A Geochemical Study on the Distribution of Some Minor Elements in Deposits and Water Samples of the Antarctic Oases

No. 1. The Ra Content of DVDP 13 Core and the Deposits of the Vestfold Hills

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南極オアシスにおける堆積物，水試料中の微量元素の分布に関する地球化学的研究

その 1. DVDP 13 コアー試料およびベストフォールド・ヒルズの堆積物中の Ra の含量

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要旨： ドライバレー地域の掘削で得られたDVDP 13コアー試料とベストフォールド・ヒルズの湖底堆積物について，過塩素酸可溶部と不溶部の炭酸ナトリウム融解抽出部のそれぞれの中の Ra 量を求めた．Ra の定量は放射平衡に達した Rn を液体シンチレーションカウンターで測定した． BG が 45 cpm のとき，その 1/8 を測定下限とすると，2 g の試料で $0.25 \pm 0.04 \times 10^{-12}$ Ci/g の Ra の測定が可能である．

U と Th との地球化学的な行動が異なることに基づいて考察すると， U は海水で運ばれ，生成した ^{230}Th が沈積しやすく，娘核種の ^{226}Ra とは一万年弱で放射平衡に達する． 放射平衡に達するまで ^{226}Ra の量は次第にふえ， それから 7.5×10^4 年の半減期で減少していく．ゆえに過塩素酸可溶部と炭酸ナトリウム融解部の Ra を定量することにより， 堆積生成以来のおよその年代の古さを知り得る． ドライバレー地域では前者の値が後者より数倍も多く今回の試料中で最も古く， スチニア湖湖底堆積物は最も新しいと推定した．

Abstract: The ignition loss and the Ra content in the 10% $HClO_4$-soluble fraction and Na_2CO_3-fusion fraction were respectively determined for the 17 core samples (DVDP 13 core), down to the depth of 50 meters and for the four lake deposits in the Vestfold Hills. The determination of Ra was performed by measuring the activity of Rn in radioactive equilibrium state with a liquid scintillation counter. The detection limit of Ra with 2 grams of sample was $(0.25 \pm 0.04) \times 10^{-12}$ Ci/g, taking one-eighth of the BG counting rate, 45 cpm, as the limit in this case.

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Based on the differences between U and Th in geochemical behaviors, it is thought that U is transported into sea water and decays to ^{230}Th which tends to precipitate in the site. From ^{230}Th is produced ^{226}Ra which attains the radioactive equilibrium within a little under ten thousand years. And then, the ^{226}Ra content gradually increases with a half life of 7.5×10^4 years. Therefore, by determining the ratio of Ra in the $HClO_4$-soluble fraction to that in the Na_2CO_3-fusion fraction of a sample, it is possible to determine its age since the time of sedimentation. The results obtained indicate that the Dry Valley sediment is the oldest while the Lake Stinear sediment is the latest because the ratio is the largest for the former and the smallest for the latter.

1. Introduction

There are many lakes and ponds along the coast and in the ice-free areas called the Antarctic oases. Geochemical studies of these lakes, especially saline ones, have been carried out for more than ten years by the Japanese parties in the Dry Valleys of Victoria Land and on the Prince Olav Coast in the Antarctic, and have obtained interesting information regarding the formation of lakes, the salt origin, and also for the solution of some Quaternary problems (TORII, 1975).

Investigation of the distribution of minor elements of the deposits in and around the lakes will provide an important clue to elucidation of the oases formation. This paper, as the first effort, discusses the geochemical behaviors of radium in these areas.

Samples used for the present experiment were the core samples of DVDP 13 drilled at Don Juan Pond in Victoria Land and the evaporites and lake sediments collected from the Vestfold Hills by the Australian party.

2. Experimental

2.1. Sample treatment

2.1.1. Ignition loss

The sample was treated in the approved ways of volcanic ash treatments and then was ground into powder in a silica mortar. The prescribed amount of the powder was red-heated in a platinum crucible to obtain the ignition loss.

2.1.2. Preparation of sample solution

a) $HClO_4$-soluble fraction

One to 2.5 grams of the powder dried at 110°C to constant weight, was weighed, added with 30 ml of 10% $HClO_4$ solution, then heated for one hour on a water bath and filtered. The residue was washed five times with water. The washing solutions and filtrate were collected and made up to 250 ml with water, which is called hereafter the $HClO_4$-soluble fraction.

b) Na_2CO_3-fusion fraction

The residue was weighed after heating that at 110°C to constant weight, and then fused with 6 to 7 grams of sodium carbonate flux. The fused mass was leached with water and HCl and was made up to 250 m*l* with water, hereafter called Na_2CO_3-fusion fraction.

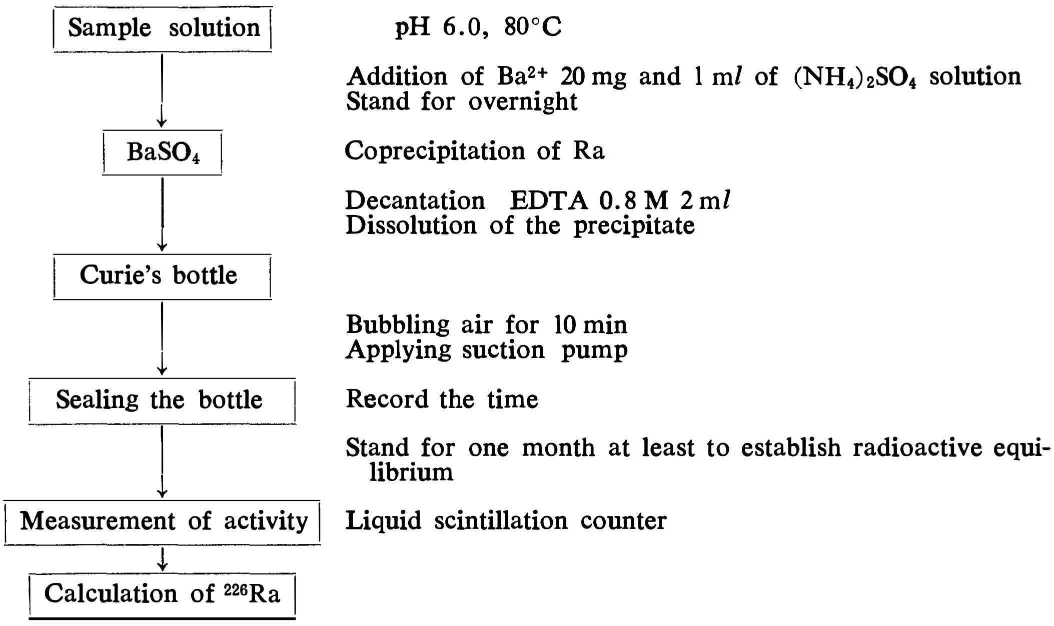
2.2. Determination of radium

The sample was brought into a solution and Ra was separated by coprecipitating with barium sulfate. It was then left standing in a Curie's bottle for a month. Determination of Ra was carried out by measuring the activity of Rn in the radioactive equilibrium state, and from the activity the quantity of Ra was calculated.

2.2.1. Separation of radium

The solution thus obtained, prewarmed at 80°C, was added with 1 m*l* of $BaCl_2$ solution (35.6 g/*l*) and was adjusted to pH 6.0 with either 1N NaOH or 6N HCl. One milliliter of $(NH_4)_2SO_4$ solution (30 g/*l*) was then added with constant stirring and left standing for overnight. After the supernatant was removed by decantation, the resultant barium sulfate was dissolved, while being warmed at 80°C, by adding 2 m*l* of 0.8 M EDTA tetra-sodium salt solution and by alkalizing the solution with 1 m*l* of 1N NaOH. The solution was transferred into a Curie's bottle with 10 m*l* washing solution. Air was bubbled into the bottle through a sodalime tube and a cotton stopper with the aid of a water suction

Table 1. Procedures for the determination of Ra in $HClO_4$-soluble fraction and Na_2CO_3-fusion fraction.



pump. The bottle was then sealed at the two branches under a reduced pressure and the time of sealing was recorded as the initiation time of Rn generation.

2.2.2. Separation of radon

After the radioactive equilibrium was attained between ^{226}Ra and ^{222}Rn, the Curie's bottle was connected to ^{222}Rn gas handling manifold. Breaking the two branches, the ^{222}Rn gas formed in the bottle was forced out by air circulation in the system and was condensed into toluene in the collection vessel cooled with an acetone-dry ice freezing mixture. The toluene was transferred into a counting vial and dissolved with a liquid scintillator (PPO 4 g, POPOP 0.1 g/*l* toluene) by thorough shaking. Since ^{222}Rn decays with a half-life of 3.825 days and establishes equilibrium in 190 minutes with daughter nuclides such as RaA, B, C and C′, the measurement was performed after 190 minutes with the liquid scintillation counter by applying the integral counting method (HOMMA *et al.,* 1977).

2.2.3. Lowest limit of detection

The counting method used in the present experiment provided the detection limit 5.62 cpm corresponding to 0.50×10^{-12} Ci of ^{226}Ra, which is one-eighth of the background 45 cpm. Therefore when the maximum 2 g of the original sample was used, each measurement for 100 minutes of the background and sample should detect $0.25\pm0.04\times10^{-12}$ Ci/g of sample as the lowest limit of detection.

3. Results and Discussion

3.1. Ra in DVDP 13 core

The results obtained from DVDP 13 core samples are given in Table 2 and are discussed, referring to the geological log map (MUDREY *et al.,* 1975) and to the distribution patterns of Ra, by grouping the samples into four, A to D.

The samples of D group, No. 15, 16 and 17 provided by H. KURASAWA, were collected from the basement rock on which there was a sediment layer of 12.6 m thickness. The upper part of the basement rock consists of 52.15 m thick dolerite which intrudes the granite layer (MUDREY *et al.,* 1975). The three samples represent the upper, middle and lower parts of the dolerite, respectively. The Ra distribution in dolerite is uniform in these three Na_2CO_3-fusion fractions with the average 1.09×10^{-12} Ci/g, whereas those in the $HClO_4$-soluble fraction of the upper samples, No. 15 and No. 16, are relatively high.

This fact seems to be explained as follows. The upper part of the basement rock has numerous vertical and horizontal fractures, and the fracture surfaces abound in calcite and other secondary minerals. Thus Ra seems to have been transported there by water and deposited on the surfaces with Ca, etc. Or the anomalously high content of Ra in $HClO_4$-soluble fraction of No. 16 sample may be due to the partial dissolution of the minerals abounding in Ra. This problem

Table 2. Ra content in DVDP 13 core.

	Samples		Ignition loss %	$HClO_4$-soluble fraction		Na_2CO_3-fusion fraction	
	Groups	Depth cm		%	Ra × 10^{-12} Ci/g	%	Ra × 10^{-12} Ci/g
A	1	97.7	12.82	18.5	1.59	81.5	2.19
	2	156	7.30	10.5	5.18	89.5	2.11
	3	258	8.63	19.6	4.05	80.4	1.64
	4	306	6.21	12.1	2.19	87.9	2.54
	5	604	6.03	8.5	2.04	91.5	1.69
	6	700	8.44	11.1	3.18	88.9	1.80
	7	792.5	6.48	11.4	3.20	88.6	1.76
B	8	817	6.48	10.0	1.69	90.0	1.16
	9	898	7.00	9.9	1.93	90.1	1.09
	10	918	5.96	10.1	1.23	89.9	1.43
C	11	1005	8.99	11.8	6.03	88.2	1.94
	12	1102	8.85	14.3	3.34	85.7	1.89
	13	1139	5.18	13.4	2.30	86.6	1.70
	14	1200	7.66	11.1	7.16	88.9	2.13
D	15	1558	0.56	12.7	1.16	87.3	1.09
	16	2409	0.30	9.6	2.01	90.4	1.05
	17	5012	1.73	10.0	0.95	90.0	1.14

is subjected to further examination.

The A, B and C groups in sediment layers showed higher content of Ra, ranging from 2.54 to 1.09×10^{-12} Ci/g, in the Na_2CO_3-fusion fraction than those of the basement rock samples. This may be attributed to the presence of another kind of rock of different origin sedimented there in the later stage. This explanation is plausible especially for the samples of No. 4 and No. 14 in which the presence of uncommon pebbles was obvious in the log map, and also for samples of No. 11 and No. 12. The Ra content of all samples of A, B and C groups is generally higher in the $HClO_4$-soluble fraction than in the Na_2CO_3-fusion fraction. But it is especially high in group C which was deposited directly upon the basement rock relative to the results with group B. This was caused probably by the old dead water retained for a long period by the impermeable basement rock and by the subsequent deposition of ^{226}Ra and/or ^{230}Th. The group B samples are composed mainly of fine sand, hence they are unable to retain the water for a long period which contains the radioactive elements.

Among the samples taken from the deeper parts than No. 4, the percent of $HClO_4$-soluble fraction and the ignition loss show relatively small differences from each other. The high Ra content in the $HClO_4$-soluble fraction of sample

No. 2 is probably due to the silty and clayed property of the sample which is shown by the log map. The positive relationships between the $HClO_4$-soluble fraction and the ignition loss were observed as shown in Figs. 1 and 2. But samples No. 1 to No. 3 show larger ignition loss and higher percentage of $HClO_4$-soluble fraction. This is accounted for by that these samples can be of surface soil layers.

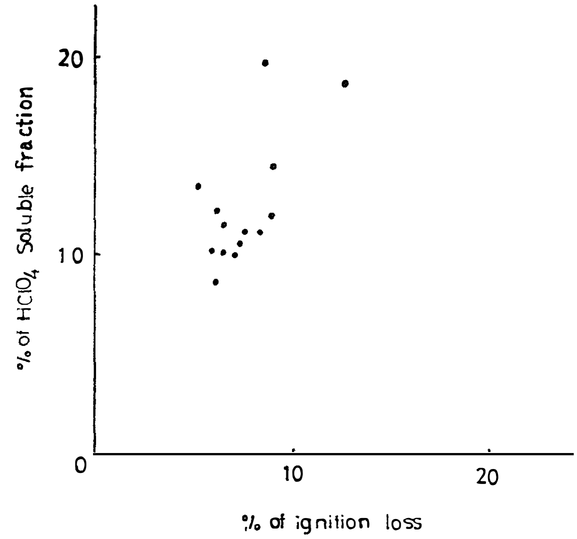


Fig. 1. Relationship between % of $HClO_4$-soluble fraction and ignition loss in DVDP 13 core samples.

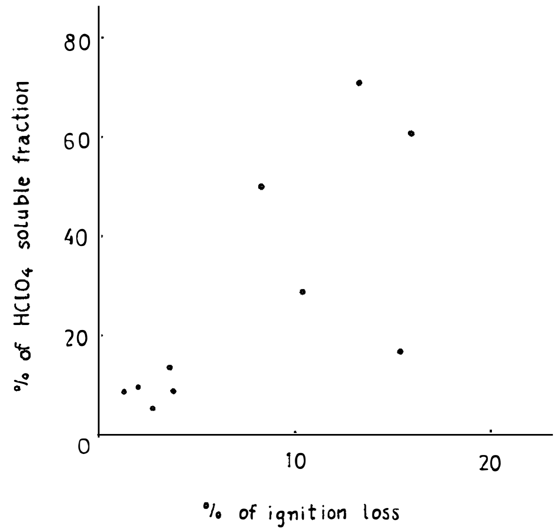


Fig. 2. Relationship between % of $HClO_4$-soluble fraction and ignition loss in Oval Lake samples.

3.2. Radium distribution in the deposits of the Vestfold Hills

There are about 34 saline lakes of various sizes in the Vestfold Hills and many evaporites have been found around the lakes (KERRY *et al.*, 1974).

Eleven samples were collected on the coast of Oval Lake and were grouped into α, β, δ, ε layers by the collector according to the appearances and other characteristics. Table 3 shows the results obtained for these samples. The α layer has an appearance similar to the currently forming lake deposit. No. 1 and No. 2 samples of α layer are both taken from the surface level, but from different sites, A and B. The β layer is a hard pan of 1 cm thickness. Although no samples of this layer are available, samples No. 5 and No. 6 were taken immediately above and below this layer respectively. The δ layer has a tinge of green and its ignition loss, averaging 12.78%, is several times larger than that of the α layer. The ε layer contains a large quantity of mirabilite ($Na_2SO_4 \cdot 10H_2O$) which is a deposit at the height of 7.1 m above the present lake level and 34 m below the old strand lines of the paleolake.

Table 3. Ra content in the deposits near Oval Lake.

Samples				Ignition loss %	$HClO_4$-soluble fraction		Na_2CO_3-fusion fraction	
	Depth cm		Description		%	Ra × 10^{-12} Ci/g	%	Ra × 10^{-12} Ci/g
No. 1	α	A0	Coarse sediment	2.64	5.19	0.35	94.8	0.59
2		B0		3.42	13.29	0.58	86.7	0.80
3		20		1.21	8.51	0.56	91.5	0.39
4		40		1.83	9.31	0.45	90.7	1.21
5		50		3.73	8.97	0.63	91.0	1.21
	β		Hard pan					
6	δ	51	Green material	10.26	28.4	0.75	71.6	1.79
7		71		15.31	16.8	0.47	83.2	0.85
8	ε	86	Mirabilite	15.98	60.9	0.84	39.1	1.42
9		106		8.16	49.9	1.24	50.1	1.55
10		116		13.21	70.8	1.35	29.2	1.32
11		226		—	49.9	0.56	50.1	0.78

The average Ra content in the $HClO_4$-soluble fraction and Na_2CO_3-fusion fraction of these layers was found as follows: for α layers 0.51 and 0.84×10^{-12} Ci/g, for δ layers 0.69 and 1.35×10^{-12} Ci/g, and for ε layers (except sample No. 11) 1.14 and 1.43×10^{-12} Ci/g. The higher Ra content in $HClO_4$-soluble fraction of ε layer, compared with those of the other layers, may be due to the large concentration of sulfate which caused by the formation of mirabilite layer and to the codeposition of Ra with gypsum.

Tables 4, 5 and 6 give the results obtained on the deposits of the other saline lakes in the Vestfold Hills. Three samples of Deep Lake have similar compositions, containing silica, feldspar, pyroxene and mica. The average Ra contents are 0.50 and 1.23×10^{-12} Ci/g respectively in the $HClO_4$-soluble and Na_2Co_3-fusion fractions. The former is more than twice smaller than in the latter fraction.

Table 4. Ra content in lake deposits of Deep Lake.

Samples depth m	Ignition loss %	$HClO_4$-soluble fraction		Na_2CO_3-fusion fraction	
		%	Ra × 10^{-12} Ci/g	%	Ra × 10^{-12} Ci/g
1	2.92	6.7	0.60	93.3	1.23
32	10.74	26.4	0.40	73.6	1.06
33	10.75	52.3	0.58	47.7	1.40

Three samples of Lake Stinear show nearly the same results as those from Deep Lake with respect to the Ra content in $HClO_4$-soluble and Na_2CO_3-fusion fractions, and to the percent of $HClO_4$-soluble fraction and of ignition loss. On

Table 5. Ra content in lake deposits of Lake Stinear.

Samples depth m	Ignition loss %	$HClO_4$-soluble fraction		Na_2CO_3-fusion fraction	
		%	Ra × 10^{-12} Ci/g	%	Ra × 10^{-12} Ci/g
10	7.06	20.23	0.63	79.8	1.07
13.5	12.45	79.0	0.22	21.0	0.54
18	—	79.0	0.13	21.0	1.66

the other hand, the sample at the depth of 18 m which has gypsum is abundant in Ra in the Na_2CO_3-fusion fraction, showing a value 1.66×10^{-12} Ci/g. This feature is similar to the cases of No. 8 and No. 9 samples of Oval Lake.

The data of the lake deposits in Triple Lake show that the $HClO_4$-soluble fractions contain less Ra except for the surface samples as seen in those of the above three lakes. The Na_2CO_3-fusion fractions of these samples still contain less Ra, averaging 0.87×10^{-12} Ci/g, than those of Deep Lake and Lake Stinear, averaging 1.23 and 1.09×10^{-12} Ci/g respectively.

Table 6. Ra content in lake deposits of Triple Lake.

Samples	Ignition loss %	$HClO_4$-soluble fraction		Na_2CO_3-fusion fraction	
		%	Ra × 10^{-12} Ci/g	%	Ra × 10^{-12} Ci/g
1	4.77	15.2	0.43	84.8	1.28
2	0.55	6.7	0.96	93.3	0.58
3-1	1.34	8.1	0.42	91.9	0.80
3-2	11.91	14.9	0.58	85.1	0.71
3-3	28.09	45.6	0.54	54.5	0.72
4	15.77	21.2	0.38	78.8	1.14

3.3. Discussions

Concerning the analytical processes used in the present experiment, the ignition loss obtained is mostly attributable to decomposition of carbonates, hydrates and various organic substances. The $HClO_4$ leaching dissolves many water-insoluble Ca salts as well as water-soluble components (MORIKAWA *et al.*, 1975). Radium seems to readily dissolve even in sulfate form with $HClO_4$ leaching since secondarily deposited Ra is present in carrier-free state. A positive correlation is clearly seen between the content of Ca and Ra in the $HClO_4$-soluble fraction of the Dry Valley, providing the basis to conclude that Ra was deposited with Ca.

The ignition loss in the case of the Dry Valleys and Oval Lake samples is apparently related to the Ra content in the $HClO_4$-soluble fractions. On the

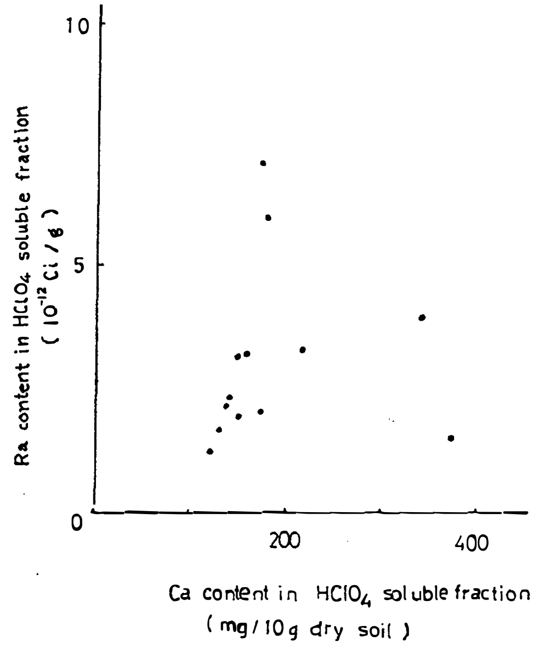


Fig. 3. Relationship between Ra content and Ca content in $HClO_4$-soluble fraction of DVDP 13 core samples.

other hand, Ra in the rock-forming minerals can be dissolved only by Na_2CO_3-fusion. Therefore the observation of different Ra contents in the Na_2CO_3-fusion fraction should be attributed to the differences in the origin of rocks included in the deposits.

The presence of ^{226}Ra indicates the original presence of ^{238}U, or at least is attributed to the occurrence of the α decay process of $^{230}Th \rightarrow {}^{226}Ra$. The geochemical behaviors of U and Th are definitely different; U, being hexavalent under oxyphilic conditions, readily forms water-soluble carbonate complex and therefore is transported by fresh and sea water without deposition, whereas tetravalent Th tends to precipitate by being absorbed on hydrates of Fe, Al and Mn, SiO_3^{2-} gels and clays. On the other hand, U(IV) which is easily formed from U(VI) under reduction circumstances also precipitates and tends to be absorbed on carboneous materials. Therefore the ignition loss provides some information to delineate the processes described above, although being indirect. Radium thus acquired in the later stage is regarded to be soluble at $HClO_4$ leaching.

The areas in question were the sea beds in the past and so was subjected to sea water reaction (Mudrey *et al.*, 1975). To provide a clue to the geochemical history of U, Th and Ra, Table 7 is cited which shows the contents of U, Th and ^{226}Ra in ocean and in marine deposit (Riley *et al.*, 1971). The marine deposit shown in this table is continuously in contact with sea water and is located in the site where Ra diffuses back into the sea water from the upper layer about 20 cm thick. This area had once been covered with marine deposits and in the later stage was covered with another thick sediment layer. Though this table dose

Table 7. Average concentration of ^{238}U, ^{232}Th and ^{226}Ra in sea and marine deposit.

Nuclides	Concentration in sea water (g/l)	Concentration in surface layer of marine deposit (g/g)
^{238}U	3.0~3.2×10^{-6}	1.0×10^{-6}
↓		
^{230}Th	0.02~0.3×10^{-12}	2~20×10^{-12}
↓		
^{226}Ra	0.1×10^{-12}	30~40×10^{-12}
^{232}Th	1×10^{-9}	5×10^{-6}

not give a direct evidence, it is helpful to understand the geochemical history of the area.

Calculations of the amount of ^{226}Ra in radioactive equilibrium with ^{238}U in sea water and marine deposits based upon the data of Table 7 were performed and gave 1.02 to 1.09×10^{-12} and 0.34×10^{-12} Ci of ^{226}Ra respectively. It may be expected from the calculation that about 3.5×10^{6} years are necessary to establish the equilibrium between ^{238}U and ^{226}Ra while about 10 thousands of years are enough between ^{226}Ra and the direct parent nuclide ^{230}Th. Since ^{238}U decays into ^{230}Th by emitting 2α and $2\beta^-$, the amount of ^{226}Ra, direct decay product of ^{230}Th, present in sea water is one order of magnitude less than the above equilibrium value. This is caused by the geochemical behavior of ^{230}Th which is rapidly lost from the sea to the marine deposits. In the deposits, on the contrary, its content is actually larger than thus estimated equilibrium value by a factor more than ten. This fact supports the precipitation mechanisms described above, and accordingly the discussions on the positive relationship between the percentages of the ignition loss and $HClO_4$-soluble fraction seem to be confirmed.

Next, the Ra content in the $HClO_4$-soluble fraction of the Dry Valleys core is one order of magnitude higher than the equilibrium value of marine deposits, 0.34×10^{-12} Ci/g. And those of Oval Lake (significantly), Deep Lake and Triple Lake also exceed the equilibrium value of marine deposits, while they are nearly the same as those of the Lake Stinear samples. If it is admitted that ^{226}Ra measured is mainly formed by decay of ^{230}Th which is generated from U transported to the site by sea water, about 10^{4} years are required for establishing the radioactive equilibrium between ^{230}Th and ^{226}Ra. Therefore, the amount of Ra keeps increasing till the attainment of this equilibrium and then decreases with the half life equal to that of ^{230}Th, 7.5×10^{4} years (ATTREE *et al.*, 1962), until the next equilibrium among ^{238}U, ^{230}Th and ^{226}Ra is achieved in about 10^{6} years. After that they decay with a half life of 4.5×10^{9} years of ^{238}U.

On the other hand, ^{226}Ra in rock which is not subject to weathering is typically represented by the Na_2CO_3-fusion (fraction) because ^{226}Ra in it has been kept insoluble until now and the equilibrium of these daughter nuclides with ^{238}U is thought to be still retained. It is hence useful to compare the ratio of ^{226}Ra in the two fractions in order to understand the ages of the deposit layers.

From the above arguments, the sediment in the Dry Valleys should have the long history after sedimentation because the ratio of the ^{226}Ra content in the $HClO_4$-soluble fraction to that in the Na_2CO_3-fusion fraction is significantly large. On the other hand, the Lake Stinear samples with the smallest value of this ratio can be estimated to have experienced shortest period of time after sedimentation. In order to further confirm this conclusion, it is desirable to directly determine ^{230}Th or ^{238}U and Al, Mn, La and Ca which readily form hydrates and catch Ra on it. This is under investigation now.

It is of course a matter of concern that ^{224}Ra, the decay product from ^{232}Th which has four times as much Clark's number as ^{238}U, coprecipitates with ^{226}Ra and may come into the counting. A calculation of the equilibrium amount of ^{224}Ra from the content of ^{232}Th in the sea water and in the marine deposit gives 1.11×10^{-16} and 5.55×10^{-13} Ci respectively. These values are definitely smaller than the equilibriated amount of ^{226}Ra with ^{238}U. The coprecipitated ^{224}Ra, if occurs, should raise a certain effect on its content. But since ^{224}Ra has short half life of 3.64 days and the counting is done 190 minutes after the Rn condensation into the scintillator, the measurement method used here would not be affected by the presence of ^{224}Ra.

Acknowledgments

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