STUDIES ON Ra, U, Th AND MINOR ELEMENT CONTENTS IN DVDP CORES AND DEPOSITS FROM VESTFOLD HILLS*

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Abstract: The ignition loss and the Ra contents in the 10% $HClO_4$-soluble fraction and Na_2CO_3-fusion fraction were respectively determined for the DVDP 13 and 14 cores and four lake deposits in the Vestfold Hills.

The powdered sample dried at 110°C to constant weight, was weighed, added with 10% $HClO_4$ solution, then heated on a water bath and filtered. The filtrate is called the $HClO_4$-soluble fraction. The residue was fused with sodium carbonate. The fused mass was leached with water and HCl, which is called the Na_2CO_3-fusion fraction. Radium in each fraction was separated by coprecipitation with barium sulfate. It was then left standing in a Curie's bottle for a month. Determination of Ra was carried out with a liquid scintillation counter by measuring the activity of Rn in the radioactive equilibrium.

The other radioactive elements such as U and Th and other minor elements were determined in the same samples. The U content was obtained by the fluorometry and the Th content by the colorimetry of thorin after separation of some interfering ions with cation exchange resins. For minor elements, the nondestructive neutron activation method was employed and 23 elements were determined by irradiating the samples with the reactor (TRIGA Mark II) at St. Paul's University, followed by the γ-ray spectrometry with a multichannels pulse height analyzer. Some of the results are shown in Tables.

Discussion will be based upon these data.

1. Introduction

The authors previously reported on the Ra content of the DVDP 13 core and the deposits from the Vestfold Hills, and discussed briefly on the age of the deposits in these areas (HORIUCHI *et al.*, 1977). In this paper, the contents of U, Th, Ra and minor elements in the DVDP cores and the deposits in the Vestfold Hills were analyzed further to study the distribution and geochemical behaviors of these elements. The U and Th contents of 10 samples of DVDP 14 core in addition to those samples studied previously were determined, fluorometrically or colorimetrically. In addition to U and Th, 23 minor elements were determined by the activation analysis, of which pertinent data are shown in Table 1. The age of the deposits and the geochemical behaviors of U, Th and Ra are discussed by presenting the results of analysis.

Table 1. Radioactive nuclides and γ-ray used for neutron activation analysis.

Short-lived nuclides				Long-lived nuclides				
Nuclides	Half-life	γ-ray used	Nuclides	Half-life	γ-ray used	Nuclides	Half-life	γ-ray used
		MeV			MeV			MeV
^{49}Ca	8.8 m	3.084	^{59}Fe	45 d	1.095	^{141}Ce	32.5d	0.145
^{27}Mg	9.46m	0.844	^{86}Rb	18.6 d	1.078	^{152}Eu	12.7y	1.408
^{23}Al	2.3 m	1.780	^{46}Sc	84 d	0.889	^{160}Tb	72.1d	0.299
^{24}Na	15.1 h	1.369	^{51}Cr	27.8 d	0.320	^{169}Yb	32 d	0.177
^{42}K	12.4 h	1.524	^{60}Co	5.26y	1.173	^{177}Lu	6.8d	0.208
^{52}V	3.75m	1.434	^{131}Ba	12.0 d	0.496	^{181}Hf	42.5d	0.482
^{56}Mn	2.57h	0.847	^{122}Sb	2.68d	0.564	^{182}Ta	115 d	1.122
^{51}Ti	5.8 m	0.320	^{134}Cs	2.05y	0.796			

2. Experimentals

2.1. Sample treatment

The treatment methods of samples are the same as in the previous report (HORIUCHI *et al.*, 1977) with a minute variation.

2.1.1. Ignition loss

The sample was treated as in the case of treating volcanic ash usually and was ground into powder in a silica mortar. One to 2.5 g of the powder was red-heated for 30 min 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 g of the powder, dried at 110°C to constant weight, was weighed, added with 30 m*l* of 10% $HClO_4$ solution, and heated for one hour on a water bath and the mixture was filtered. The residue was washed with 150 m*l* of water. The filtrate and washings were combined and made up to

250 ml with water, which is called hereafter the $HClO_4$-soluble fraction.

b) Na_2CO_3-fusion fraction: The above residue was weighed after heating to constant weight at 110°C, and was fused with 6 to 7 g of sodium carbonate flux. The fused mass was leached with water and HCl, and was made up to 250 ml with water. This part hereafter is called the Na_2CO_3-fusion fraction.

2.2. Determination of Ra

Following the procedure reported in the previous paper (HORIUCHI et al., 1977), Ra dissolved in the $HClO_4$-soluble and the Na_2CO_3-fusion fractions was coprecipitated with $BaSO_4$. The precipitate was again dissolved in an EDTA solution in alkaline medium and the resultant solution was sealed in a Curie's bottle. It was left standing for approximately one month to attain a radioactive equilibrium. Radon gas formed in the bottle was collected into toluene in a counting vial with the gas handling manifold (HOMMA et al., 1977). After the scintillator was applied to the vial, the activity was measured by a liquid scintillation counter. The detection limit of Ra was 0.25×10^{-12} Ci/g in 2 g sample.

2.3. Determination of U

The U content was determined fluorometrically as follows. Approximately 0.5 g of finely powdered sample was fused with KOH and the resultant cake was dissolved in nitric acid. Uranium was extracted from the resultant solution with ethylacetate. After the extract was carefully heated on a platinum plate to burn out ethylacetate, an aliquot (usually 2 g) of the flux mixture (NaF 18, K_2CO_3 91, Na_2CO_3 91 g) was added and gently fused at the temperature lower than 700°C. The U content of the fused cake was determined by a fluorometric method. The U content of most samples was less than 50 μg as U_3O_8.

2.4. Determination of Th

The content of Th was determined colorimetrically. Approximately 0.5 g of sample (Th content 0–50 μg) was fused with alkali flux and dissolved in HCl and water. Thorium in the solution was adsorbed on a cation exchange resin (Amberlite CG-120) and thorium was eluated with 3 M H_2SO_4. The thorium in the eluant was determined by colorimetry with Arsenazo III (0.05% solution). The lower limit of Th determination by measuring the intensity at 660 nm was 0.01 μg.

2.5. Analysis of minor elements by activation analysis

Minor elements in samples were non-destructively analyzed by a thermal neutron activation method. 100 mg of sample dried at 110°C was irradiated with thermal neutron (1.2×10^{12}n/cm^{2}s with F-Ring and 10^{11} n/cm^{2}s with RSR) of the reactor (TRIGA Mark II) at St. Paul's University. Gamma ray spectra were recorded with a Ge (Li) solid state detector (45 ml) connected to a 2048 or 4096 channels pulse hight analyzer. Table 1 shows the produced radionuclides with their half-lives and γ-ray energies used for their determination. When a sample was irradiated

for 5 min to determine several elements which produce short-lived nuclides, γ-ray spectra were recorded immediately after the irradiation. Eight elements, *i.e.* Ca, Mg, Al, Na, K, V, Mn and Ti, were determined in this way. Further irradiation was made for 24 hours to determine the elements which produce long-lived nuclides. The samples irradiated were cooled for more than 4 days before the spectra were recorded. Thus, 15 elements including Fe, Rb, Sc, Cr, Co, Ba, Sb, Cs, Ce, Eu, Tb, Yb, Lu, Hf and Ta were successfully determined.

3. Distribution of U, Th and Ra

The Ra, U and Th contents and ignition losses in the DVDP 13 and 14 cores, and in the deposits of four lakes in the Vestfold Hills are shown in Tables 2–6.

From the results obtained it may be said that ^{226}Ra in these samples was formed mostly from the parent nuclide ^{230}Th and partly formed as a decay product of ^{238}U in the sediments. Sample No. 1 of DVDP 13 core was chosen as an example to discuss. It contained 2.33 ppm of U. Assuming that ^{226}Ra is in equilibrium with ^{238}U actually determined (0.78×10^{-12} Ci), the amount of ^{226}Ra would be 0.78×10^{-12} Ci. This value is approximately one order of magnitude smaller than the determined value, 3.78×10^{-12} Ci which is the sum of ^{226}Ra determined in the HClO$_4$-

Table 2. Ra, U and Th contents in the DVDP 13 core.

	Depth (cm)	Ignition loss (%)	HClO$_4$-soluble fraction		Na$_2$CO$_3$-fusion fraction		U (ppm)	Th (ppm)
			(%)	(Ra×10^{-12}Ci/g)	(%)	(Ra×10^{-12}Ci/g)		
	97.7	12.82	18.5	1.59	81.5	2.19	2.33	22.0
	156	7.30	10.5	5.18	89.5	2.11	2.67	8.0
	258	8.63	19.6	4.05	80.4	1.64	1.36	8.0
A	306	6.21	12.1	2.19	87.9	2.54	0.43	10.02
	604	6.03	8.5	2.04	91.5	1.69	1.59	10.02
	700	8.44	11.1	3.18	88.9	1.80	1.70	10.02
	792.5	6.48	11.4	3.20	88.6	1.76	0.93	32.0
	817	6.48	10.0	1.69	90.0	1.16	1.74	54.0
B	898	7.00	9.9	1.93	90.1	1.09	1.19	—
	918	5.96	10.1	1.23	89.9	1.43	1.31	1.40
	1005	8.99	11.8	6.03	88.2	1.94	1.53	22.0
C	1102	8.85	14.3	3.34	85.7	1.89	1.62	12.0
	1139	5.18	13.4	2.30	86.6	1.70	1.24	24.0
	1200	7.66	11.1	7.16	88.9	2.13	1.36	16.0

— Not determined.

Table 3. Ra, U and Th contents in the deposit near Oval Lake.

Sample			Ignition loss (%)	HClO₄-soluble fraction		Na₂CO₈-fusion fraction		U (ppm)	Th (ppm)
Depth (cm)		Description		(%)	(Ra×10⁻¹²Ci/g)	(%)	(Ra×10⁻¹²Ci/g)		
No. 1	A0	Coarse sediment	2.46	5.19	0.35	94.8	0.59	1.27	8.0
2	B0		3.42	13.29	0.58	86.7	0.80	0.50	8.0
3	20		1.21	8.51	0.56	91.5	0.39	0.38	2.02
4	40		1.83	9.31	0.45	90.7	1.21	0.43	12.0
5	50		3.73	8.97	0.63	91.0	1.21	0.39	4.0
Hard pan									
6	51	Green material	10.26	28.4	0.75	71.6	1.79	3.54	—
7	71		15.31	16.8	0.47	83.2	0.85	3.18	—
8	86		15.98	60.9	0.84	39.1	1.42	1.23	—
9	106		8.16	49.9	1.24	50.1	1.55	1.14	—
10	116	Mirabilite	13.21	70.8	1.35	29.2	1.32	1.26	—
11	226		—	49.9	0.56	50.1	0.78	0.76	—

Table 4. Ra, U and Th contents in lake deposits (Deep Lake and Stinear Lake).

Samples depth (m)	Ingition loss (%)	HClO₄-soluble fraction		Na₂CO₃-fusion fraction		U (ppm)	Th (ppm)
		(%)	(Ra×10⁻¹²Ci/g)	(%)	(Ra×10⁻¹²Ci/g)		
Deep Lake							
1	2.92	6.7	0.60	93.3	1.23	0.24	8.0
32	10.74	26.4	0.40	73.6	1.06	0.40	4.0
33	10.75	52.3	0.58	47.7	1.40	0.19	4.0
Stinear Lake							
10	7.06	20.23	0.63	79.8	1.07	0.093	0.88
13.5	12.45	79.0	0.22	21.0	0.54	0.009	4.0
18	—	79.0	0.13	21.0	1.66	0.35	10.02

Table 5. Ra, U and Th contents in the deposit of Triple Lake.

Sample No.	Ignition loss (%)	HClO₄-soluble fraction		Na₂CO₃-fusion fraction		U (ppm)	Th (ppm)
		(%)	(Ra×10⁻²Ci/g)	(%)	(Ra×10⁻¹²Ci/g)		
1	4.77	15.2	0.43	84.8	1.28	0.47	4.0
2	0.55	6.7	0.96	93.3	0.58	0.36	4.0
3-1	1.34	8.1	0.42	91.9	0.80	0.36	8.0
3-2	11.91	14.9	0.58	85.1	0.71	1.27	2.0
3-3	28.09	45.6	0.54	54.5	0.72	1.61	0.88
4	15.77	21.2	0.38	78.8	1.14	4.37	2.0

Table 6. Ra, U and Th contents in DVDP 14 core.

Depth (cm)	Ignition loss (%)	HClO₄-soluble fraction		Na₂CO₃-fusion fraction		U (ppm)	Th (ppm)
		(%)	$(Ra \times 10^{-12}Ci/g)$	(%)	$(Ra \times 10^{-12}Ci/g)$		
25- 28	2.41	8.8	25.38	91.2	1.97	0.92	5.98
200- 205	2.01	7.4	6.43	92.6	2.74	0.58	18.02
420- 425	1.15	7.6	3.10	92.4	3.21	0.86	10.02
461- 466	10.44	13.6	2.72	86.4	—	0.98	8.0
920- 925	2.09	9.4	2.98	90.6	2.19	0.56	5.98
970- 975	10.08	20.2	4.64	79.8	2.69	1.41	10.09
1290-1295	8.71	17.7	3.86	82.3	3.26	1.09	10.02
2145-2150	14.02	29.3	3.24	70.3	1.84	1.75	8.96
2340-2345	9.15	16.6	2.70	83.4	3.11	2.02	8.06
2738-2743	8.83	17.2	1.84	82.8	1.94	1.42	16.0

— Not determined.

soluble and the Na₂CO₃-fusion fractions.   This large excessive amount of Ra suggests the presence of another source to form [226]Ra as a decay product.   [226]Ra is the decay product of [230]Th and [234]Th of the U-series, and could not be formed from [232]Th of the Th-series.   On the other hand, the amount of Th determined in sample No. 1 is mostly [232]Th, and [230]Th is supposed to be a fairly small portion of Th determined.

As the geochemical behaviors of Th and U are definitely different, Th easily precipitates but U can the present in water as a soluble form.   Therefore, it is quite natural to consider that [230]Th was separated from the parent nuclide [238]U, deposited with other Th and was concentrated more in the sediments than in water.   The excessive amount of [226]Ra must be produced from the direct parent nuclide [230]Th precipitated during the formation of the sediment.   This is supported by the data shown in Table 7.   The average concentration of [230]Th in marine deposit was 2–20 × 10^{-10} g (Riley and Chester, 1971).   The [226]Ra contents in equilibrium with these

Table 7. Equilibrium amount of Ra calculated from U and Th in marine deposits and core.

	Content		Equilibrium amount of [226]Ra (calculated by the authors)	Remarks
Marine deposit g/g	[238]U	1.0×10^{-6}g	0.34×10^{-12} Ci	Riley and Chester
	[230]Th	$2 \sim 20 \times 10^{-10}$g	$4.25 \sim 42.5 \times 10^{-12}$ Ci	
Core sample g/g	U	2.33×10^{-6}g	0.78×10^{-12} Ci	
	Th	22.0×10^{-6}g	2.42×10^{-12} Ci (as [232]Th)	This work
	Ra	3.78×10^{-12}Ci	4.57×10^{-7} Ci (as [230]Th)	

^{230}Th were calculated by the authors as $4.25\text{--}42.5 \times 10^{-12}$ Ci, which agreed well with all the values determined in this study. This result strongly suggests that ^{230}Th is the main source of ^{226}Ra as mentioned above.

The amount of ^{230}Th was a small portion of the total Th content in the deposit. Assuming that all the Th determined was ^{230}Th, the amount of ^{226}Ra in equilibrium with it would be 4.57×10^{-7} Ci, which is 5 orders of magnitude larger than the determined value, 3.78×10^{-12} Ci. A similar tendency was found in other core samples. In the depositional process of Th, the role of Fe, Al, Mn and rare earth elements was important as will be discussed later. There must be a significant effect of sea water during the formative processes of these sediments in both Dry Valleys and Vestfold Hills, as reported in the former work (HORIUCHI et al., 1977).

The contents of U, Th and Ra are summarized in Table 8. Ra in the $HClO_4$-soluble fraction was formed from ^{230}Th as mentioned above, and Ra in the rock-forming minerals, which was extracted to the Na_2CO_3-fusion fraction, could not move out of the rock. The ratios of Ra in both fractions were calculated. It was found that the ratios are extremely higher in DVDP 13 and 14 core samples than those in the samples of other four salt lakes. These facts give us a clue to estimate the time of deposition.

The ^{226}Ra content will increase naturally with increasing age of deposits because the equilibrium between ^{230}Th and ^{226}Ra should be established in 10^4 years. Thereafter, the amount of ^{226}Ra should decrease with the half-life of 7.5×10^4 year (the half-life of ^{230}Th). The autors' calculation shows that 10^6 years are required before the equilibrium is reached between ^{238}U and ^{230}Th. It may be said on the basis of

Table 8. *Comparison of U, Th and Ra in core and deposits.*

Deposits	Ra in $HClO_4$-fracion $\times 10^{-12}$ Ci	$\dfrac{\text{Ra in } HClO_4}{\text{Ra in } Na_2CO_3}$	Average contents U (ppm)	Th (ppm)	Th/U
Lake Stinear	0.13–0.63	0.37	0.15	4.94	32.43
Deep Lake	0.40–0.60	0.43	0.27	5.33	19.74
Triple Lake	0.38–0.76	0.74	0.81	4.32	5.33
Oval Lake	0.35–1.35	0.75	Not determined*		—
DVDP 13 core					
A layer	1.59–5.18	1.61	1.58	14.3	0.91
B layer	1.23–1.69	1.36	1.41	34.0	24.11
C layer	2.30–7.16	2.40	1.44	18.5	12.85
Basement rock	0.95–2.01	1.27	0.60	7.3	12.17
DVDP 14 core	0.87–2.35	1.39	1.16	10.11	8.72

*Shortage of sample.

these results that the age of deposits in the Vestfold Hills is younger than that in the Dry Valleys. The deposit of Stinear Lake in the Vestfold Hills is the youngest among them.

4. Results of Activation Analysis

4.1. Behavior of minor elements

The results of activation analysis are presented in Tables 9, 10 and 11. The vertical distribution of minor elements, radioactive elements such as U, Th and Ra, and SO_4^{2-}/Cl^- are shown in Fig. 1. The role of Fe, Al, Mn and rare earth elements in the deposits should be discussed in both oxidizing and reducing environments. The chemical behaviors of these elements are shown in Table 12, by contrasting

Table 9. Results of activation analyses of DVDP 13 core.

	Depth (cm)	Ca (%)	Mg (%)	Fe (%)	Al (%)	Na (%)	K (%)	Rb (ppm)	V (ppm)	Sc (ppm)	Cr (ppm)
	97.7	4.66	2.83	1.91	4.00	1.04	0.79	0	81.9	10.4	80.2
	156	2.66	3.06	3.19	4.48	1.10	1.02	0	119.6	15.2	100.1
	258	5.09	2.36	2.66	3.65	0.82	0.65	13	42.5	13.6	76.7
A	306	3.81	2.66	5.20	4.80	1.22	0.74	68	175.8	23.4	144.4
	604	2.24	2.45	2.52	3.76	0.88	0.60	52	84.1	14.3	72.1
	700	4.36	1.51	1.74	5.25	1.37	1.00	12	106.6	11.2	53.3
	792.5	3.27	2.61	3.07	8.03	1.28	0.87	21	126.5	16.5	81.5
	817	2.42	2.39	2.23	6.43	1.96	1.61	80	69.9	10.6	50.6
B	898	2.66	1.60	2.02	5.61	1.49	1.13	77	52.3	8.96	52.4
	918	1.93	2.20	1.37	5.48	1.87	1.24	0	55.6	6.43	35.4
	1005	4.72	1.91	3.17	4.30	1.12	0.84	25	95.2	16.8	104.7
C	1102	2.97	2.61	3.41	5.16	1.44	1.07	50	101.7	17.7	110.8
	1139	5.03	2.49	3.31	4.96	1.43	0.93	30	101.6	16.0	90.4
	1200	4.18	2.49	1.30	5.57	1.63	1.42	0	78.5	11.6	60.8

	Depth (cm)	Co (ppm)	Mn (ppm)	Ba (ppm)	Ce (ppm)	Eu (ppm)	Tb (ppm)	Yb (ppm)	Lu (ppm)	Hf (ppm)	Ta (ppm)
	97.7	10.2	500	60.0	38.5	0.32	0.31	0.52	0.20	2.35	0.22
	156	14.6	597	327.2	96.5	—	0.36	1.29	0.17	3.10	—
	258	15.2	483	320.1	26.5	0.85	0.02	—	0.17	2.38	0.23
A	306	25.3	927	518.4	90.6	1.19	0.34	1.41	0.45	6.20	0.44
	604	14.9	508	389.9	29.0	0.29	0.22	0.82	0.29	1.82	0.14
	700	11.3	609	97.8	49.4	—	0.14	0.88	0.22	1.58	—
	792.5	18.6	582	304.4	46.8	0.85	0.11	0.77	0.26	2.49	0.47
	817	28.6	500	803.8	46.6	1.30	0.28	0.86	0.13	2.67	0.40
B	898	11.1	445	397.2	39.0	0.89	0.21	0.47	0.14	3.70	0.25
	918	10.1	434	568.7	48.4	—	0.32	1.08	0.20	0.39	0.27
	1005	28.6	837	502.9	66.8	0.25	0.13	0.73	0.20	2.02	0.26
C	1102	20.7	647	451.3	46.2	0.53	0.37	0.98	0.25	2.82	0.31
	1139	19.0	703	423.6	53.8	1.13	0.30	1.44	0.27	2.56	0.26
	1200	5.5	787	173.9	75.4	—	0.24	—	0.22	—	—

Table 10. Results of activation analyses of the deposits of Vestfold Hill's salt lakes.

Sample location		Ca (%)	Mg (%)	Al (%)	Na (%)	K (%)	V (ppm)	Mn (ppm)	Ti (%)	Fe (%)	Rb (ppm)	Sc (ppm)
Oval Lake	A0cm	2.06	1.98	6.81	3.90	3.02	22.0	174	0.15	1.27	152	2.87
	B0	2.85	3.84	7.36	3.95	1.29	132	590	0.56	5.71	77	16.3
	20	2.54	2.57	5.16	2.89	1.92	69.4	599	0.47	4.89	—	16.7
	40	2.30	3.80	6.74	2.80	1.57	136	743	0.84	6.60	47	19.9
	50	3.27	3.49	7.91	3.04	2.05	75.7	701	0.54	4.68	62	15.2
	51	2.78	2.21	3.61	4.06	0.94	104	369	0.28	3.86	87	7.56
	71	2.42	1.46	3.09	3.81	0.90	61.6	263	0.34	2.87	0	7.02
	86	2.72	1.69	4.01	5.46	1.20	94.0	398	0.48	4.55	29	8.18
	106	1.57	1.51	3.23	11.3	—	31.5	323	0.35	2.23	0	6.99
	116	—	1.04	1.77	15.0	0.34	39.4	256	—	1.34	32	3.39
	226	2.72	2.23	4.51	11.2	0.98	73.6	353	0.28	3.05	0	6.76
Deep Lake	1m	3.21	3.02	5.88	1.95	0.74	110	1000	0.26	5.23	—	18.8
	32	2.24	2.95	5.86	5.20	—	102	617	0.39	6.10	—	13.5
	33	1.70	1.55	4.95	14.3	—	44.5	201	0.19	3.14	0	8.07
Stinear Lake	10m	2.18	0.92	2.44	15.2	—	38.5	225	0.19	1.86	0	5.29
	13.5	1.57	0.86	1.63	19.0	—	24.9	171	0.11	0.96	0	2.81
	18	2.48	3.23	5.82	4.68	1.76	105	580	0.39	6.71	0	16.2
Triple Lake	No. 1	1.82	3.66	6.40	3.96	1.79	155	742	0.58	3.48	—	13.0
	2	4.78	4.37	3.11	2.97	1.96	67.7	796	0.48	5.05	0	18.9
	3-1	3.15	2.95	6.79	2.74	1.86	107	710	0.39	6.04	0	18.1
	3-2	6.12	2.08	4.79	2.83	1.25	92.5	509	0.51	3.86	69	9.22
	3-3	2.30	1.28	1.69	7.96	—	43.0	175	0.16	1.62	0	4.03
	4	2.18	2.51	3.87	4.14	1.27	116	313	0.31	3.68	0	9.27

Sample location		Cr (ppm)	Co (ppm)	Ba (ppm)	Sb (ppm)	Cs (ppm)	Ce (ppm)	Eu (ppm)	Tb (ppm)	Yb (ppm)	Lu (ppm)	Hf (ppm)	Ta (ppm)
Oval Lake	A0cm	9.77	3.03	1543	—	0.60	116	1.73	0.66	1.46	0.24	3.30	0.35
	B0	100	20.3	1359	—	—	105	3.34	0.37	3.74	0.55	6.17	0.53
	20	88.5	20.9	1262	2.24	—	91.1	3.35	0.38	2.37	0.35	4.37	0.21
	40	109	21.8	1027	—	0.51	83.6	3.18	0.29	2.00	0.44	5.58	—
	50	69.2	17.2	1166	—	1.51	89.6	3.59	0.26	1.30	0.33	2.59	0.17
	51	62.3	17.9	833	—	—	73.5	0.57	0.36	1.14	0.54	3.96	—
	71	62.2	9.95	—	—	0.87	68.3	3.00	0.25	0.98	—	2.51	0.22
	86	42.9	12.2	489	—	0.27	76.2	2.58	0.34	0.81	—	4.64	0.08
	106	56.0	9.74	855	—	0.20	49.1	1.50	0.14	0.65	0.73	2.01	0.05
	116	32.5	5.85	—	—	1.16	33.8	5.92	0.09	0.29	1.74	1.69	0.11
	226	44.3	12.2	468	—	0.36	56.7	2.32	0.12	0.90	0.61	2.14	—
Deep Lake	1m	121	23.2	1296	—	—	52.5	1.79	0.22	2.83	—	3.66	—
	32	192	17.1	—	—	1.02	166	2.78	0.32	2.07	—	3.71	0.35
	33	79.1	15.2	—	—	—	60.9	2.10	0.22	1.52	—	2.65	0.19
Stinear Lake	10m	46.1	9.38	—	—	0.83	34.0	1.01	0.14	0.72	—	1.99	0.19
	13.5	19.6	4.23	—	—	0.18	15.3	0.42	0.05	—	—	1.31	—
	18	176	33.3	—	—	1.71	122	2.60	0.38	2.32	3.23	7.02	0.61
Triple Lake	No. 1	119	14.0	1103	—	—	53.2	2.11	0.37	1.55	0.80	6.47	0.10
	2	95.6	15.0	724	—	—	115	2.15	0.57	—	—	3.30	—
	3-1	103	22.3	490	—	—	83.8	3.56	0.34	1.68	—	2.85	—
	3-2	58.9	17.9	1266	—	—	74.7	3.01	0.09	0.89	—	5.56	0.30
	3-3	33.1	6.90	—	—	1.39	36.8	1.33	0.09	1.66	—	1.21	—
	4	64.0	13.5	947	—	—	79.5	2.13	0.17	1.00	—	3.14	—

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Table 11. Results of activation analyses of DVDP 14 core.

Sampling depth (cm)	Fe (%)	Rb (ppm)	Sc (ppm)	Cr (ppm)	Co (ppm)	Ba (ppm)	Sb (ppm)	Cs (ppm)	Ce (ppm)	Eu (ppm)	Tb (ppm)	Yb (ppm)	Lu (ppm)	Hf (ppm)	Ta (ppm)
25- 28	4.20	75	19.7	104	23.0	738	0.30	2.05	66.2	0.99	0.40	2.30	0.28	4.41	2.20
60- 65	4.85	34	25.2	115	26.8	680	0.52	4.73	176	1.00	0.47	1.95	0.37	3.12	0.78
100- 105	6.03	42	34.6	162	37.3	388	—	0.97	29.0	0.41	0.18	1.17	—	3.21	0.51
150- 155	5.13	65	26.4	62	32.3	712	—	2.83	13.3	0.42	0.21	1.31	0.30	2.34	0.68
200 -205	5.15	39	32.3	170	35.6	576	—	0.45	28.6	2.99	0.36	1.96	0.35	2.91	1.37
220- 225	4.43	72	18.3	78	21.5	722	0.68	3.55	21.7	1.72	0.84	2.98	0.36	5.54	2.46
300- 305	4.55	58	18.5	77	21.4	803	0.59	8.22	52.9	0.88	0.52	2.75	0.50	5.33	2.54
373- 378	4.32	42	23.2	107	23.2	337	0.69	3.21	44.4	1.52	0.39	1.77	0.36	5.21	0.88
420- 425	4.33	70	23.6	98	22.0	1101	0.98	7.93	39.9	1.22	0.37	1.77	0.23	4.99	0.53
461- 466	4.88	102	19.8	76	21.1	941	0.52	4.09	60.6	1.25	0.54	1.27	0.45	5.09	3.37
550- 555	4.58	68	20.4	86	22.5	741	0.60	1.82	54.4	1.34	0.32	3.40	0.38	6.74	1.89
695- 700	4.01	74	21.2	102	21.4	1008	0.28	1.73	52.2	1.30	0.30	2.27	0.33	5.40	1.54
700- 705	4.49	76	19.8	80	46.8	908	—	1.71	22.9	1.18	0.48	1.96	0.37	5.65	2.49
806- 811	4.20	106	21.4	9	4.08	3627	0.18	1.69	568	2.91	1.53	3.63	0.66	15.23	2.26
920- 925	4.72	44	26.0	133	27.6	353	—	1.20	24.6	1.24	0.22	2.00	0.15	3.58	0.98
970- 975	5.13	92	18.4	75	23.5	775	1.42	8.92	78.3	1.37	0.55	2.60	0.38	4.62	2.66
1040-1045	4.51	52	23.8	116	26.3	799	1.02	2.08	45.0	0.98	0.48	1.73	0.17	3.10	1.10
1110-1115	4.36	66	21.8	90	25.5	567	—	3.85	39.3	0.89	0.55	2.69	0.35	7.32	1.80
1190-1195	4.47	86	18.8	76	22.7	655	—	4.49	53.2	1.96	0.54	6.63	0.24	5.60	22.9
1210-1215	3.76	98	19.6	87	22.5	567	—	2.19	39.6	1.44	0.39	2.30	0.16	3.80	1.13
1290-1295	3.63	80	19.1	84	21.7	826	—	3.35	36.6	0.90	0.32	2.49	0.21	2.82	1.16
1357-1262	—	34	—	69	16.6	—	—	2.95	42.5	N.D.	N.D.	1.95	N.D.	3.59	N.D.
1440-1445	4.11	44	24.6	125	25.6	770	—	2.71	32.2	0.70	0.26	2.01	0.40	3.05	—
1540-1545	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
1580-1585	3.11	50	15.4	82	17.3	700	—	3.79	32.1	1.01	0.27	1.25	0.13	3.09	0.53
1647-1652	3.34	70	17.9	107	19.9	548	—	1.53	38.7	0.96	0.32	0.86	0.20	3.67	0.29
1946-1951	3.35	42	16.3	70	18.7	210	2.23	24.3	53.4	1.28	0.36	2.06	0.24	3.07	0.78
2040-2050	3.28	54	15.5	79	17.9	260	—	6.53	35.5	0.87	0.24	2.40	0.13	2.73	0.57
2145-2150	3.28	56	10.8	40	14.7	623	6.85	67.5	54.8	1.06	0.42	2.89	0.33	5.71	1.35
2220-2225	3.48	98	11.8	43	13.3	601	1.22	7.08	57.9	0.85	0.52	2.54	0.43	5.24	2.60
2340-2345	4.50	56	16.4	103	21.6	570	0.26	10.2	44.9	0.87	0.46	3.89	0.66	3.73	2.41
2500-2505	4.60	102	15.3	99	22.8	204	—	9.35	51.8	0.70	0.51	1.13	0.43	3.80	1.83
2600-2606	3.67	52	14.2	83	17.7	300	1.40	5.07	64.4	1.53	0.35	1.82	0.49	5.18	2.83
2640-2645	3.87	44	19.1	121	21.8	496	5.31	2.62	43.2	0.76	0.43	0.88	0.18	4.15	2.51
2738-2743	5.02	49	17.9	93	23.5	411	—	7.32	55.0	2.28	0.46	1.55	0.35	3.06	2.36
2781-2786	3.60	76	14.5	92	20.5	1078	1.62	6.10	68.6	1.10	0.42	1.65	0.24	3.67	1.10

N.D.: not detected.
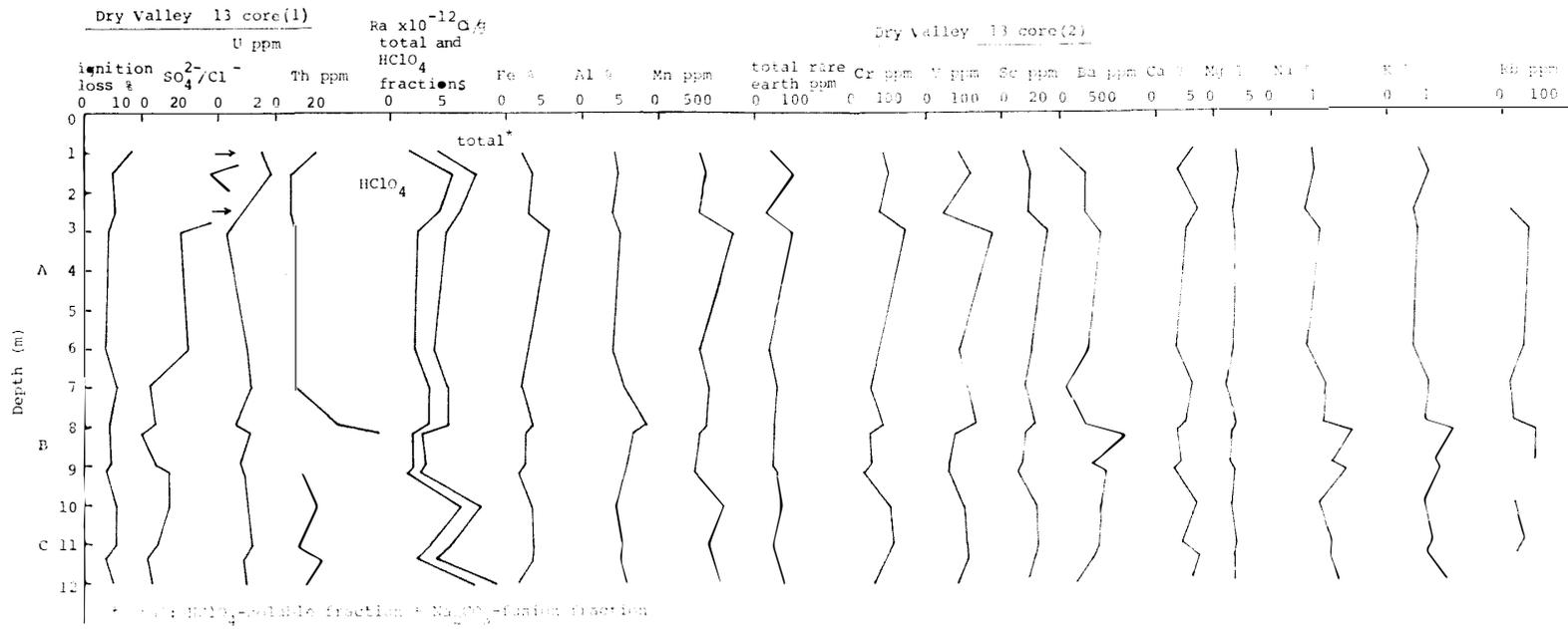
Fig. 1.   The vertical distribution of minor elements and radioactive elements in DVDP 13 core.

Table 12.   *The difference of chemical behaviors of some ions in oxidizing and reducing environments.*

Element	Oxidizing environment		Reducing environment
U	VI $UO_2(CO_3)_3{}^{4-}$ Soluble complex	$\xrightleftharpoons{}$ O_2 in water	III, IV Insoluble hydroxide
Th	IV ——————— Insoluble $Th(OH)_4$ depend upon pH (>5)	—— IV	
Ra	II ——————— Carrier-free, insoluble $RaSO_4$, $RaCo_3$ etc.	—— II	
Fe	III Insoluble $Fe(OH)_3$	easily $\xrightleftharpoons{}$	II Insoluble FeS
Mn	IIII, IV Insoluble hydroxide	easily $\xrightleftharpoons{}$ O_2 in water	II Soluble salts
Al	III ——————— Insoluble $Al(OH)_3$ depend upon pH	——— III	
S	VI $SO_4{}^{2-}$	$\xrightleftharpoons{}$ O_2 in water	II S^{2-}
Cl	V, VII $ClO_3{}^-$ $ClO_4{}^-$	easily $\xrightleftharpoons{}$ not easily	I Cl^-

the difference between oxidizing and reducing environments.   Uranium usually takes the valency state of VI in an oxidizing environment which is easily soluble in water as uranyl carbonate complex or organo-uranyl complex ions, while in a reducing environment the valency of uranium changes to III or IV.   In this valency state U tends to precipitate as a hydroxide or to be adsorbed on organic matter (Kolodny *et al.,* 1973).   The valency of Th is always IV in both environments and Th easily gives hydroxide at the pH-value above 3.5.   The chemical state of [226]Ra formed as a decay product is intrinsically in a carrier free state and the solubility products of its insoluble compounds such as carbonate and sulfate are fairly small.   However, the concentrations of [226]Ra in carrier-free state can not exceed the solubility products of these compounds.   If Ra was found in the deposits, it must have been coprecipitated together with the precipitate of other elements.

Iron takes the valency of III in an oxidizing environment and precipitates as $Fe(OH)_3$.   It takes the valency of II in a reducing environment and precipitates as FeS.   On the contrary, aluminium has always the valency of III in both environments, and hydroxide is formed in the pH range of 3–7, but it starts to dissolve at the pH-value above 8.   On the other hand, the precipitate of $Fe(OH)_3$, though it precipitates at higher pH-value than 3, does not dissolve at higher pH-value than 8.

Manganese becomes Mn (II) in a reducing environment and the compounds of Mn (II) generally have high solubility in water.   But in an oxidizing environment, Mn precipitates as Mn (II, III) oxide hydrate.   Thus, the geochemical behaviors of Fe and Mn are quite similar to each other and Al behaves similarly in some respects with these elements.   The main difference among their chemical behaviors is due to the range of pH-value affecting the precipitation.   This similarity of chemical behavior suggests that precipitates of Fe, Mn and Al would be an important coprecipitant to concentrate U, Th or Ra in the sediments.

4.2. Discussion

Ignition loss is a measure to estimate the amount of organic matters, hydroxides and carbonates.   These materials are decomposed easily on heating and result in large ignition loss.   The ratio of SO_4^{2-}/Cl^- was calculated, because it will be a good measure to judge the environment in which the deposits are formed.   Sulfur forms SO_4^{2-} ions in an oxidizing environment, but in a reducing environment it occurs as S^{2-} ions.   Chlorine is present as Cl^- in a reducing environment and in a moderately oxidizing environment.   It can form ClO_3^- and ClO_4^- in an extremely strong oxidizing environment, but it is sometimes difficult to keep this state for a long period. There are two causes to decrease the ratio of SO_4^{2-}/Cl^-; one is the reduction of SO_4^{2-} into S^{2-} which usually occurs in a reducing environment, and the other is the remarkable increase of Cl^-, which is mainly due to invasion of sea water.   If the invasion occurred, it would cause a marked decrease in the SO_4^{2-}/Cl^- ratio.

If U was present in the valency of VI, it would tend to be leached away in a
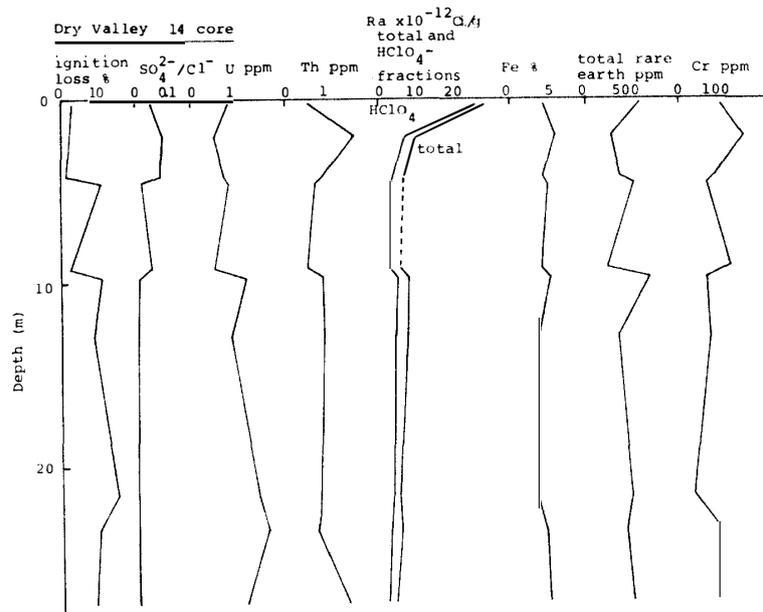
Fig. 2.   The vertical distribution of minor elements and radioactive elements in DVDP 14 core.
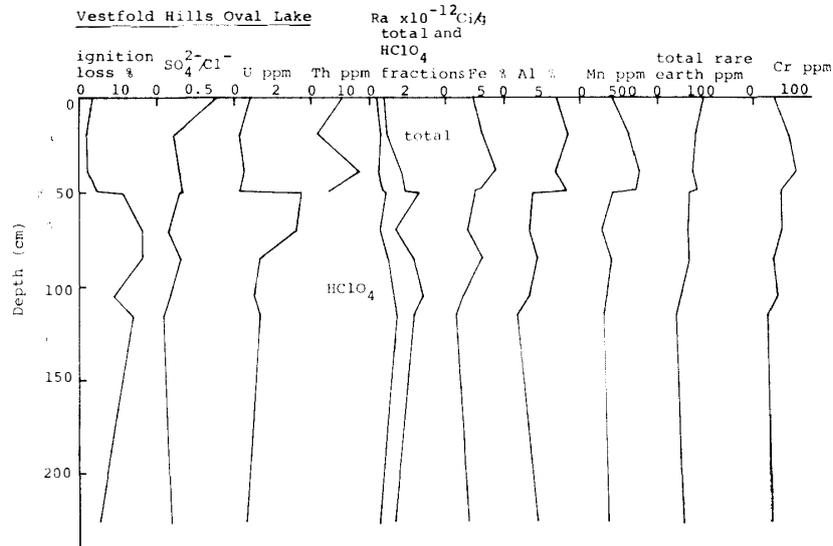
Fig. 3. The vertical distribution of minor elements and radioactive elements in Oval Lake of the Vestfold Hills.

form of carbonate complex ion. Thorium and iron easily precipitate as hydroxides in the same environment. On the other hand, Al tends to be slightly dissolved in a form of aluminate ion. Geochemically, U and Ra often behave similarly under certain circumstances, but the concentration of U and Th in the deposit varied in the opposite direction in most cases as shown in Figs. 1, 2 and 3. The concentration of Fe and U changed either similarly or oppositely. The change in the opposite direction appeared more frequently except in the three samples of DVDP 13 core, which were collected near the ground surface.

With the increasing U content the ignition loss tends to increase, while the SO_4^{2-}/Cl^- ratio tends to decrease except in the case of the above three samples. Therefore, more U would be precipitated in a reducing environment than in an oxidizing environment. These results suggest that the reducing environment would have prevailed during the period of deposition. The exemption in this discussion of three samples collected near the ground surface may be justified, because an oxidizing environment in recent years is assumed to affect these samples.

The total content of rare earth elements in DVDP 14 core changes oppositely to those of Fe and Al. This is quite different from the results of the DVDP 13 core, in which the contents of Cr and total rare earth elements changed similarly to those of Fe and Al. These results suggest that regardless of the environment the valency of rare earth elements was always III, in which state these elements easily form hydroxides.

The concentration of U and Th changes always oppositely in the DVDP 13 and 14 cores and in the deposits of the Vestfold Hills. Similar tendency is also

found in the samples at Oval Lake, which is shown in Fig. 3. However, in the deposits of Oval Lake the ratio of the Ra content in the $HClO_4$-soluble fraction to that in the Na_2CO_3-fusion fraction was much smaller than those in the DVDP 13 and 14 cores. This fact means that the age of deposits in Oval Lake is much younger than those of the DVDP 13 and 14 cores, as stated before. The statement mentioned above is based on a small number of data obtained by this work. For making further discussion, results of more detailed analysis simultaneously applying a plenty of geological data are urgently required.

5. Concluding Remarks

In summary, the authors would mention the following points.

I) Geochemical behaviors of U and Th are clearly different as in the case of other areas. Uranium precipitates in a reducing environment only, but thorium can precipitate in both reducing and oxidizing environments.

II) The ratio of SO_4^{2-}/Cl^- is a good measure to know an oxidizing or a reducing environment and the ignition loss is also a good indication of the presence of organic matters or volatile compounds, which may have a close relation to the formation of the deposits.

III) The value of SO_4^{2-}/Cl^- ratio in the deposits suggests that the invasion of sea water occurred in both the Dry Valleys and the Vestfold Hills.

IV) The age of deposits can be estimated by the ratio of Ra content in the $HClO_4$-soluble fraction to that in the Na_2CO_3-fusion fraction. Ra in the $HClO_4$-soluble fraction is closely related to Th and also to the water environment in which the concentrating effect of other elements such as Fe, Al and Mn is present.

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