Note

Abundance of Uranium and Thorium in Rock Salts

—Partition of Uranium and Thorium between Solid and Solution Phases
in Neutral Environments in Nature—[†]

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Uranium and thorium contents of German rock salts were determined by neutron activation analysis. Mean contents of nine samples were 1.07 ppb and 96 ppt for U and Th, respectively. U thus was thought to be depleted and Th was enriched in the solid phase in evaporation of sea water. Similar tendency was observed for other halite samples in nature. These results are consistent with the existence of the stable uranyl tricarbonate anion in the solution phase.

Key Words: neutron activation analysis, uranium, thorium,
rock salt, partition

1. Introduction

Uranium (U) and thorium (Th) are widely but rather sparsely distributed terrestrially¹⁾. U comprises 2.3 ppm of the earth's crust and Th is at 8.1 ppm. Their existence sometimes causes environmental problems because of their radioactivity. While Th is more abundant in the earth's crust than U, a much higher concentration of U (3.3 ppb) exists in sea water than Th (0.1 ppt)²⁾. This large difference existing in sea water is attributed to the stable U carbonate, i.e., uranyl tricarbonate anion ($\text{UO}_2(\text{CO}_3)_3^{4-}$)³⁾.

In elucidation of material cycles and distributions of U and Th at the surface of the earth, it is important to understand their partitioning behaviors between the solid and fluid phases. In this context, we chose halite as the solid phase and directed our efforts 1) to determine U and Th contents in halite samples and 2) to examine the partition of U and Th between the halite (NaCl) phase and mother solutions. In this paper, we report the determination of U and Th contents of rock salts and discuss the solid-solution partition of U and Th under the circumstances where halite deposits from neutral solutions in nature.

2. Experimental

2.1 Samples

The samples were nine rock salts from Stassfurt in Germany⁴⁾. We designate them as sample I, sample II, ... sample IX, with the sample of a

[†] 岩塩中のウランとトリウム存在量——天然中性環境下におけるウランとトリウムの固液分配——。油井瑞明, 木川田喜一, 大井隆夫, 本多照幸*, 野崎徹也*: 上智大学理工学部化学科, 102-8554 東京都千代田区紀尾井町 7-1, *武蔵工業大学原子力研究所 215-0013 神奈川県川崎市麻生区王禅寺 971。

younger number being collected in general at a shallower location underground. Most of them are collected as drilling cores. The samples are of marine origin, formed by the evaporation of water from sea water.

2.2 Determination of U and Th

A block of each rock salt sample was crushed into small granules with diameters of less than 2 mm and dried at 140°C for two days. An accurately weighed aliquot (1.2–1.8 kg) of the sample was dissolved in 6.0 dm³ dilute HCl solution (about 0.012 M). When insoluble matter remained, it was removed by filtration. The procedure for the preparation of the samples for neutron irradiation (irradiation samples) from the filtrates is in principle the same as the procedure for hot spring waters and solutions of solar salts^{5),6)}.

Neutron irradiation, γ -ray measurements and the data analysis are the same as in the previous works^{5),6)}. From 8.2 to 105.3 mg of the samples were neutron irradiated in the Rikkyo University Research Reactor (100 kW) at Yokosuka under two different conditions; 12 h irradiation without Cd wrapping at the thermal neutron flux (ϕ_{th}) of $1.4 \times 10^{12} \text{ n} \cdot \text{cm}^{-2} \text{ s}^{-1}$ and 6 h irradiation with Cd wrapping at the same ϕ_{th} and with the cadmium ratio of 3.4. The γ -ray was measured by an ultra-pure Ge semiconductor detector and a 4096 channel pulse-height analyzer. The cooling time was 1 or 2 weeks for U and 1 or 2 months for Th. The γ -ray spectra digitally recorded were analyzed with a set of new versions of computer programs by Suzuki⁷⁾ to give the final contents of U and Th of the rock salt samples.

The 228.2 or 277.6 keV γ -ray of ²³⁹Np in the reactions,

was measured for the determination of U. For Th, the 311.8 keV γ -ray of ²³³Pa in the reactions,

was used.

2.3 Other measurements

Contents of alkali metal ions were measured by flame photometry, those of other cationic species were measured by ICP-AES, and anions were determined by ion chromatography. Powder X-ray diffraction (XRD) patterns were recorded to identify rock-forming minerals in each sample by a Rigaku RAD-IIA X-ray diffractometer.

3. Results and Discussion

As examples of the γ -ray spectra obtained, those of sample IV measured after 12 h neutron irradiation followed by one-week cooling and one-month cooling are shown in Figs. 1 (a) and (b), respectively. The peaks of ²³⁹Np and ²³³Pa are observed and the contents of U and Th are calculated from the areas of the peaks.

The contents of U and Th of the rock salts determined in the present work are summarized in Table 1. Except for Th of sample VIII, the two elements are found in every sample examined, with uncertainty in the γ -ray counting (1 σ) being satisfactorily low, several % at most. The U content varies from 197 ppt to 2.68 ppb and the arithmetic mean of the nine data is 1.07 ppb (the geometric mean is 820 ppt). The Th content is between 49 and 213 ppt, with the arithmetic mean of 96 ppt (the geometric mean is 83 ppt). These values are much lower than the average values in the earth's crust.

Since the irradiation samples were prepared from dilute-HCl soluble parts of the rock salt samples, the contents of U and Th of rock salt determined in this work do not necessarily mean

Fig. 1 γ -Ray spectrum of sample IV.

Irradiation and measuring conditions are : amount of sample=26.6 mg ; $\phi_{th} = 1.4 \times 10^{12} \text{ n} \cdot \text{cm}^{-2} \text{ s}^{-1}$; irradiation time=12 h ; without Cd wrapping ; cooling time=1 week (a), =1 month (b) ; measuring time=2 000 s (a), =6 000 s (b).

the contents of U and Th in a strict meaning. XRD identifies anhydrite (CaSO_4) and polyhalite ($\text{K}_2\text{Ca}_2\text{Mg}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$) other than halite (NaCl) as minerals in the original samples. Anhydrite is found in those samples whose contents of calcium and sulfate ions are relatively high, and polyhalite is identified in such samples whose

contents of potassium and magnesium ions, in addition to those of calcium and sulfate ions, are relatively high. Only anhydrite is identified in the insoluble parts of the samples. Hence, the soluble parts of the samples mostly consist of halite, and consequently, the contents of U and Th determined in this work most likely represent the con-

Table 1 Contents (ppt) of U and Th in rock salts

Sample	U	Th
I	2 680±30	56± 2
II	300±10	150±10
III	1 330±30	84± 3
IV	197± 5	49± 2
V	800±10	60± 2
VI	800±20	103± 3
VII	614± 8	49± 2
VIII	1 510±30	ND
IX	1 380±20	213± 4
(Mean	1 070	96)

± : Errors (1 σ) in γ -ray counting.

ND : Not detected.

tents of U and Th of the halite phases of the rock salts.

Table 2 summarizes U and Th contents of halite in nature. The data for the Australian solar salt and the Chinese brine deposit are cited from our previous works^(6),8). XRD identified only halite in those salt samples. The present rock salt and solar salt are of marine origin while the brine deposit from a neutral salt lake water in China is of non-marine origin. The U content of the present rock salt is higher than those of Australian solar salt and Chinese brine deposit, while the Th content is lowest of the three. The number of data points is so scant that it would be inappropriate to emphasize the difference in U and Th contents among three different halites. We may say, at the present stage, that the U and Th contents of halite

formed from neutral mother solutions in nature are at sub ppb – ppb levels and at one-tenth ppb – sub ppb levels, respectively.

Table 2 also summarizes the values of the enrichment factor, α

$$\alpha = [A]_{\text{halite}} / [A]_{\text{ERMS}},$$

where $[A]_{\text{halite}}$ denotes the concentration of A ($A = \text{U or Th}$) in the sample and $[A]_{\text{ERMS}}$ denotes that expected for the evaporated residue of mother solution. When it is assumed that U and Th in sea water are 3.3 ppb and 0.10 ppt, respectively, and saline components occupy 3.5 weight % of sea water as a whole²⁾, $[U]_{\text{ERMS}}$ and $[Th]_{\text{ERMS}}$ would be 94 ppb and 2.9 ppt, respectively. For the evaluation of the α values for rock salt, we further assume that U and Th contents of sea water have been unchanged since the era when our rock salts were formed and only a part of the sea water was evaporated to give the rock salts. The value of $[A]_{\text{ERMS}}$ ($A = \text{U}$) of the evaporated residue of the brine is estimated to be 1.26 ppb based on the composition of the major components of the brine⁸⁾. Unfortunately, Th of the brine is not determined.

The values of α for U and Th are 0.011 and 33, respectively, for the present rock salt. This indicates that, when the rock salts were formed, Th preferred to move to the solid (halite) phase than to remain in the solution (sea water) phase, whereas U tended to stay in the solution phase. Similar tendency is also observed for the other

Table 2 U and Th Contents of natural halite in ppt and enrichment factor

Sample	Rock salt*		Solar salt**		Brine deposit***	
	Content	α	Content	α	Content	α
U	1 070	0.011	570	0.0061	880	0.70
Th	96	33	480	166	120	—

*This work.

**Ref.6. Average for four Australian solar salts.

***Ref.8. Average for two Chinese brine deposits.

halites, although, unfortunately, the datum of Th for the brine deposit is missing; in every case, $\alpha < 1$ for U and $\alpha > 1$ for Th. These observations are most likely attributable to the fact that U can stay, without being precipitated, in a neutral solution as a stable carbonate complex anion ($\text{UO}_2(\text{CO}_3)_3^{4-}$)³⁾ whereas Th does not form such a stable complex. The much large α value (but still less than unity) for U of the brine deposit with the non-marine origin compared to those of the other kinds of halites with the marine origin indicates that the U carbonate complex is not so predominant in the brine as it is in sea water.

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