

Uranium

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Introduction

The geochemistry of uranium is intimately associated with that of thorium. Consequently, the preparation of separate chapters on thorium and uranium has necessitated a subdivision of topics involving these two elements. In this chapter on uranium, the writers have included a discussion of both thorium and uranium in connection with heat production in the earth, autoradiographic studies, fractionation of thorium and uranium during weathering and sedimentation, and the utilization of nuclear energy. The chapter on thorium (90) includes a discussion of age dating by means of radioactive disequilibria, Th/U ratios in igneous rocks, and the general problem of the relationship of thorium and uranium to igneous petrology. The chapter on lead (82) Section B includes a discussion of U/Pb and Th/Pb age dating.

A number of reviews of the geochemistry of thorium and uranium have been published. ADAMS, OSSMOND, and ROGERS prepared one in 1959. DYBEK (1962) reviews the geochemistry of uranium and EL SHAZLY (1962) provides a detailed bibliography. An extensive review now in preparation by PETERMAN was available in preliminary form in 1963. Owing to the enormous volume of published material, no effort is made in this chapter to refer to all papers dealing with the geochemistry of uranium. Reference is made to those papers from which numerical data have been obtained and to recent summary papers which will introduce readers to specific sub-topics.

92-B. Isotopes in Nature; Heat Production in Common Rocks

I. Varieties of Isotopes

Naturally-occurring uranium consists of three different isotopes: U^{238} , U^{235} , and U^{234} . The U^{238} and U^{235} are parent isotopes for two separate decay series which ultimately yield Pb^{206} and Pb^{207} respectively. No natural isotopic fractionation of U^{238} and U^{235} has been observed, and today all natural materials have a ratio of U^{238}/U^{235} equal to 137.5 ± 0.5 . In the past this ratio has systematically increased to the present value, owing to the fact that U^{235} has a half-life of 7.1×10^8 years, which is much less than that of U^{238} (4.5×10^9 years). The U^{238}/U^{235} ratio 4.5 $\times 10^9$ years ago, the presumed age of the earth, was 3.45. The third isotope of uranium, U^{234} , is an intermediate in the decay series of U^{238} and is formed from U^{238} by emission of an alpha followed by two beta particles; consequently, the abundance ratio of U^{234}/U^{238} is proportional to the ratio of their half-lives. The half-life of U^{234} is 2.5×10^5 years, making U^{234} equal to 0.0056 percent of total natural uranium.

Uranium, but generally not its daughter products, is incorporated from sea water into calcium carbonate shells and other precipitates. As a result of this selective fixation, the daughter of U^{234} (Th^{230} by alpha decay) is largely absent in freshly deposited carbonate, and thus the rate of building of Th^{230} can be used to date the carbonate materials; (see THURBER, 1965, for a review). For reasons not wholly understood, sea water contains about 15 percent more U^{234} than would be expected to be in secular radioactive equilibrium with the U^{238} in the water. Apparently the intermediate daughters formed in the decay process permit chemical fractionation of the U^{238} and U^{234} . Consequently, the rate at which the U^{234}/U^{238} ratio approaches that of secular radioactive equilibrium in carbonate shells may be used to check U^{234}/Th^{230} dating (THURBER, 1965). RICHARDSON (1964) detected a 15 percent deficiency in U^{234} in weathered samples of the Conway granite, New Hampshire. This deficiency in U^{234} correlates well with the apparent excess of U^{234} in sea water.

II. Heat Production in the Earth

The study of the flow of heat through the earth's surface has recently assumed great importance¹. As examples, two of the questions involved are: 1) determination of whether or not the earth has the bulk composition of chondritic meteorites (the "chondritic hypothesis"); and 2) comparison of oceanic and continental heat flows, possibly for the purpose of establishing compositional differences in the upper mantle underlying continental and oceanic areas. Studies of heat flow in the earth have recently been summarized by a number of writers, including BIRCH (1965) and LEE and UYEDA (1965).

One major line of evidence for the chondritic hypothesis is the fact that the total terrestrial heat flow can be accounted for by the heat generated by radioactive elements

¹ See Chapter 6, Section V in Volume I of this handbook.

92-A. Crystal Chemistry

The 5-f element uranium in the ground state has the probable electronic structure $5f^3 6d^1 7s^2$ and the formal valence states vary between 2+ and 6+. In minerals, however, only the valences 4+, 5+ and 6+ are known. With many elements (e.g. C, N, Si, P, S etc.), binary compounds of uranium are semimetallic and often non-stoichiometric.

I. Metallic Uranium

Metallic uranium (melting point 1,132° C) has three crystalline modifications; α -uranium (below 660° C) crystallizes orthorhombic, and each uranium atom is coordinated by twelve neighbors at distances between 2.75 and 3.34 Å (STURKEN and POST, SR 1960, 240). β -uranium (between 660° and 760° C) is probably tetragonal and non-centrosymmetric, and the coordination number of the six structurally different uranium atoms is between 12 and 15 (THEWLIS and STEEPLE, SR 1954, 304; STEEPLE and ASHWORTH, 1966). Because of some uncertainties in the indexing of the powder data (DONOHUE and EINSPAHR, 1971), it is possible that the structure determination is not quite correct. The phase γ -uranium (from 760° C up to the melting point) is cubic, body-centered (THEWLIS, SR 1951, 123) with U—U distances of 3.0 Å (8×).

II. Formally Di-, Tri- and Penta-valent Uranium

One example of a compound with divalent uranium is UO_2 , crystallizing in the NaCl-type (RUNDLE *et al.*, SR 1947—1948, 220).

For trivalent uranium the structures of some artificial halides are the best known. The layer structure of UF_3 is isotypic with CeF_3 ; in the hexagonal arrangement the uranium atoms have a [2+3+6] coordination of fluorine. The fluorides AUF_6 ($A = Sr, Ba, Pb$) with formally tetravalent uranium are isotypic with UF_3 and the atoms A and U seem to be randomly distributed over the metal sites (ZACHARIASEN, SR 1949, 164). UCl_3 and UBr_3 crystallize in the $Y(OH)_3$ structure type. Uranium is surrounded by nine halogen neighbors at nearly equal distances, e.g. U—Cl ~ 2.9 Å (ZACHARIASEN, SR 1947—1948, 277). The fourth halogenide, UI_3 crystallizes orthorhombic and each U is coordinated by 8 iodine neighbors (ZACHARIASEN, SR 1947—1948, 282).

Pentavalent uranium occurs in two tetragonal modifications of UF_5 . In the α -form each uranium is coordinated by six fluorine neighbors in the form of an octahedron with distances U—F ~ 2.2 Å. The β -form shows a seven-fold coordination to uranium, with U—F distances between 2.18 and 2.29 Å (ZACHARIASEN, SR 1949, 169). In UCl_5 , the uranium atoms are coordinated octahedrally by six chlorine atoms (U—Cl distances between 2.43 and 2.70 Å); two such octahedra share an edge to form U_2Cl_{10} units (SMITH *et al.*, 1967).

In the system involving UO_2 and U_3O_8 (which is only tentatively known — GRONVOLD, 1955), the crystal structures of only a few compounds have been determined. UO_2 crystallizes in the CaF_2 -type (see below) and the compound U_4O_9 has been reported to crystallize in a cubic superstructure of UO_2 with 4 times the UO_2 cell dimensions (MASAKI and DOI, 1972). In U_3O_8 there are two crystallographically different uranium atoms: U(1) is coordinated by six oxygens with U—O distances of 2.07 (2×) and 2.18 Å (4×) (after ANDRESEN, SR 1958, 296) and is pentavalent; U(2) has the typical [2+5] coordination of hexavalent uranium with U—O distances of 2.07 (2×), 2.17 (2×), 2.21 and 2.42 (2×). The system U—O is very complex and deviations from stoichiometry are the rule, but only the UO_2 to U_3O_8 region seems to be significant for the natural occurrence of uranium oxides.

III. Formally Tetravalent Uranium

The structures of two halogenides are well-known. UF_4 crystallizes in a monoclinic structure, isotopic with ZrF_4 , and uranium is coordinated by 8 fluorine atoms (ZACHARIASEN, SR 1949, 168). UCl_4 is tetragonal with four chlorine atoms at distances of 2.41 Å, and four at 2.09 Å (MOONEY, SR 1949, 166).

The coordination number of oxygen around U(IV) is six or eight and examples are given in Table 92-A-1. In minerals with structures similar to columbite, (Fe, Mn) (Nb, Ta)₂O₆ (STURDIVANT, SB 1928—1932, 337), the atoms (Fe, Mn) with six-fold coordination (octahedral) can probably be partially substituted by uranium. In the

Table 92-A-1. Structural data of some uranium (IV) compounds

Mineral name	Chemical formula	Coordination number and form of the polyhedron about uranium	U—O distances (Å)	References
Coffinite	$\text{U}[\text{SiO}_4]$	[4+4] two-fold dispshenoide	2.32 (4×) 2.52 (4×)	FUCHS and GEBERT (SR 1958, 504)
Uraninite	UO_2	[8] cube	2.37 (8×)	several authors (SB 1913—1928, 148 and 212)
	UTi_2O_6^*	[6] octahedron	~2.3 (6×)	RÜH and WÄOSLET (1966)
	UGeO_4	[8] two-fold dispshenoide	~2.3 to 2.5 (8×)	DURIF (SR 1956, 283)
	$\text{U}[\text{SO}_4](\text{OH})_2$	[8] square Archimedean antiprism	~2.3 (8×)	LUNDGREN (SR 1952, 287)
	$\text{U}_8\text{O}_4[\text{SO}_4]_6(\text{OH})_4$	[8] square Archimedean antiprism	~2.3 (8×)	LUNDGREN (SR 1952, 287)
	$\text{U}[\text{SO}_4]_2 \cdot 4 \text{ H}_2\text{O}$	[8] square Archimedean antiprism	~2.4 (8×)	KIERKEGAARD (SR 1956, 354)

* UTi_2O_6 is isotopic to brannerite, $(\text{U}, \text{Ca}, \text{Th}, \text{Y})(\text{Ti}, \text{Fe})_2\text{O}_6$.

pyrochlore-like structures, $(\text{Ca}, \text{Na})_2(\text{Nb}, \text{Ta})_2\text{O}_8$ ($\text{O}, \text{OH}, \text{F}$) (several authors; SB 1928—1932, 340), uranium can probably occupy the position of (Ca, Na) with a [2+6] coordination of oxygens. In both these minerals, the valency state of the substituting uranium is not known exactly.

IV. Formally Hexavalent Uranium

The compound UF_6 is orthorhombic and each uranium is octahedrally coordinated by six fluorines at distances between 2.01 and 2.13 Å (HOARD and STROUPE, 1958). The uranium atoms are arranged in the octahedral holes of the double-hexagonal close-packing of fluorine atoms. In UCl_6 the chlorine atoms form a nearly perfect octahedron about uranium with $\text{U}-\text{Cl}$ distances of 2.4 Å (ZACHARLASEN, SR 1947—1948, 479); the chlorine atoms are arranged in a hexagonal close-packing.

The coordination number of hexavalent uranium against oxygen is six, seven or eight. Two oxygens having significantly shorter distances to the central atom (2.0 Å

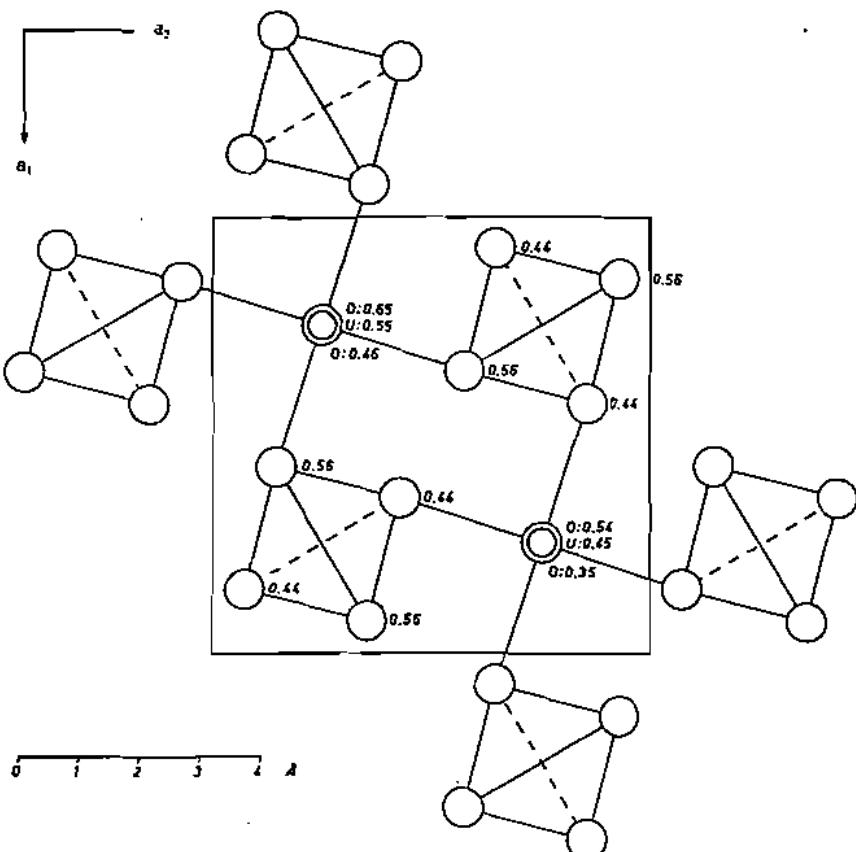


Fig. 92-A-1. Ahernathyite, projection of a single $[\text{UO}_2]-[\text{AsO}_4]$ sheet of (001). The numbers are the z parameters of the atoms in the tetragonal arrangement ($c_0 = 18.13$ Å). The As-atoms in the center of the tetrahedra with $z = \frac{1}{3}$ are not drawn

Table 92-A-2. Structural data of some uranium(VI) compounds

Mineral name	Chemical formula	U-O distances in the uranyl group (Å)		U-O distances in the plane perpendicular to the uranyl group (Å)		References
<i>A) Coordination number [2+4]</i>						
Abernathyite	K[UO ₂][AsO ₄]·3 H ₂ O	1.81	1.70	2.35 (4 ×)		Ross and Evans (1964)
Meta-autunite	Ca[UO ₂] ₂ [PO ₄] ₃ ·6 H ₂ O	1.99	1.79	2.32 (4 ×)		MAKAROV and IVANOV (SR 1960, 412)
Meta-torber- nite	Cu[UO ₂] ₂ [PO ₄] ₃ ·8 H ₂ O*	1.82	1.77	2.33 (4 ×)		Ross <i>et al.</i> (1964)
		1.80	1.94	2.31 (4 ×)		
Meta-zeunerite	Cu[UO ₂] ₂ [AsO ₄] ₃ ·8 H ₂ O	1.94	1.78	2.18 (4 ×)		HANIC (SR 1960, 415)
	Ba[UO ₂]O ₃	1.90	1.90	2.12 (2 ×)	2.22 (2 ×)	SAMSON and SILLÉN (SR 1947—1948, 441)
	Mg[UO ₂]O ₃	1.92	1.92	2.16 (2 ×)	2.20 (2 ×)	ZACHARIASEN (SR 1954, 463)
	K ₂ [UO ₂]O ₃	1.90	1.90	2.17 (4 ×)		
	Rb ₂ [UO ₂]O ₃	1.91	1.91	2.17 (4 ×)		
	Cs ₂ [UO ₂]O ₃	1.91	1.91	2.19 (4 ×)		
						KOVBA <i>et al.</i> (SR 1958, 320)

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$\beta\text{-Na}_2[\text{UO}_3]\text{O}_4$	1.93	1.93	2.12 (4 x)	} KOVBA <i>et al.</i> (SR 1958, 321)
$\alpha\text{-Li}_2[\text{UO}_3]\text{O}_2$	1.89	1.89	1.98 (4 x)	
$\alpha\text{-Na}_2[\text{UO}_3]\text{O}_4$	1.90	1.90	2.24 (4 x)	
$\text{NH}_4[\text{UO}_3][\text{AsO}_4] \cdot 3 \text{H}_2\text{O}$	1.81	1.73	2.37 (4 x)	} Ross and Evans (1964)
$\text{K}(\text{H}_2\text{O})[\text{UO}_3]_2[\text{AsO}_4] \cdot 6 \text{H}_2\text{O}$	1.77	1.70	2.33 (4 x)	
$\text{Cu}[\text{UO}_3]\text{O}_4$	1.90	1.90	2.15 2.24 (2 x) (2 x)	
$\beta\text{-}[\text{UO}_3](\text{OH})_3$	1.81	1.81	2.27 2.32 (2 x) (2 x)	BANNISTER and TAYLOR (1970)
$[\text{UO}_3]_2\text{O}_2(\text{OH})_3$ ^b	1.83	1.83	2.07 2.42 (2 x) (2 x)	SIEGEL <i>et al.</i> (1972)
$\text{Ca}_2[\text{UO}_3]\text{O}_4$ ^c	2.02	1.91	2.26 2.16 2.24 (2 x)	} RIETVELD (1966)
$\text{Sr}_2[\text{UO}_3]\text{O}_4$ ^c	1.86	1.85	2.39 2.11 2.42 2.36	

B) Coordination number [2+5]

"Anhydrous carnotite"	$\text{K}_2[\text{UO}_3]_2[\text{V}_2\text{O}_5]$	1.8	1.8	2.2 to 2.4 (5 x)	APPLEMAN and EVANS (1965)
Curielite	$\text{Pb}[\text{UO}_3]_2[\text{V}_2\text{O}_5] \cdot 5 \text{H}_2\text{O}$	1.67	1.66	2.39 2.37 2.30 2.29 2.27	BORÈNE and CESBRON (1971)
Dumontite	$\text{Pb}_2[\text{UO}_3]_3[\text{PO}_4]_3(\text{OH})_4 \cdot 3 \text{H}_2\text{O}$ ^b	1.76	1.76	2.33 2.37 2.32 (2 x) (2 x)	PIRET-MEUNIER, LEONARD and VAN MEERSCHE (SR 1962, 583)

Table 92-A-2 (continued)

Mineral name	Chemical formula	U-O distances in the uranyl group (Å)		U-O distances in the plane perpendicular to the uranyl group (Å)					References	
Jachimovite	$CuH_2[UO_4]_2[SiO_4]_2 \cdot 5 H_2O^{aa}$	1.90	1.87	2.27	2.63	2.36	2.26	2.45	PIRETT-MEUNIER and van MEERSCHE (1963)	
Kasolite	$Pb[UO_4][SiO_4] \cdot H_2O$	1.71	1.72	2.22	2.15	2.50	2.21	2.47	MOKEEVA (1964a)	
Sklodowskite	$MgH_2[UO_4]_2[SiO_4]_2 \cdot 6 H_2O^{aa}$	1.7	1.7	2.2	2.3	2.5	2.7 (2 ×)		MOKEEVA (1964b)	
Uranophane	$Ca(H_2O)_2[UO_4]_2[SiO_4]_2 \cdot 3 H_2O$	1.91	1.91	2.5 (2 ×)	2.3 (2 ×)	2.2			SMITH, GRUNER and LIPSKOMB (SR 1957, 338)	
β -Uranophane	$Ca[UO_4]_2[UOOH][SiO_4][SiO_3OH] \cdot 4 H_2O^{a,b}$	1.77	1.81	2.27	2.35	2.38	2.41 (2 ×)		SMITH and STOHL (1972)	
	$Ca_2[UO_4]_2[SO_4]_2$	1.76	1.81	2.26	2.34	2.35	2.38	2.48		
	$Ca_2[UO_4]_2[V_2O_8]$	1.74	1.74	2.37 (2 ×)	2.47 (2 ×)	2.46			ROSS and EVANS (SR 1960, 389)	
	$Ni[UO_4]_2[V_2O_8] \cdot 4 H_2O$	1.77	1.77	2.40	2.37	2.38	2.25	2.29	APPLEMAN and EVANS (1965)	
	$UV_2O_8^{bb}$	1.79	1.84	2.33	2.29	2.34	2.35	2.21	BORÈNE and CESBRON (1970)	
	$[UO_4]_2O_2(OH)_2^b$	2.05	2.07	2.34	2.18 (2 ×)	2.25 (2 ×)			CHEVALIER and GASPERIN (1970)	
		1.74	1.78	2.48	2.33	2.27	2.31	2.40	SIEGEL <i>et al.</i> (1972)	
<i>C) Coordination number [2+6]</i>										
Cliffordite	$[UO_4]Tc_2O_7^a$	2.04	2.04	2.30 (6 ×)					FISCHER <i>et al.</i> (1969)	
		1.96	1.96	2.51 (6 ×)					GALY and MEUNIER (1971)	

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Dumontite	$Pb_3[UO_4]_3[PO_4]_2(OH)_4 \cdot 3 H_2O^b$	1.76	1.76	2.11 (2 x)	2.73 (4 x)	PIRET-MEUNIER, LEONARD and VAN MEERSCHE (SR 1962, 583)
Rutherfordin	$[UO_4][CO_3]$	~1.9	~1.9	~2.5 (4 x)	~2.4 (2 x)	CHRIST, CLARK and EVANS (resp. CROMER and HARPER; SR 1955, 425)
	$Ca[UO_4]O_2$	1.91	1.91	2.29 (6 x)		ZACHARIASEN (SR 1948, 323)
	$Sr[UO_4]O_2$	1.91	1.91	2.33 (6 x)		
	$[UO_4][NO_3]_3 \cdot 6 H_2O$	1.77	1.75	2.50 (2 x)	2.55 (2 x) 2.40 (2 x)	TAYLOR and MUELLER (1965)
	$Rb[UO_4][NO_3]_3$	1.78	1.78	2.48 (6 x)		BARCLEY <i>et al.</i> (1965)
	$[UO_4]Nb_3O_8^{bb}$	1.95	1.95	2.42 (4 x)	2.57 (2 x)	CHEVALIER and GASPERIN (1968)
	$[UO_4]TiNb_3O_8$	1.79	1.79	2.34 (4 x)	2.50 (2 x)	CHEVALIER and GASPERIN (1969)
	$\alpha-[UO_4](OH)_2$	1.71	1.71	2.46 (4 x)	2.51 (2 x)	TAYLOR (1971)

^a Two structurally different U-positions with essentially identical coordination.^b For one of the two structurally different U-positions.^c Uranium (VI) compounds with an insignificant "uranyl-group."^{aa} The bond of the two H atoms is unknown.^{bb} Valency of V and Nb with respect to U not clearly defined by composition.

and less) compared to the other atoms (between 2.2 and 2.5 Å) are characteristic for the so-called "uranyl-group". The O—U—O angle within this group is 180° (metazenerite) or nearly this value ($\text{Ni}[\text{UO}_2]_2[\text{V}_2\text{O}_8] \cdot 4\text{H}_2\text{O}$). Equal distances of the two oxygens lead to a symmetric UO_2 -group as in rutherfordine. An asymmetric UO_2 -group has been found in meta-zeunerite, abernathyite and meta-torbernite where the other oxygens of the uranium polyhedron are arranged in a plane, perpendicular to the axial direction of the linear uranyl group.

To summarize, EVANS (1963) has made an attempt to explain the different relations in the coordination of hexavalent uranium. This author also tabulated the crystal structures with uranyl groups according to the varying coordination within these groups; similarly, the coordination and U—O distances of some uranium(VI) compounds are listed in Table 92-A-2.

In the minerals of the torbernite group, isolated [2+4] uranium polyhedra, and $[\text{PO}_4]$ or $[\text{AsO}_4]$ tetrahedra are linked together in two dimensions (Fig. 92-A-1). Interlayered water and partially hydrated metal-atoms connect these sheets in the third direction. For the first time, BEINTEMA (SB 1938, 24) has described these structural elements in the proposed crystal structure of autunite.

A large number of synthesized "uranates" show the same [2+4] coordination principle. In $\text{Mg}[\text{UO}_2]\text{O}_2$, the uranium polyhedra linked by two shared edges form endless chains in one direction. $\text{Ba}[\text{UO}_2]\text{O}_2$ has a layer structure built up by uranium octahedra with four shared corners.

The [2+5] coordination plays an important role in uranyl vanadates and silicates. In curienite and also in $\text{Cs}_2[\text{UO}_2]_2[\text{V}_2\text{O}_8]$, the Cs-analogue of carnotite (cf. Fig. 23-A-5, this Handbook), the uranium polyhedra share edges, forming U_2O_{12} units. Uranophane and β -uranophane show typical sheet-structures, in which uranium polyhedra and silicon tetrahedra are connected in two dimensions.

$[\text{UO}_2]\text{Te}_3\text{O}_7$ contains UO_2 groups in a $(\text{Te}_3\text{O}_7)^{2-}$ framework; cliffordite crystallizes in the same structure type. Rutherfordine has a sheet-structure in which the carbonate groups and [2+6] coordinated uranium atoms share edges. Synthetic $[\text{UO}_2][\text{NO}_3]_2 \cdot 6\text{H}_2\text{O}$ is characterized by two O—O edges of NO_3 groups belonging to the coordination polyhedron around U^{6+} ; a similar coordination is found in $\text{Rb}[\text{UO}_2][\text{NO}_3]_3$ where three edges of nitrate groups coordinate one uranyl group.

Several forms of uranium trioxide are known. α - UO_3 crystallizes hexagonally, and each uranium is coordinated by eight oxygens ($\text{U}—\text{O}: 2.08$ (2×), 2.39 (6×); ZACHARIASEN, SR 1947—1948, 224), but the structure now seems to be more complicated (LOOPSTRA and CORDFUNKE, 1966) than described here. The form β - UO_3 has five structurally different uranium atoms, with [6] and [7] coordination of oxygens and U—O distances between 1.52 and 2.77 Å (DEBETS, 1966). In γ - UO_3 the oxygens form distorted octahedra around uranium (ENGMANN and WOLFF, 1963) and δ - UO_3 is said to be isostructural with ReO_3 (WAIT, SR 1955, 356). Finally, in a high pressure form of UO_3 uranium has a seven-fold coordination with U—O distances from 1.80 to 2.56 Å (SIEGEL *et al.*, 1966).

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in an earth having the composition of an average chondrite. Taking into account regional variations in heat flow, the average flow through the earth's surface each year is about 2×10^{20} calories for the entire earth. The total amount of heat produced by radioactive decay in a chondritic earth can be calculated from the average concentrations of radioactive elements in chondrites. Tables 92-C-1 and 90-C-1 show the average uranium and thorium concentrations in chondrites as approximately 10^{-2} and 4×10^{-8} ppm respectively. (The data of STARIK and SHATS (1956) are not included in the averages because their values are so markedly different from those of other workers.) The average concentration of potassium in chondrites is 0.1 percent. The amount of heat generated by one gram of the metal of each of these three elements plus the daughter products in secular radioactive equilibrium with the uranium and thorium is:

potassium	2.7×10^{-5} cal/gm/yr
thorium	0.20 cal/gm/yr
uranium	0.73 cal/gm/yr.

From these data plus the mass of the earth, the total heat produced by radioactivity in a chondritic earth would be approximately 2×10^{20} calories per year, a figure which matches that of the observed heat flow.

Most studies seem to indicate an approximate uniformity of heat flow in oceanic and continental areas. Consequently, any models proposed for the crust and upper mantle must provide roughly the same total amount of radioactive material underlying equal surface areas of continents and ocean basins. The heat produced by rocks commonly used in such models is shown below in terms of the amount of heat generated in one year in a column of rock one kilometer long and having a cross-sectional area of one square centimeter. Thorium and uranium concentrations are taken from Tables 90-E-1 and 92-E-1 respectively, and potassium concentrations are from Chapter 19 (courtesy of Dr. K. S. Heier).

	Th ppm	U ppm	K ppm metal	Heat cal/cm ² /yr for 1 km of rock
Granite (> 70% SiO ₂)	18	4	3.6×10^4	2.0
Oceanic tholeiitic basalt	0.18	0.10	0.17×10^4	0.05
Plateau basalt	1.96	0.53	0.75×10^4	0.3
Dunite and peridotite	< 0.05	0.01	10—20	0.01
Pipe eclogite	0.22	0.05	$0.1\text{--}0.2 \times 10^4$	0.03
Eclogite in metamorphic terranes	0.46	0.20	$0.1\text{--}0.2 \times 10^4$	0.1

The table clearly shows the extreme concentration of radioactive elements in continental-type rocks. Thus, an approximate equality of heat flow in continental and oceanic areas presumably indicates that the upper mantle under the oceans contains a higher concentration of radioactive elements than it does under the continents. This fact has been used to argue against a continental drifting by means of some simple shifting of continental masses over a more plastic mantle (see discussion by BIRCH, 1965, and MACDONALD, 1965).

Comparison of average concentrations of thorium and uranium in chondrites (Tables 90-C-1 and 92-C-1) with the concentrations in crustal rocks shown above clearly indicates extreme outward migration of thorium and uranium in the earth. TILTON and REED (1963) point out that the abundances of radioactive elements in chondrites are much lower than those required to account for the observed oceanic heat flow, which must come largely from the mantle, unless the oceanic upper mantle has undergone considerable fractionation from a chondritic earth. A mantle with the composition of the average dunite also would not be sufficiently radioactive to account for oceanic heat flow, and TILTON and REED conclude that eclogites may be important constituents of the oceanic upper mantle.

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

I. Meteorites

The exceptionally low concentrations of radioactive elements in meteorites have made their determination difficult. The refinement of neutron activation techniques, however, has made it possible to estimate the small concentrations present even in the iron meteorites. The concentrations of uranium in a variety of meteorites are given in Table 92-C-1. Measurements of the concentration of thorium in meteorites are far less abundant than those of uranium. The thorium concentrations and Th/U ratios where available are given in Table 90-C-1.

Table 92-C-1. Contents of uranium in meteorites

Name	Class symbol	No. of samples	$U \times 10^4 \times ppm$	Method	Reference
<i>Stones</i>					
<i>Acbondrites</i>					
Angra dos Reis	Aa	2	19.85	N	MORGAN and LOVERING (1964)
Binda	Ap	2	2.27	N	MORGAN and LOVERING (1964)
Bishopville	Ae	2	0.517	N	MORGAN and LOVERING (1964)
Cumberland Falls	Ac	1	1.0	R	DAVIS (1950)
Ellemecet	Ab	2	0.151	N	MORGAN and LOVERING (1964)
Johnstown	Ab	2	0.22	N	KÖNIG and WÄNKE (1959)
		1	1.1	N	BATE and HUIZENGA (1963)
		2	1.15	N	MORGAN and LOVERING (1964)
Moore Co.	Ap.	2	1.96	N	MORGAN and LOVERING (1964)
Nakhla	Ado	2	4.92	N	MORGAN and LOVERING (1964)
Norton Co.	Ae	1	1.00	I	PATTERSON <i>et al.</i> (1953)
Nuevo Laredo	Ap	1	12.6	N	HAMAGUCHI <i>et al.</i> (1957)
		2	15.5	N	REED <i>et al.</i> (1960)
fragment II		2	13.2	N	MORGAN and LOVERING (1965a)
fragment III		2	13.9	N	MORGAN and LOVERING (1965a)
Pasamonte	Aor	1	5.42	N	KÖNIG and WÄNKE (1959)
Sioux Co.	Ap	1	6.30	N	KÖNIG and WÄNKE (1959)
Staroe Pas' Yanoe	Ae		17-18	L and N	STARIK and SHATS (1960)

Table 92-C-1 (continued)

Name	Class symbol	No. of samples	U $\times 10^3$ ppm	Method	Reference
<i>Chondrites</i>					
Abel	Ce	3	1.10	N	REED <i>et al.</i> (1960)
		2	1.50	N	GOLES and ANDERS (1962)
Akaba		1	0.9	N	HERNEGGER and WÄNKE (1957)
		1	0.8	N	EBERT <i>et al.</i> (1957)
Beardsley	CH	3	1.20	N	REED <i>et al.</i> (1960)
		1	1.13	N	KÖNIG and WÄNKE (1959)
Breitscheid		1	1.5	N	HERNEGGER and WÄNKE (1957)
		1	1.23	N	EBERT <i>et al.</i> (1957)
		1	1.24	N	KÖNIG and WÄNKE (1959)
Bruderheim	CL	3	1.50	N	GOLES and ANDERS (1962)
Elenovka (total)	CL	1	11.0	L and N	STARIK and SHATS (1960)
chondrules		2	21.4	L and N	STARIK and SHATS (1956)
matrix		2	28.6	L and N	STARIK and SHATS (1956)
Ergheo	CL	1	2.1	N	GOLES and ANDERS (1962)
Forest City	CH	1	1.02	N	HAMAGUCHI <i>et al.</i> (1957)
		2	1.50	N	REED <i>et al.</i> (1960)
Holbrook	CL	2	1.26	N	HAMAGUCHI <i>et al.</i> (1957)
		4	1.60	N	REED <i>et al.</i> (1960)
Hvitri	Ce	2	0.619	N	LOVERING and MORGAN (1964)
Indarch	Ce	1	1.6	N	REED <i>et al.</i> (1960)
		3	0.9	N	GOLES and ANDERS (1962)
Karoonda	CHL	2	1.37	N	LOVERING and MORGAN (1964)
Kunashak		4	22.7	L and N	STARIK and SHATS (1956)
Mighei	Cc ₂	1	1.6	N	REED <i>et al.</i> (1960)
		2	1.4	N	GOLES and ANDERS (1962)
Mocs	CL	1	1.1	N	GOLES and ANDERS (1962)
Modoc	CL	1	1.1	I	PATTERSON <i>et al.</i> (1953)
		1	1.08	N	HAMAGUCHI <i>et al.</i> (1957)
		4	1.40	N	REED <i>et al.</i> (1960)
		4	2.7	I	PATTERSON in HAMAGUCHI <i>et al.</i> (1957)
Mokoia	CHL	1	1.04	N	KÖNIG and WÄNKE (1959)
		2	1.40	N	LOVERING and MORGAN (1964)
Murray	Cc ₂	3	2.00	N	GOLES and ANDERS (1962)
Orgueil	Cc	2	0.8	N	REED <i>et al.</i> (1960)
		2	2.42	N	LOVERING and MORGAN (1964)
Pultusk	CH or CL	1	1.20	N	EBERT <i>et al.</i> (1957)
		1	1.23	N	KÖNIG and WÄNKE (1959)

Uranium

92-C-3

Table 92-C-1 (Continued)

Name	Class symbol	No. of samples	U $10^3 \times \text{ppm}$	Method	Reference
Richardton	CR	2	1.22	N	HAMAGUCHI <i>et al.</i> (1957)
		1	1.3	N	GOLES and ANDERS (1962)
Saratov (total)	CL		8.5—9.0	L and N	STARIK and SHATS (1960)
Chondrules		1	20.0	L and N	STARIK and SHATS (1956)
Matrix		1	33.2	L and N	STARIK and SHATS (1956)
St. Marks	Ce	1	0.9	N	GOLES and ANDERS (1962)
Ställdalen	CH or CL	1	1.1	N	GOLES and ANDERS (1962)
<i>Stony irons</i>					
Antofagasta (metal)	P	1	1.0	R	DAVIS (1950)
Brenham (olivine) (metal)	P	1	0.79	R	DAVIS (1950)
		1	<0.09	R	DAVIS (1950)
		1	0.06	R	REASBECK and MAYNE (1955)
(stone)		1	0.64	R	REASBECK and MAYNE (1955)
(metal)		1	0.0005	N	REED <i>et al.</i> (1958)
		1	0.012	N	REED <i>et al.</i> (1958)
Salta (metal) (olivine)	P	1	1.9	R	DAVIS (1950)
		1	0.12	R	DAVIS (1950)
<i>Irons</i>					
Cañon Diablo (metal)	Og		0.0005 to 0.0014	N	REED <i>et al.</i> (1958)
(troilite)		1	<0.06	N	GOLES and ANDERS (1962)
		1	0.35	N	GOLES and ANDERS (1962)
		1	0.4	N	REED <i>et al.</i> (1960)
		1	0.9	I	PATTERSON <i>et al.</i> (1953)
Carbo	Om		0.0003 to 0.007	N	REED <i>et al.</i> (1958)
Chebankol	Og	1	1.68	L and N	STARIK and SHATS (1956)
Chinghe	D	1	1.73	L and N	STARIK and SHATS (1956)
Grant (metal)	Of	1	<0.05	N	GOLES and ANDERS (1962)
(troilite)		1	0.65	N	GOLES and ANDERS (1962)
Sardis (troilite)		1	0.65	N	GOLES and ANDERS (1962)
Sikhote-Alin	H	2	2.19	L and N	STARIK and SHATS (1956)
		1	<0.002	N	FIREMAN and FISHER (1961)
Soroti (troilite)	uncl.	1	1.7	N	GOLES and ANDERS (1962)
Thunda			0.0005 to 0.032	N	REED <i>et al.</i> (1958)
Toluca (metal)	Om	2	<0.015	N	GOLES and ANDERS (1962)
(troilite)		1	1.0	N	GOLES and ANDERS (1962)
(troilite)		1	<1.3	N	REED <i>et al.</i> (1960)

With regard to the various types of meteorites, the abundance of uranium is particularly low in the irons. Early determinations in the range of hundredths of a part per million uranium in the irons are probably not accurate, and the more recent data are in the range of tenths of a part per billion. The abundances of uranium in the stony meteorites are higher than in the irons, with the chondrites averaging 0.01 to 0.02 part per million of the metal, roughly two orders of magnitude greater than in the irons. The achondrites may contain slightly more uranium than the chondrites.

II. Tektites

The abundances of uranium in various tektites are shown in Table 92-C-2. Comparable values for thorium and the Th/U ratio are given in Table 90-C-2. Tektites are interesting in view of the possibility that they might be of extraterrestrial origin. The concentrations of radioactive elements in tektites, however, are at least two orders of magnitude greater than in meteorites. In fact, concentrations of radioactive materials in tektites are rather similar to those found in surficial materials on the earth. This similarity, of course, does not prove terrestrial origin but is at least

Table 92-C-2. *Contents of uranium in tektites and glasses*

Name	No. of samples	U ppm	Method	Reference
Australite	2	2.6	R	DUBEY (1933)
	4	1.6	L	ADAMS (1956)
	1	1.74	I	TILTON (1958)
	6	2.0	R	CHERRY (1962)
	1	2.7	R	CHERRY and ADAMS (1963)
	8	2.1	R	BALACEK and ADAMS (1966)
Bediasite	4	1.3	L	ADAMS <i>et al.</i> (1959)
	2	1.5	R	CHERRY and ADAMS (1963)
	10	1.9	R	BALACEK and ADAMS (1966)
Billitonite	1	2.7	R	DUBEY (1933)
Ivory Coast Tektite	1	0.91	L	FRIEDMAN (1958)
Indochinite	2	1.7	L	ADAMS (1956)
	1	2.24	L	HEIDE (1961)
	3	2.2	L	STARIK <i>et al.</i> (1961b)
	4	2.1	R	CHERRY and ADAMS (1963)
	5	2.2	R	BALACEK and ADAMS (1966)
	4	2.7	R	DUBEY (1933)
Moldavite	1	1.8	L	ADAMS <i>et al.</i> (1959)
	2	1.9	L	HEIDE (1961)
	2	2.2	L	STARIK <i>et al.</i> (1961b)
	1	2.1	R	CHERRY and ADAMS (1963)
	1	1.6	L	ADAMS (1956)
Philippinite	1	2.5	L	STARIK <i>et al.</i> (1961b)
	1	1.85	R	CHERRY and ADAMS (1963)
	12	2.6	R	BALACEK and ADAMS (1966)
	1	1.4	R	DUBEY (1933)
Darwin glass	1	1.9	L	ADAMS (1956)
	1	0.8	L	STARIK <i>et al.</i> (1961b)
	2	18.4	R	CHERRY and ADAMS (1963)
Tektites Ave.		1—2		ADAMS (1956)

a strong indication of that possibility. Regional differences in the abundances of thorium and uranium in tektites have recently been summarized by BALACEK and ADAMS (1966), who also report a large number of new analyses. The origin of these regional differences has not been established.

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III. Lunar Materials

The results from approximately 700 uranium analyses of lunar rocks can be found in the literature, but it is very difficult to summarize them in a meaningful way. The reason for this is that rock types are often ill defined or form only small portions of larger rocks, e.g. breccias. An additional problem with many analyses is that the samples analyzed were very small and far from being representative for a particular hand specimen or rock type. On the other hand, it seems that at each landing site the U concentration of a particular rock type keeps close to a specific concentration level with rather small variation. The large number of analyses therefore, probably provides a good estimate of the U concentration of the various petrographic units. Agreement between average concentrations obtained by neutron activation, mass spectrometry, γ -ray spectrometry of natural radioactivity and occasionally fission track counting is good. Spark source mass spectrometry in many cases yields clearly deviating values and therefore these data were not used.

Table 92-C-3 lists the average uranium concentrations, their range and standard deviations for the various rock types encountered at each landing site. The grouping of the rocks is to a very large degree arbitrary and an example of this is the melt rocks. They comprise the so-called anorthositic, troctolitic, very high alumina and Apollo 14 KREEP basalts which contain clastes or xenolithic materials and frequently show evidence of shock or reaction with the melt matrix containing them (IRVING, 1975, P VI, 363)¹; the Apollo 15 and 17 KREEP basalts were also included with this group. It is certainly possible to subdivide a particular group on petrographic grounds, but in most cases there is either no consensus on the classification or the differences are not borne out in the uranium concentrations, e.g. for the mare basalts.

Table 92-C-3. *Uranium in lunar rocks*

	Mean ppm U	Range ppm U	s	Number of analyses	References
<i>Apollo 11</i>					
Soils	0.56	0.29-1.2	0.17	22	15, 22, 26, 28, 49, 60, 67, 69, 77, 78, 85, 88, 90
Breccias	0.56	0.36-0.69	0.08	31	26, 27, 49, 59, 67, 69, 77, 85
High-K basalts	0.75	0.47-0.88	0.12	29	26, 27, 31, 49, 59, 60, 66 67, 69, 77, 85, 86
Low-K basalts	0.23	0.14-0.41	0.06	27	26, 27, 49, 59, 60, 67, 69, 77, 85

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 (1970-1975).

Table 92-C-3 (continued)

	Mean ppm U	Range ppm U	s	Number of analyses	References
<i>Apollo 12</i>					
Soils	1.85	0.9-3.27	0.54	42	4, 13, 23, 38, 57, 61, 63, 65, 72, 80, 86, 90
Breccias	5.25	2.19-10.3	3.02	11	23, 51, 57, 61, 63, 72, 87
Basalts	0.23	0.11-0.37	0.05	52	4, 9, 13, 37, 38, 51, 57, 61, 63, 65, 72, 86
<i>Apollo 14</i>					
Soils	3.34	2.1-4.07	0.39	24	8, 16, 21, 41, 42, 62, 71, 73, 81, 89
Breccias	3.52	1.24-5.4	0.93	28	5, 16, 21, 29, 37, 81, 89
Melt rocks	3.15	2.6-3.9	0.37	11	5, 16, 37, 41, 62, 71, 74
Basalt 14053	0.58	0.52-0.64	0.05	4	37, 71, 74
1 Anorthositic fragment 14161	0.58	—	—	1	33
<i>Apollo 15</i>					
Soils	1.11	0.51-1.89	0.26	42	3, 20, 25, 37, 41, 58, 62, 81
Breccias	0.83	0.35-1.46	0.32	12	35, 37, 58
KREEP-rich breccias	3.15	2.9-3.28	0.17	4	37, 62
Melt rocks	1.51	1.17-1.84	—	2	35
Basalts	0.15	0.10-0.20	0.03	12	3, 29, 37, 58, 62, 83
Anorthosites	0.0076	0.0015-0.043	0.0065	5	33, 37, 83
<i>Apollo 16</i>					
Soils	1.11	0.51-1.89	0.26	42	29, 40, 50, 52, 53, 75, 82, 91
Breccias	0.57	0.062-1.31	0.37	49	6, 12, 17, 19, 29, 35, 39, 50, 53, 83, 84
KREEP-rich breccias	2.35	1.7-3.2	0.45	8	6, 12, 17, 39, 45, 53
Melt rocks	0.61	0.28-1.10	0.34	11	2, 3, 12, 17, 19, 35, 53
Anorthosites	0.026	<0.0006-0.101	0.31	11	12, 35, 52, 53, 75, 83, 84, 91
<i>Apollo 17</i>					
Soils	0.46	0.16-1.0	0.26	66	6, 11, 18, 19, 25, 39, 52, 54, 64, 84
Breccias	1.27	0.51-2.06	0.41	27	7, 18, 25, 35, 39, 55, 83, 84
Melt rocks	0.29	0.20-0.41	0.06	12	35, 56
Basalts	0.13	0.07-0.22	0.03	33	7, 18, 25, 54, 83, 84
<i>Luna 16</i>					
Soils	0.29	0.1-0.36	0.10	6	1, 34, 73, 79
<i>Luna 20</i>					
Soils	0.32	0.22-0.41	0.07	6	2, 48, 68, 70, 75

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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The variation within each group at one particular landing site is, in general, smaller than between analogous rock groups of different landing sites.

With respect to many incompatible elements, e.g. K and U, the composition of the great majority of the soils, breccias and most other rocks, except the anorthositic ones, can be approximated by a two-component mixing model with varying pro-

portions of the end-members (e.g. SCHONFIELD, 1974, P V, 1135). For Apollo 11 these are low-K ($\lesssim 0.06\%$ K, ~ 0.2 ppm U) and high-K ($\sim 0.25\%$ K, 0.75 ppm U) mare basalt. For the other lunar landing sites the end-members are low-K mare basalt and the hypothetical rock KREEP. The latter is very rich in K, REE, P and other incompatible elements like Th and U which are present due to concentration by differentiation processes. In general, the U content of a rock is dominated by its KREEP component which provides up to 3–4 ppm U in some breccias. No pure KREEP, however, has ever been found. The highest U concentration of 6–10 ppm was encountered in a granitic differentiate (white portion of breccia 12013), the lowest of < 0.0006 ppm U in an almost monomineralic anorthosite (rock 63315). The average for anorthosites is 0.02 ppm U. The emerald green glass of Apollo 15, which is considered a representative of the least differentiated mare basalt contains 0.045 ppm U (average of 445 fission track analyses, FLEISCHER *et al.*, 1974, P V, 2251; STORZER *et al.*, 1973, P IV, 2363), average low-K mare basalts ~ 0.2 ppm U and high-K mare basalts ~ 0.75 ppm U. The melt rocks are all uranium-rich types with uranium contents around 1 ppm.

Geochemically the uranium in lunar rocks is characterized by its stronger coherence with Th than in terrestrial rocks. This is probably due to the absence of hexavalent uranium on the moon, which prevents a possible separation of the two elements. Fission track studies have shown, that uranium in lunar rocks is very inhomogeneously distributed and that the uranium content of the rock-forming minerals is extremely low: Pyroxenes, feldspars, olivines, cristobalites and ilmenites contain < 5 ppb U (BURNETT *et al.*, 1971, P II, 1503; CROSAZ *et al.*, 1970, P I, 2051; LOVERING *et al.*, 1970, P I, 627). Most of the uranium in volcanic rocks is localized in indeterminate interstitial areas of possibly glassy material enriched in Si, K, P. It probably represents a quenched residual magmatic liquid which concentrates uranium until the very last stage of crystallization. Only then does the uranium enter discrete phases leaving the glassy matrix essentially devoid of uranium (BURNETT *et al.*, 1971, P II, 1503; LOVERING *et al.*, 1970, P I, 627; 1971, P II, 151, and 1972, P III, 281; RICE *et al.*, 1971, P II, 159). These phases are baddeleyite, zircon, tranquillityite, a mineral which perhaps is zirconolite, whitlockite and apatite. In lunar breccias the uranium is less strictly confined to certain phases of interstitial material (LOVERING *et al.*, 1970, P I, 627) and the distributed uranium may amount up to 95% (GRAF *et al.*, 1973, P IV, 2145) of the total. Table 92-C-4 gives an indication of the uranium content in the uranium concentrating minerals and Table 92-C-5 is an example of the uranium balance in two lunar magmatic rocks.

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. Since the Th/U ratio on the moon is very constant at 3.65 ± 0.3 , these data permit the conclusion to be drawn that on average the highlands contain ~ 0.25 ppm U, the maria 0.9 ppm U and the average crustal rock on the lunar surface 0.6 ppm U. Although these numbers deviate from averages that may be calculated from the values for the soils of Table 92-C-3 they are probably representative, since for the least heterogeneous landing sites (Apollo 11 and 16) the orbital data are close to the averages of the soils. The U and Th concentrations in the crust are due to strong enrichment. Based on element correlations, geochronology and heatflow measurements (LANGSETH *et al.*, 1972, The Moon 4, 390) and depending

Uranium

92-C-9

Table 92-C-4. *U content of U concentrating phases^a*

Mineral	Typical values ppm U	Range ppm U	No. of grains analyzed	Rock numbers	References ^b
Apatite	40–60, 100–200	31–430	27	1084, 12013, 14305, 14321, 72315, 72395	9, 30, 36, 76
Whitlockite	20–80	10–880	34	12013, 12040, 14301, 14318, 7225	9, 29, 30, 36
Monazite	270	—	1	10047	46
Zircon	100–400	<10–1,500	24	10084, 12013, 14301, 14311	9, 14, 24, 30
Baddeleyite	50–150, ~10–1,500 300–450	>20		10047, 10057, 10069, 12002, 12020, 12022, 12028, 12040, 12051, 12053, 14301, 14306, 14310, 14311	9, 14, 24, 43, 44
Tranquillityite ^{c)}	50–300	40–~1,000	>13	10047, 10057, 10069, 12002, 12020, 12022, 12051, 12053	44, 47
Zirkelite ^{d)}	2,000	1,900–2,200	5	12036	10

^a Besides the minerals listed, there are other major U carriers which were not yet identified. They are all Zr-Ti or phosphate minerals which probably are tranquillityite, zirkelite or zirconolite and unresolved intergrowths of apatite and whitlockite. The highest U concentration (3.6%) was reported for a Zr-Ti mineral in rock 12013 containing also much Fe, Y, Nb, REE, Th and Pb (Reference 30).

^b For references see footnote of Table 92-C-3.

^c $\text{Fe}^{2+}(\text{Zr} + \text{Y})_2\text{Ti}_3\text{Si}_2\text{O}_{24}$.

^d CaZrTiO_4 .

Table 92-C-5. *Uranium balance in the lunar rocks 12013 and 12040 (Taken from reference 9 of Table 92-C-3)*

Phase	12013		12040	
	U (ppm)	% of total U	U (ppm)	% of total U
Apatite	170	25	^a	^a
Whitlockite	190	25	104	78
Zircon	330	17	^a	^a
Baddeleyite	^a	^a	840	10
Zr-Ti phase	2,000	10	1,300	5
Distributed	6 ^{b)}	20	^{c)}	^{c)}
		97		100

^a Not present.

^b Dark areas rich in P.

^c From major minerals, both from buried sources and distributed.

on the model of lunar evolution, overall uranium concentrations of between 30 and 86 ppb were estimated, with values of around 60 ppb being the most probable ones (PAPANASTASSIOU *et al.*, 1971, Earth Planet. Sci. Letters 11, 37; SOLOMON *et al.*, 1973,

Phys. Earth Planet. Interiors 7, 15; Toksöz *et al.*, 1973, The Moon 7, 251; WÄNKE *et al.*, 1973, P IV, 1461; SCHONFIELD *et al.*, 1974, P V, 1135; GANAPATHY *et al.*, 1974, P V, 1181; HUBBARD *et al.*, 1975, P VI, 1057; CONEL *et al.*, 1975, The Moon 14, 263).

The $^{238}\text{U}/^{235}\text{U}$ ratio in lunar rocks is the same as in terrestrial samples: 137.8 ± 0.3 (BARNES *et al.*, 1972, P III, 1465 and 1973, P IV, 1197; FIELDS *et al.*, 1970, P I, 1729 and 1972, P III, 1637; ROSHOLT *et al.*, 1970, P I, 1499 and 1971, P II, 1577; WANLESS *et al.*, 1970, P I, 1729). As a 10^7 year difference in the time of nucleosynthesis of the U isotopes would be reflected in a 1% difference in the $^{238}\text{U}/^{235}\text{U}$ ratios of lunar and terrestrial uranium, this implies that the U in the two bodies has a common origin within ± 5 million years. The ^{234}U daughter is in radioactive equilibrium with parent ^{238}U in the lunar rocks (ROSHOLT *et al.*, 1971, P II, 1577).

92-D. Abundances in Rock Forming Minerals (I), Uranium Minerals (II)

I.

Uranium occurs in a variety of minerals but characteristically is concentrated in a few species of minor abundance. Where uranium is present as trace quantities in such major minerals as quartz and the feldspars, its mode of occurrence is uncertain, though the following possibilities may be listed: (1) isomorphous substitution in the lattice, (2) concentration in lattice defects, (3) adsorption along crystal imperfections and grain borders, and (4) inclusion as microcrystals of uranium minerals. Table 92-D-1 summarizes the abundances of uranium in rock-forming minerals and uraniferous accessories in igneous rocks. Comparable concentrations of thorium and Th/U ratios are given in Table 90-D-1.

Table 92-D-1. *Contents of uranium in minerals in igneous rocks*

	U in ppm	References (No. of samples)
<i>Major minerals</i>		
Quartz	1.7 0.1-10	P (20) A (3); C (3); D (1); F (2); L (6); M (3); P (20); Q (2); R (2); U (1)
Feldspar (including potassium feldspar and plagioclase)	2.7 0.1-10	P (42) A (5); C (3); D (1); F (2); L (6); M (3); N (2); P (42); Q (7); R (2); U (1)
Biotite	8.1 1-60	P (23) A (1); C (3); F (2); L (6); M (3); N (2); P (23); Q (5); R (2); U (1)
Muscovite	2-8	C (1); M (2); P (4)
Hornblende	7.9 0.2-60	P (19) A (1); C (2); L (4); P (19); Q (5); R (2); U (1)
Pyroxene	3.6 0.1-50	P (11) A (1); P (11); Q (1); R (2)
Olivine (from dunite)	~ 0.05	T (20)
<i>Accessory minerals</i>		
Allanite	200 30-1,000	J (10) B (1); C (1); J (10); L (6); M (3); N (2); P (10); R (2); S (5); U (1)
Apatite	65 10-100	H (29) C (2); D (1); F (2); H (29); L (6); M (3); N (2); P (14); Q (7); U (1)
Epidote	43 20-200	H (9) H (9); P (3)
Garnet	6-30	C (2); P (4)

Table 92-D-1 (Continued)

	U in ppm	References (No. of samples)
Huttonite	$3 \times 10^3 - 7 \times 10^4$	V (individual grains from one rock)
Magnetite (and other opaque minerals)	1—30	A (12); C (2); D (1); F (2); L (6); M (3); N (2); P (23); Q (6); R (1); U (1)
Monazite	3000	H (11)
	500—3000	C (2); H (11); K (4); M (3); N (2); P (4); R (1)
Sphene	280	H (25)
	10—700	D (1); F (2); H (25); L (6); M (3); Q (4)
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)	
Xenotime	$300 - 4 \times 10^4$	C (2); P (3)
Zircon	1330	H (43)
	100—6000	C (3); D (1); G (21); H (43); L (6); M (3); N (2); P (14); Q (7); U (1); V (1)

Ranges of concentrations shown are those within which uranium values commonly lie, rather than the extreme values of the various mineral suites. Average values are reported for: major minerals in several batholiths of the western U.S.A. analyzed by reference P, using fluorimetric methods; accessory minerals from a sampling of North American granites by reference H, using gamma-spectrometric methods; and a suite of allanite separates by reference J, using radiometric methods. References listed below are cited for each mineral, and the numbers in parentheses in the table by each reference indicate the number of samples analyzed.

A. KEEVIL (1944); B. HUTTON (1951); C. LARSEN JR. and PHAIR (1954); D. TILTON *et al.* (1955); E. LARSEN JR. *et al.* (1956); F. TAUSON (1956); G. WEBBER *et al.* (1956); H. HURLEY and FAIRBAIRN (1957); J. W. L. SMITH *et al.* (1957); K. TILTON and NICOLAYSEN (1957); L. LEONOVA and TAUSON (1958); M. CHENTSOV (1959); N. BARANOV and DU (1961); P. LARSEN JR. and GOTTFRIED (1961); Q. LEONOVA and POGIBLOVA (1961); R. MELIKSETYAN (1961); S. LEONOVA (1962); T. HEIER and CARTER (1964); U. LEONOVA and RENNE (1964); V. RICHARDSON (1964).

Four papers which give preliminary data on mineral compositions but which are not cited in the table are GOTTFRIED and LARSEN JR. (1954); LARSEN JR. (1954); PHAIR (1955); and PHAIR (1956).

A major method of investigation of alpha-emitting elements in rocks is autoradiography. It is possible to construct autoradiographic techniques which discriminate between uranium and thorium, but the common and easily used methods involving thin films or plates of alpha-sensitive emulsions do not permit such a distinction. Modern techniques have been summarized by RAGLAND (1964), who also gives an extensive bibliography of autoradiographic investigations. The principal conclusions derived from autoradiographic studies of igneous rocks may be summarized as follows: (1) Most granites have a major portion of their alpha activity concentrated in small grains of accessory minerals. In many granites, however, there is also appreciable concentration on grain borders or disseminated through the major minerals. (2) Gabbros and other basic igneous rocks have their alpha activity distributed fairly evenly among the various major constituents. (3) Volcanic rocks

have a uniform distribution of radioactivity among their constituent phases. These facts lead to the conclusion that most minerals containing appreciable concentrations of thorium and uranium form quite late in the igneous crystallization sequence. In addition to the summary by RAGLAND (1964) cited above, other papers which might be consulted for an introduction to the field are those of MERLIN *et al.* (1957), ROGERS and ADAMS (1957), SPEARS (1961), and COPPENS (1950).

Variation of thorium and uranium abundances within individual crystals of accessory minerals has recently been demonstrated by SILVER and DEUTSCH (1963). By selectively dissolving various layers of zircon grains, they showed variations in abundances of thorium and uranium from place to place in single grains by as much as an order of magnitude. AHRENS (1965) has recently proposed a lognormal frequency distribution of uranium concentrations in accessory zircons of granites.

II. Uranium Minerals

The most abundant uranium mineral is uraninite, with a formula varying from UO_2 to U_3O_8 . The variability of chemical composition apparently results largely from oxidation of UO_2 to U_3O_8 after deposition, and all compositions between the end members are found. Some geologists use the term "pitchblende" as synonymous with uraninite, whereas others restrict it to the more oxidized form. Uraninite is the common black ore of uranium and occurs in hydrothermal vein and disseminated deposits and also in sedimentary rocks throughout the world. A more complete mineralogic description of uraninite is given by PALACHE *et al.* (1944).

A characteristic feature of uranium is its ability to be oxidized to the highly soluble uranyl ion (UO_2^{++}). This ion is easily mobilized in surface and near-surface waters; consequently, regardless of their origin, most uranium deposits contain an assemblage of supergene minerals which are invariably bright yellow, green, or orange and are generally fluorescent. In some cases these minerals are widely dispersed and not obviously associated with the original, primary mineralization. The various minerals in this category consist of carbonates, phosphates, vanadates, silicates, sulfates, etc., commonly in combination with uranium plus some other cation. A complete list of uranium minerals is given in Table 92-D-2; the list represents an addition of some 25 new species to those given by FRONDEL (1956).

Table 92-D-2. Minerals containing uranium as an essential constituent

Oxides	
Becquerelite	$7\text{UO}_3 \cdot \text{H}_2\text{O}$
Billietite	$\text{BaO} \cdot 6\text{UO}_3 \cdot 11\text{H}_2\text{O}$
Clarkeite	$(\text{Na}, \text{K}, \text{Ca}, \text{Pb})_2\text{U}_2\text{O}_7 \cdot n\text{H}_2\text{O}$
Compeignacite	$\text{K}_2\text{O} \cdot 6\text{UO}_3 \cdot 11\text{H}_2\text{O}$ (PROTAS, 1964)
Curite	$3\text{PbO} \cdot 8\text{UO}_3 \cdot 4\text{H}_2\text{O}$
Fourmarierite	$\text{PbO} \cdot 4\text{UO}_3 \cdot 7\text{H}_2\text{O}$
Ianthinite	$\text{UO}_3 \cdot 5\text{UO}_3 \cdot 10.56\text{H}_2\text{O}$ (GUILLEMIN and PROTAS, 1959)
Masuyite	$\approx \text{UO}_3 \cdot 2\text{H}_2\text{O}$
Richetite	Hydrated oxide of U and Pb (?)
Schoepite	$2\text{UO}_3 \cdot 5\text{H}_2\text{O}$
Uraninite	UO_2
Uranospherite	$(\text{BiO})(\text{UO}_2)(\text{OH})_3$ (?)
Vandenbrandeite	$\text{Cu}(\text{UO}_2)\text{O}_3 \cdot 2\text{H}_2\text{O}$
Vandendriesscheite	$\text{PbO} \cdot 7\text{UO}_3 \cdot 12\text{H}_2\text{O}$

Table 92-D-2 (Continued)

<i>Carbonates</i>	
Andersonite	$\text{Na}_2\text{Ca}(\text{UO}_2)(\text{CO}_3)_3 \cdot 6\text{H}_2\text{O}$
Bayleyite	$\text{Mg}_2(\text{UO}_2)(\text{CO}_3)_3 \cdot 18\text{H}_2\text{O}$
Diderichite	Identical with rutherfordine
Liebigite	$\text{Ca}_2(\text{UO}_2)(\text{CO}_3)_3 \cdot 10 - 11\text{H}_2\text{O}$
Rabbitite	$\text{Ca}_3\text{Mg}_5(\text{UO}_2)_2(\text{CO}_3)_6(\text{OH})_4 \cdot 18\text{H}_2\text{O}$
Rutherfordine	$(\text{UO}_2)(\text{CO}_3)$
Schroeckingerite	$\text{NaCa}_3(\text{UO}_2)(\text{CO}_3)_3(\text{SO}_4)\text{F} \cdot 10\text{H}_2\text{O}$
Sharpite	$(\text{UO}_2)(\text{CO}_3) \cdot \text{H}_2\text{O}(?)$
Studtite	Pb, uranyl carbonate (?)
Swartzite	$\text{CaMg}(\text{UO}_2)(\text{CO}_3)_3 \cdot 12\text{H}_2\text{O}$
Voglite	Ca, Cu, uranyl carbonate (?)
Wyartite	$3\text{CaO} \cdot \text{UO}_2 \cdot 6\text{UO}_3 \cdot 2\text{CO}_2 \cdot 12 - 14\text{H}_2\text{O}$ (GUILLEMIN and PROTAS, 1959)
<i>Sulfates</i>	
Johannite	$\text{Cu}(\text{UO}_2)_2(\text{SO}_4)_2(\text{OH})_2 \cdot 6\text{H}_2\text{O}$
Meta-uranopilite	Doubtful basic uranyl sulfate
Peligotite	Identical with johannite
Uranopilite	$(\text{UO}_2)_2(\text{SO}_4)(\text{OH})_{10} \cdot 12\text{H}_2\text{O}$
Zippeite	Near $2\text{UO}_3 \cdot \text{SO}_3 \cdot 5\text{H}_2\text{O}$
<i>Phosphates-Arsenates</i>	
Abernathyite	$\text{K}_4(\text{UO}_2)_3(\text{AsO}_4)_3 \cdot 8\text{H}_2\text{O}$
Arsenuranylite	$\text{Ca}(\text{UO}_2)_2(\text{AsO}_4)_2(\text{OH})_4 \cdot 6\text{H}_2\text{O}$ (BELOVA, 1958)
Autunite	$\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8 - 12\text{H}_2\text{O}$
Bassetite	$\text{Fe}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$
Bergenite	$\text{Ba}(\text{UO}_2)_2(\text{PO}_4)_2(\text{OH})_4 \cdot 8\text{H}_2\text{O}$ (BÜLTEMANN and MÖH, 1959)
Dewindtite	Doubtful Pb, uranyl phosphate
Dumontite	$\text{Pb}_2(\text{UO}_2)_3(\text{PO}_4)_2(\text{OH})_4 \cdot 3\text{H}_2\text{O}$
Fritzscheite	Doubtful Mn, uranyl phosphate-vanadate
Hallimondite	$\text{Pb}_2(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot n\text{H}_2\text{O}$ (WALENTA and WIMMENHAUER, 1961)
Heinrichite	$\text{Ba}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 10 - 12\text{H}_2\text{O}$ (GROSS <i>et al.</i> , 1958)
Hügelite	$\text{Pb}_2(\text{UO}_2)_2(\text{AsO}_4)_2(\text{OH})_4 \cdot 3\text{H}_2\text{O}$ (WALENTA and WIMMENHAUER, 1961)
Kahlcrite	$\text{Fe}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$
Lermontovite	$(\text{U}, \text{Ca}, \text{TR})_2(\text{PO}_4)_4 \cdot 6\text{H}_2\text{O}$ (G. and S., p. 199)
Meta-aurunite	$\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 6 - 8\text{H}_2\text{O}$
Metaheinrichite	$\text{Ba}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$ (GROSS <i>et al.</i> , 1958)
Metakahlerite	$\text{Fe}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$ (WALENTA, 1958)
Meta-kircheimerite	$\text{Co}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$ (WALENTA, 1958)
Metanovacekite	$\text{Mg}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$
Metatorbernite	$\text{Cu}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 6 - 8\text{H}_2\text{O}$
Meta-uranocircite	$\text{Ba}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$
Meta-uranospinitite	$\text{Ca}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$ (WALENTA, 1958)
Metazunerite	$\text{Cu}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$
Novacekite	$\text{Mg}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 8 - 10\text{H}_2\text{O}$
Parsonite	$\text{Pb}_2(\text{UO}_2)_2(\text{PO}_4)_2(\text{OH})_4 \cdot 7\text{H}_2\text{O}$
Phosphuranylite	$\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2(\text{OH})_4 \cdot 7\text{H}_2\text{O}$
Przhevalskite	$\text{Pb}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ (G. and S., p. 213)
Renardite	$\text{Pb}(\text{UO}_2)_2(\text{PO}_4)_2(\text{OH})_4 \cdot 7\text{H}_2\text{O}$
Sahugalite	$\text{HAl}(\text{UO}_2)_2(\text{PO}_4)_4 \cdot 16\text{H}_2\text{O}$
Salcite	$\text{Mg}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8 - 10\text{H}_2\text{O}$
Torbemite	$\text{Cu}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 12\text{H}_2\text{O}$
Troegerite	$\text{H}_2(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$

Table 92-D-2 (Continued)

Uramphite	$\text{NH}_4(\text{UO}_2)(\text{PO}_4) \cdot 3\text{H}_2\text{O}$ (NEKRASOVA, 1957)
Uranocircite	$\text{Ba}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8-10\text{H}_2\text{O}$
Uranospathite	$\text{Cu}(\text{UO}_2)_2(\text{AsO}_4, \text{PO}_4)_2 \cdot 16\text{H}_2\text{O}$ (?)
Uranospinite	$\text{Ca}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 10\text{H}_2\text{O}$
Walpurgite	$\text{Bi}_4(\text{UO}_2)(\text{AsO}_4)_2 \cdot 3\text{H}_2\text{O}$
Zeunerite	$\text{Cu}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 8-10\text{H}_2\text{O}$
<i>Vanadates</i>	
Carnotite	$\text{K}_2(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 1-3\text{H}_2\text{O}$
Ferghanite	$\text{U}_3(\text{VO}_4)_2 \cdot 6\text{H}_2\text{O}$
Francevillite	$(\text{Ba}, \text{Pb})(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 5\text{H}_2\text{O}$ (BRANCHE <i>et al.</i> , 1957)
Metatyuyamunite	$\text{Ca}(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 5-7\text{H}_2\text{O}$
Rauvite	$\text{CaO} \cdot 2\text{UO}_3 \cdot 2\text{V}_2\text{O}_5 \cdot 16\text{H}_2\text{O}$ (?)
Sengierite	$\text{Cu}(\text{UO}_2)(\text{VO}_4)(\text{OH}) \cdot 4-5\text{H}_2\text{O}$
Tyuyamunite	$\text{Ca}(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 7-11\text{H}_2\text{O}$
Uvanite	$\text{U}_2\text{V}_6\text{O}_{21} \cdot 15\text{H}_2\text{O}$ (?)
Vanuralite	$\text{Al}_2\text{O}_3 \cdot 2\text{V}_2\text{O}_5 \cdot 4\text{UO}_3 \cdot 17\text{H}_2\text{O}$ (BRANCHE <i>et al.</i> , 1963)
<i>Silicates</i>	
Beta-uranophane	$\text{Ca}(\text{UO}_2)_4(\text{SiO}_4)_2(\text{OH})_2 \cdot 5\text{H}_2\text{O}$
Boltwoodite	$\text{K}_2(\text{UO}_2)_3(\text{SiO}_4)_2(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ (FRONDEL and ITO, 1956)
Coffinite	$\text{U}(\text{SiO}_4)_2 \cdot (\text{OH})_4$
Cuproskłodowskite	$\text{Cu}(\text{UO}_2)_2(\text{SiO}_4)_2(\text{OH})_2 \cdot 5\text{H}_2\text{O}$
Gastunite	Ca, Pb, uranyl silicate
Kasolite	$\text{Pb}(\text{UO}_2)(\text{SiO}_3)(\text{OH})_3$
Orlite	$3\text{PbO} \cdot 3\text{UO}_3 \cdot 4\text{SiO}_2 \cdot 6\text{H}_2\text{O}$ (G. and S., p. 239)
Pilbarite	$\text{UO}_3 \cdot \text{PbO} \cdot \text{ThO}_2 \cdot 2\text{SiO}_2 \cdot 4\text{H}_2\text{O}$ (?)
Ranquilité	$1.5\text{CaO} \cdot 2\text{UO}_3 \cdot 5\text{SiO}_2 \cdot 12\text{H}_2\text{O}$ (de ABELECO, 1960)
Skłodowskite	$\text{Mg}(\text{UO}_2)_2(\text{SiO}_4)_2(\text{OH})_2 \cdot 5\text{H}_2\text{O}$
Soddyite	$(\text{UO}_2)_6(\text{SiO}_4)_2(\text{OH})_2 \cdot 5\text{H}_2\text{O}$
Uranopbanc	$\text{Ca}(\text{UO}_2)_2(\text{SiO}_3)_2(\text{OH})_2 \cdot 5\text{H}_2\text{O}$
Ursilite	$2(\text{Ca}, \text{Mg}) \cdot 0.2\text{UO}_3 \cdot 5\text{SiO}_2 \cdot 9-10\text{H}_2\text{O}$ (CHERNIKOV <i>et al.</i> , 1957)
Weeksite	$\text{K}_2(\text{UO}_2)_2(\text{Si}_2\text{O}_5)_3 \cdot 4\text{H}_2\text{O}$
<i>Niobates — Tantalates — Titanates</i>	
Betafite	$(\text{U}, \text{Ca})(\text{Nb}, \text{Ta}, \text{Ti})_3\text{O}_9 \cdot n\text{H}_2\text{O}$
Brannerite	UTi_2O_6
Lodochnikovite (Lodochnikite)	$2(\text{U}, \text{Th})\text{O}_2 \cdot 3\text{UO}_2 \cdot 14\text{TiO}_2$ (GERASIMOVSKY, 1956)
Pisekite	U, Ti, Th, rare-earth niobate-tantalate
<i>Molybdates</i>	
Calcarmolite	$\text{Ca}(\text{UO}_2)(\text{MoO}_4)_2(\text{OH})_2 \cdot 11\text{H}_2\text{O}$ (FEOROV, 1963)
Iriginitite	$\text{UO}_3 \cdot 2\text{MoO}_3 \cdot 4\text{H}_2\text{O}$ (G. and S., p. 197)
Moluranite	$\text{UO}_3 \cdot 3\text{UO}_3 \cdot 7\text{MoO}_3 \cdot 20\text{H}_2\text{O}$ (G. and S., p. 196)
Mourite	formula uncertain; contains U and Mo (KOPCHENOVА <i>et al.</i> , 1962)
Umohoite	$(\text{UO}_2)(\text{MoO}_4) \cdot 4\text{H}_2\text{O}$

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. G. and S. refer to GETSEVA and SAVALEVA (1957). 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.

92-E. Abundances in Common Igneous Rocks

The abundances of uranium in igneous rocks are discussed under three subheadings. The first is a generalized discussion of the content of uranium in rocks broadly classified as granites, basalts, etc. The second category for discussion concerns the variation in abundances of uranium in cogenetic suites of rocks, and the third category discusses the variation of abundance of uranium within individual plutons.

I. Abundances in Major Rock Types

The fact that the uranium and thorium concentrations of igneous rocks are both so closely related to the compositions of those rocks makes it difficult to subdivide igneous rocks into meaningful radiometric groups. For example, the phrase "uranium content of basalt" is a meaningless term because the basalts clearly do not represent one petrological population, and sufficient work on contents of radioactive materials has been done to indicate radiometric differences between different varieties of basalt. The data given in Table 92-E-1, therefore, represent only average compositions of those groups of rocks which might possibly be considered single populations. Indeed, many of the groups shown in Table 92-E-1 probably do not actually represent one homogeneous population. Similar groups are used in Table 90-E-1, which gives the contents of thorium and the Th/U ratios in igneous rocks.

Table 92-E-1 shows the general tendency for uranium to increase in abundance toward the more silicic varieties of igneous rocks. The average uranium content of various igneous rocks is summarized graphically in Figs. 92-E-1 to 92-E-2. In view of the marked concentration of uranium toward the outer parts of the earth (see Section 92-B), the fact that uranium increases in abundance toward the later members of igneous rock series further demonstrates the tendency of uranium to become segregated from other rock-forming constituents during general petrologic evolution.

The average concentration of uranium in the earth's continental crust can be variously estimated according to the proportions of rock types assumed to constitute the crust. As discussed by ROGERS (1966), there is a general tendency to overestimate the abundance of granite in cratonic areas. Assuming that granites constitute about half of the continental crust, and that the remainder of the crust contains little radioactive material, the average concentration of uranium in continental masses must lie in the range of 1–4 ppm and is probably somewhere near the middle of this range. PHAIR and GOTTFRIED (1964) estimate an average uranium content of 2.8 ppm for continental areas.

The concentration of uranium in dunites and other ultrabasic rocks is extremely low. The average of 0.014 ppm from the data of HEIER and CARTER (1964) is about one order of magnitude below that estimated for the upper mantle from heat flow studies (BIRCH, 1965). The dunites and peridotites included in this average come both from major intrusive bodies and from inclusions in basalts. Most of them, though not all, are from continental arcs, and it is possible that they represent the upper mantle

Tables 92-E-1. Uranium contents of selected igneous rock suites

Suite	No. of sam- ples	U ppm	Method	Reference
<i>Granitic rocks</i>				
<i>France</i>				
Luzy granites (Paleozoic)	167	4.2	L	COULOMB (1959)
Paleozoic granites of western France	814	6.1	L	HUSSEIN (1961) and COULOMB (1959)
<i>Russia</i>				
Precambrian mica granites of Ukrainian shield (Middle Dnepr area)	100	5.7	emanation	FILIPPOV and KOMLEV (1959)
Tertiary Meghrinsk intrusions of Southern Armenia; alkalic granodiorites to alkalic granites of 2nd intrusive phase	16	5.1		MELIKSETYAN (1961)
Paleozoic Susamyr batholith of Tien Shan; granodiorites to granites	152	3.4	emanation	TAUSON <i>et al.</i> (1958)
Northern Tien Shan; weighted average of all crystalline rocks		4.1		KRYLOV (1963)
Paleozoic granites and syenites of Central and western Tuva	47	3.9	radiochemical	ABRAMOVICH (1959)
<i>United States</i>				
Conway granite, New Hampshire; Triassic, alkalic	1051	15	R	ROGERS <i>et al.</i> (1965)
New England granites	123	6.2	R	ROGERS (1964)
Enchanted Rock batholith, Texas; granite	81	3.5	R	ROGERS (1964)
Precambrian granites of Front Range, Colo.	38	5.0 (weighted)	L	PHAIR and GOTTFRIED (1964)
Laramide stocks of Front Range, Colorado	27	7.6	L	PHAIR and GOTTFRIED (1964)
Laramide stocks west of Front Range, Colo.	25	2.2	L	PHAIR and GOTTFRIED (1964)
Precambrian granites of Middle Rocky Mountains	25	2.2	L	PHAIR and GOTTFRIED (1964)
Idaho batholith; Laramide; tonalites and granodiorites	23	2.3	L	LARSEN JR. and GOTTFRIED (1961)
qtz. monzonites and granites	9	3.7	L	
Sierra Nevada batholith, Cal.; granodiorites to granites; Jurassic	20	5.4	various	ROGERS (1964)
Laramide granites of Idaho and Boulder batholiths and northern Washington	38	2.5	various	ROGERS (1964)

Uranium

92-E-3

Table 92-E-1 (Continued)

Suite	No. of sam- ples	U ppm	Method	Reference
Granites and granodiorites of Southern California batholith; Cretaceous	54	2.4	various	ROGERS (1964)
<i>Gabbroic and ultramafic rocks</i>				
General average for "gabbroid" rocks	34	0.84	various	HEIER and CARTER (1964)
Dunite (intrusive and nodules)	24	0.014	various	HEIER and CARTER (1964)
Dunite nodules (Hawaii, Germany, Arizona)	3	0.003 to 0.009	I and N	TILTON and REED (1963)
<i>Eclogites</i>				
Pipe eclogite (Africa)	10	0.26	R	HEIER (1963)
Pipe eclogite (Africa-1; Australia-3)	4	0.052	N	LOVERING and MORGAN (1963)
Eclogite nodules (Hawaii)	2	0.030 to 0.043	I	TILTON and REED (1963)
Average eclogite from metamorphic terranes (Nor- way and central Europe)	9	0.20	various	HEIER and CARTER (1964)
<i>Alkaline intrusive rocks</i>				
Nepheline syenites from northern Norway	16	0.04	R	HEIER (1962a)
Variscan alkalic syenites and nepheline syenites of southern Tien Shan	26	1.4	L	LEONOVIA (1964)
Lovozero massif, Kola Peninsula, Russia:				SAFRYKINA (1959)
first intrusive phase (neph. syenites)	14	9.9	L	
second intrusive phase (lujavrites, urtites, and foyaites)	25	15.3	L	
third intrusive phase (mainly lujavrites)	19	19.7	L	
fourth intrusive phase (monchiquites)	2	2.8	L	
<i>Silicic extrusive rocks</i>				
Rhyolites and dacites of western U.S.A.	116	5.0	—	COATS (1956)
<i>Basaltic rocks</i>				
Oceanic tholeiitic basalts	22	0.10	I	TATSUMOTO <i>et al.</i> (1965)
Basalts and basaltic andesites of Mariana Islands	20	0.56	L	GOTTFRIED <i>et al.</i> (1963)
Tholeiitic basalts of Hawaii	6	0.18	R L	HEIER <i>et al.</i> (1964) LARSEN, 3d, and GOTTFRIED (1960)

Table 92-E-1 (Continued)

Suite	No. of sam- ples	U ppm	Method	Reference
Alkali basalts of Hawaii	2	0.99	R L	HEIER <i>et al.</i> (1964) LARSEN, 3d, and GOTTFRIED (1960)
Japan:				
tholeiitic basalts	2	0.15	R	HEIER and ROGERS (1963)
high-alumina basalts	2	0.22	R	HEIER and ROGERS (1963)
alkali-olivine basalts	2	0.53	R	HEIER and ROGERS (1963)
Caribbean Island arc:				
spilites	6	0.22	R	ROGERS and DONNELLY (1966)
intrusive keratophyres	5	0.77	R	ROGERS and DONNELLY (1966)
extrusive keratophyres	4	0.29	R	ROGERS and DONNELLY (1966)
basaltic andesites	12	0.79	R	ROGERS and DONNELLY (1966)
Plateau basalts (ave.)	26	0.53	various	HEIER and CARTER (1964)
Columbia River	2	0.36	R	HEIER and ROGERS (1963)
Palisades diabase (New York)	5	0.35	R	HEIER and ROGERS (1963)

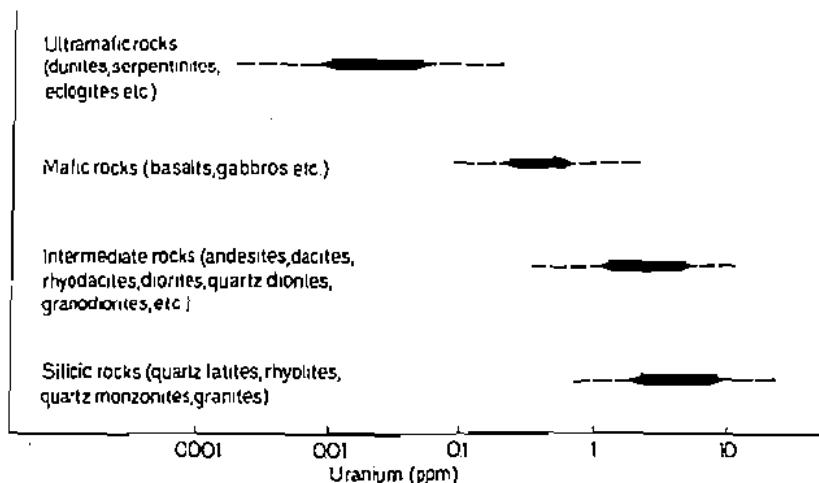


Fig. 92-E-1. Generalized distribution of uranium in various broad groups of igneous rocks.
[From PETERIAN, Z. E.: unpublished communication (1963)]

under the continent that has been depleted in thorium and uranium during separation of the cratonic materials. Data are not yet adequate to determine whether or not there are differences between oceanic and continental dunites and peridotites. It is interesting to note that the concentration of 0.2 ppm found by HEIER and CARTER for pipe eclogites is comparable to that presumed for the upper mantle (also see TILTON and

REED, 1963). With regard to upper mantle studies, MORGAN and LOVERING (1965b) have recently reported the uranium and thorium abundances in the basalt of the Guadalupe experimental Mohole. This basalt contained 0.195 ppm uranium.

The alkaline rocks reported in Table 92-E-1 are merely a few representatives of a broad sampling of such rocks that have been studied radiometrically. The wide variability of uranium concentrations in such alkaline rocks is discussed in more detail by PETERMAN (1963). The areas which have been primarily studied include the Kola Peninsula of Russia (Table 92-E-1 summarizes data on 60 samples by

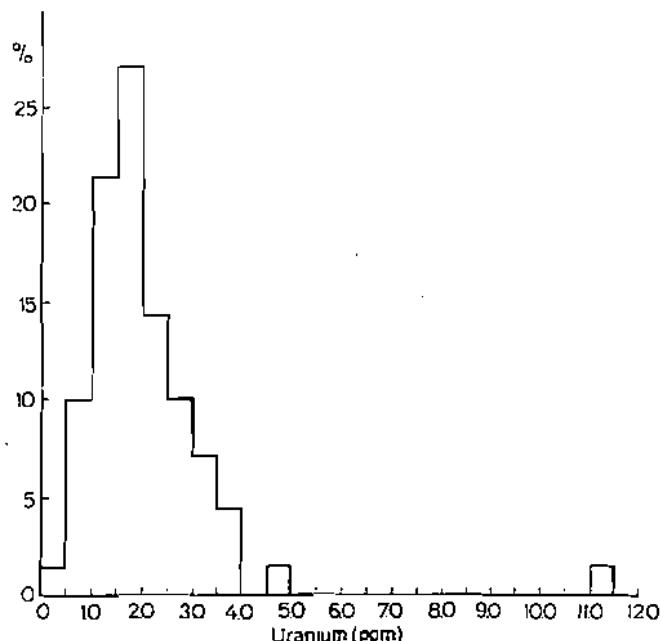


Fig. 92-E-2. Histogram of uranium concentrations in silicic igneous rocks. Plot represents 242 individual analyses and 3 average values for volcanic rocks and 194 individual analyses and 96 average values for plutonic and hypabyssal rocks. [From PETERMAN, Z.E.: unpublished communication (1963); data are summarized variously in Table 92-E-1]

SAPRYKINA, 1959), several suites of rocks from the southern Urals and Tien Shan area (e.g., see YESHOVA *et al.*, 1962), the rocks of Stjernoy in northern Norway (HEIER, 1962a), a suite from Magnet Cove, Arkansas (ERICKSON and BLADE, 1963) (Fig. 90-E-3), and rocks from Virginia and Texas (GOTTFRIED *et al.*, 1962) (Fig. 90-E-6). The extreme variability between and within groups makes averaging almost useless, and the only valid generalization concerning the uranium content of alkaline rocks is that it is generally high. It should be noted in this regard that the K/U ratio varies only slightly between igneous rocks of wide petrologic differences (HEIER and ROGERS, 1963).

The averages and general ranges of uranium concentrations shown in Table 92-E-1 for various types of rocks are similar for intrusive and extrusive rocks of compositional equivalence. The chances of occurrence of very large concentrations of uranium are, of course, higher for intrusive than for extrusive rocks.

II. Variations within Rock Suites

The almost universal tendency for the concentration of uranium to increase toward the later members of an igneous differentiation series has been documented repeatedly. Many of these investigations are thoroughly summarized by PETERMAN (1963). In his manuscript, the sequences in Table 92-E-2 show a tendency toward increasing uranium content during igneous differentiation (Figs. 92-E-3; 90-E-3 to 90-E-6). Note that some differentiation sequences do not show the tendency to

Table 92-E-2. Sequences of igneous rocks showing increase in uranium content toward the younger rocks

Extrusive series

Lassen Volcanic National Park (AOAMS, 1955; LARSEN, 3d, and GOTTFRIED, 1960)
 Modoc area, California (GOTTFRIED and LARSEN JR., 1958; LARSEN, 3rd, and GOTTFRIED, 1960)
 San Juan Mountains, Colorado (LARSEN JR. *et al.*, 1958)
 Valles Mountains, New Mexico (LARSEN, 3d, and GOTTFRIED, 1960) (Fig. 90-E-5)
 Chaîne des Puys, France (GOLDSZTEIN and GUILLERMO, 1961)
 Big Bend National Park, Texas (GOTTFRIED *et al.*, 1962) (Fig. 90-E-6) (part intrusive)
 Marianas Islands (GOTTFRIED *et al.*, 1963) (Fig. 90-E-4)
 Mt. Garibaldi area, British Columbia (GOTTFRIED *et al.*, 1963)
 Strawberry Mountains, Oregon (GOTTFRIED *et al.*, 1963)

Sills and shallow intrusives (Fig. 92-E-3)

Dillsburg sill, Pennsylvania (GOTTFRIED, 1959)
 Skaergaard, Greenland (HAMILTON, 1959)
 Duluth gabbro, Minnesota (HEIER and ROGERS, 1963)
 Augusta County, Virginia (GOTTFRIED *et al.*, 1962)

Plutonic sequences

Southern California Batholith (LARSEN, 3d, 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; AOAMS *et al.*, 1962)
 Oliverian series, New Hampshire (ROGERS and RAGLAND, 1961; LYONS, 1961)

increase in uranium content toward younger rocks. Most such series merely show no detectable trends in composition, but the Honolulu series of Hawaii, studied by LARSEN, 3rd, and GOTTFRIED (1960) shows a decrease in uranium with increasing silica content (Fig. 90-E-2).

Plots of uranium content against some type of differentiation index are much smoother in extrusive sequences than in intrusive ones. Most extrusive series show consistent trends when plotted against silica content, the Larsen differentiation index, and potassium content. In intrusive rocks the scatter of values is quite high in plots of uranium abundance versus silica content. The most consistent variation of uranium in intrusive rocks is shown by a comparison of uranium and potassium abundances. In fact the K/U ratio is about 10^4 in all crustal materials (HEIER and ROGERS, 1963). The use of this ratio for the earth's mantle, however, creates difficulties in explaining the earth's thermal history; (see calculations of MACDONALD, 1965). Discrepancies between the K/U ratio of chondrites and the apparent ratio for the whole earth are discussed by GAST (1960).

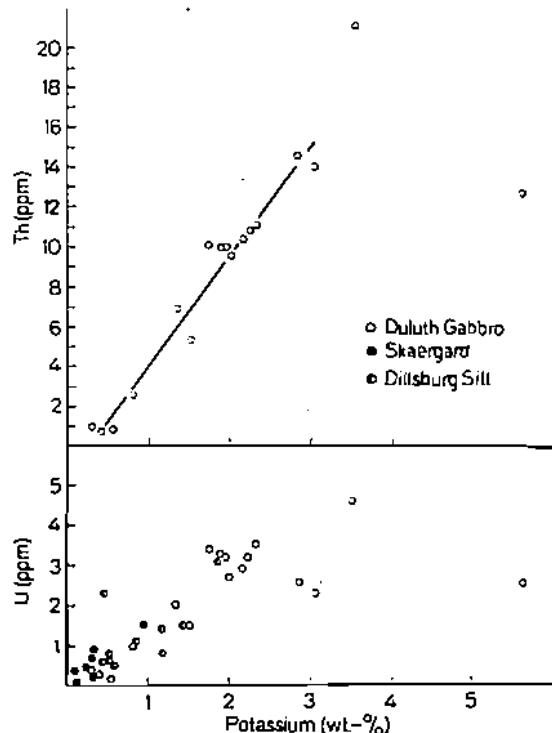


Fig. 92-E-3. Variation of thorium and uranium concentrations in three gabbro-granophyre sequences. [From PETERMAN, Z. E.: unpublished, personal communication (1963); data on the Skaergaard intrusion, Greenland, are from HAMILTON, 1959; data on the Dillsburg sill, Pennsylvania, U.S.A. are from GOTTFRIED, 1959; data on the Duluth complex, Minnesota, U.S.A. are from HEIER and ROGERS, 1963]

III. Variation within Batholithic Complexes

Economic interest in uranium has led to considerable investigation of the distribution of uranium within individual plutons and associated wallrocks and also within complex batholiths. In many complexes such as that of the Colorado Front Range (PHAIR and GOTTFRIED, 1964), variability in uranium content within plutons and between members of the plutonic complex is not simply related to some differentiation index. In some studied plutonic complexes or individual plutons there are progressive changes in uranium concentration toward wallrocks. Most of the work on these problems has been done by Russian workers; their studies are summarized by PETERMAN (1963). Surficial redistribution of uranium makes detection of areal trends difficult (e.g., see Fig. 92-E-4).

92-E-8

Uranium

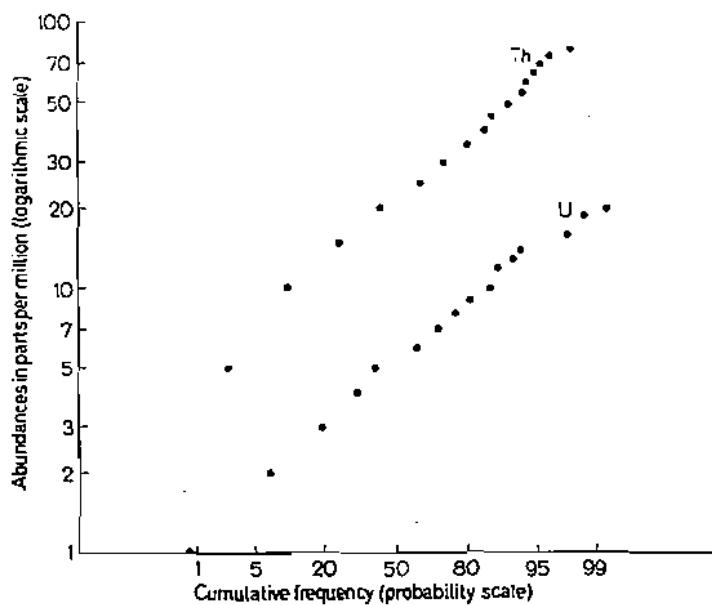


Fig. 92-E-4. Cumulative percentage plot of uranium concentrations in granitic rocks of New England, U.S.A. The lognormality shown on this logarithmic-probability diagram may indicate the importance of surficial processes in redistributing uranium. (From ROGERS, 1964)

92-F. Behavior during Processes Connected with Magmatism

As mentioned above in Section 92-D, uranium commonly occurs in veins as the mineral uraninite or pitchblende. Uraninite has also been found in pegmatites along with uranium-bearing varieties of such rare earth minerals as samarskite and euxenite. The economic geology of uranium in magmatically-derived ore deposits is summarized by a number of workers. A discussion in English is provided by MCKELVEY *et al.* (1955) along with a description of the general economic geology of uranium. KOTLYAR (1961) has published a summary in Russian of the various types of uranium deposits.

92-G. Behavior during Weathering and Rock Alteration

Few studies have been oriented directly toward an understanding of the behavior of uranium during weathering and alteration. The tendency of uranium to be oxidized to the comparatively soluble uranyl ion permits uranium to be mobilized easily in surficial processes. This oxidation is primarily responsible for the wide variations in Th/U ratios shown by surficial material. The comparatively insoluble thorium is concentrated in resistate minerals or is adsorbed on clays, whereas uranium is redistributed in surface and ground waters. The solubilities and oxidation potentials pertinent to these processes are given in Section 92-H.

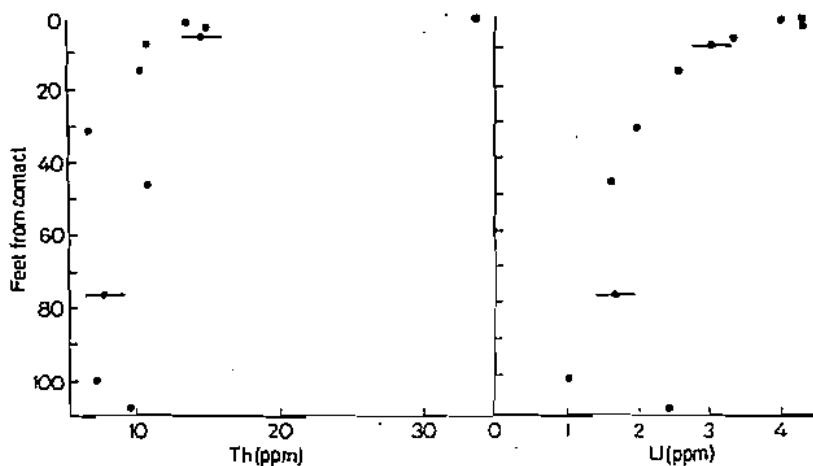


Fig. 92-G-1. Variation in thorium and uranium concentrations in the weathering zone in the granodiorite on Flagstaff Mountain, Colorado, U.S.A. (From PILLER and ADAMS, 1962b)

One study of the behavior of uranium during weathering was made by PILLER and ADAMS (1962b) (Fig. 92-G-1). In the Pennsylvanian weathering profile on a granodiorite at Flagstaff Mountain, Colorado, the variation in both thorium and uranium contents can be investigated throughout the soil profile. The profile is somewhat lateritic and clearly results from humid, subtropical weathering. The uranium which is retained in the soil is held primarily in resistate minerals such as the zircons, whereas thorium is incorporated both in resistate minerals and also in clays formed during the weathering process. The highest concentrations of both elements are found in the residual clays at the top of the soil profile. Artificial leaching experiments on the granodiorite with dilute acid indicate that the vast bulk of the uranium was removed by natural leaching whereas the thorium was less affected (Fig. 92-G-2). These results correlate well with the enrichment of thorium relative to uranium in the soil zone. A generalized study of weathering by HARRISS and ADAMS

Uranium

92-G-2

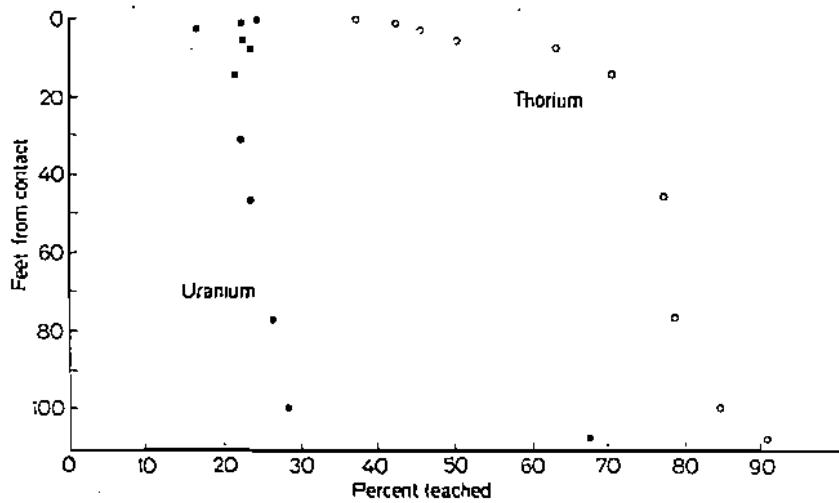


Fig. 92-G-2. Variation in the percentage of leachable thorium and uranium in the weathering zone in the granodiorite on Flagstaff Mountain, Colorado, U.S.A. (From PILLER and ADAMS, 1962b)

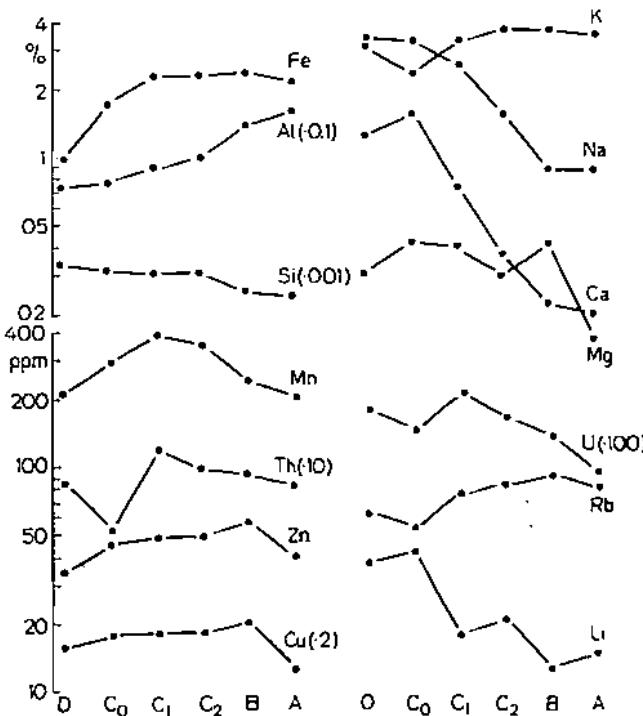


Fig. 92-G-3. Variation of thorium and uranium concentrations in a soil zone compared with variations in abundances of other elements. Tishomingo granite, Oklahoma, U.S.A. (From HARRISS and ADAMS, 1966)

(1966) (Fig. 92-G-3 and 92-G-4) provided information about the mobilization of thorium and uranium, and the results of this study are roughly similar to those found by PILLER and ADAMS (1962b) and indicate the generally greater ease of mobilization of uranium than of thorium.

Investigations of the radioactivity of the Conway granite, New Hampshire, have involved the drilling of cores into unaltered rock below surficially weathered

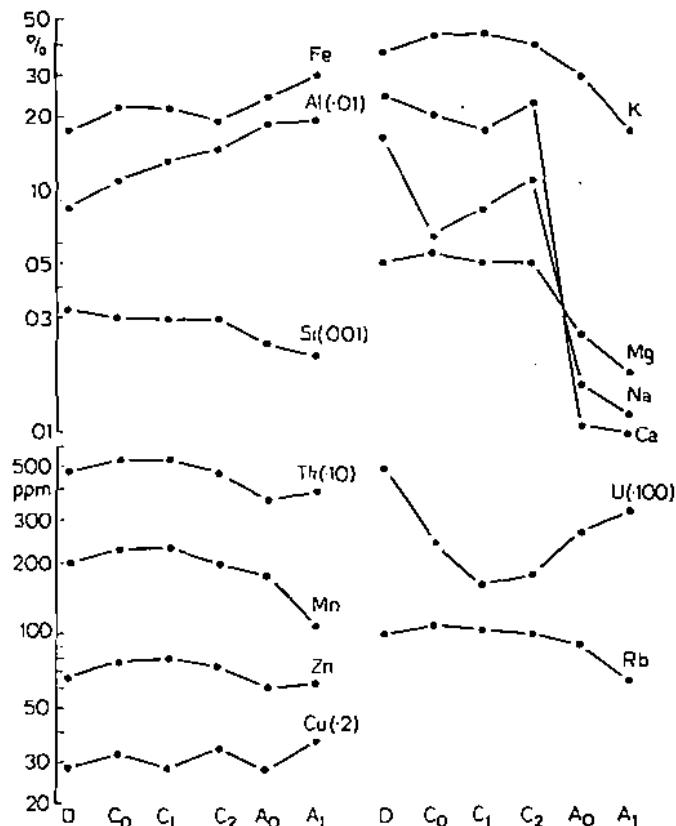


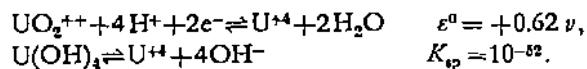
Fig. 92-G-4. Variation of thorium and uranium concentrations in a soil zone compared with variations in abundances of other elements. Elberton granodiorite, Georgia, U.S.A. (From HARRISS and ADAMS, 1966)

material. Data reported by RICHARDSON (1964) and ROGERS *et al.*, (1965) indicate a near-surface depletion of uranium except in a few zones where the mobilized uranium is redeposited by circulating ground water. In some areas, the remobilization of uranium extends to depths of several hundred feet, generally in zones of fracturing and ground water movement. As reported by RICHARDSON (1964), in some of the weathered rocks the U^{234} isotope is about 15 percent less abundant than it should be for secular equilibrium with U^{238} .

Surficially deposited uranium minerals consist of the complex uranyl salts listed in Section 92-D.

92-H. Solubilities in Waters; Valence States

The solubility and redox data pertinent to the distribution of uranium under surficial conditions are:



The uranyl (UO_2^{++}) ion is almost completely soluble, whereas the uranous (U^{+4}) ion can be precipitated easily in alkaline solutions. The uranyl ion precipitates in nature only in the uranyl salts listed in Table 92-E-1 and in certain laboratory preparations. The carbonate ion strongly complexes the uranyl ion and inhibits precipitation; a dissociation constant of 10^{-10} (approx.) has been proposed for the uranyl carbonate complex $(\text{UO}_2)(\text{CO}_3)_2^{--}$. Uranyl salts coprecipitate with calcium phosphates, but the true solubility products of naturally-occurring uranyl phosphates and other salts are unknown.

Uranium is known to be adsorbed from solution by organic material (see SWANSON, 1963) and also by clays (GOLDSZTAUB and WEY, 1955). The amount adsorbed by clays is proportional to the normal base exchange capacity of the clay, and GOLDSZTAUB and WEY report the following grams of uranium adsorbed from a 1-percent solution of uranyl nitrate:

montmorillonite	7.5 g/100 g calcined clay
kaolinite	2.0 g/100 g calcined clay.

92-I. Abundance in Natural Waters

Uranium concentrations are constant in sea water and are in the range of $1-4 \times 10^{-8}$ ppm (1-4 ppb) (Table 92-I-1). These values may be compared with an average of 10^{-5} to 10^{-6} ppm for thorium (Table 90-I-1); it is clear that the Th/U ratio in sea water is extremely small. The geochemistry of uranium in sea water is discussed in various papers by F. Koczy and coworkers and also by TATSUMOTO and GOLDBERG (1959).

Concentrations of uranium in fresh water are considerably more variable than in the oceans. The concentrations are clearly controlled by a variety of factors, such as rock type leached by the water, rate of flow and rate of evaporation, etc. The concentrations of a number of samples of continental waters are shown in Table 92-I-2. Variability in concentrations of uranium in continental ground and underground waters has been used for commercial purposes such as prospecting for uranium (see, for example, CANNON and KLEINHAMPL, 1956; ILLSLEY, 1957). Some efforts have also been made to provide mass balances of uranium in source areas and in surface and ground waters (for example, AGAMIROV, 1965; LOPATKINA, 1964). The general concentration of uranium in most fresh waters may be somewhat less than in sea water.

Table 92-I-1. Contents of uranium in sea water

Location	U ppb	Method	Reference
Atlantic, Pacific	1.5	L	FØYN <i>et al.</i> (1939)
Atlantic, Pacific	1.1-1.5	L	G. KOCZY (1950)
Pacific (deep ocean)	2.82	L	NAKANISHI (1951)
Pacific (mouth of Ito Bay)	1.18	L	NAKANISHI (1951)
Pacific (surface, 1 km off Aomori Pref.)	0.46	L	NAKANISHI (1951)
North Atlantic	0.3-1	L	RONA and URRY (1952)
Atlantic	1.15	L	SMITH and GRIMALDI (1954)
Gulf of Mexico	3.15	L	SMITH and GRIMALDI (1954)
Pacific	2.5	L	STEWART and BENTLEY (1954)
Atlantic, Pacific, Gulf of Mexico	3.3	I	RONA <i>et al.</i> (1956)
Baltic Sea	0.8-5.9	L	F. KOCZY <i>et al.</i> (1957b)
Bering Sea	2.2	L	STARIK <i>et al.</i> (1958)
Barents Sea	1.6	L	STARIK <i>et al.</i> (1958)
White Sea (eastern)	1.4	L	STARIK <i>et al.</i> (1958)
White Sea (Onezh Bay)	1.8	L	STARIK <i>et al.</i> (1958)
Sea of Azov	3.3	L	STARIK <i>et al.</i> (1958)
Caspian Sea	3-10	L	STARIK <i>et al.</i> (1958)
Indian Ocean (SW part)	2.7	L	BARANOV and KHRISSIANOVA (1959)
Indian Ocean (central)	1.8	L	BARANOV and KHRISSIANOVA (1959)
Black Sea	2	L	NIKOLAEV <i>et al.</i> (1960)
English Channel and Bay of Biscay	3.3	various	WILSON <i>et al.</i> (1960)

Table 92-I-2. Contents of uranium in continental waters

Location	U ppb	Method	Reference
Colorado ground water	0.4—4	L	BRUCE and FERGUSON (1951)
Illinois ground water	< 0.3	L	BRUCE and FERGUSON (1951)
Florida ground water	< 1.0	L	BRUCE and FERGUSON (1951)
Three N. American Rivers	0.026	L	RONA and URRY (1952)
River water, by calculation	0.09—1.1	L	HOLLAND and KULP (1954)
Great Salt Lake, Utah	4.8	L	STEWART and BENTLEY (1954)
Texas ground water	2.3—10	L	JUDSON and OSMOND (1955)
Wisconsin and Illinois ground waters	0.8	L	JUDSON and OSMOND (1955)
Mineralized Aquifer	100—460	L	JUDSON and OSMOND (1955)
Mineralized Aquifer	10—250	L	DENSON <i>et al.</i> (1956)
Mineralized Aquifer	20—200	L	FIX (1956)
Thermal Springs	< 7	L	FIX (1956)
U.S.A., Alaska, regional average	0.1	L	FIX (1956)
Colorado Plateau	0.5—3	L	FIX (1956)
France, Springs	0.35—7.68	L	JURAIN (1957)
Baltic region, igneous drainage	0.5	L	KOCZY <i>et al.</i> (1957 b)
Baltic region, sedimentary drainage	1—13	L	KOCZY <i>et al.</i> (1957 b)
Llano Estacado, Texas ground water	0.9—46	L	BARKER and SCOTT (1958)
New Mexico ground water	1.2—4.7	L	BARKER and SCOTT (1958)
Austria, Vienna Basin; Springs	1.4—12	L	HECHT <i>et al.</i> (1958)
Austria, Tyrol; Springs	0.25—40	L	HECHT <i>et al.</i> (1958)
Austria, Danube River	0.5—2.3	L	HECHT <i>et al.</i> (1958)
Austria, Tyrol; Rivers	0.2—2.8	L	HECHT <i>et al.</i> (1958)
Wales, Spring	1.3	L	SMITH and CHANDLER (1958)
Jamaica, Rivers	1.5—5.9	L	SMITH and CHANDLER (1958)
Uganda, Spring	1.3	L	SMITH and CHANDLER (1958)
England, Cornish Waters	0.6—40	L	SMITH and CHANDLER (1958)
Germany, Saale River	0.34—4.27	L	HEIDE and PROFT (1959)
Germany, Saale River	0.03—0.28		HEIDE and PROFT (1959)
dissolved			
suspended			
Great Central Plains, Wells (ground water)	9.5	L	LANDIS (1960)
Great Central Plains, Springs (ground water)	11.3	L	LANDIS (1960)
Pacific NW, ground water in silicic, subsilicic rocks	< 0.1—10	L	BARKER and SCOTT (1961)
Pacific NW, ground water in Idaho batholith	< 0.1—13	L	BARKER and SCOTT (1961)
Pacific NW, ground water in Snake River basalt	< 0.1—2.6	L	BARKER and SCOTT (1961)
Pacific NW, ground water in Columbia River basalt	< 0.1—0.6	L	BARKER and SCOTT (1961)
Nevada (Truckee Meadows)	0.1—43	L	COHEN (1961)
England, surface waters	≤ 1.1	L	PEACOCK (1961)
U.S.A. (general)	< 0.1—120	L	SCOTT and BARKER (1962)
India, surface water	0.03—4.2	L	KAMATH <i>et al.</i> (1964)
River water of Japan	0.34—1.23	L	MIYAKE <i>et al.</i> (1964)
Waters of Florida	0.9	R	OSMOND (1964)

92-K. Abundance in Common Sedimentary Rocks

The concentrations of uranium in sedimentary rocks are difficult to summarize because of the various designations used by different authors to describe the rocks which they study. Thus, for example, the term "graywacke" means different things to different geologists. (For definition see Chapter 8 of Volume I of this Handbook.) The names used for various rocks in this section are thought to be reasonably standard, and the abundances of uranium in different types are listed in Table 92-K-1. A correlative summary of thorium values is given in Table 90-K-1.

Table 92-K-1. Contents of uranium in sedimentary rocks

Rock type	No. of samples	U ppm	Method	Reference
<i>Sandstones</i>				
<i>Orthoquartzites</i>				
North American av.	16	0.45	R	MURRAY and ADAMS (1958)
Mesa Verde	8	1.7	R	PLILER and ADAMS (1962a)
Gulf Coast beach sands	29	0.59	R	МАНДАВИ (1964)
Atlantic Coast beach sands	54	3.21	R	МАНДАВИ (1964)
<i>"Volcanic" graywackes</i>				
Caribbean	14	0.5-1	R	ROGERS and DONNELLY (1966)
Umpqua (Oregon)	4	1.3	R	ROGERS (1966)
Other graywackes (estimated average)		2.1		ROGERS and RICHARDSON (1964)
Arkoses (estimated average)		1.5		ROGERS and RICHARDSON (1964)
<i>Shales</i>				
North American gray and green	52	3.2	L	ADAMS and WEAVER (1958)
Russian platform (comp)	178	4.1	emanation	BARANOV et al. (1956)
Mancos	102	3.7	R	PLILER and ADAMS (1962a)
Red and yellow	10	~2	L	ADAMS and WEAVER (1958)
Black (average)	numerous	8	various	SWANSON (1961)
<i>Black Shales</i>				
Marine black shales (excluding geo-synclinal)		20	L	SWANSON (1961)
All black shales		8	L	SWANSON (1961)
Chattanooga		79	L	SWANSON (1961)
Alum shale; Cambrian; Sweden	309	168	L	from summary by „ BATES and STRAHL (1958)

Uranium

92-K-2

Table 92-K-1 (Continued)

Rock type	No. of samples	U ppm	Method	References
Reedsville; Ord; Pennsylvania	4	4	L	.. BATES and STRAHL (1958)
Ohio shale; Devonian; Ohio	220	10	L	.. BATES and STRAHL (1958)
Woodford; Devonian; New Mexico	116	9	L	.. BATES and STRAHL (1958)
Hamilton; Devonian; Pennsylvania	6	6	L	.. BATES and STRAHL (1958)
Chemung; Devonian; Pennsylvania	4	3	L	.. BATES and STRAHL (1958)
St. Hippolyte; Carb.; France	150	1244	L	.. BATES and STRAHL (1958)
Allegheny; Penn.; Pennsylvania	34	4	L	.. BATES and STRAHL (1958)
Kansas shale; Penn.; Kansas	21	16	L	.. BATES and STRAHL (1958)
Kupferschiefer; Perm.; Germany	4	39	L	.. BATES and STRAHL (1958)
Bauxites	29	11.4	R	ADAMS and RICHARDSON (1960)
Bentonites	64	5.0	various	ADAMS and WEAVER (1958)
<i>Limestones</i>				
North American av.	25 (comp)	2.2	L and R	ADAMS and WEAVER (1958)
Russian platform	128 (comp)	2.1	emanation	BARANOV <i>et al.</i> (1956)
Eniwetok cores				
calcite		0.35		SACKETT and POTRATZ (1963)
aragonite		2.3		SACKETT and POTRATZ (1963)
Eniwetok core E-1	21	2.34		SACKETT and POTRATZ (1963)
Miscellaneous	49	2		BELL (1963)
<i>Dolomites</i>				
Dolomites and dolomitic limestones	100	0.03—2.0	L	DEININGER (1964)
<i>Phosphate rock</i>				
Marine phosphorites		50—300	mostly L	from summary by MCKELVY (1956), based on a variety of published and unpublished measurements
Residual phosphorites		50		
River-pebble deposits		unknown; probably low		
Guano		negligible		
Phosphatized rock		negligible (?)		
Fossil bone		50—300		
<i>Evaporites</i>				
Estimate of pure evaporite minerals		<0.1		BELL (1960)

Table 92-K-1 (Continued)

Rock type	No. of samples	U ppm	Method	Reference
<i>Pacific ocean sediments</i>				
Sands	5	3.0		
Muds	3	2.3		
Clayey muds	6	2.7		
Siliceous and diatomaceous muds and clayey muds	7	3.6		
Pelagic clays	13	4.0	various	summary by BARANOV and KHRISSIANOVA (1963)
Pelagic clays	5	1.5—2.5	L	HAHOFER and HECHT (1954)
<i>Indian ocean sediments</i>				
Various muds		0.2—0.5	various	summary by BARANOV and KHRISSIANOVA (1960)
<i>Atlantic ocean sediments</i>				
Globigerina oozes	5	0.74	L	ROSHOLT <i>et al.</i> (1961)
<i>Caribbean sediments</i>				
Globigerina oozes	17	1.0	L	ROSHOLT <i>et al.</i> (1961)
<i>Black sea sediments</i>				
Muds	41	3.7		STARIK <i>et al.</i> (1961a)
<i>Organic matter</i>				
Lignite; Great Plains, U.S.A.	80		L	VINE (1956)
Coal; Eocene; Wyoming	30		L	VINE (1956)
Coaly shale; Cret.; Idaho	20		L	VINE (1956)
Coal and coaly shale; Cret.; New Mexico	< 6000		L	VINE (1956)
Lignite; Tertiary; Nevada	< 50		L	VINE (1956)
Coal; Upper Paleozoic eastern U.S.A.	mostly < 10		L	VINE (1956)
Oil; ranges of regional averages:			L	HYDEN (1956)
Mid-continent, U.S.A.	36	5—77 in ash $(0.17—10) \times 10^{-3}$ in oil		
Rocky Mts., U.S.A.	61	4—46 in ash $(0.4—3.1) \times 10^{-3}$ in oil; omitting one very large value		
California	10	4.5 in ash 7.0×10^{-3} in oil		
Asphalts from western U.S.A.	45	10—3760; normal range of 100—500	L	HAIL <i>et al.</i> (1956)
Black muds; Norwegian Fjords	10	36 (13—60 range)	L	SWANSON (1963)
Black and gray muds; Baltic Sea	10	48 (22—103 range)	L	SWANSON (1963)

I. Sandstones

Sandstones are subdivided into three categories in Table 92-K-1. The average concentration of uranium in the orthoquartzites is reasonably well known because the range of values among various orthoquartzitic suites is comparatively small. In orthoquartzites, uranium may occur both disseminated in the quartz or as heavy resistate grains. The sites of radioactivity have been investigated by both MURRAY and ADAMS (1958) and ROGERS and RICHARDSON (1964). Both investigations showed that most of the uranium is held within the quartz grains themselves.

Two special groups of graywackes are reported in Table 92-K-1 in addition to an estimated "average" for all graywackes. The Caribbean "volcanic" graywackes are important because they represent the average composition of rocks of the Caribbean orogen. As ROGERS and DONNELLY (1966) have pointed out, the low thorium and uranium contents of eugeosynclinal materials indicates derivation from nearly undifferentiated material of the upper mantle. The Umpqua graywackes of Oregon are similar geologically and also radiometrically to the Caribbean orogenic wackes. The average graywacke estimate in Table 92-K-1 includes both the highly-volcanic, generally uranium-poor, graywackes of the Caribbean and Oregon areas and also some more-highly radioactive rocks of the type which are generally classified as graywacke simply because of their high clay content. Arkoses have not been well studied, and the estimate in Table 92-K-1 for their uranium content is highly tentative.

II. Shales

The abundance of uranium in common shales (Fig. 92-K-1) shown in Table 92-K-1 is well established by several independent studies. Both ADAMS and WEAVER (1958), working with North American shales, and BARANOV *et al.* (1956), working with shales of the Russian platform arrived at almost identical values of approximately 3.7 ppm for the average uranium content. It is interesting to note that both the average thorium contents (Table 90-K-1) and uranium contents of ordinary shales are very close to the values commonly cited for the average concentration in the continental crust.

Both black and red shales are distinct from the ordinary green and gray shales in thorium and uranium contents. The black shales have been studied by numerous workers, and only summary reference is made in Table 92-K-1. A discussion of the economic significance of the black shales is given by BATES and STRAHL (1958). The black shales characteristically have a very high uranium concentration and comparatively low thorium content with a consequently low Th/U ratio. The high concentration of uranium results presumably from absorption of uranium by organic material in the shale and/or reduction of uranyl ion in sea water to the less soluble uranous form by the decay of organic matter and consequent precipitation of uranium oxide. The red and yellow shales are comparatively enriched in thorium, and their relatively low uranium content (1—2 ppm) gives them a high Th/U ratio. Depletion of uranium in the red shales presumably results from the solubility of the oxidized uranyl ion. This discussion of shales shows the value of the Th/U ratio for the interpretation of the environment of formation of sedimentary rocks (Fig. 92-K-2).

92-K 5

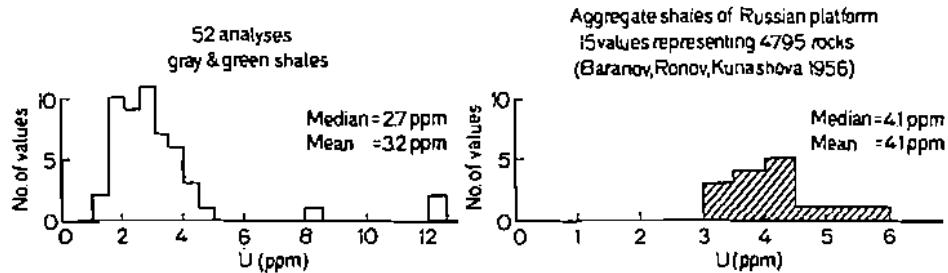
Uranium

Fig. 92-K-1. Histogram of uranium concentrations in North American gray and green shales. (From ADAMS and WEAVER, 1958; Russian platform data from BARANOV *et al.*, 1956)

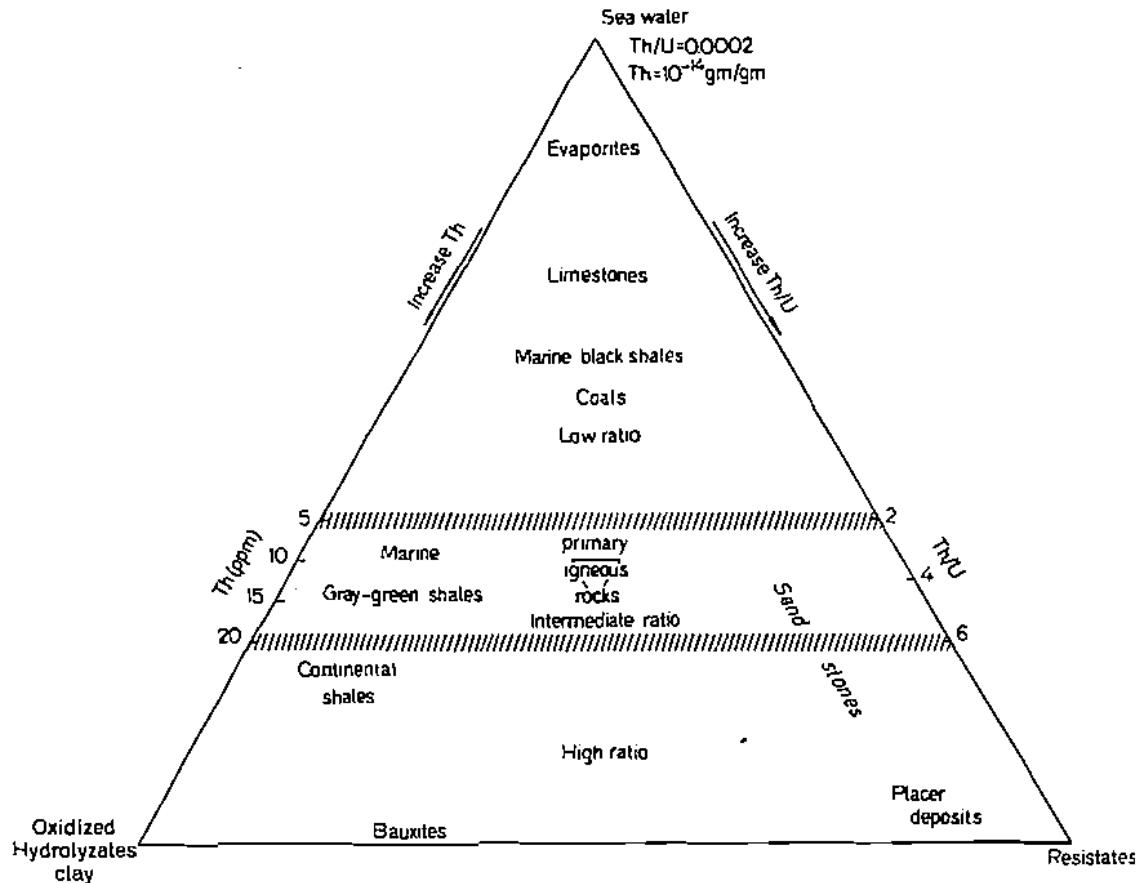


Fig. 92-K-2. Generalized distribution of thorium and uranium in sedimentary rocks. (From ADAMS and WEAVER, 1958)

III. Bauxites, Bentonites

Bauxites and bentonites are examples of the concentration of thorium and uranium in clays. In bauxites, the average uranium content (11.4 ppm) and thorium content (45.6 ppm; Table 90-K-1) are both abnormally high. Presumably during

weathering both the thorium and uranium have been concentrated in resistate residues and adsorbed on clays. Some tendency for greater retention of thorium than of uranium is shown by the generally high Th/U ratios.

IV. Carbonate Rocks

Carbonate rocks (Fig. 92-K-3) have uranium concentrations in the range found for typical calcareous organisms. The uranium in calcium carbonate apparently substitutes in the lattice in place of calcium, although some may accompany thorium in the insoluble residue fraction of limestones; (see Section 90-K). Several studies have been made of the concentration of uranium in calcareous organic material, and reference may be made to TATSUMOTO and GOLDBERG (1959), SACKETT and POTRATZ

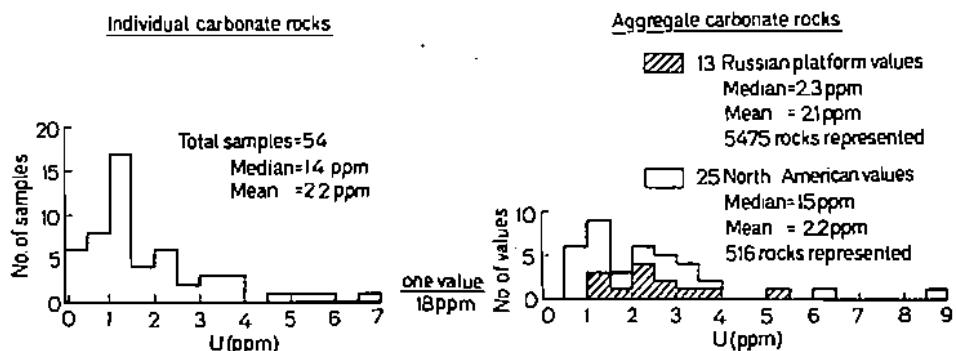


Fig. 92-K-3. Histogram of uranium concentrations in aggregate samples of carbonate rocks. (From ADAMS and WEAVER, 1958; Russian platform data from BARANOV, RONOV, and KUNASHOVA, 1956)

(1963), ROSHOLT and ANTAL (1963), and BELL (1963). Estimates of the average uranium content of carbonate rocks are quite uniform at approximately 2 ppm. These estimates include the North American limestones studied by ADAMS and WEAVER (1958), the carbonate rocks of the Russian platform studied by BARANOV *et al.* (1956), and the highly assorted suite of limestones investigated by BELL (1963). DENINGER (1964) shows, in general, little variation between limestones and dolomites with respect to uranium content.

V. Phosphates

Phosphate rocks, listed in Table 92-K-1, generally have a high concentration of uranium. A large number of studies have been made on the uranium in phosphate rocks and in apatite minerals because of the potential economic importance of uranium recovery from such rocks. The references are summarized in a paper by MCKELVEY (1956) cited in the table.

VI. Oceanic Sediments

Uranium contents are given in Table 92-K-1 for a variety of modern oceanic sediments. With the exception of studies made primarily for the purpose of dating cores by means of various disequilibrium methods, not a great deal of atten-

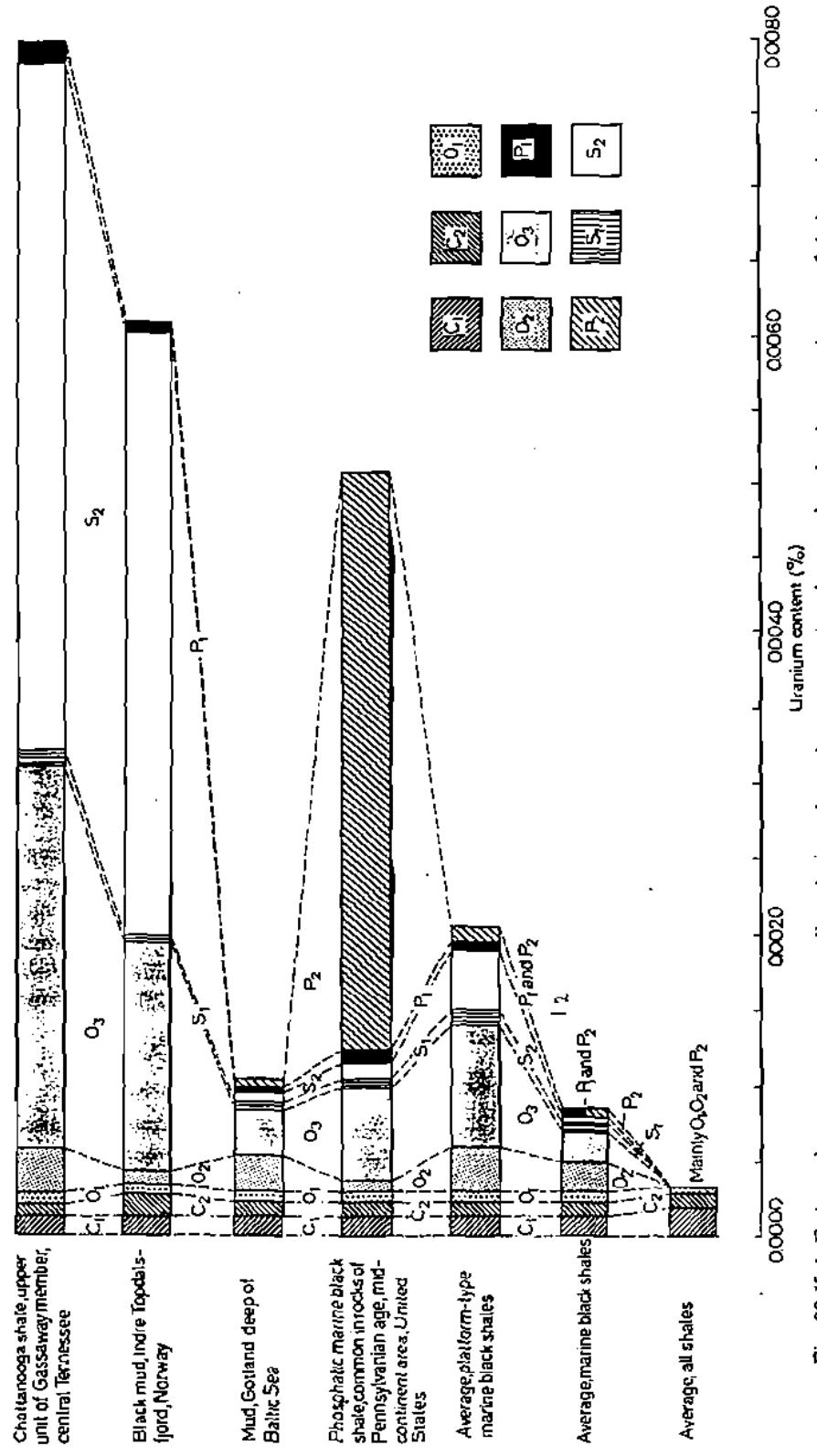


Fig. 92-K-4. Estimated average amount contributed to total uranium content by nine uranium-bearing constituents of shales and muds.
(From SWANSON, 1963); For list of symbols see p. 92-K-8

Fig. 92-K-4 (Continued). List of symbols:

- C₁: Uranium in main mass of clastic mineral sediment, particularly clay minerals, but exclusive of resistates.
- C₂: Uranium in resistates or heavy minerals, such as zircon, apatite, and sphene.
- O₁: Uranium inherent to living plants or animals, either land or marine types.
- O₂: Uranium sorbed from sea water by solid or colloidal carbonaceous remains of plankton settling from surface waters to bottom.
- O₃: Uranium sorbed from stream water and sea water by either solid or colloidal organic matter derived from decaying land plants of the humic type.
- P₁: Uranium in phosphate precipitated on and within sediment as oolites and nodules where hydrogen sulfide environment extends into overlying water; also uranium in phosphatic fossil shells and bones.
- P₂: Uranium in phosphate precipitated from, settling through and exposed to sea water above sediment-water interface, and formed where hydrogen sulfide environment confined to sediment.
- S₁: Uranium precipitated as colloidal-size uraninite(?) from connate water by hydrogen sulfide formed and confined within sediment.
- S₂: Uranium precipitated as colloidal-size uraninite(?) from sea water by hydrogen sulfide generated within and above sediment by anaerobic bacteria, and diffused into overlying water.

tion has been paid to the radioactive contents of oceanic materials. The low Th/U ratios reported by BARANOV and KHRISTIANOVA (1963) certainly do not match the ratios obtained for similar sediments by other investigators.

In many sedimentary rocks uranium is commonly associated with organic matter. A typical example of this occurrence is the Colorado Plateau Province of the western United States, where uranium is found absorbed in petrified logs and also intimately admixed with asphaltic bands in sandstones. The nature of the uranium mineral or minerals in these occurrences has been investigated in detail (KELLEY, 1963). On a broader scale, the general association of uranium with organic material is well documented by the high uranium concentrations in black shales and also in coals, asphalts, and oil (Table 92-K-1). The site of uranium in these organic materials is uncertain. Some asphaltic deposits contain admixed uraninite, but the organic phases themselves also seem to be rich in uranium, which may be in the form of some organic complex. The term "thucholite" has been proposed for mineraloids containing thorium, uranium, carbon, hydrogen, and oxygen.

The reasons for the association of thorium and uranium with organic material have never been fully ascertained. Experimental work has clearly demonstrated that wood and other organic material are capable of absorbing uranium from solution. It has also been proposed that the radioactivity of the thorium and uranium may aid in polymerization of organic materials around the two metals. Organic uranium geochemistry is discussed more fully by BREGER and DEUL (1956). SWANSON (1963) shows quantitatively the amounts of uranium contributed to black muds and shales by various processes (Fig. 92-K-4).

92-L. Biogeochemistry

Uranium is not known to be an essential element for the life process of any organism. The several parts per million concentration of uranium in carbonate shells is probably explained by substitution of uranium in the calcium carbonate lattice. The concentration of uranium in woody and other plant residues is not easily understood. Possibly the organic matter simply acts as a reducing agent which causes precipitation of the comparatively insoluble uranous form. It is also possible, however, that the uranium occurs in some particularly stable organo-metallic complexes. Sulfate-reducing bacteria may play a role in the reduction and fixation of uranium (JENSEN, 1963). The association of uranium with organic and woody material is discussed in a number of papers summarized by BREGER and DEUL (1956). The biochemical importance of uranium is summarized by F. KOCZY (1963) and EDGINGTON (1966). Some analyses of animal and plant materials are given by HOFFMANN (1941, 1943). BOWIE and ATKIN (1956) report 2,700 ppm uranium in an unusual fossil fish skeleton.

92-M. Abundance in Common Metamorphic Rock Types

The abundances of uranium have been determined in a number of different metamorphic rocks, and the data are given in Table 92-M-1. The names used for rock designations are those given by the original authors. As might be expected for rocks derived from a variety of parent materials under a variety of conditions, the range of compositions is quite broad.

HEIER and CARTER (1964) have summarized studies of the radiometry of various eclogites from metamorphic environments. They find an average of 0.20 ppm uranium and 0.38 ppm thorium in a total of 14 samples analyzed by various methods.

Table 92-M-1. *Contents of uranium in metamorphic rocks*

Rock type	No. of samples	U ppm	Method	References
Gneiss, Japan	1	2.3	R	EVANS and GOODMAN (1941)
Augen Gneiss, Finland	1	2.1	R	EVANS and GOODMAN (1941)
Eclogite, Switzerland	1	0.2	R	EVANS and GOODMAN (1941)
Amphibolite (Schwarzwald, Germany)	3	3.5	R	HUSMANN (1956)
Biotite-Hornbl. Paragneiss (Schwarzwald, Germany)	2	2.0	R	HUSMANN (1956)
Paragneiss (Schwarzwald, Germany)	4	7.0	R	HUSMANN (1956)
Granulite (Schwarzwald, Germany)	2	4.9	R	HUSMANN (1956)
Orthogneiss (Schwarzwald, Germany)	4	3.6	R	HUSMANN (1956)
Metatectite (Schwarzwald, Germany)	4	4.8	R	HUSMANN (1956)
Diatectite (Schwarzwald, Germany)	4	11.2	R	HUSMANN (1956)
Cordierite Gneiss (Schwarzwald, Germany)	1	5.8	R	HUSMANN (1956)
Orthoclase metacrysts (Schwarzwald, Germany)	1	45	R	HUSMANN (1956)
Marble	2	0.17	L	PLILER (1956)
Slate (mainly Michigan)	14	2.7	L	PLILER (1956)
Phyllite (mainly Arizona — New Mexico)	7	1.9	L	PLILER (1956)
Schist (New Mexico)	4	2.5	L	PLILER (1956)
Mafic Rocks (Terskei Ala Tau Mts.)	82	3.2 (comp)	W	KRYLOV (1958)
Idaho Batholith Gneisses (Almandine-Amph. Facies)	12	2.2	L	LARSEN JR. and GOTTFRIED (1961)
Gneiss (Texas)	13	2.82	R	BILLINGS (1962)

92-M-2

Uranium

Table 92-M-1 (Continued)

Rock type	No. of samples	U ppm	Method	Reference
(Almandine-Amph. Facies) Amphibolite (Texas)	14	0.33	R	BILLINGS (1962)
(Almandine-Amph. Facies) Graphitic Schist (Texas)	3	3.49	R	BILLINGS (1962)
Marble (Grenville Province)	2	0.36	L	DOE (1962)
(Amphibolite Facies) Light Gneiss (Langøy, Norway)	5	<2.5	R	HEIER (1962b)
(Amphibolite Facies) Amphibolite (Langøy)	7	<1.06	R	HEIER (1962b)
(Retrograde Gneiss) Monzonite (Langøy)	2	<1.25	R	HEIER (1962b)
(Retrograde Gneiss) Granite (Langøy)	8	<0.94	R	HEIER (1962b)
Biotite Schist (Front Range, Colorado)	9	4.7	L	PHAIR and GOTTFRIED (1964)
Biotite Hornblende Schist and Amphibolite (Front Range)	4	4.7	L	PHAIR and GOTTFRIED (1964)
(High Granulite Facies) Monzonite (Langøy, Norway)	3	0.61	R	HEIER and ADAMS (1965)
(High Granulite Facies) Banded Gneiss (Langøy)	4	0.22	R	HEIER and ADAMS (1965)
(Low Granulite Facies) Gneiss (Langøy)	5	0.88	R	HEIER and ADAMS (1965)
(High Amphibolite Facies) Gneiss (Langøy)	3	1.22	R	HEIER and ADAMS (1965)

92-N. Behavior in Metamorphic Reactions

The mobility of the uranyl ion in surface waters plus the tendency for potassium and uranium to occur together lead to the presumption that uranium is highly involved in metasomatic activity. Unfortunately, data for metamorphic rocks are not yet adequate to test the hypothesis. HEIER and ADAMS (1965) have proposed that high-rank rocks in one area in Norway are impoverished in uranium in comparison with lower-rank rocks owing to upward movement of uranium. This evidence of mobility, however, has not been confirmed in other areas owing to lack of adequate samples.

92-O. Economic Utilization

Aside from very minor uses as a pigment and chemical reagent, the economic utilization of uranium has been dominated in the first 40 years of this century by a demand for radium and since 1942 by a demand for fissionable materials. The demand for radium for medical and industrial purposes led to widespread exploration for the parent uranium in the first quarter of this century, but this exploration was drastically cut back after the discovery in 1923 of the rich uranium deposits in Katanga (then the Belgian Congo). The Katanga source and the Great Bear Lake, Canada, sources of rich pitchblende discovered in 1930 were more than adequate to meet the demand for radium.

Beginning in 1943 a second widespread exploration effort was initiated to develop uranium supplies for military purposes. This military demand for uranium was substantially oversaturated in the U.S.A. by 1958, when guaranteed prices were restricted and new import arrangements ceased to be made. A steady exploration effort continued in France, Sweden, and other countries.

As of this writing (1966) uranium-fueled nuclear reactors are competitive in many areas with conventional power plants for the generation of electricity for civilian uses. To the extent that this competition continues to shift in favor of the nuclear reactors, a new and still larger demand for uranium will be created, leading to a third widespread exploration effort.

The last year for which world production figures of uranium are reasonably available is 1963. Among the countries reporting production, the leader is the United States, with 14,218 short tons of U_3O_8 during the year; the U.S. is followed by Canada, with 8,141 short tons, and South Africa, with 4,532 short tons. Other countries reporting significant production are the Congo, France, and Portugal.

Most of the uranium production in the United States is from mineralized sandstones in the Colorado Plateau province centering around Wyoming, Utah, and New Mexico. Canadian production comes primarily from vein deposits in the Northwest Territories, with large reserves in the Blind River conglomerate. South African production is almost exclusively a by-product of gold mining in the Witwatersrand area, where pitchblende mineralization has apparently accompanied gold deposition. The largest reserves are disseminated in sediments, usually sandstones. The majority of smaller deposits are pitchblende veins such as those of Great Bear Lake, Canada; Erzgebirge, Germany and Czechoslovakia; Katanga, Congo; and Portugal.

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