are shown for all of the Surinam samples, but the Arkansas alumina sample, having an alpha activity of only 0.8 cph, was not amenable to gamma ray spectrometry. The uranium content of the Surinam bauxite, and the thorium content of the Surinam red mud were also measured independently by chemical methods that gave good agreement with the spectral analyses. Fluorometric uranium determinations for the Arkansas bauxite gave markedly lower values than the gamma ray method. This may have been the result of incomplete extraction of the uranium in the fluorometric procedure. Such a problem was encountered with the sample of Arkansas bauxite cited by Adams, Richardson and Templeton, but the radioactive decay series were shown to be in equilibrium in that sample.

The samples of calcined alumina produced from both Surinam and Arkansas bauxites have very low radioactivities. Most of the thorium and uranium introduced in the feed bauxite is concentrated in the waste products of the Bayer process: the red mud and the classifier sand. The red mud makes up 80 to 90 percent of the waste material, and it contains much more of the thorium and uranium than the classifier sand. The red mud from the Surinam bauxite treatment plant contains 281 ppm of thorium and 11.6 ppm of uranium; this is 96 percent of the thorium and 82 percent of the uranium that was originally contained in the bauxite. The red mud from the Arkansas bauxite treatment plant contains 120 ppm of thorium and 39.8 ppm of uranium; this represents 73 percent of the thorium and 93 percent of the uranium from the feed bauxite.

The concentrations of uranium in the red mud and coarse sand samples of the Surinam material balance are essentially the same, but the Th/U ratio is 24.2 in the mud and 11.9 in the sand. This indicates that in the Surinam bauxite the modes of occurrence of thorium and uranium may be different, with the thorium occurring in finer grained particles than the uranium. In the Arkansas material balance the Th/U ratio of the red mud is much less than the Th/U ratio of the classifier sand.

Samples elutriated from Surinam and Arkansas red muds, consisting of the less than 6 micron size fraction, were alpha counted. The measured activities, 1215 and 1040 counts per hour, respectively, are not greatly changed from the activities of the whole red mud samples. Thus, the alpha emitting nuclides can be retained in very fine grained material.

A portion of the less than 6 micron Surinam sample was leached with hydrochloric acid. Much of the iron was removed, and the sample weight was reduced by approximately 70 percent. The measured alpha activity of the residue was 1,480 counts per hour, and the calcined leach, whose mass is approximately twice that of the residue, had an alpha activity of 1,230 counts per hour.

Without distinguishing parent from daughter elements, or thorium from uranium series, the results of the leaching experiment show that roughly 1/3 of the alpha emitters resist severe leaching, and remain in the residue of the red mud. The retention of these elements suggests that they are held in resistate minerals. It is also possible that some of the radioactive material in the leach was removed from resistates. A further indication that thorium occurs in resistate minerals is the fact that this element is in equilibrium with its daughters in the Surinam red mud sample (Table VII). The existence of radioactive equilibrium in this sample would be extremely unlikely, unless the entire radioactive decay series were within a closed system, i.e. within resistate mineral grains.

X-ray diffraction analysis of the leached red mud residue showed this

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Table VIII. Zirconium in Bauxites

Sample	2	by wt.
muxites der	ived from carbonate rocks	
KR-3		
KR-3B		0.05
KR-h		0.049
KR-4B		0.05
KR-5L		0.053
KR-11L		0.022
		0.040
KR-121		0.040
KR-13L KR-14L		0.062
101-141		0.061
KR-15L		
KR-23L		0.048
	Average	0.049
Bauxites der	lved from shales	- Contraction
KR-9L		
KR-17L		0.022
KR-18		0.044
		0.10
KR-22		0.07
	Average	0.059
Bauxites des	rived from basic igneous rocks	
KR-2L		120 1201
KR-7L		0.030
KR-6L		0.132
KR-10		0.02
KR-201		0.057
and the second second	Average	0.069
Bauxites de	rived from acid igneous rocks	
KR-1		0.65
KR-6L		0.153
KR-26		0.076
88-27		a sta
KH-27		0.242
in ja	Average	0.120
		and the second
Arkaneas se	mples	
KR-55	relatively fresh nepheline syenit	te 0.055
XR-56		0.064
KR-57	kaolinized nepheline syenite	0.103
KR-79	drill core syenite	0.085
KR-74	drill core bauxite	0.251
KR-69	drill core bauxite	0.253
Trestment r	lant samples	
Surinam b		
	calcined alumina	0.01
KR-33 KR-28	classifier sand classifier sand	0.113
AL-20	CAMPORALUT BRIDE	0.010
KR-32	red mud	0.34
	red mud (-6 micron)	0.17
A subscription of some or	Bauxite	
KR-29	classifier sand red mud (-6 micron)	0,460

material to consist mainly of anatase, with rutile, quartz, and possibly gypsum and gibbsite in minor accounts.

The small amounts of thorium and uranium present in samples of calcined alumina (Table VII) indicate that similar low radioactivity should be

characteristic of reduced aluminum metal. A number of aluminum metal samples discussed by Adams and Richardson had alpha counting rates only slightly above background.

Zirconium in Bauxites .- Because of the chemical similarities between thorium, uranium and zirconium many of the bauxite and associated samples were analyzed for this element. Table VIII gives zirconium determinations for 25 bauxite samples, 6 bauxite and nepheline syenite samples from Arkansas, and 7 samples from bauxite treatment plants.

The concentration of zirconium in bauxite appears to be related to the type of rock from which the bauxite is derived. A histogram of the distribution of zirconium concentrations, Figure 6, illustrates this relationship. The zirconium contents of bauxites derived from carbonates are uniformly low, ranging from 0.022 to 0.062 percent and averaging 0.048 percent. Bauxites derived from shales and basic igneous rocks have a wider range





Zirconium data on bauxites.

of zirconium concentrations, with average values of 0.059 and 0.069 percent, respectively. Bauxite daughters of acid igneous rocks have zirconium contents ranging from 0.076 to 0.65 percent, and averaging 0.248 percent. The relative zirconium concentrations in the 4 groups of bauxites compare closely with the relative zirconium concentrations quoted by Degenhardt for each of the 4 types of parent rocks.

There appears to be no relationship between the zirconium contents of bauxites and the thorium or uranium contents. A positive relationship between these elements might be expected if thorium and uranium were present in zirconium minerals. Degenhardt refers to the corrosion of zircons in laterites, and Frederickson states that portions of the bauxite drill core that he studied showed high assays for zirconium and contained no zirconium minerals. With these considerations, the absence of a correlation between thorium or uranium content and zirconium content in bauxites is not improbable.

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Colorimetric zirconium determinations on Arkansas samples show a concentration of 0.055 percent Zr in the freshest nepheline syenite sample, increasing to 0.103 percent Zr in the weathered syenite, and reaching 0.257 percent Zr in the bauxite. This compares favorably with Gordon and Murata's spectrographic determination of 0.050 percent Zr in the nepheline

TABLE IX.

POTASSIUM IN BAUXITI

Sample	A STASSICM IN BAUXITES	
KR-1	Description, Location	
KR-2L	Bauxite, French Cal	% K
KR-3	Dauxite, Gold Coost	0.03
July-D	Bauxite, Dominican Republic	0.07
KR-3B		0.29
KR-4	Bauxite, Dominican Republic	
KR-4B	Dauxice, famaica	0.04
ACIC-TD	Bauxite, Jamaica	-0.05
KR-5L		0.24
KR-6L	Bauxite, Jamaica	
KR-7L	Bauxite, Brazil	0.15
RR-IL	Bauxite, British Guiana	0.27
KR-8L		0.21
KR-9L	Bauxite, India	
KR-10	Bauxite, Bintan, East Indies	0.14
KR-10	Bauxite, Palau Islands	0.12
LTD AAT		0.04
KR-11L	Bauxite, Istria, Yugoslavia	
KR-12L	Bauxite, Dalmatia, Yugoslavia	0.13
KR-13L	Bauxite, Italy	0.3
1000		0.21
KR-14L	Bauxite, France	
KR-15L	Bauxite, Greece	0.08
KR-17L	Bauxite, Henry, Georgia	0.30
	shuarte, rienry, Georgia	0.22
KR-18	Low grade bauxite, Georgia	
KR-20L	Composite sand	0.24
KR-22	Composite sample, Oregon	0.12
	Low grade bauxite, Mississippi	0.19
KR-23L	Diama Ol AN	
KR-26	Diaspore Clay, Missouri	1.3
KR-27	Bauxite, Surinam	0.21
IXIX-21	Bauxite, Arkansas	0.41
KR-31		
	Bauxite, Surinam material balance	0.15
KR-32	Red mud. Surinam material balance	0.60
KR-33	Classifier sand, material balance	-0.04
		-0.04
KR-34	Calcined alumina. Surinam material balance	-0.22
KR-37	Red mud, Arkansas material balance	0.21
KR-38	Bauxite, Arkansas material balance	-0.10
	on and the transfer material balance	-0.10
KR-55	Nepheline syenite, Arkansas	
KR-64 '		5.62
111-04	Granitic textured bauxite. Arkansas	0.02
KR-67	C-1 1 11 11	
	Carbonaceous clay, Arkansas drill core	0.21
KR-68	Clay and bauxite, Arkansas drill core	0.03
KR-76	Bauxite. Arkansas drill core	0.09
KR-79	Nepheline syenite. Arkansas drill core	2.11
KR-83	Bauxite, Jamaica	0.3

From the size of the negative values and other considerations, the estimated error in these measurements is less than 0.1 percent K.

syenite, but is double their value of 0.13 percent Zr in the bauxite. Degenhardt gives values averaging 0.071 percent Zr for nepheline syenites, and 0.051 percent Zr for European bauxites derived from limestones.

The Surinam material balance samples show that approximately 75 percent of the zirconium in the bauxite is concentrated in the red mud. The zirconium concentration increases from 0.126 percent in the bauxite (KR-31) to 0.346 percent in the red mud. Zirconium is present in the calcined alumina in an extremely low concentration. Because the concentration of zirconium in the classifier sand and in the less than 6 micron fraction is lower than in the red mud, zirconium must occur in an intermediate grain size fraction. In contrast to the Surinam samples, the Arkansas classifier sand and less than 6 micron fraction of the red mud contain equally high zirconium concentration, 0.46 percent. This suggests a more uniform distribution of zirconium in all grain sizes in the Arkansas bauxite.

ECONOMIC CONSIDERATIONS

The relatively high concentration of thorium and uranium in bauxites presents a convenient radiometric method of prospecting for this ore.

Although more detailed work would be required on individual bauxite deposits, it is suggested that a usable relationship between the radioactivity and the grade of the ore might favor the substitution of a field radiometric technique for some of the drilling and laboratory analyses now used in bauxite mining operations.

Another economic consideration is that of recovering thorium as a byproduct of the alumina process. The concentration of 281 ppm of thorium in the red mud of the East St. Louis alumina plant indicates that for each ton of alumina produced, 1 lb of thorium is concentrated in approximately 1 ton of red mud. This alumina plant alone, having an annual capacity of more than 300,000 short tons, might produce 40,000 lbs of thorium per year, assuming 50 percent recovery.

SUMMARY AND CONCLUSIONS

The principal conclusions of this study are:

1. Bauxites generally contain concentrations of thorium and uranium greater than the earth's crustal average.

2. A relationship exists between the type of rock from which a bauxite is derived and the thorium, uranium and zirconium contents of the bauxite.

3. There are a number of indications that thorium and uranium are held in either primary or secondary resistate minerals in bauxites.

4. In the process of extracting alumina from bauxite, over 70 percent of the thorium and uranium are concentrated in the red mud. The alumina and aluminum metal contain very small amounts of these elements.

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RADIOACTIVITY OF ALUMINUM METAL

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During a recent study of the thorium and uranium concentrations in bauxites (2, 5), it was found that in the processing of bauxite, much of the thorium and uranium is concentrated into the red mud, and calcined alumina contains very small amounts of these elements. For this reason, aluminum metal might also be expected to have rather low radioactivity. The radioactivities of a number of aluminum samples were measured by alpha counting, and the results are presented in this paper.

Table 1 gives the gamma ray spectrometer data on Surinam material balance samples. Adams, Richardson, and Templeton (2) give the procedures. These samples, obtained through the courtesy of the Aluminum Company of America, consist of Surinam bauxite, calcined alumina, red mud, and classifier sand, from the East St. Louis alumina plant. Some of the gamma ray determinations were verified by chemical analyses, indicating that the thorium and uranium are in equilibrium with their daughter products in the bauxite and red mud samples. The results in Table 1 show that more than 80 percent of the thorium and uranium in the bauxite is concentrated in the red mud, and less than 5 percent of these elements is extracted with the alumina. The calcined alumina contains 4.9 ppm of thorium and 0.3 ppm of uranium, and has an alpha activity of 0.054 counts per hour per square centimeter. A sample of alumina produced from Arkansas bauxite has an alpha activity of 0.039 counts per hour per square centimeter. These alpha activities were measured a few weeks after the alumina was produced. Counting of the same samples approximately two years later indicated an increase in activity of approximately 100 percent, but this apparent change may have no statistical significance.

The alpha counting technique that was used in this study is the same as that described by Adams, Richardson and Templeton (2). The powdered material balance samples were counted in a 2 inch diameter planchet with a depth of $\frac{1}{8}$ inch. The alpha activities of the aluminum samples were measured on metal discs of the same diameter and thickness as the planchets.

The metal samples that were studied included 7 modern aluminum samples in varying degrees of purity, 3 samples of aluminum produced 30 to 40 years ago, and three National Bureau of Standards aluminum alloy samples. The alpha activities of the samples are listed in Table 2, with more detailed sample descriptions. The statistical error in these low level measurements ranges approximately from ± 20 to ± 90 percent of the measured activity.

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TABLE 1

Sample	Weight, Ibs	Th. ppm	U. ppm	Alpha* activity	% Th	% U
Bauxite Calcined alumina Fine red mud Classifier sand	1.9 1.0 0.48 0.05	74.2 4.9 281 122	3.6 0.3 11.6 10.1	16.8 0.054 65.6 31.0	3.5 96 4.3	5 82 7.4

THORIUM AND URANIUM DATA ON SURINAM MATERIAL BALANCE

* Alpha activities in counts per hour per square cm.

The average alpha activity of the seven relatively recently produced metal samples, KR-45 to KR-51, is 0.089 counts per hour per square centimeter. Measurement of the activities of these samples two years before the counts listed in Table 2 were made gave an average value twice as great. However, the activity of the metal being only slightly above background, its apparent decrease is within statistical limits of error.

The gradational decrease in purity in the series of samples KR-46 through KR-51 does not cause a change, within statistical limits of error, in the radioactivities of the samples. A sample taken from an anode of the electrolytic aluminum purification process has a measured alpha activity of 4.3 counts per hour per square centimeter. This is approximately the activity that would be expected for a sample containing 5 to 10 ppm of thorium and

TABLE 2

		ALPHA ACTIVITY OF ALUMINUM METAL SAMPLES
Sample number	Alpha activity	Sample description
KR-39	0.13 0.16	N.B.S. # 601: 4.38% Cu, 0.39% Mg, 0.88% Si, 0.52% Fe, 0.81% Mn, 0.020% Cr, 0.015% Ti.
KR-40	0.16 0.18	N.B.S. # 602: 4.44% Cu, 1.49% Mg, 0.130% Si, 0.28% Fe, 0.63% Mn, 0.007% Cr, 0.012% Ti.
KR-41	0.34 0.33	N.B.S. #603: 0.29% Cu, 1.01% Mg, 0.52% Si, 0.21% Fe, 0.24% Cr, 0.037% Ti.
KR-42	0.79 0.69	Aluminum produced from Arkansas bauxite in 1918.
KR-43	0.41 0.24	Aluminum produced from Arkansas bauxite in 1920.
KR-44	0.24	Aluminum produced from French or Irish bauxite in 1907.
KR-45	0.074	Aluminum produced recently from Surinam bauxite,
KR-46 KR-47 KR-48 KR-49 KR-50 KR-51	0.089 0.14 0.069 0.11 0.059 0.089	Aluminum samples KR-46 to KR-51 are produced from Arkansas bauxite. This series grades from 99.9% purity in KR-46 to 94% in KR-51. KR-48 has the composition typical of modern aluminum.

* Alpha activities in counts per hour per sq cm from solid metal surface.

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uranium. Gamma ray spectral analysis of this sample indicates concentrations of less than 1 ppm for both of these elements. The radioactive decay series must, then, be out of equilibrium. Because the sample is over two years old, the alpha activity must be due to a concentration of some of the longer-lived nuclides.

The National Bureau of Standards samples, KR-39, KR-40, and KR-41, containing 93 to 98 percent aluminum (see chemical analyses in Table 2),

TABLE 3

ALPHA ACTIVITIES OF SOME METALS

Material	Alpha counts per hour per 100 cm ²
Steel (commercial)	3
Brass (commercial)	5
Copper (commercial)	9
Aluminum (commercial)	31
Tin (commercial)	121

exhibit alpha activities somewhat greater than the samples of modern aluminum. Probably the increased radioactive content was added to these alloys with one or more of their minor metal constituents.

The three old aluminum samples, KR-42, KR-43, and KR-44, are two to eight times more active than the modern samples. This might be due to a greater radioactive impurity in the samples at the time of production, or to a build-up of radioactive daughters from a non-equilibrium condition.

TABLE 4

BETA ACTIVITIES OF SOME METALS

Material Copper tubing	Beta counts per minute per 100 cm ²
Brass rod	0.05
Steel scale	2
	5
Aluminum (2S)	
Aluminum (superpure)	6
	4
Lead (modern)	
Lead (16th century)	11
	1

Bearden (3) measured the alpha activities of materials commonly used in the construction of radiometric equipment, and some of these are listed in Table 3. Table 4 gives more recent measurements (4) of the beta activities of some metals. These data show that, although aluminum is produced from an ore with relatively high radioactivity, the radioactivity of aluminum metal is comparable with that of other common metals.

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