

33. URANIUM AND THORIUM ISOTOPES: DEEP SEA DRILLING PROJECT, LEG 23¹

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INTRODUCTION

Sediment samples taken from Sites 228 and 229 were received for analyses of the longer-lived uranium and thorium series nuclides; namely, U^{238} , U^{234} , Th^{230} , and Th^{232} . These sediments were of the silty calcareous ooze type with varying calcium carbonate contents and with colors ranging from dusty yellow to greenish gray. Site 229 samples were more grayish and, when received at our laboratory, were in the form of pressed cakes with interstitial water already extracted for chemical studies.

Measurements of the above-mentioned isotopes were carried out for the following purposes:

1) To attempt to delineate sedimentation rates from the amount of the excess Th^{230} (i.e., uranium-unsupported) present in these sediments;

2) To detect from the ratios Th^{230}/U^{234} and U^{234}/U^{238} if any post-depositional migration of uranium and thorium isotopes had occurred, as samples from great depths, because of their ages, would be expected to show radioactive equilibrium relationship among these nuclides;

3) To assess the uranium and thorium concentrations in sediments of this relatively land-locked oceanic basin and compare them with those of open-ocean, pelagic deposits.

PROCEDURES

Samples were digested with HCl, then fumed with a mixture of HF-HClO₄ to effect total dissolution. Known amounts of U^{232} and Th^{228} were added to the solutions to serve as yield tracers. Uranium and thorium isotopes were then separated and purified through ion-exchange and solvent extraction steps and mounted as thin sources for alpha-spectral analyses. Detailed procedures followed essentially those described by Ku (1965). Calcium carbonate contents were assayed by gasometric measurement of CO₂ released upon acidification using a LECO (Laboratory Equipment Corporation) instrument (Kolpack and Bell, 1968).

RESULTS AND DISCUSSION

Table 1 lists the analytical results. The errors indicated are standard deviations (one sigma) based on counting statistics. Precision of the CaCO₃ measurements is about ±1%.

The Th/U ratio generally reflects the oxidation potential of a depositional environment (Goldberg, 1965). The larger the ratio, the more oxidizing sedimentary regime it denotes. The explanation involves the difference in solubilities of

uranium in its two oxidation states: U^{+4} and U^{+6} . Under oxidizing conditions, uranium is in +6 state and can be strongly held in solution through the uranyl complexes such as $UO_2(CO_3)_3^{-4}$. Thus Th/U increased from shales (~4) to deep-sea clays (~5) and manganese nodules (as high as 20). The consistently low Th/U ratio of the Red Sea sediments (Table 1) attests to the fact that they represent a redox potential system much lower than open ocean deposits. Data on Site 228 sediments are very similar to those of a nearby piston core (154P) reported earlier (Ku, 1969). Their uranium contents are comparable to those of average shales and pelagic clays (~2-3 ppm). Their thorium content, however, is distinctively lower (5-7 ppm on a carbonate-free basis as opposed to 10-12 ppm for shales and deep-sea clays). Sediments at Site 229 are characterized by abnormally high uranium. This further lowers the Th/U ratios and denotes highly reducing conditions. The question arises: Did such enrichment of uranium occur post-depositionally or syngenetically?

Table 1 shows that in the two deep sections of Hole 229A, Th^{230} is greatly depleted relative to U^{234} . With a sedimentation rate on the order of 580 m/m.y. (cf. Report on Sedimentation Rate, Site 229), the age of 229A-5-6 is about 130,000 years. If all of its uranium were syngenetic, i.e., uranium was incorporated into the sediments when the latter were accumulated, then the sediments would initially be totally devoid of Th^{230} in order to acquire the present Th^{230}/U^{234} ratio of 0.66 ± 0.07 . In other words, the Th^{230}/U^{234} ratio of the sediments would be zero at the time of deposition. Although possible, the fact that a significant amount of Th^{232} is found in the deposits makes the zero Th^{230} hypothesis highly improbable. In 229A-5-6, the activity ratio of Th^{232}/U^{234} is equal to 0.15. The introduction of Th^{232} into the sediments must have also been accompanied by some of its isotope, Th^{230} . Since the average crustal Th^{232}/Th^{230} (activity ratio) as determined by the relative abundance of uranium to thorium is about one, it can be argued that the sediments initially had a finite Th^{230}/U^{234} value on the order of 0.15 instead of zero. This means that the age of 229A-5-6 should be about 80,000 years rather than 130,000 years. In the case of 229A-2-1, its having initially contained Th^{230} is almost certain in view of its shallow depth and young age (~50,000 yr if a rate of 580 m/m.y. is assumed). Therefore, unless the above-mentioned sedimentation rate estimate is unreasonably low, a more consistent interpretation of the Th^{230}/U^{234} data calls for a post-depositional migration of uranium. As decay of organic matter in the sediments was taking place, uranium could have been transported through the pore solution medium and continuously precipitated in the more reduced layers. Such a process could have also operated at Site 228, though to a far less extent. This

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TABLE I
Uranium and Thorium Isotopes in Leg 23 Sediments

Sample ^a	Depth ^b (cm)	CaCO ₃ (%)	U ^c (ppm)	Th ^c (ppm)	Th U wt	$\frac{U^{234d}}{U^{238}}$	$\frac{Th^{230d}}{U^{234}}$	Th _{ex} ^{230e} (dpm/g)
228-1-1	0-10	22.2	1.38 ± 0.06 (1.77 ± 0.08)	3.72 ± 0.16 (4.78 ± 0.21)	2.70	0.93 ± 0.05	1.25 ± 0.09	0.24 ± 0.07
228-1-2	105-107	9.0	3.21 ± 0.14 (3.53 ± 0.15)	5.44 ± 0.23 (5.97 ± 0.25)	1.70	1.12 ± 0.06	0.78 ± 0.04	-0.59 ± 0.14
228-1-3	286-288	14.8	1.66 ± 0.07 (1.95 ± 0.11)	4.27 ± 0.27 (5.01 ± 0.32)	2.57	0.95 ± 0.05	0.91 ± 0.07	-0.10 ± 0.09
228-1-4	484	54.5	1.53 ± 0.07 (3.36 ± 0.15)	2.38 ± 0.21 (5.23 ± 0.46)	1.56	1.04 ± 0.06	0.82 ± 0.05	-0.21 ± 0.06
228-3-1	2440	18.3	2.23 ± 0.13 (2.73 ± 0.16)	4.89 ± 0.38 (5.98 ± 0.47)	2.19	0.98 ± 0.07	1.08 ± 0.09	0.13 ± 0.07
228-5-1	3300	32.1	1.90 ± 0.05 (2.80 ± 0.07)	3.89 ± 0.20 (5.73 ± 0.29)	2.05	1.03 ± 0.03	1.10 ± 0.05	0.14 ± 0.05
229-1-CC	200-210	69.4	18.6 ± 0.37 (60.8 ± 1.2)	2.49 ± 0.13 (8.14 ± 0.42)	0.13	1.02 ± 0.01	0.91 ± 0.03	-1.20 ± 0.42
229A-2-1	2900-2910	64.9	8.13 ± 0.18 (23.2 ± 0.51)	2.75 ± 0.08 (7.82 ± 0.23)	0.33	1.11 ± 0.02	0.58 ± 0.02	-2.79 ± 0.17
229A-5-6	7250-7260	45.8	8.57 ± 0.45 (15.8 ± 0.83)	4.13 ± 0.66 (7.61 ± 1.21)	0.48	1.08 ± 0.04	0.66 ± 0.07	-2.03 ± 0.25

^aSite-core-section.

^bDepth in sediment column.

^cNumbers in parentheses are for values recalculated on a carbonate-free basis.

^dActivity ratio.

^eExcess Th²³⁰ = dpm/gTh²³⁰ - dpm/gU²³⁴; dpm = disintegration per minute.

suggestion of diagenetic uranium enrichment can be more definitely verified if future measurement on samples deeper than 229A-5-6 from the Hole 229A yields Th²³⁰/U²³⁴ ratios less than 0.66.

It is notable that for the three samples with low Th²³⁰/U²³⁴ (228-1-2, 229A-2-1, 229A-5-6), their U²³⁴/U²³⁸ values are relatively high, implying a significant portion of their uranium as having originated from seawater or pore solution. For 229-1-CC, however, both U²³⁴/U²³⁸ and Th²³⁰/U²³⁴ data point to the possibility that the majority of its high uranium content is of detrital origin.

The present study at best enables us to make an order-of-magnitude estimation of the more recent sedimentation rate at Site 228. It will be assumed from the 228-1-1 data that surface sediments at the site contain about 0.3 dpm/g (disintegrations per minute per gram) excess Th²³⁰. Since precipitation of Th²³⁰ produced by decay of U²³⁴ in the sea is quantitative, i.e., less than 1% of the Th²³⁰ formed remaining in the sea (Moore and Sackett, 1964), one can estimate that each square centimeter of the Red Sea floor receives about 2.6 dpm of Th²³⁰ per thousand years (assuming 1 km to be the mean depth of the Red Sea and each liter of its water containing about 3.3 μg uranium). The concentration of the "authigenic" Th²³⁰, or Th_{ex}²³⁰, in a newly deposited sediment will then be approximately $2.6/\rho \times R$ (dpm/g) where R is the sedimentation rate in cm/10³ yr, and ρ the water-free, uncompressed bulk density of the surface sediments in g/cm³. By taking ρ to be 0.9 g/cm³ (cf. Report on Physical Properties and Water Contents, Site 228), Th_{ex}²³⁰ to be 0.3 dpm/g, R should be of the order of 10 cm/³ yr. This

corroborates with the radiometric results obtained previously on lutite cores retrieved from that part of the Red Sea (Ku et al., 1969; Ku, 1969).

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