

*Hill in "Handbook of
Geochemistry"*

Thorium

90

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Introduction

Owing to the geochemical similarity of thorium and uranium, it is necessary in the chapters on each element to refer to the geochemistry of the other. The chapter on uranium (92) specifically considers a number of topics pertaining to both elements, namely: the contribution of radioactive elements to heat flow; autoradiography; fractionation of thorium and uranium during weathering and the use of Th/U ratios as indices of sedimentary depositional environments; and the utilization of nuclear fuels as energy resources. This chapter on thorium includes a discussion of age dating by disequilibrium methods involving both the thorium and uranium series; the Th/U ratio in igneous rocks; and the regional variation in the abundances of radioactive elements in igneous rocks and the petrologic conclusions which can be drawn from these variations. A discussion of Th/Pb and U/Pb dating can be found in Chapter 82 (lead), Section B.

Reviews of the geochemistry of thorium have been published in a number of places. The present writers presented a review of the geochemistry of thorium and uranium (ADAMS *et al.*, 1959), and PETERMAN (1963) prepared a preliminary version of a very detailed description of the abundances of thorium and uranium in various materials. A bibliography of the geology of uranium and thorium has been published by EL SHAZLY (1962). The present sections 90-B to 90-O are based primarily on world-wide literature published prior to 1965 with a few references to later papers. In the case of some papers which are difficult to obtain or are in a language other than English, German, or French, the data reported in this chapter have been taken from PETERMAN's 1963 summary.

90-B. Isotopes in Nature

Only two long-lived isotopes of thorium occur in nature. The major one is Th^{232} , which is the parent nuclide of a long decay series terminating with Pb^{208} . The half-life of Th^{232} is 1.39×10^{10} years, which is considerably longer than that of either U^{238} or U^{235} . The other important natural isotope of thorium, Th^{230} , is generally present in minerals which contain uranium. Thorium-230 is the decay product of U^{234} , an intermediate in the decay of U^{238} . The half-life of Th^{230} is 80,000 years.

The fact that thorium and uranium are geochemically separable during sedimentation and other surficial processes permits disequilibrium dating of sediments in which some of the isotopes occur. The various techniques are summarized in a number of papers, including ROSHOLT *et al.* (1961, 1962), ROSHOLT and ANTAL (1963), SACKETT and POTRATZ (1963), SACKETT (1965), and THURBER (1965). In outline form, the various dating techniques are as follows:

(1) Uranium is precipitated from sea water in calcareous organisms or other forms of calcium carbonate. The calcium carbonate does not incorporate the thorium daughter products, and thus the rate of accumulation of Th^{230} is a measure of the age of the precipitated carbonate.

(2) The limited amounts of Th^{230} and Pa^{231} in sea water are absorbed in clay sediments. Because the thorium and protoactinium are unsupported by their parent uranium, which is not incorporated in the sediments, the rate of disappearance of thorium and protoactinium can be used to date the formation of the sediment. The ratio $\text{Pa}^{231}/\text{Th}^{230}$ has a half-life of 60,100 years.

(3) The excess of U^{234} commonly found in sea water above the amount required for secular equilibrium permits a check on other methods of dating. The 15 percent excess of U^{234} gradually disappears in deposited sediments which incorporate uranium in any form, such as in the calcium carbonate lattice. The rate of establishment of secular equilibrium permits dating the sediment.

In addition to the two thorium isotopes discussed, four other short-lived isotopes also occur naturally:

- Th^{234} — a member of the U^{238} decay series
- Th^{231} — a member of the U^{235} decay series
- Th^{228} — a member of the Th^{232} decay series
- Th^{227} — a member of the U^{235} decay series.

90-A. Crystal Chemistry

I. Introduction

Thorium belongs to the series of actinide elements which are characterized by an incomplete 5f shell, analogous to the rare earth elements with incomplete 4f shells; such elements, therefore, may occur in a variety of valence states. Thorium is predominantly stable in the tetravalent state but is sometimes 3-valent and 2-valent in some halides and chalcogenides. It is the largest of the tetravalent cations with an ionic radius comparable to that of U^{4+} and Ce^{4+} (see Table 12-8 of Volume I of this handbook; also SHANNON and PREWITT, 1969).

The similarities in ionic size, outer electron configuration and bond character are the main reasons for the close relationship between the crystal chemistry of thorium, cerium, uranium and zirconium. There are many examples for isostructural compounds, e.g. ThS, US, CeS, ZrS (NaCl-type); ThO_2 , UO_2 , CeO_2 , ZrO_2 (fluorite-type); $TbSiO_4$, $USiO_4$, $ZrSiO_4$ (zircon-type); $ThGeO_4$, $UGeO_4$, $CeGeO_4$, $ZrGeO_4$ (scheelite-type); and $BaThO_3$, $BaUO_3$, $BaCeO_3$, $BaZrO_3$ (perovskite-type). Although there is a definite preference by Th for 8- and 6-fold coordination in nonmetallic compounds, higher coordination numbers such as 9, 10 and 11 are also found. Pure thorium minerals, like thorianite (ThO_2) or thorite ($ThSiO_4$), are rather rare, but this element occurs as a minor constituent of a large number of minerals containing uranium and rare earths as monazite (see Section 90-D-2; also FRONDEL, 1958).

II. Metallic Compounds, Borides, Carbides, Nitrides, etc.

Elemental thorium exists in two modifications. The face-centered cubic α -form is stable from room temperature upto 1,400° C. Above this temperature it transforms reversibly into the body-centered cubic β -modification. The existence of many intermetallic compounds of thorium, varying greatly in composition and structure, has been reported by MAKAROV (1959) and NEVITT (1963); most of these structures are close-packed with high coordination numbers for thorium.

The stable carbides of thorium are ThC (NaCl-type like other IV-B group carbides) and ThC_2 (structurally closely related to NaCl). The C_2 -groups instead of Cl-atoms change their orientation with temperature and ThC_2 is therefore known in three modifications: monoclinic from room temperature to 1,430° C, tetragonal from 1,430—1,480° C, and cubic above 1,480° C (BOWMAN *et al.*, 1968). The silicides of thorium have compositions ThSi, $ThSi_2$ and Th_3Si_2 (JACOBSON, FREEMAN, THARP and SEARCY, SR 1956, 191).

The nitride ThN crystallizes in the NaCl-structure, Th_2N_3 in the hexagonal A-type structure of the rare earth sesquioxides (ZACHARIASEN, SR 1949, 172), and Th_3N_4 in a special close-packed configuration of thorium atoms where nitrogen occupies octahedral and tetrahedral holes (BENZ, 1966). This structure is closely related to that of Th_2N_2O where the thorium atoms are in hexagonal close-packing. The compounds $Th_2(N, O)_2X$ ($X = P, S, As$ or Se) crystallize in the Ce_2O_2S structure which is related to Th_2N_3 (BENZ and ZACHARIASEN, 1969).

III. Oxides and Oxosalts

The very stable oxide ThO_2 (thorianite) crystallizes in the fluorite structure; natural thorianite contains varying amounts of UO_2 and also rare earth oxides (ROBINSON and SABINA, 1955). On the other hand thorium is usually present in the minerals uraninite (UO_2) and cerianite (CeO_2). A continuous series of solid solutions exists between the isostructural oxides ThO_2 and UO_2 . Thorium oxide may also form defect fluorite-type phases with Y_2O_3 (SCHUSTERIUS and PADUROV, SR 1955, 377) and with rare earth oxides (GINGERICH, SR 1961, 493). At higher sesquioxide concentrations the structure changes to the C-type of the rare earth oxides.

Various compounds between ThO_2 and other oxides, and also oxosalts of tetravalent thorium, are known. A compilation of such compounds is given in Table 90-A-1; in a few cases the crystal structure is not known. Oxide and silicate minerals containing thorium as a major constituent are listed in Subsection 90-D-3, Table 90-D-2; many of such minerals occur in the metamict state.

Thorium germanate crystallizes in the scheelite structure below $1,100^\circ\text{C}$ and in the zircon structure above this temperature. The high temperature form of ThTi_2O_6 is isostructural with UTi_2O_6 and with the mineral brannerite. The linking of the (TiO_6) octahedra is similar to that in anatase. Thoro-aeschynite and thorbastnaesite, which are listed in Subsection 90-D-3, contain upto 30% ThO_2 and 47% ThO_2 .

Table 90-A-1. Oxide compounds and oxosalts of thorium

Compound	Coordination number of Th	Reference
ThO_2	8	GOLDSCHMIDT and THOMASSEN (SB 1913-28, 208)
$\alpha\text{-Th[GcO}_4]$	8	BERTAUT and DURIF (SR 1954, 451)
$\beta\text{-Th[GcO}_4]$	8	BERTAUT and DURIF (SR 1954, 451)
$\alpha\text{-ThTi}_2\text{O}_6$	6+2	HARARI and THERY (1969)
$\beta\text{-ThTi}_2\text{O}_6$	6	RUH and WADSLEY (1966)
$\alpha\text{-ThMo}_2\text{O}_8$	8	THORET <i>et al.</i> (1970)
$\beta\text{-ThMo}_2\text{O}_8$	8	THORET <i>et al.</i> (1968)
SrThO_3 , BaThO_3 , PbThO_3	6	NARAY-SZABO (SR 1947/48, 456)
$\text{Th}_2(\text{OH})_2[\text{NO}_3]_4 \cdot (\text{H}_2\text{O})_8$	11	JOHANSSON (1968)
$\text{Th}[\text{NO}_3]_4 \cdot 5 \text{H}_2\text{O}$	11	TAYLOR <i>et al.</i> (1966)
$\text{Th}[\text{NO}_3]_4 \cdot 6 \text{H}_2\text{O}$	8	TEMPLETON and DAUBEN, (SR 1951, 278)
$\text{Th}[\text{P}_2\text{O}_7]$	6	BURDESE and BORLERA (SR 1960, 405)
$\text{NaTh}_2[\text{PO}_4]_2$, $\text{KTh}_2[\text{PO}_4]_2$	9	MATKOVIC <i>et al.</i> (1970)
$\text{CaTh}[\text{PO}_4]_2$ (Ca, Ce, La, Th)[PO_4]	9	BOWIC and HORNE (SR 1953, 540)
$\text{Me}^{2+}\text{Th}[\text{PO}_4]_2$	9	SCHWARZ (1965)
$\text{Me}^{2+}\text{Th}[\text{AsO}_4]_2$	9	SCHWARZ (1965)
$\text{Me}^{2+}\text{Th}[\text{VO}_4]_2$ ($\text{Me}^{2+} = \text{Cd, Ca, Sr, Ba, Pb}$)	8	SCHWARZ (1965)
$\text{Th}_2[\text{VO}_4]_4$	8	LE FLEM <i>et al.</i> (1965)
$\text{Th}[\text{V}_2\text{O}_7]$	8	QUARTON, <i>et al.</i> (1970)
$\text{Th}(\text{OH})_2[\text{SO}_4]$	8	LUNDGREN (SR 1950, 327)
$\text{Th}(\text{OH})_2[\text{CrO}_4] \cdot \text{H}_2\text{O}$	8	LUNDGREN and SILLÉN (SR 1949, 254)

respectively (ES'KOVA *et al.*, 1964; PAVLENKO *et al.*, 1965). Cheralite, (Ca, Ce, La, Th) $[\text{PO}_4]_3$, and its synthetic analogue $\text{CaTh}[\text{PO}_4]_2$ are isostructural with huttonite, ThSiO_4 . Table 90-A-1 demonstrates the importance of thorium-containing phosphates and their corresponding vanadates. $\text{Th}_3[\text{VO}_4]_4$ crystallizes in the zircon structure with partly unoccupied Zr positions; $\text{PbTh}[\text{VO}_4]_2$ occurs in three modifications, scheelite, huttonite and zircon.

IV. Silicates

In spite of the close crystal chemical relationship between thorium and zirconium, only a few thorium silicates are known so far as compared to the large number of Zr-containing silicates (see Subsection 40-A-IV). By far the most important silicate is the orthosilicate ThSiO_4 and its substituted derivatives. It occurs in two modifications, in the tetragonal structure of zircon as thorite, and in the monoclinic structure of monazite as huttonite. Contrary to expectation the denser huttonite structure is stable at high temperature and is formed irreversibly from thorite above $1,225^\circ\text{C}$ (FINCH *et al.*, 1964). The more abundant thorite is usually found in the metamict state and frequently contains U, RE, Pb or Zr e.g. uranothorite, calcliothorite, eucrasite and thorumgumite (PABST, SR 1951, 307). A continuous series of solid solutions probably exists between USiO_4 and ThSiO_4 in the zircon structure (FUCHS and GEBERT, 1958); also partial replacement of $[\text{SiO}_4]^{4-}$ by $[\text{OH}_4]^{4-}$ is found in the thorite-variety thorumgumite, as in zircon (FRONDEL, SR 1953, 565; FRONDEL and COLETTE, 1957). The monoclinic huttonite form seems to be inherently much more stable and is not so easily decomposed to a metamict state as thorite.

The metamict silicate, thoroostenstrupine, contains thorium instead of the rare earth elements in sreenstrupine (see Table 90-D-2). The rare mineral ekaonite, (Th, U) $(\text{Ca, Fe, Pb})_2\text{Si}_2\text{O}_6$, is also found in the metamict state; it recrystallizes above 650°C to some unknown phases and to huttonite (ANDERSON *et al.*, SR 1961, 538). A new thorium-beryllium-silicate, $\text{ThBe}_2\text{Si}_2\text{O}_6$, is probably structurally related to anorthite (GREBENSHCHIKOV, 1964).

V. Chalkogenides, Phosphides and Halides

A large number of thorium sulfides, selenides and tellurides is known. ThS and ThSe crystallize in the NaCl-structure and ThTe in the CsCl-structure (ZACHARIASEN, SR 1949, 139; D'EYE *et al.*, SR 1952, 135; FERRO, SR 1955, 289); ThS_2 occurs in the orthorhombic PbCl_2 structure (ZACHARIASEN, SR 1949, 155) as is ThSe_2 (D'EYE, SR 1953, 257). A typical layer structure (PbFCl-type) is present in the compounds ThOS (Fig. 90-A-1), ThOSe , and ThOTe (ZACHARIASEN, SR 1949, 217; FERRO, SR 1955, 289). Th_2S_3 and Th_2Se_3 are isostructural with Sb_2S_3 (ZACHARIASEN, SR 1949, 381), and Th_7S_{12} and $\text{Th}_7\text{Se}_{12}$ have a special structure type with 8- and 9-fold coordinated thorium (ZACHARIASEN, SR 1949, 184; D'EYE, SR 1953, 257).

Most of the phosphides, arsenides and antimonides of thorium are also isostructural (FERRO, SR 1955, 57 and SR 1956, 37), e.g. ThP , ThAs , ThSb (NaCl-type), ThAs_2 , ThSb_2 , ThBi_2 (anti- Fe_2As -type), and Th_3P_4 , Th_3As_4 , Th_3Sb_4 , Th_3Bi_4 (cubic Th_3P_4 -type).

The simple halides of thorium are listed in Table 90-A-2.

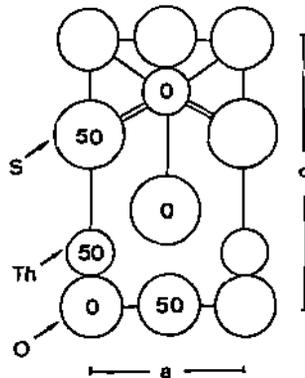


Fig. 90-A-1. The atomic arrangement in ThOS (PbFCl-structure) projected along one of the *a*-axes (FERRO, SR 1955, 289)

Table 90-A-2. *Thorium halides*

Compound	Structure type	Coordination number of Th	Reference
ThF ₄	UF ₄	8	ZACHARIASEN (SR 1949, 168)
ThCl ₄	UCl ₄	8	MOONEY (SR 1949, 167) MUCKER <i>et al.</i> (1969)
ThBr ₄	UCl ₄	8	D'EYE (SR 1950, 188)
ThI ₄	CdI ₂	6	ANDERSON and D'EYE (SR 1949, 159)
ThOF	CaF ₂	8	RANNON and LUCAS (1969)
ThO _{0.5} F _{2.5}	LaF ₃	11	RANNON and LUCAS (1969)
ThOF ₃	LaF ₃	11	ZACHARIASEN (SR 1949, 165)

Complex thorium fluorides have been reported representing a wide variety of compositions and structures: CaThF₆, SrThF₆, BaThF₆, PbThF₆ (LaF₃-type; ZACHARIASEN, SR 1949, 165); (NH₄)₄ThF₈ (RYAN *et al.*, 1969); (NH₄)₃ThF₇ (PENNE-MANN *et al.*, 1971); (Na, Li)₇Th₆F₃₁ (BRUNTON and SEARS, 1969); α-KTh₆F₂₅ (BRUNTON, 1972); RbTh₃F₁₃ (BRUNTON, 1971a); and K₇Th₆F₃₁ (BRUNTON, 1971b).

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90-C. Abundance in Meteorites, Tektites, and Lunar Materials

I. Meteorites and Tektites

The abundance of thorium and the Th/U ratios in meteorites are shown in Table 90-C-1. The uranium values from which the Th/U ratios are calculated are given in Table 92-C-1. Owing to the greater difficulty in analyzing for thorium than uranium, there are many more analyses for uranium than for thorium.

The average concentration of thorium in chondritic meteorites is in the range of 0.04 ppm. The average for achondrites is higher and the range is much greater than

Table 90-C-1. Contents of thorium and Th/U ratios in meteorites

Name	Class symbol	No. of sam- ples	Th $10^3 \times$ ppm	Th/U	Me- thod	Reference
<i>Stones</i>						
<i>Achondrites</i>						
Angra dos Reis	Aa	2	96.7	4.88	N	MORGAN and LOVERING (1964)
Binda	Ap	2	6.31	2.78	N	MORGAN and LOVERING (1964)
Bishopville	Ae	2	4.46	8.61	N	MORGAN and LOVERING (1964)
Ellemeet	Ab	2	0.379	2.51	N	MORGAN and LOVERING (1964)
Johnstown	Ab	2	0.57		N	BATE <i>et al.</i> (1957, 1959)
Juvinas		1	60		R	ROWE <i>et al.</i> (1963)
Moore Co.	Ap	2	6.20	3.16	N	MORGAN and LOVERING (1964)
Nakhla	Ado	2	19.0	3.86	N	MORGAN and LOVERING (1964)
Nuevo Laredo	Ap	1	54		N	BATE <i>et al.</i> (1957)
		2	47.6		N	BATE <i>et al.</i> (1959)
		1	47		R	ROWE <i>et al.</i> (1963)
fragment II		2	45.9	3.5	N	MORGAN and LOVERING (1965)
fragment III		2	49.2	3.5	N	MORGAN and LOVERING (1965)
Pasamonte	Aor	1	52		R	ROWE <i>et al.</i> (1963)
Sioux Co.	Ap	1	35		R	ROWE <i>et al.</i> (1963)
Stannern		1	50		R	ROWE <i>et al.</i> (1963)
<i>Chondrites</i>						
Beardsley	CH	1	4.3		N	BATE <i>et al.</i> (1957)
		1	4.77		N	BATE <i>et al.</i> (1959)
Forest City	CH	2	4.35		N	BATE <i>et al.</i> (1957)
		1	3.87		N	BATE <i>et al.</i> (1959)
Holbrook	CL	2	3.80		N	BATE <i>et al.</i> (1959)
Hvittis	Ce	2	3.11	5.02	N	LOVERING and MORGAN (1964)
Karoonda	CHL	2	5.66	4.13	N	LOVERING and MORGAN (1964)
Nodoc	CL	1	4.5		N	BATE <i>et al.</i> (1957)
		2	3.92		N	BATE <i>et al.</i> (1959)
Mokoia	CHL	2	6.05	4.32	N	LOVERING and MORGAN (1964)
Orgueil	Cc	2	6.48	2.68	N	LOVERING and MORGAN (1964)
Richardton	CH	2	3.80		N	BATE <i>et al.</i> (1959)

Table 90-C-1 (continued)

Name	Class symbol	No. of samples	Th $10^3 \times$ ppm	Th/U	Method	Reference
<i>Stony irons</i>						
Brenham	P					
(metal)		1	<0.07		R	REASBECK and MAYNE (1955)
(stone)		1	5.3		R	REASBECK and MAYNE (1955)
(olivine)		1	1.1		N	BATE <i>et al.</i> (1958)
<i>Irons</i>						
Arispe I		1	0.0015		N	BATE <i>et al.</i> (1958)
Arispe II		1	0.00058		N	BATE <i>et al.</i> (1958)
Sandia Mts.		1	0.001		N	BATE <i>et al.</i> (1958)

Table 90-C-2. Contents of thorium and Th/U ratios in tektites and glasses

Name	No. of samples	Th ppm	Th/U	Method	Reference
Australite	2	11.7	4.8	R	DUBET (1933)
	1	9.19	5.28	I	TILTON (1958)
	6	9.4	5.0	R	CHERRY (1962)
	1	12.9	4.8	R	CHERRY and ADAMS (1963)
	1	12.2		R	ROWE <i>et al.</i> (1963)
	8	12.7	6.1	R	BALACEK and ADAMS (1966)
Bediasite	3	4	3.3	R	ADAMS <i>et al.</i> (1959)
	2	8.6	5.9	R	CHERRY and ADAMS (1963)
	2	9.0		R	ROWE <i>et al.</i> (1963)
	10	7.2	3.9	R	BALACEK and ADAMS (1966)
Billitonite	1	9.6	3.6	R	DUBET (1933)
Indochinite	2	10.5	6.5	R	ADAMS (1956)
	4	13.0	6.4	R	CHERRY and ADAMS (1963)
	1	11.9		R	ROWE <i>et al.</i> (1963)
	5	12.7	5.9	R	BALACEK and ADAMS (1966)
Moldavite	4	15.4	5.8	R	DUBET (1933)
	1	11	6	R	ADAMS (1956)
	1	9.8	4.7	R	CHERRY and ADAMS (1963)
Philippinite	1	15	9	R	ADAMS (1956)
	1	15.7	8.5	R	CHERRY and ADAMS (1963)
	4	14.7		R	ROWE <i>et al.</i> (1963)
	12	14.6	5.8	R	BALACEK and ADAMS (1966)
Darwin glass	1	11.3	8.1	R	DUBET (1933)
Libyan Desert glass	1	3.3		R	ROWE <i>et al.</i> (1963)
Peruvian glass	2	3.6	0.2	R	CHERRY and ADAMS (1963)

for the chondrites. The thorium content of iron meteorites is extremely small. The average Th/U ratio for all of the stony meteorites is in the range of 3-4, with a few exceptional ones outside of this range. The average Th/U ratio is presumed to

be the fundamental ratio for the solar system, and calculations of the age of the earth based on lead isotope data are generally based on the assumption of a primordial Th/U ratio of 3.5. The reported values of Th/U ratio are, in some cases, based on uranium measurements by one investigator and thorium measurements on other pieces of the same meteorite by another investigator. The combination of separate values clearly yields less precision than determination of the Th/U ratio by measurements by the same investigator on the same sample; Table 90-C-1 reports Th/U ratios only for measurements on the same sample.

Thorium concentrations in tektites are reported in Table 90-C-2, and comparable uranium values are given in Table 92-C-2. The thorium concentrations in tektites are much higher than in meteorites and average about 8 to 10 ppm, which is very close to the average concentration in the continental crust. The Th/U ratios for tektites are also reported in Table 90-C-2, and the uranium values on which they are based are given in Table 92-C-2. The Th/U ratios in tektites are on the order of 4 to 5 and seem to be somewhat higher than in meteorites or in most crustal materials. The origin of these slightly higher ratios is unknown. As discussed in Chapter 92, the high thorium and uranium contents of tektites are difficult to explain in terms of an extra-terrestrial origin.

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II. Lunar Materials

More than 500 analyses of thorium in lunar rocks obtained by neutron activation, γ -ray spectroscopy of natural radioactivity, and mass spectrometry have been summarized in Table 90-C-3 (spark source mass spectrometry data were not included). As the distribution of thorium in lunar rocks is intimately associated with that of uranium, the same rocks as in Table 92-C-3 are grouped together. The same problems, that existed with uranium with proper classification of rock types and with the inadequacy of the sample sizes also exist with thorium. The rock groups of Table 90-C-3 could certainly be arranged in many other ways. The variation within a rock group at one particular landing site is, in general, smaller than between similar rock groups of different landing sites. If the rocks are classified as in Table 90-C-3, the relative standard deviations from the means in 67% of the cases are less than 30% and exceed 50% only in 19% of the cases. Although hardly any sample can be claimed to be representative of a rock type, the large number of analyses and the remarkable agreement of the results by different analytical methods on rocks of the same group permits some generalizations to be made.

The lowest Th content, 0.0032 ppm, was found in an anorthosite, the highest, 34.2 ppm, in a granitic portion of a breccia. The average anorthosite contains 0.09 ppm Th and the average low-K mare basalt 0.7 ppm Th. The Th content of the other rocks is dominated by their KREEP component, the hypothetical rock which besides K, REE and P is enriched in other incompatible elements like U and Th. The different proportion of KREEP in the soils, breccias and melt rocks (anorthositic, troctolitic, very high alumina basalts and Apollo 14, 15 and 17 KREEP basalts) is reflected by their varying Th content.

The geochemical coherence of Th and U in lunar samples is even more pronounced than in terrestrial rocks. This is demonstrated by the constancy of the Th/U

Table 90-C-3. Thorium in lunar rocks

	Mean ppm Th	Range ppm Th	s	Number of analyses	References
<i>Apollo 11</i>					
Soils	2.05	1.31-2.3	0.30	12	16, 20, 39, 44, 46, 53, 60, 64, 66
Breccias	2.50	1.90-3.72	0.65	6	38, 44, 60
High-K basalts	3.33	2.80-4.03	0.38	17	21, 38, 39, 44, 46, 60, 61
Low-K basalts	0.82	0.53-1.08	0.19	12	38, 39, 46, 60, 61
<i>Apollo 12</i>					
Soils	6.73	3.2-13.5	1.98	39	2, 9, 17, 36, 40, 49, 53, 55, 61, 63, 66
Breccias	16.85	8.45-34.2	8.45	13	17, 19, 31, 36, 40, 49, 62, 63
Basalts	0.90	0.24-2.19	0.31	58	2, 9, 19, 24, 31, 36, 40, 43, 49, 55, 61, 63
<i>Apollo 14</i>					
Soils	13.30	11.3-15.9	1.38	23	6, 10, 15, 27, 28, 41, 48, 50, 56, 65
Breccias	14.14	4.2-21	3.65	21	3, 10, 15, 24, 56, 65
Melt rocks	11.37	8.6-13.3	1.29	11	3, 10, 24, 27, 41, 48, 51
Basalts	2.19	1.98-2.38	0.18	4	24, 48, 51
<i>Apollo 15</i>					
Soils	4.07	1.8-7.35	1.05	44	1, 14, 18, 24, 26, 27, 37, 41, 56, 58
Breccias	3.39	2.0-5.9	1.19	11	24, 37
KREEP-rich breccias	12.25	12.0-12.6	0.30	4	24, 41
Basalts	0.52	0.40-0.70	0.10	11	1, 24, 37, 41, 58
Anorthosites	0.065	0.028-0.102	—	2	24
<i>Apollo 16</i>					
Soils	1.91	0.51-2.77	0.50	65	1, 4, 8, 11, 13, 26, 30, 32, 52, 57, 58, 67
Breccias	2.10	0.22-7.8	1.68	50	4, 8, 11, 13, 22, 25, 30, 32, 58, 59
KREEP-rich breccias	9.15	8.1-10.34	0.82	8	4, 8, 11, 25, 29, 32
Melt rocks	2.23	0.63-3.55	1.16	7	1, 8, 11, 13, 22, 32
Anorthosites	0.096	0.0032-0.49	0.18	7	8, 22, 32, 52, 67
<i>Apollo 17</i>					
Soils	1.69	0.3-3.0	0.87	53	4, 7, 12, 13, 18, 25, 33, 42, 58, 59
Breccias	4.48	1.86-6.05	1.29	26	5, 12, 18, 22, 25, 34, 58, 59
Melt rocks	1.03	0.4-1.49	0.29	11	22, 25, 35
Basalts	0.38	0.17-0.79	0.11	32	5, 12, 13, 18, 25, 33, 58
<i>Luna 16</i>					
Soils	0.94	0.47-1.23	0.33	4	23, 50, 54
<i>Luna 20</i>					
Soils	1.09	0.73-1.54	0.29	5	26, 45, 47, 52

References: Abbreviations P I to P VI = Proceedings of the Lunar Science Conferences, *Geochim. et Cosmochim. Acta*, Supplements 1 to 6; GCA = *Geochim. et Cosmochim. Acta*; EPSL = *Earth Planet. Sci. Letters*.

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ratio for whole rock samples. The mean and median Th/U ratio of 477 determinations on the same rock samples (for references see Table 90-C-3) is 3.65, with 67% within ± 0.3 of this value. The smallest ratio reported is 1.8 in an anorthosite of Apollo 16 and the largest 6.1 in a breccia of Apollo 11. However, on a small scale there exist differences of two orders of magnitude: apparently U and Th concentrate during crystallization differentiation and are enriched in interstitial residual liquids. They enter discrete minerals only in the very last stage of crystallization; it is then that the two elements segregate. BURNETT *et al.* (1971, P II, 1503)¹ report Th/U ratios for zircon of between 0.2 and 3.6, for a Zr-Ti-mineral of 2.9, for apatite $\sim 5 \pm 1$ and for whitlockite, of between 6.8 and 20. ANDERSEN *et al.* (1972, EPSL 14, 195) found Th/U ratios of 0.5–0.8 in zircon, 0.5 in baddeleyite, 1.6–1.7 in zirkelite, 2.2 in a Ti-Zr

¹ The abbreviations P I to P VI refer to the Proceedings of the First to Sixth Lunar Science Conferences, *Geochim. Cosmochim. Acta* Supplements 1 to 6. EPSL means Earth and Planetary Science Letters.

silicate, and 5.5 in REE phosphate and 20 in a whitlockite. BUSCHE *et al.* (1972, EPSL 14, 313) report Th/U ratios of between 1.8 and 2.6 for a mineral which is probably zirkelite and HAINES *et al.* (1971, EPSL 12, 145 and 1975, PVI, 3527) report ratios of 8-14 in whitlockite and 1.5 in a REE-rich Zr-Ti phase (in this the highest Th content of 4.1% was found). From these data it is obvious that Th is preferably incorporated in phosphates and U in Zr-minerals. These differences probably explain part of the spread for whole rock Th/U ratios because many of the samples analyzed were extremely small.

The orbital γ -ray mapping experiment (METZGER *et al.*, 1974, P V, 1067) yielded average Th concentrations of 0.9 ppm for the highlands, 3.2 ppm for the maria, and 2.2 ppm as an average for the surface. Although these numbers are very different from those that may be calculated from the soil data of Table 90-C-3 they are probably more representative. The reason for this is that the orbital data for the least heterogeneous landing sites (Apollo 11 and 16) agree well with the averages of the soils. As is the case with uranium, these concentrations are due to strong enrichment in the lunar crust. Many models for the evolution of the moon (for references see Sect. 92-C-III) arrive at ~ 0.06 ppm U as the average for the entire moon. Under the assumption that the ratio Th/U = 3.65 is constant this implies that the average Th content of the moon is ~ 0.2 ppm.

The isotopic composition of lunar thorium was studied by ROEHOLT *et al.* (1970, P I, 1499 and 1595; 1971, P II, 1577). They measured the $^{230}\text{Th}/^{232}\text{Th}$ ratio by α -particle spectrometry. Comparison of the measured ratio with the ratio which has to be expected from the ^{232}Th and ^{238}U contents revealed excesses at the α -particle energy of the ^{230}Th 4.68 MeV peak in some crystalline rocks. This excess seems to increase with the KREEP component and may reach 80%. As the effect cannot be explained by disequilibrium in the ^{238}U - ^{234}U - ^{230}Th decay sequence, the existence of an isomer of ^{232}Th ($^{232\text{m}}\text{Th}$) is suggested which emits α -particles of ~ 4.7 MeV and which is accompanied by a decay series collateral to the regular decay series for ^{232}Th . It is possible that a variable cosmogenic history for ^{232}Th and $^{232\text{m}}\text{Th}$ may exist.

90-D. Abundance in Rock Forming Minerals (I); Thorium Minerals (II); Phase Equilibria (III)

I. Rock Forming Minerals

The concentrations of thorium in various rock-forming minerals are given in Table 90-D-1. The Th/U ratios shown in the table are calculated with the aid of the uranium data given in Table 92-D-1. As discussed in Chapter 92, Section D, the precise location of radioactive elements in rock-forming minerals is uncertain. In minerals such as allanite, huttonite, and monazite, the thorium clearly occupies one or more of the cation sites in the lattice as a major constituent. In zircon it may be presumed that thorium substitutes for zirconium, and in fact the Th/Zr ratio is relatively constant for a variety of crustal materials (for discussion see ADAMS *et al.*, 1959). In minerals such as epidote or potassium feldspar, it is uncertain whether thorium occurs in lattice sites, interstitial positions, submicroscopic defects, or perhaps in the form of individual small grains of thorium minerals.

The Th/U ratios of the various minerals reflect the ability of crystal lattices to discriminate between thorium and uranium. Thus allanite, huttonite, and monazite are primarily thorium minerals and have high Th/U ratios, whereas xenotime is primarily a uranium mineral. Zircon and sphene, common accessory minerals in granite, have Th/U ratios of 1–2, which contrasts with the general 3.5–4 ratios for whole igneous rocks. Whether these low ratios for zircon and sphene reflect differential inclusion of uranium in the mineral or possibly precipitation from an early magma of lower Th/U ratio than the magma from which the final rock crystallized is uncertain.

II. Thorium Minerals

Thorium is a major cation in a variety of minerals, none of which are at all common. Table 90-D-2, based largely on FRONDEL (1956), lists the various thorium minerals. The scarcity of thorium, its ability to substitute for other elements in crystal lattices, and the absence of a geochemical method of concentration of the element all combine to render thorium a highly dispersed material. Dispersal contrasts markedly with the tendency of uranium to become concentrated by precipitation from waters carrying the soluble, oxidized uranyl ion (see Chapter 92). Thorium occurs naturally only as the comparatively insoluble tetravalent ion.

Mineral formulas are those given by FRONDEL (1956) except in the case of minerals discovered since 1956 or minerals whose formulas have been modified by later work. References are given in each case of more recent discovery or new description. Papers consulted only secondarily through summaries in the *American Mineralogist* are shown in the reference list with a parenthetical reference to volume and page in the *American Mineralogist*.

Table 90-D-1. Contents of thorium and Th/U ratios in minerals in igneous rocks

	Th in ppm	Th/U	References (no. of samples)
<i>Major minerals</i>			
Quartz	0.5—10	1—5	A (3); C (1); J (6); K (5); M (1)
Feldspar (including potassium feldspar and plagioclase)	0.5—10	1—6	A (5); C (1); J (6); K (5); M (1)
Biotite	0.5—50	0.5—3	A (1); J (6); K (5); M (1)
Hornblende	5—50	2—4	A (1); J (4); M (1)
Olivine (from dunite)	0.02	low	L (2)
<i>Accessory minerals</i>			
Allanite	9100 1 × 10 ³ to 2 × 10 ⁴	high high	G (10) B (1); F (4); G (10); J (6); K (5); M (1); N (1)
Apatite	70 50—250	1.3 ~1	E (29) C (1); E (29); J (6); K (5); M (1)
Epidote	200 50—500	4.8 2—10	E (9) E (9)
Huttonite	nearly pure ThSiO ₄		N (individual grains in one rock)
Magnetite (and other opaque minerals)	0.3—20		A (12); C (1); J (6); K (5); M (1)
Monazite	125,000 49,700 2 × 10 ⁴ to 2 × 10 ⁶	high ~25 high	F (15) E (11) E (11); F (15); H (4)
Sphene	510 100—1,000	1.7 1—3	E (25) C (1); E (25); J (6); K (5)
Thorianite and Uraninite	varies from ThO ₂ to UO ₂		
Thorite and Uranothorite	varies from ThSiO ₄ to USiO ₄ (?) (solid solution may not be complete)		
Zircon	560 100—10 ⁴	0.4 0.2—2	E (43) C (1); D (21); E (43); J (6); K (5)

Ranges shown in the table are those within which thorium concentrations and Th/U ratios commonly occur rather than the extreme ranges for suites of samples. Averages are given only for: suites of minerals separated from North American rocks and reported by reference E, using gamma-radiometric methods; monazites reported by reference F, using dilution; and allanites reported by reference G, using radiometric methods.

A: KEEVIL (1944); B: HUTTON (1951); C: TILTON *et al.* (1955); D: WEBBER *et al.* (1956); E: HURLEY and FAIRBAIRN (1957); F: MURATA *et al.* (1957); G: W. L. SMITH *et al.* (1957); H: TILTON and NICOLAYSEN (1957); J: LEONOVA and TAUSON (1958); K: LEONOVA (1962); L: HEIER and CARTER (1964); M: LEONOVA and RENNE (1964); N: RICHARDSON (1964).

Data on Th/U ratios are given by HURLEY and FAIRBAIRN (1955), and preliminary data on accessory allanite is provided by PHAIR (1955).

III. Phase Equilibria

MUMPTON and ROY (1961) have investigated the system ThO₂—UO₂—SiO₂ both dry and in the presence of water. A preliminary diagram of the system is shown in Fig. 90-D-1. Their conclusions may be summarized as follows:

1. Huttonite (monoclinic) is the stable form of ThSiO_4 at all temperatures, and thorite (tetragonal) is metastable.

2. Thorite dissolves not more than about 35 mol percent " USiO_4 " (which does not exist as a separate phase), although other workers have reported considerable isomorphism between ThSiO_4 and the hypothetical " USiO_4 ".

3. ThO_2 and UO_2 are completely isomorphous at high temperatures; (experiments were performed at 1,350 degrees C.).

4. ThSiO_4 melts incongruently near 2,000 degrees C. to ThO_2 and SiO_2 ; (this conclusion is a citation of the work of another author).

5. Zircon dissolves less than 1 mol percent ThSiO_4 and 5 mol percent " USiO_4 ".

The frequency distribution of thorium concentrations in zircons has been studied by AHRENS (1965). The presumed lognormality of this distribution is also characteristic of uranium.

Table 90-D-2. Minerals containing thorium as a major constituent

Brockite	$\text{Ca}_{0.43}\text{Sr}_{0.03}\text{Ba}_{0.01}\text{Th}_{0.41}\text{RE}_{0.11}(\text{PO}_4)_{0.43}(\text{CO}_3)_{0.17} \cdot 0.9 \text{H}_2\text{O}$ (FISHER and MEYROWITZ, 1962)
Cheralite	(Th, Ca, Ce) $(\text{PO}_4, \text{SiO}_4)$
Ekanite	(Th, U) $(\text{Ca, Fe, Pb})_2\text{Si}_6\text{O}_{20}$ (ANDERSON <i>et al.</i> , 1961)
Huttonite	ThSiO_4
Monazite	(Ce, Y, La, Th) PO_4
Thorbastnaesite	$\text{Th}(\text{Ca}_{0.8}\text{RE}_{0.2})(\text{CO}_3)_2\text{F}_2 \cdot 3 \text{H}_2\text{O}$ (PAVLENKO <i>et al.</i> , 1965)
Thorianite	ThO_2
Thorite	ThSiO_4
Thorogummite	$\text{Th}(\text{SiO}_4)_{1-x}(\text{OH})_{4x}$
Thorosteenstrupine	$(\text{Ca, Th, Mn})_2\text{Si}_4(\text{O}_{11.24}\text{F}_{0.95})_{17.2} \cdot 5 \text{H}_2\text{O}$ (KUTRIYANOVA <i>et al.</i> , 1962)
Thoutite (Smimovite)	ThTi_2O_6 (GOYMAN and KHAPAEV, 1958)
Uranothorianite	$(\text{Th, U})\text{O}_2$
Uranothorite	$(\text{Th, U})\text{SiO}_4$ solid solution may be incomplete

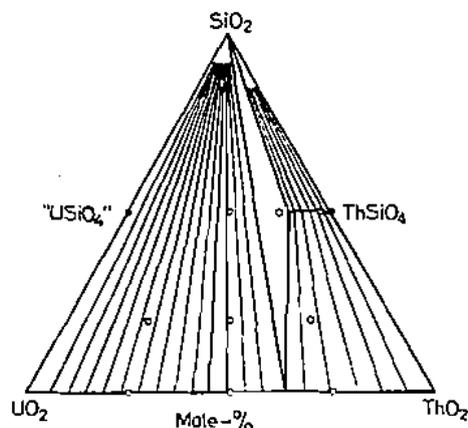


Fig. 90-D-1. Possible, though not completely verified, phase diagram of the ThO_2 - UO_2 - SiO_2 system in the neighborhood of 1350° C. (From MURPHY and ROY, 1961)

90-E. Abundances in Common Igneous Rocks

Thorium contents and the Th/U ratios in various types of igneous rocks (Table 90-E-1) are discussed under several subheadings. This section includes a description of the average thorium content and Th/U ratios of various major rock groups, the variation in thorium content and Th/U ratios in differentiation sequences, the recognition of provinces of high thorium and uranium abundance, and various problems concerning the homogeneity of the distribution of thorium and uranium within the earth. The Th/U ratios shown in Table 90-E-1 are calculated using uranium data presented in Table 92-E-1.

Table 90-E-1. Thorium contents and Th/U ratios of selected igneous rock suites

Suite	No. of samples	Th ppm	Th/U	Method	Reference
<i>Granitic rocks</i>					
Russia:					
Precambrian mica granites of Ukrainian shield (middle Dnepr area)	100	33	5.8	emanation	FILIPPOV and KOMLEV (1959)
Tertiary Megrinsk intrusions of Southern Armenia; alkalic granodiorites to alkalic granites of 2nd intrusive phase	7	32	6.3		MELIKSETYAN (1961)
Northern Tien Shan; weighted av. of all crystalline rocks	—	15	3.7		KRYLOV (1963)
Paleozoic granites and syenites of Central and Western Tuva	47	16.0	4.1	radio-chemical	ABRAMOVICH (1959)
United States:					
Conway granite, New Hampshire, Triassic, alkalic	1,265	56	3.7	R	ADAMS <i>et al.</i> (1962); ROGERS <i>et al.</i> (1965)
New England granites	123	26	4.5	R	ROGERS (1964)
Enchanted Rock batholith, Texas, granite	81	20	6	R	ROGERS (1964)
Precambrian granites of Front Range, Colorado	38	25.5	5.1	C	PHAIR and GOTTFRIED (1964)
Laramide stocks of Front Range, Colorado	23	30	4.0	C	PHAIR and GOTTFRIED (1964)
Laramide stocks west of Front Range, Colorado	25	9.7	4.5	C	PHAIR and GOTTFRIED (1964)

Table 90-E-1 (Continued)

Suite	No. of samples	Th ppm	Th/U	Method	References
Precambrian granites of middle Rocky Mts.	24	16	—	C	PHAIR and GOTTFRIED (1964)
Idaho batholith; Laramide: tonalites and granodiorites	17	11	5.0	C	LARSEN JR. and GOTTFRIED (1961)
gtz. monzonites and granites	9	17.8	4.7	C	LARSEN JR. and GOTTFRIED (1961)
Sierra Nevada batholith, Cal.; granodiorites to granites; Jurassic	20	18	3.5	various	ROGERS (1964)
Laramide granites of Idaho batholith, Boulder batholith, and northern Washington	38	10	4.7	various	ROGERS (1964)
Granites and granodiorites of Southern Cal. batholith; Cretaceous	54	8	3.8	various	ROGERS (1964)
<i>Gabbroic and ultramafic rocks</i>					
General average for "gabbroid" rocks	24	3.84	4.3	various	HEIER and CARTER (1964)
Dunite (North America)	3	0.05	low	various	HEIER and CARTER (1964)
<i>Eclogites</i>					
Pipe eclogite (Africa)	10	0.44	2.3	R	HEIER (1963)
Pipe eclogite (Africa-1; Australia-3)	4	0.22	4.2	N	LOVERING and MORGAN (1963)
Average eclogite from metamorphic terranes (Norway and central Europe)	9	0.46	2.2	various	HEIER and CARTER (1964)
<i>Alkaline intrusive rocks</i>					
Nepheline syenites (northern Norway)	16	0.55	6	R	HEIER (1962a)
Nepheline syenites of Lovozero massif, Kola Peninsula; weighted av.	—	35	—	C	POLYAKOV and KOT (1964)
Variscan alkalic syenites and nepheline syenites of southern Tien Shan	26	17	5.6	C	LEONOVA (1964)
Various suites from Kola Peninsula, Russia:					
Lesnaya Varaka (olivinite)	2	0.65		C	POLYAKOV and VOLYNETS (1961)
Afrikanda (pyroxenite)	10	21.5		C	POLYAKOV and VOLYNETS (1961)
Lake Varaka (alkalic)	5	27.8		C	POLYAKOV and VOLYNETS (1961)

Table 90-E-1 (Continued)

Suite	No. of Th samples	Th ppm	Th/U	Method	References
<i>Basaltic rocks</i>					
Oceanic tholeiitic basalts	22	0.18	1.8	I	TATSUMOTO <i>et al.</i> (1965)
Basalts and basaltic andesites of Mariana Islands	20	1.1	2.2	C	GOTTFRIED <i>et al.</i> (1963)
Tholeiitic basalts of Hawaii	6	0.69	4.0	R	HEIER <i>et al.</i> (1964)
	23	0.95	3.0	C	LARSEN, 3d, and GOTTFRIED (1960)
Alkali basalts of Hawaii	2	3.9	3.7	R	HEIER <i>et al.</i> (1964)
	7	5.4	3.1	C	LARSEN, 3d, and GOTTFRIED (1960)
<i>Japan</i>					
tholeiitic basalts	2	0.19	1.6	R	HEIER and ROGERS (1963)
high-alumina basalts	2	0.78	3.7	R	HEIER and ROGERS (1963)
alkali-olivine basalts	2	3.9	7.6	R	HEIER and ROGERS (1963)
<i>Caribbean Island arc spilites</i>					
intrusive keratophyres	6	0.26	1	R	ROGERS and DONNELLY (1966)
extrusive keratophyres	5	0.84	1	R	ROGERS and DONNELLY (1966)
basaltic andesites	4	0.39	1.4	R	ROGERS and DONNELLY (1966)
	12	1.90	2.4	R	ROGERS and DONNELLY (1966)
Plateau basalts (av.)	21	1.96	4.2	various	HEIER and CARTER (1964)
Columbia River	2	1.0	3.3	R	HEIER and ROGERS (1963)
Palisades (New York)	5	1.8	5.3	R	HEIER and ROGERS (1963)

I. Abundances in Various Rock Groups

Table 90-E-1 shows the thorium contents and Th/U ratios for a variety of groups of igneous rocks. These groups represent suites of rocks or large assemblages of similar rock types which may be considered as individual populations. No effort has been made in Table 90-E-1 to summarize all of the measurements of thorium in igneous rocks.

Although an average thorium concentration for granites, for example, is essentially unobtainable owing to the extreme variation in thorium content from one type of granite to another, it is possible, nevertheless, to indicate the general range of thorium concentrations for major rock types. As shown in Table 90-E-1 the thorium content of granite is in the range of 10–20 ppm and decreases steadily through the

intermediate rock types to a concentration in the range of 0.5—2 ppm for various types of basalt and gabbro. The thorium concentration thus shows the same increase in abundance as the uranium concentration toward the more petrologically differentiated rock types. In fact, the K/Th ratio has been found to have a nearly constant value of approximately 3×10^3 in a large variety of igneous rocks (HELER and ROGERS, 1963). This constancy of the K/Th ratio has been noted in sediments as well as in igneous rocks by PLILER and ADAMS (1962a), and the K/Th ratio is, in general, even more constant than the K/U ratio in surficial materials. The extremely high concentration of thorium in alkaline rocks is noteworthy in view of the general tendency for thorium and potassium to occur together. Table 90-E-1 shows no significant differences between extrusive and intrusive rocks in regard to their thorium contents or their Th/U ratios.

The average thorium content of the continental crust may be estimated from the data given in Table 90-E-1 providing that the proportion of various rock types composing the crust is known. This problem has been discussed by a number of authors including PHAIR and GOTTFRIED (1964) for thorium and uranium and ROGERS (1966) for the general problem of geochemical balances. The abundance of granite in the earth's crust is almost certainly less than 50 percent, and most of the other rock types contain much less thorium and uranium than granite. Thus the average thorium content of the continental crust may be estimated in the range of 6—10 ppm, approximately one half the concentration in the highly differentiated granites. As discussed in Section 92-E, the uranium content of the continental crust is approximately 2 ppm, and thus the Th/U ratio for the continental crust should be about 3—4.

The average Th/U ratio for igneous rocks is shown by Table 90-E-1 to be in the range of 3.5 to 4. As discussed in Section 90-C, a primordial Th/U ratio of 3.5 is commonly used for calculations of the age of the earth by lead isotope methods. The similarity of crustal and cosmic ratios, however, does not indicate that the crust is a comprehensive sample of the cosmos. As pointed out, for example, by GAST (1960) and a number of other workers, the ratio of K/U and K/Th in the average chondritic meteorite is not the same as in crustal rocks. Furthermore, as discussed below, the Th/U ratio in rocks derived directly from the upper mantle is generally in the range of 1 to 2, thus indicating some type of preferential enrichment of thorium in crustal materials during igneous evolution.

The thorium and uranium contents and Th/U ratios in the upper mantle are of considerable interest in connection with heat flow studies, isotopic studies of lead, and also in regard to understanding the separation of the continental crust. The subject of heat flow is discussed more completely in the chapter on uranium (Section 92-B).

Obviously no direct measurements of the upper mantle are possible, but the study of primitive basalts derived from the mantle gives some information concerning its composition. TATSUMOTO *et al.* (1965) have determined the thorium and uranium contents of some mid-oceanic tholeiitic basalts. As discussed in that paper and references cited by it, these oceanic basalts appear to be the most primitive direct derivatives from the upper mantle. The values obtained by TATSUMOTO *et al.* of approximately 0.1 ppm uranium and 0.18 ppm thorium in the tholeiitic basalts correlate rather well with the thorium and uranium contents of the spilites reported by ROGERS

and DONNELLY (1966) from the Caribbean area and some similar early-orogenic basalts from western Oregon. Apparently, as discussed by ROGERS and DONNELLY, the early stages of eugeosynclinal activity represent a tapping of relatively undifferentiated upper mantle material. The thorium and uranium content of the Caribbean and other eugeosynclinal materials gradually increases from the low values found in the spilites characteristic of early volcanic stages, and the orogenic sequence presumably terminates with the development of the typical silicic, highly radioactive rocks of a continental craton.

The thorium and uranium contents of the primitive oceanic tholeiitic basalts and eugeosynclinal spilites are essentially identical to the abundances of the elements estimated by heat flow studies for the upper mantle (see, for example, BIRCH, 1965).

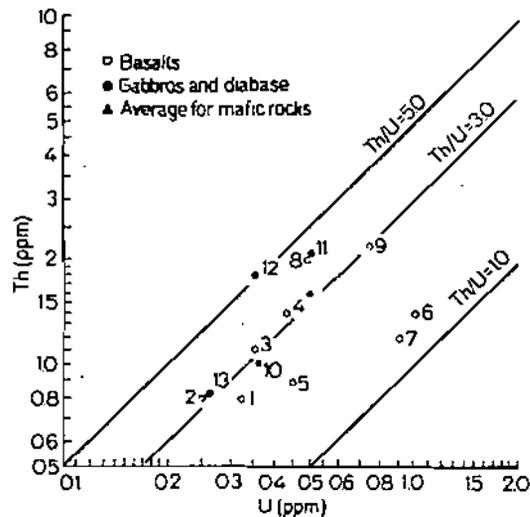


Fig. 90-E-1. Thorium and uranium contents of selected groups of mafic igneous rocks. Note the general tendency toward Th/U ratios of 3.0 or less. [From PETERMANN, Z. E.: unpublished, personal communication (1963)]

The similarity cannot, of course, result from bulk melting in the upper mantle, and it must be concluded that the fractional melting of the basaltic lava in the mantle takes place without fractionation of thorium and uranium between the solid and liquid phases. If there is no fractionation during partial melting, then the Th/U ratio of the upper mantle is the same as in the oceanic tholeiitic basalts (approximately 2). In view of a cosmic Th/U ratio of about 3.5, this ratio of 2 is probably not representative of the mantle as a whole. Additional data are needed, however, before this conclusion can be verified.

The fact that the Th/U ratio of primitive basalts is low (Fig. 90-E-1), plus the dissimilarity of the K/U ratio between rocks of the continental crust and the presumed bulk composition of the earth (e.g., see GASR, 1960) indicate segregation of radioactive constituents during continental evolution. It may be that the continental masses represent an ultimate stable segregate from the remainder of the earth, and thus their thorium and uranium concentrations and Th/U ratio of 3.5 to 4 give a comprehensive estimate of the radioactivity of terrestrial material. It is also possible,

however, that different elements such as thorium and uranium diffuse upward out of the mantle at different rates, and the continents may not represent the ultimate differentiate. The fact that the Th/U ratio in continental crusts is similar to that assumed for the universe as a whole probably indicates that the craton is a stable ultimate differentiate from the mantle, although considerable doubt must be attached to this conclusion.

II. Variation within Igneous Rock Series

As mentioned in the preceding section, the thorium concentration of igneous rocks generally increases toward the silicic, more differentiated members of a series.

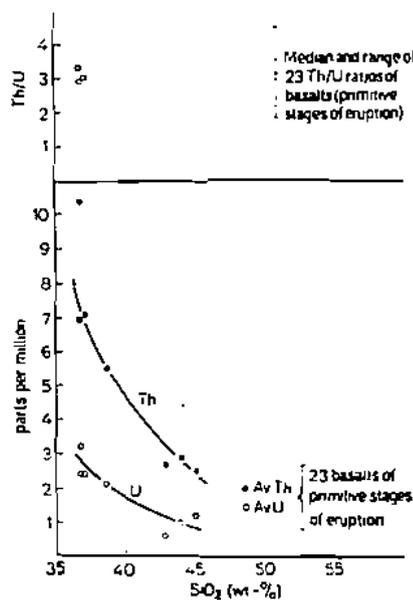


Fig. 90-E-2

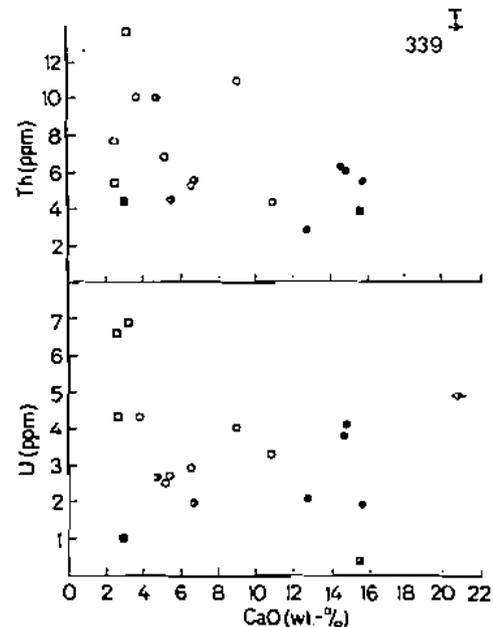


Fig. 90-E-3

Fig. 90-E-2. Variation of thorium and uranium concentrations and Th/U ratios in rocks of the Honolulu Series, Hawaiian Islands. The Honolulu Series is a group of alkalic basalts younger than the main tholeiitic basalts. [From PETERMAN, Z. E.: unpublished, personal communication (1963); based on data from LARSEN, 3rd, and GOTTFRIED, 1960]

Fig. 90-E-3. Distribution of uranium and thorium in rocks of the Magnet Cove igneous complex. Concentrations are plotted against CaO content. Plots of thorium and uranium concentrations against other major element abundances show no better correlation. [From PETERMAN, Z. E.: unpublished, personal communication (1963); based on data from ERICKSON and BLAOG, 1963]

A large number of differentiation sequences is described by PETERMAN (1963), and the only one in which thorium content decreases towards the younger rocks is the Honolulu sequence of Hawaii (Fig. 90-E-2). As mentioned in section 92-E, the Honolulu series is also the only one in which uranium content decreases with differentiation. Plots of thorium content against silica content in differentiation sequences are generally more scattered (Figs. 90-E-2 to 90-E-7) than plots of thorium against other differentiation indexes such as the Larsen index or the potassium

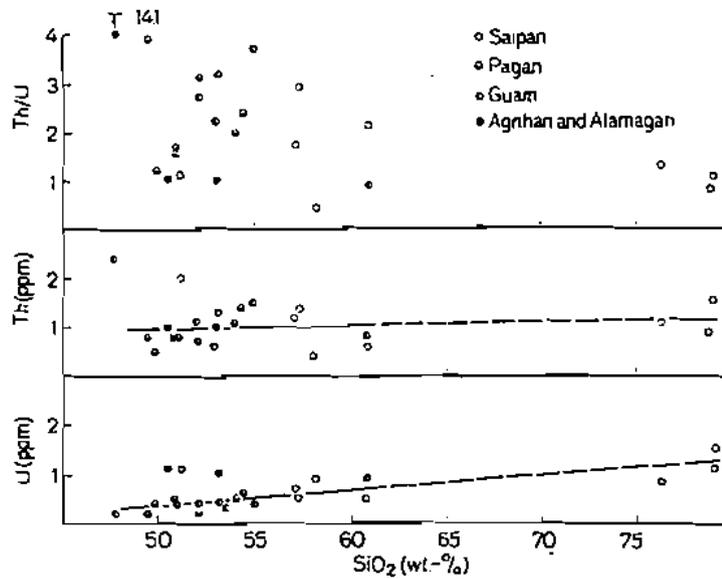


Fig. 90-E-4. Variation of thorium and uranium concentrations and Th/U ratios in volcanic rocks of the Marianas Islands. (From PETERMAN, Z. E.: unpublished, personal communication (1963); based on data from GOTTFRIED *et al.*, 1963)

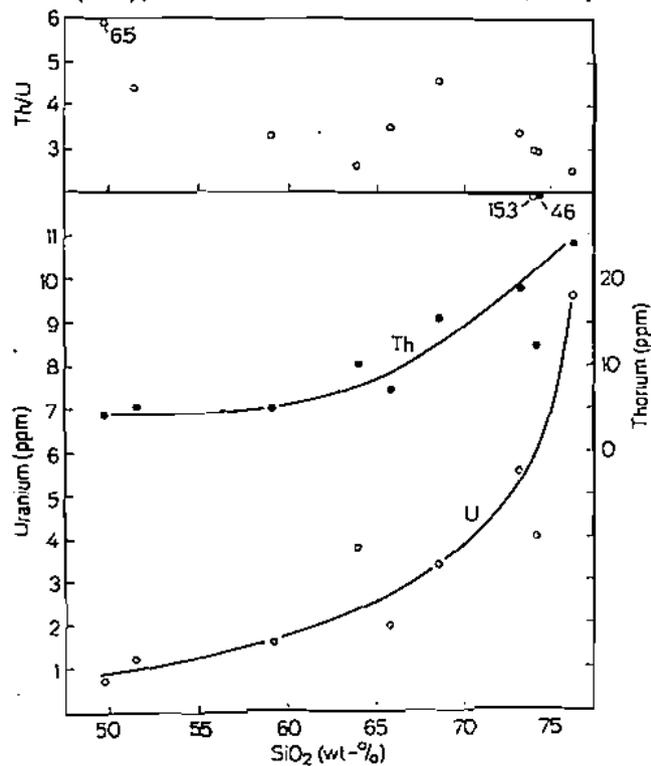


Fig. 90-E-5. Variation of thorium and uranium concentrations and Th/U ratios in rocks of the Valles Mountains, New Mexico, U.S.A. [From PETERMAN, Z. E.: unpublished, personal communication (1963); based on data from LARSEN, 3rd, and GOTTFRIED, 1960]

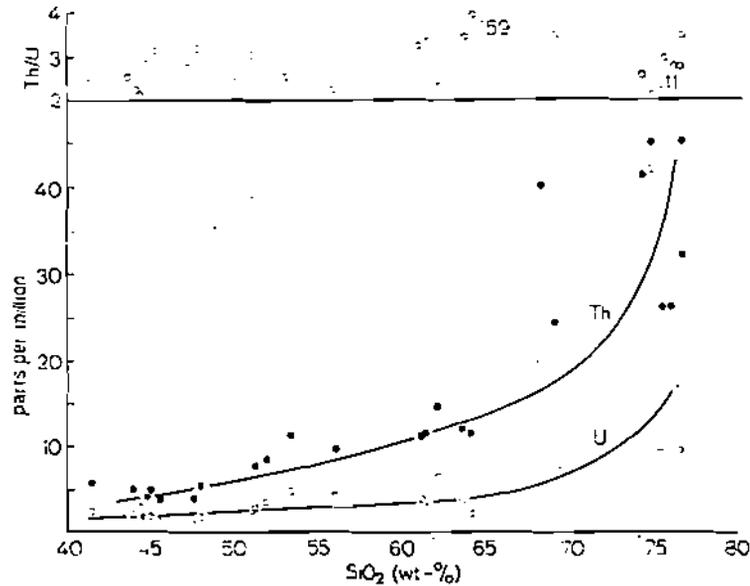


Fig. 90-E-6. Variation of thorium and uranium concentrations and Th/U ratios in alkalic volcanic and hypabyssal rocks of Big Bend National Park, Texas, U.S.A. [From PETERMAN, Z. E.: unpublished, personal communication (1963); based on data from LARSEN and GOTTFRIED, 1960]

content. Plots of thorium against potassium are almost invariably quite linear. In PETERMAN's (1963) summary, the number of differentiation sequences in which thorium has been studied is less than the number in which uranium has been studied. The sequences in which uranium content increases with differentiation are listed in Table 92-E-2. Among those sequences are several in which the thorium content has been found to increase toward the younger members of the sequence; these are listed in Table 90-E-2 (Figs. 90-E-5 to 90-E-8).

Variation in the Th/U ratios in igneous rock series has been a topic of considerable discussion. LARSEN, 3rd and GOTTFRIED (1960) found no general relationship between the ratios and position in several differentiation sequences. Among the sequences summarized by PETERMAN (1963), however, some increase in the Th/U ratio toward the younger members of the series is shown by the White Mountain and Oliverian intrusive sequences, whereas the extrusive sequences in the Mariana Islands, Lassen Park, and the Valles Mountains show a decrease in the Th/U ratio with increasing differentiation. A general increase in the Th/U ratio with differentiation has been proposed in several papers. ROGERS and RAGLAND (1961) found a weak, though statistically valid, relationship between Th/U ratios and potassium content for a large suite of silicic intrusive rocks (Fig. 90-E-9). The increase in ratio with differentiation is attributed to the oxidation proposed by OSBORN (1959) as necessary for the evolution of granitic magmas. HEIER and ROGERS (1963) found a linear relationship between Th/U ratio and potassium content for various apparently primary basalts (Fig. 90-E-10). As shown in Table 90-E-1, the Th/U ratio for many basic rocks is somewhat lower than for silicic ones.

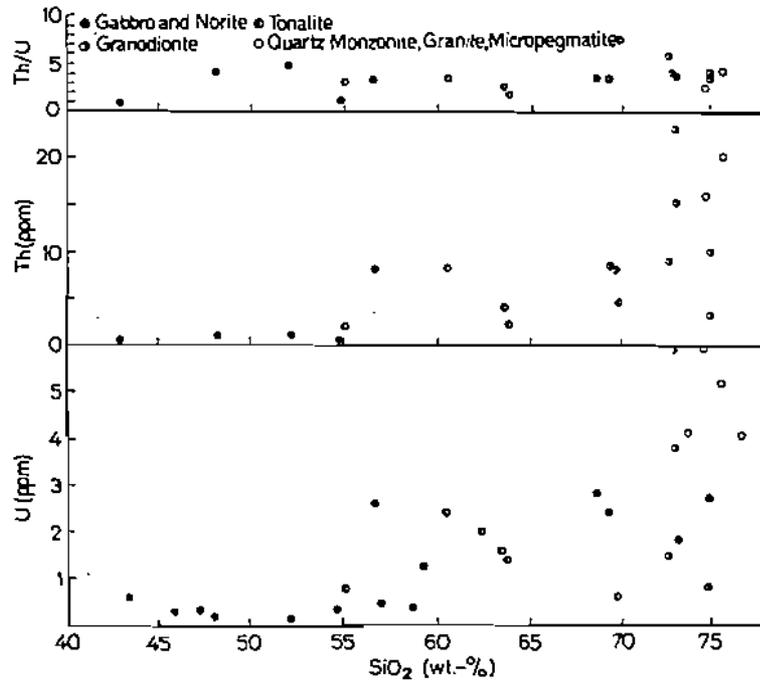


Fig. 90-E-7. Variation of thorium and uranium concentrations and Th/U ratios for the Southern California Batholith, U.S.A. [From PETERMAN, Z. E.: unpublished, personal communication (1963); based on data from LARSEN, 3d, and GOTTFRIED, 1960; LARSEN JR., and GOTTFRIED, 1961; WHITFIELD *et al.*, 1959; ROGERS and RAGLAND, 1961; HEIER and ROGERS, 1963; and personal communication from D. GOTTFRIED]

Table 90-E-2. Sequences of igneous rocks showing increase of thorium content toward the younger rocks

Extrusive series

Lassen Volcanic National Park (ADAMS, 1955; LARSEN, 3rd, and GOTTFRIED, 1960)
 Modoc area, California (GOTTFRIED and LARSEN JR., 1958; LARSEN, 3rd, and GOTTFRIED, 1960)
 Valles Mountains, New Mexico (LARSEN, 3rd, and GOTTFRIED, 1960) (Fig. 90-E-5)
 Big Bend National Park, Texas (GOTTFRIED *et al.*, 1962) (part intrusive) (Fig. 90-E-6)
 Mt. Garibaldi area, British Columbia (GOTTFRIED *et al.*, 1963)
 Strawberry Mountains, Oregon (GOTTFRIED *et al.*, 1963)

Sills and shallow intrusives

Augusta County, Virginia (GOTTFRIED *et al.*, 1962)
 Duluth gabbro, Minnesota (HEIER and ROGERS, 1963)

Plutonic sequences

Southern California batholith (LARSEN, 3rd, and GOTTFRIED, 1960; LARSEN JR. and GOTTFRIED, 1961; WHITFIELD *et al.*, 1959; ROGERS and RAGLAND, 1961; HEIER and ROGERS, 1963) (Fig. 90-E-7)
 White Mountain magma series, New Hampshire (BUTLER, 1961; ROGERS and RAGLAND, 1961; ADAMS *et al.*, 1962)
 Olivecian series, New Hampshire (ROGERS and RAGLAND, 1961; LYONS, 1961) (Fig. 90-E-8,

90-E-10

Thorium

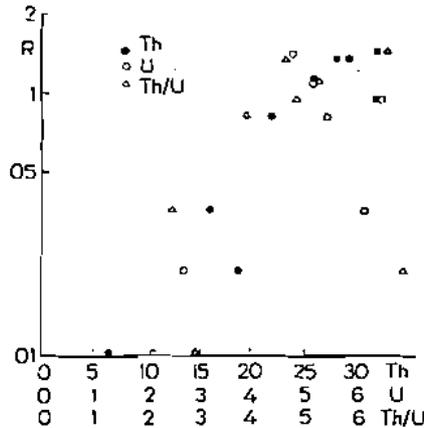


Fig. 90-E-8. Variation of thorium and uranium concentrations and Th/U ratios in the Oligo-verian series of mantled gneiss domes, New Hampshire, U.S.A. with R (ratio of potassium feldspar to plagioclase). (From ROGERS and RAGLAND, 1961)

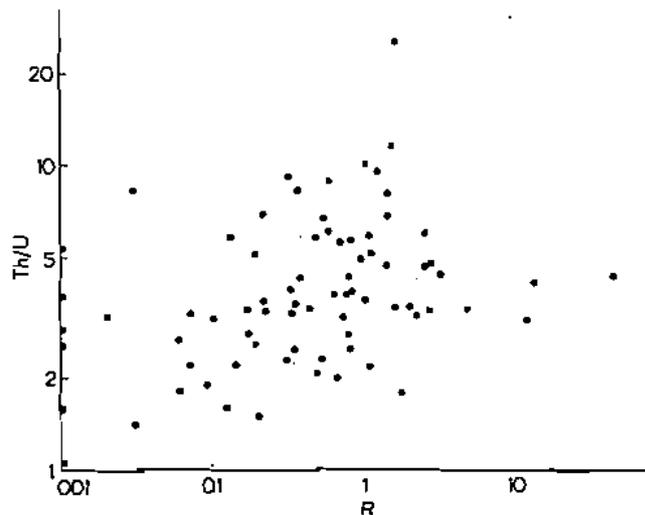


Fig. 90-E-9. Th/U ratio vs. the ratio of potassium feldspar to plagioclase (R) for 77 granitic rocks. Rocks with R values of less than 0.01 are plotted along the 0.01 line. The correlation coefficient of the logarithms of the ratios is 0.31, which is significant at the 99% confidence level. (From ROGERS and RAGLAND, 1961)

The preceding paragraph indicates a discrepancy in the variation of Th/U ratios which has not been satisfactorily explained. Where rocks from a variety of plutonic and/or extrusive sequences are compared, the Th/U ratio is generally higher in the more differentiated rocks, i.e., in those containing more silica or potassium. The few intrusive sequences which show systematic variation in Th/U ratios also exhibit an increase in the ratio with differentiation. Where there is variation in the Th/U ratio in extrusive sequences, however, the ratio decreases toward the younger rocks, despite the pronounced correlation between Th/U and potassium content found for apparently primary basalts. No comprehensive explanation of these observations is yet available.

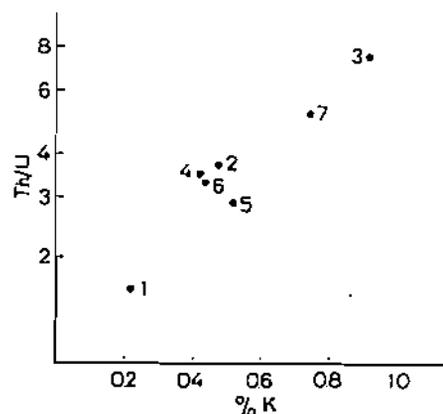


Fig. 90-E-10. Relationship between Th/U ratio and potassium content in various mafic igneous rocks. (From HEILER and ROGERS, 1963)

III. Provinces of High Thorium and Uranium Contents

High thorium and uranium concentrations appear to characterize the igneous rocks formed over considerable periods of time within certain areas. One excellent example is the Colorado Front Range, studied by PHAIR and GOTTFRIED (1964). Here thorium concentrations at least twice as large as the average for cratonic rocks are found in igneous rocks ranging in age from Precambrian through Laramide. Thorium concentrations of rocks within the Front Range area contrast markedly with the concentrations in rocks of equivalent age outside of the province.

Another area of high thorium concentration is the general New England region. Here the dominantly alkaline granites ranging in age from Paleozoic through lower Mesozoic have concentrations of thorium as high as 50 or more ppm and equivalent high abundances of uranium. The major example is the Triassic Conway granite of New Hampshire (ADAMS *et al.*, 1962). Although the data are not adequate, there seems to be some tendency for New England granites to have a slightly higher Th/U ratio than those elsewhere in the United States (ROGERS, 1964). High contents of thorium and uranium had not been found in the rocks of the Pacific Coast area until the comparatively recent work of WOLLENBERG and SMITH (1964). It is possible that the general tendency for granites from the western United States to be high in sodium and comparatively deficient in potassium, whereas those of the eastern United States are more potassic, is reflected in the tendency for higher thorium and uranium contents in the eastern granites. The concept of thorium and uranium provinces is discussed in more detail by PETERMAN (1963).

A possible relationship between age and Th/U ratios has been suggested by WHITFIELD *et al.* (1959) for granites in North America. In general, Precambrian granites in this area have a slightly higher Th/U ratio than granites of other ages. This higher ratio is primarily the result of slightly lower uranium content, and it is possible that Precambrian rocks have suffered depletion of uranium owing to upward migration of the element throughout geologic time.

The homogeneity of thorium and uranium distributions in the silicic intrusive rocks has been discussed by ROGERS (1964) and ROGERS *et al.* (1965) based on an interpretation of frequency distribution of the elemental abundances. The distribution of thorium within homogeneous bodies such as the Conway granite of New Hampshire was found to be homogeneous (lognormal), although the distribution of uranium was non-homogeneous. Presumably the thorium distribution is related to primary crystallization processes, whereas the uranium has undergone surficial redistribution which has altered the primary homogeneous distribution (Section 92-G). The thorium contents of New England rocks are not homogeneous for populations which include several plutons owing to differences in the abundances of thorium in the separate bodies. The secondary surficial control of uranium, however, yields a homogeneous distribution from the surficial rocks of a population which includes a large number of New England plutons (Fig. 92-E-2). The problem of distribution of thorium and uranium within relatively small areas of rock has also been discussed in the Russian literature; (see, for example, LEONOVA and RENNE, 1964).

90-F. Behavior during Processes Connected with Magmatism

The tendency of thorium to be incorporated in primary minerals in igneous rocks reduces its ability to concentrate in late-stage fluids. Thorium minerals, primarily allanite, are found in some pegmatites, but high concentrations are not common. The isomorphism between uraninite and thorianite permits small concentrations of thorium to accompany uranium in hydrothermal deposits, but the Th/U ratio in most such ores is extremely low. In North America only one major vein deposit has been discovered, the recently developed thorianite area at Lemhi Pass on the Idaho-Montana border. The geology of this deposit is discussed in detail by ANDERSON (1961).

90-G. Behavior during Weathering and Rock Alteration

As discussed more fully in the chapter on uranium (Section 92-G), thorium and uranium are commonly fractionated during surficial processes owing to oxidation of uranium to the soluble uranyl ion. The relatively immobile thorium becomes concentrated in residual materials such as soil and weathered rocks. Two examples may be cited of the residual accumulation of thorium. One is the high concentration in bauxite as reported by ADAMS and RICHARDSON (1960), who found concentrations in the general range of 50 ppm or more. Thorium in bauxites is contained largely in resistate minerals such as zircon but also partly in the aluminum hydroxide minerals, possibly by adsorption. Residual accumulations in clays are also noted by ADAMS and WEAVER (1958).

A second example of retention of thorium during weathering and alteration is the Pennsylvanian weathering profile on the granite of Flagstaff Mountain, Colorado (PLILER and ADAMS, 1962b). Thorium concentrations in this subtropically weathered material are as high as 34 ppm in the most thoroughly kaolinized rock. The thorium is partly in resistate minerals but in large part attached to the clay (Fig. 92-G-2).

90-H. Solubilities in Waters; Valence States

Thorium occurs in nature only as the tetravalent ion. The close association of thorium and potassium in a wide variety of rocks, however, together with the concentration of all radioactive materials toward the outer part of the earth (see Section 92-C), indicates that thorium is probably closely coordinated with oxygen ions. This coordination complex provides the low density necessary for upward migration which the individual thorium ions would not show.

Thorium forms a large number of salts such as the sulfate, chloride, etc. which are soluble in acid solutions. Slightly basic solutions however, hydrolyse the thorium ion to an oxide or hydroxide precipitate. The solubility is commonly given in terms of the solubility product of $\text{Th}(\text{OH})_4$, which is approximately 10^{-42} .

90-I. Abundance in Natural Waters

The low solubility of thorium in natural waters is demonstrated in Table 90-I-1 for sea water and in Table 90-I-2 for fresh water. Solubilities are in the range of 10^{-6} to 10^{-8} ppm (10^{-2} to 10^{-3} ppb). Comparison with Tables 92-I-1 and 92-I-2, which show comparable values for uranium, indicate a Th/U ratio of about 10^{-2} to 10^{-3} for most waters. The determination of thorium concentrations in waters is extremely difficult and in some cases is inferential; the problem is discussed in various papers by F. KOCZY and co-workers.

Table 90-I-1. Contents of thorium in sea water

Location	Th ppb	Method	Reference
Scandinavian waters	<0.5	W	FØYN <i>et al.</i> (1939)
Scandinavian waters	0.00004		F. KOCZY (1956)
Scandinavian waters	<0.02	autoradio- graphic	F. KOCZY <i>et al.</i> (1957)
Pacific (deep ocean)	<0.05	R	SACKETT <i>et al.</i> (1958)
Indian Ocean	0.01		BARANOV and KRISTIANOVA (1959)
Black Sea	0.0022	W	STARIK <i>et al.</i> (1959)
Sea of Azov (central part)	0.004	R	NIKOLAEV <i>et al.</i> (1961)

Table 90-I-2. Contents of thorium in continental waters

Location	No. of samples	Th ppb	Method	Reference
River water		0.01	calcu- lation	KOCZY (1956)
River waters of Japan	10	0.027	C	MIYAKE <i>et al.</i> (1964)
Waters of Florida	7	0.4	R	OSMONO (1964)

90-K. Abundance in Common Sedimentary Rocks

As discussed in the chapter on uranium (Section 92-K), the major factors controlling the distribution of thorium and uranium in sedimentary rocks are:

1. The tendency of thorium and uranium to fractionate because of oxidation of the uranium to the soluble uranyl ion.
2. The precipitation of uranium out of solution in reducing environments, carbonates, etc.
3. The selective adsorption of thorium in clays and its retention in heavy resistant minerals.

A more complete discussion of the comparative geochemistry of thorium and uranium in sedimentary rocks is given in Section 92-K. The present section considers only the concentrations of thorium and the Th/U ratios in various sedimentary rocks. Data are given in Table 90-K-1, and comparable data for uranium are given in Table 92-K-1.

The concentrations in sandstones shown in Table 90-K-1 are based on reasonably complete sampling of orthoquartzites, fair sampling of graywackes, and very poor sampling of arkoses. The problem of sampling sandstones and also of establishing valid sandstone populations is discussed by ROGERS and RICHARDSON (1964). The volcanic graywackes shown in Table 90-K-1 are important because they represent the average composition of rocks of the Caribbean orogen and thus give an integrated average of the amount of radioactive material that has been derived from igneous sources during eugeosynclinal activity.

Ordinary shales with colors of gray, green, etc. have a thorium content of 12 ppm and a Th/U ratio in the range of 3.5 to 4 (Fig. 90-K-1). As discussed in Section 92-K, these values are similar to those for the average granite. Black shales have a variable thorium content but a low Th/U ratio owing to their high content of uranium. The high concentration of thorium in bauxites (Fig. 90-K-2) is discussed in Section 90-G. The concentration of thorium in bentonites is high for the same reason as in bauxites.

Thorium concentrations in limestone (Fig. 90-K-3) are low because thorium does not enter the carbonate lattice readily. A close relationship has been established between thorium concentration and insoluble residue content of limestones (ADAMS and WEAVER, 1958), thus demonstrating that most of the thorium in limestones is in the clay or heavy mineral fraction. The Th/U ratio of limestones is obviously very low. Thorium is almost completely absent from evaporites.

The thorium content and Th/U ratios are given in Table 90-K-1 for a variety of modern oceanic sediments. These sediments are also discussed in section 92-K. It should be noted here that the low Th/U ratios reported by BARANOV and KHRISTIANOVA (1963) are not easily explained in terms of sedimentation processes. In particular, the finding of high thorium concentrations in pelagic clays and manganese-rich sediments (see, for example, GOLDBERG and KOIDE, 1962) seems incompatible with the low Th/U ratios reported in the sediments summarized by BARANOV and KHRISTIANOVA.

Table 90-K-1. Contents of thorium and Th/U ratios in sedimentary rocks

Rock type	No. of samples	Th ppm	Th/U	Method	Reference
<i>Sandstones</i>					
Orthoquartzite					
North American av.	16	1.7	3.8	R	MURRAY and ADAMS (1958)
Mesa Verde	8	2.7	1.6	R	PLILER and ADAMS (1962a)
Gulf Coast beach sand	29	1.49	2.53	R	MAHDAVI (1964)
Atlantic Coast beach sand	54	9.05	2.82	R	MAHDAVI (1964)
Volcanic graywacke					
Caribbean	14	1—2	~2	R	ROGERS and DONNELLY (1966)
Umpqua (Oregon)	4	2.8	~2	R	ROGERS (1966)
Other graywackes (estimated average)		6.7			ROGERS and RICHARDSON (1964)
Arkose (estimated average)		5			ROGERS and RICHARDSON (1964)
<i>Shales</i>					
North American gray and green	52	13.1	4.9	R	ADAMS and WEAVER (1958)
Russian platform	178 (comp)	11.0	2.7	emanation	BARANOV <i>et al.</i> (1956)
Mancos	102	10.2	3.1	R	PLILER and ADAMS (1962a)
red and yellow	10	12—13	6—7	R	ADAMS and WEAVER (1958)
black	numerous		low	various	SWANSON (1961); BATES and STRAILL (1958)
<i>Bauxites</i>	29	48.9	5.1	R	ADAMS and RICHARDSON (1960)
<i>Bentonites</i>	64	24.0	5.8	various	ADAMS and WEAVER (1958)
<i>Limestones</i>					
North American av.	25 (comp)	1.1	0.7	R	ADAMS and WEAVER (1958)
Russian platform	128 (comp)	2.4	1.1	emanation	BARANOV <i>et al.</i> (1956)
Eniwetok core E-1	21	0.05		0.02	SACKETT and POTRATZ (1963)

90-K-2

Thorium

Table 90-K-1 (Continued)

Rock type	No. of samples	Th ppm	Th/U	Method	Reference
<i>Phosphate rocks</i>		1—5	<0.1	various	References summarized by MCKELVEY (1956)
<i>Pacific ocean sediments</i>					
Sands	5	1.2	0.4	various	Summary by BARANOV and KHRISTIANOVA (1963)
Muds	3	2.7	1.2	various	Summary by BARANOV and KHRISTIANOVA (1963)
Clayey muds	6	4.8	1.8	various	Summary by BARANOV and KHRISTIANOVA (1963)
Siliceous and diatomaceous muds and clayey muds	9	2.2	low	various	Summary by BARANOV and KHRISTIANOVA (1963)
Pelagic clays	13	6.8	1.7	various	Summary by BARANOV and KHRISTIANOVA (1963)
Pelagic clays	5	3.1—8.5	2—4	radiochemical	PICCIOTTO and WILGAIN (1954)
Pelagic clays	3	9.3—11.2		R	GOLDBERG and KOIDE (1962)
Manganese nodules	4	24—124		C	GOLDBERG and PICCIOTTO (1955)
<i>Indian ocean sediments</i>					
Various muds		1—2	3—4.5	various	Summary by BARANOV and KHRISTIANOVA (1960)
<i>Atlantic ocean sediments</i>					
Pelagic clays	2	30			EL WAKEEL and RILEY (1961)
Globigerina oozes	5	5.1	9.9	R	ROSHOLT <i>et al.</i> (1961)
<i>Caribbean sediments</i>					
Globigerina oozes	17	5.5	5.5	R	ROSHOLT <i>et al.</i> (1961, 1962)
<i>Black Sea sediments</i>					
Muds	44	7.3	3.3 (41 spls.)		STARIK <i>et al.</i> (1961)

Thorium

90-K-3

90-K-4

Thorium

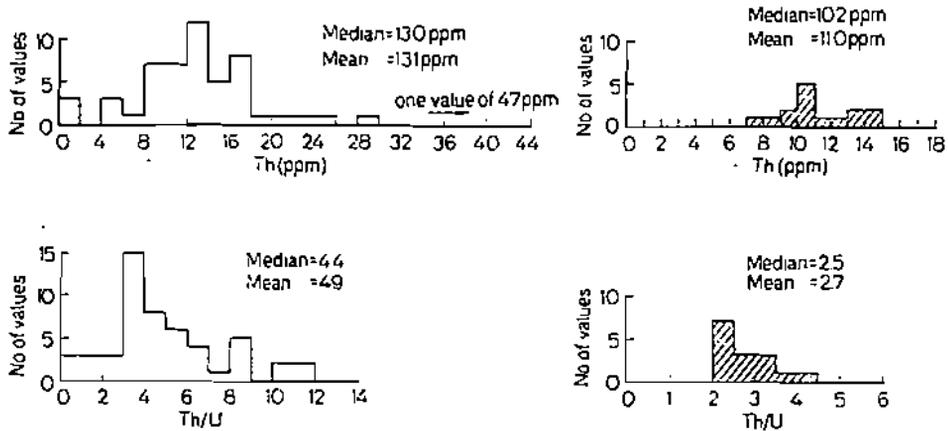


Fig. 90-K-1. Histogram of thorium concentrations and Th/U ratios in North American gray and green shales and Russian Platform shales. (From ADAMS and WEAVER, 1958; Russian Platform data from BARANDV, RONOY, and KUNASHOVA, 1956)

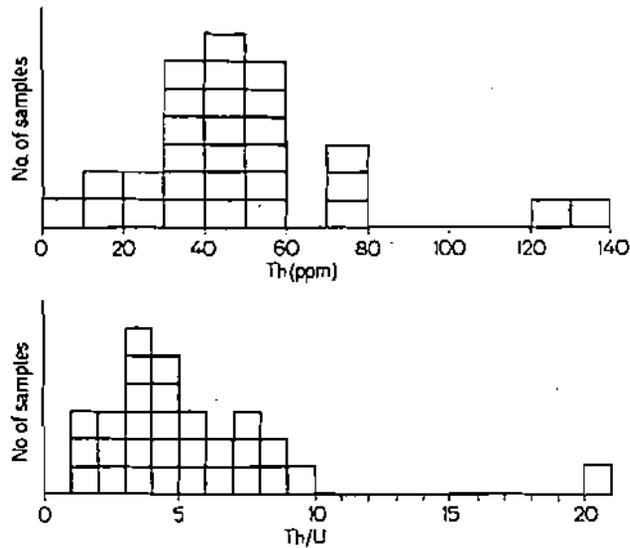


Fig. 90-K-2. Histograms of thorium concentrations and Th/U ratios in a world-wide sampling of bauxites. (From ADAMS and RICHARDSON, 1960)

It is possible, however, that some major sedimentary fractionation occurs on the sea floor, yielding high thorium concentrations in some varieties of clay and comparatively high uranium concentrations in other materials.

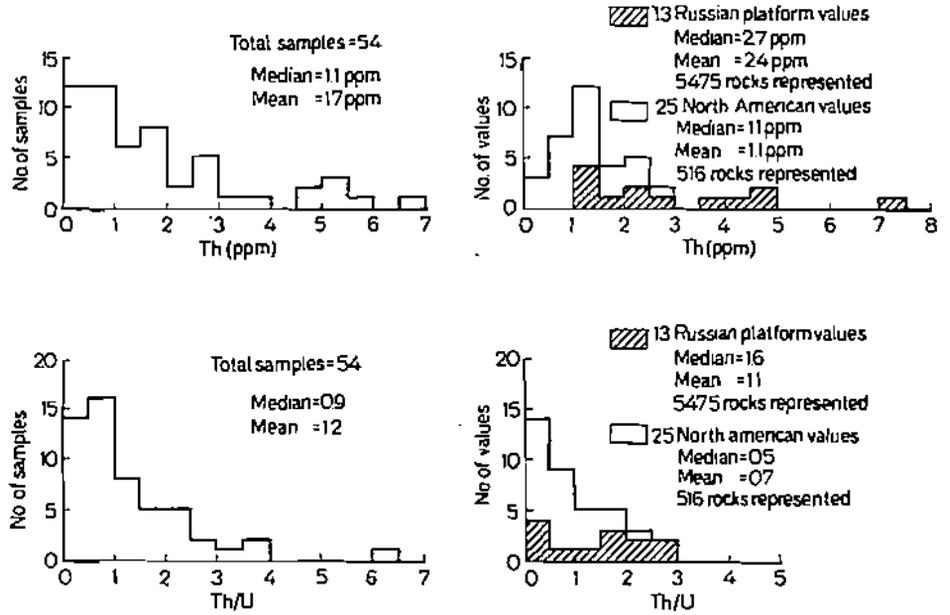


Fig. 90-K-3. Histograms of thorium concentrations and Th/U ratios in aggregate samples of carbonate rocks. (From ADAMS and WEAVER, 1958; Russian Platform data from BARANOV, RONOV, and KUNASHOVA, 1956)

90-L. Biogeochemistry

Thorium is not known to be an essential material in any organic process. BOWIE and ATKIN (1956) report a thorium concentration of as much as 4,500 ppm in a fossil fish skeleton, but most organisms and organically derived materials contain essentially no thorium. The problem of dealing with the exceptionally low thorium concentrations which occur in organic material and the possible biological significance of thorium is discussed briefly by EDGINGTON (1965).

90-M. Abundance in Common Metamorphic Rock Types

The concentration of thorium in a variety of metamorphic rocks is shown in Table 90-M-1. The Th/U ratios are also shown in this table and are based on uranium data given in Table 92-M-1. Concentrations of thorium and the Th/U ratio are highly variable from one metamorphic rock to another and clearly depend on a variety of factors, including parent rock composition, metasomatic effects, and the possible sampling difficulties caused by segregation during metamorphism. HETER and ADAMS (1965) have suggested that high-rank metamorphic rocks contain less thorium and uranium than low-rank rocks as a result of selective removal of these materials from the deeper parts of the crust. The data for this conclusion, however, are not complete. Other generalizations concerning the thorium and uranium contents of metamorphic rocks cannot be made from the small number of measurements currently available.

Table 90-M-1. *Contents of thorium and Th/U ratios in metamorphic rocks*

Rock type	No. of samples	Th ppm	Th/U	Method	Reference
Amphibolite (Schwarzwald, Germany)	3	5	1.4	R	HUSMANN (1956)
Biotite-Hornbl. Paragneiss (Schwarzwald, Germany)	2	27	13.5	R	HUSMANN (1956)
Paragneiss (Schwarzwald, Germany)	4	6.4	0.9	R	HUSMANN (1956)
Granulite (Schwarzwald, Germany)	2	21	4.3	R	HUSMANN (1956)
Orthogneiss (Schwarzwald, Germany)	4	5.5	1.5	R	HUSMANN (1956)
Metatectite (Schwarzwald, Germany)	4	22	4.6	R	HUSMANN (1956)
Diatectite (Schwarzwald, Germany)	4	3	0.3	R	HUSMANN (1956)
Cordierite Gneiss (Schwarzwald, Germany)	1	21.8	3.8	R	HUSMANN (1956)
Orthoclase metacryst (Schwarzwald, Germany)	1	67.7	1.5	R	HUSMANN (1956)
Kinzigit (Schwarzwald, Germany)	1	7		R	HUSMANN (1956)
Marble	2	0.03	0.2	R	PLILER (1956)
Slate (mainly Michigan)	14	7.5	2.8	R	PLILER (1956)
Phyllite (mainly Arizona-New Mexico)	7	5.5	2.8	R	PLILER (1956)
Schist (New Mexico)	4	7.5	3.0	R	PLILER (1956)
Mafic rocks (Terskei Ala Tau Mts.)	82	10	3.1	W	KRYLOV (1958)

Table 90-M-1 (Continued)

Rock type	No. of samples	Th ppm	Th/U	Method	Reference
Gneiss (Texas) (Almandine-Amph. Facies)	13	13.1	4.75	R	BILLINGS (1962)
Amphibolite (Texas) (Almandine-Amph. Facies)	14	0.31	0.79	R	BILLINGS (1962)
Graphite Schist (Texas) (Almandine-Amph. Facies)	3	6.16	2.66	R	BILLINGS (1962)
Light Gneiss (Langøy, Norway) (Amphibolite Facies)	5	15.08	> 7.36	R	HEIER (1962b)
Amphibolite (Langøy) (Amphibolite Facies)	7	4.2	~ 3.8	R	HEIER (1962b)
Intermediate Gneiss (Langøy) (Granulite Facies)	2	9.25		R	HEIER (1962b)
Monzonite (Langøy) (Retrograde Gneiss)	2	3.3	> 2.8	R	HEIER (1962b)
Granite (Langøy) (Retrograde Gneiss)	8	< 14.4	> 12.89	R	HEIER (1962b)
Biotite Schist (Front Range, Colorado)	11	18.8		W	PHAIR and GOTT- FRIED (1964)
Biotite-Hornbl. Schist and Amphibolite (Front Range)	4	10.6		W	PHAIR and GOTT- FRIED (1964)
Monzonite (Langøy) (High Granulite Facies)	3	1.18	1.7	R	HEIER and ADAMS (1965)
Banded Gneiss (Langøy) (High Granulite Facies)	4	0.85	3.07	R	HEIER and ADAMS (1965)
Gneiss (Langøy) (Low Granulite Facies)	5	4.09	30	R	HEIER and ADAMS (1965)
Gneiss (Langøy) (High Amphibolite Facies)	3	9.39	13.4	R	HEIER and ADAMS (1965)

90-N. Behavior in Metamorphic Reactions

As mentioned in Section 90-M, there is some possibility that thorium and uranium are depleted from high-rank rocks owing to upward movement through the crust during major metamorphism. No data are available on the behavior of thorium during metamorphism either from laboratory studies or from complete sampling of metamorphic terrains.

90-O. Economic Utilization

At the present time thorium is of minor economic interest with annual production rarely exceeding a thousand tons of metal. The metal is used in magnesium alloys and incandescent gas mantles. Current research on the breeding of Th^{232} to make fissionable U^{233} for power generation may lead to a greatly expanded market.

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