Chinese Journal of Polar Science, Vol. 12, No. 1, 21 - 30, June 2001

Geochemistry of rare-earth elements and its significance in the study of climatic and environmental change in Barrow, Arctic Alaska

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Received April 28, 2001

Abstract Geochemical characteristics of rare-earth elements (REE) and sedimentary features were studied in the borehole 96-7-1 from Elson Lagoon in Barrow, Arctic Alaska. The results show that total contents of REE (ΣREE) are lower, suggesting that physical weathering is dominate, therefore, concentrations of rare-earth elements are lower in the paleosediment environment. The chondrite-normalized distribution patterns of REEs are characterized by light REE (LREE) enrichment and Eu-depletion with the terrestrial sedimentary rock as the parent materials. In comparison with the borecore AB-67 in Elson Lagoon, the main conclusions for climatic and environmental changes are similar: before 1740 A. D., it was cold and dry with terrestrial properties, but the comparatively warming around 1400 A. D. and 1550 A. D.; after 1740 A. D., it became warming, or markedly after 1821 A. D.; but it was cold around 1890 A. D. From 1904 A. D., it got warm again, but it was relatively cold around 1971 A. D..

Key words Arctic, rare-earth elements, climate, sedimentary facies.

1 Introduction

Researches on geochemistry, especially, on rare-earth elements are few in Arctic lakes. The abundance of rare-earth elements in any sediment environment of Antarctica has been studied (Wang and Zhao 1989; Wang 1993; Yu *et al*. 1993). In recent years, geochemical investigations dealing with global changes, greenhouse and anthropogenic effects in high-latitude lakes have been increased (Cornnel 1986; Engstrom *et al*. 1990; Yang *et al*. 1996, 1997). They play important roles in paleolimnology, global and environmental changes of Holocene. Arctic, as one of the two cold sources on earth, exerts an effect on the pole-to-equator energy balances and circulation patterns that control atmosphere in turn. We examine in this paper the record of 96-7-1 sediment core from Elson Lagoon in Barrow with chemical elements assemblages as an indicator for reconstructing the climatic and environmental history and for predicting a tendency of future environmental changes.

The Barrow is located on the lowing Arctic Coastal Plain in the northeast Alaska (71°20′N and 156°40′W), facing the Chukchi Sea to the west and the Beaufort Sea to the North (Fig. 1). The climate is extremely cold in Barrow of Alaska. The mean annual temperature is − 12.4 ℃. The summer and winter mean temperatures are 2 ℃ and − 29 ℃ respectively. The mean annual precipitation is less than 250 mm. Entering into Elson Lagoon, the main rivers are short and discontinuous, they are Central Mar. Sl (the length is about 6.2 km), Ikpik Sl. (7.0 km), Mayoeak R. (7.3 km) respectively. The runoff is appeared from melting water of snow and ice and from season thawing layers of permafrost during summer.

Under the cooperative agreement between the Chinese Academy of Sciences and North Slope Borough Alaska U.S. Dr. Zhang Qingsong and Yang Weili made an observation in this area from May 25 to June 25 1996.

2 Method and materials

The 96-7-1 borehole was drilled by a piston corer in 2.4 m deep water, through 1.5 m thick of ice, 2 km away from the coast (71°20.2′N, 156°32.4′W) on Elson Lagoon (Fig. 1). The length of the sediment core was 71 cm which was sliced into 1 cm sections.

Rare-earth elements were measured by neutron activation analysis (INAA) in Ge (Li) detector-mutichannel and analyzer-personal computer system (Mao and Chai 1994).

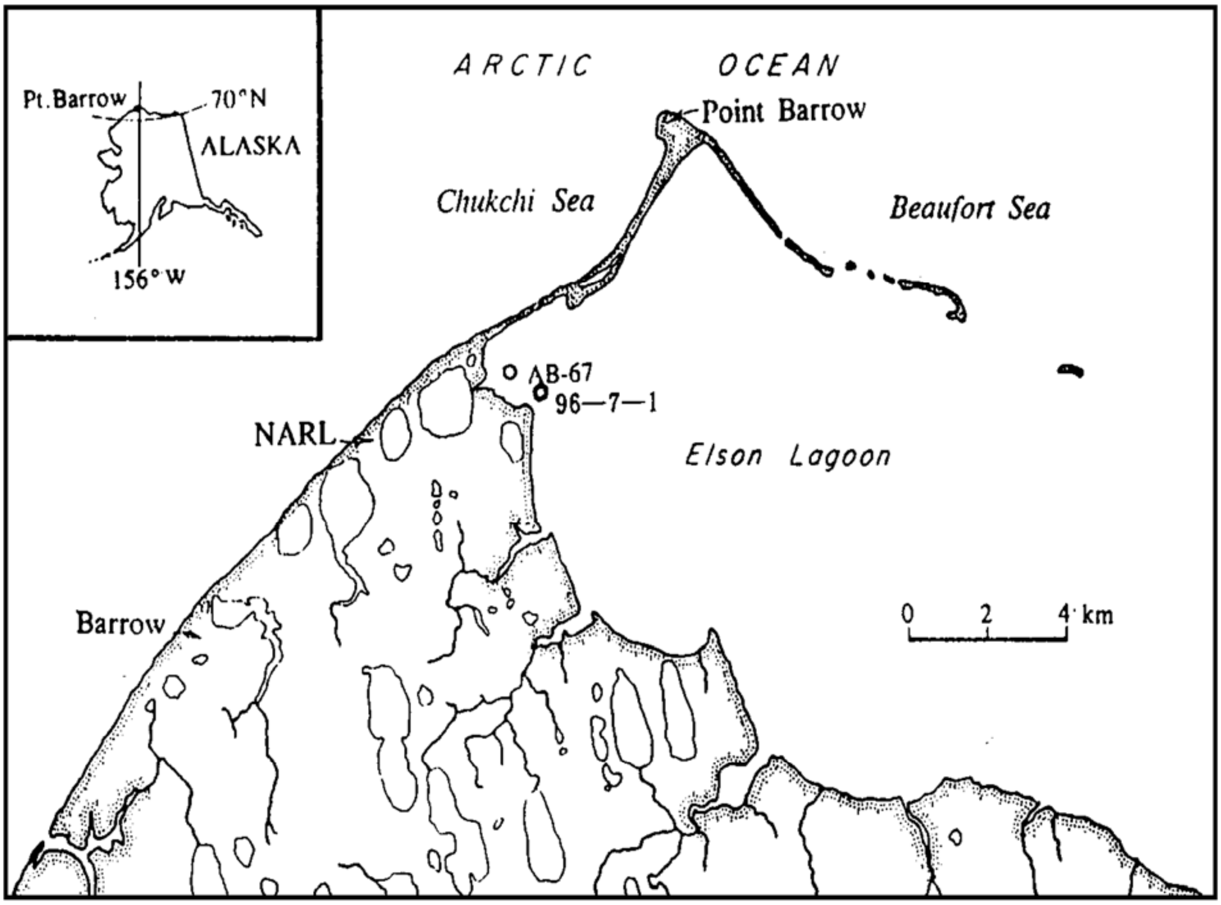

Fig. 1. Map showing 96-7-1 core site in Elson Lagoon in Barrow, Alaska.

To obtain depositional rate of the borecore 96-7-1 and to calculate the age of different depths in the borecore 96-7-1, the ^{210}Pb radiation method was used. The results are shown in Table 1. It can be seen from the table that the ^{210}Pb concentration of the lowest two samples (16 - 17 cm and 19 - 20 cm) are both 1.11 dpm/g, which reach to a balanced condition without any surplus value of ^{210}Pb. According to these values, the mean depositional rare is calculated to be 1.2 mm/a, the error for the age is ±8 a (Xia *et al*. 1983, Zhang *et al*. 1996).

Table 1. ^{210}Pb radiation concentration in the sediment core of Elson Lagoon, Barrow, Alaska

Number	Depth / cm	^{210}Pb concentration / $dpm \cdot g^{-1}$	Surplus ^{210}Pb / $dpm \cdot g^{-1}$
1	0 - 1	1.75 ±0.11	0.64
2	1 - 2	1.80 ±0.11	0.69
3	2 - 3	1.63 ±0.12	0.52
4	4 - 5	1.86 ±0.11	0.75
5	6 - 7	0.86 ±0.05	- 0.25
6	8 - 9	1.59 ±0.12	0.48
7	10 - 11	1.42 ±0.10	0.31
8	13 - 14	1.17 ±0.08	0.07
9	16 - 17	1.11 ±0.08	-
10	19 - 20	1.11 ±0.09	-

3 Results and Discussion

3.1 Depositional features

The borecore 96-7-1 in 71 cm can be divided in the three parts according to grain size distribution and sedimentary structures. The lower part (31 - 71 cm) mainly consists of grey-black fine sand and silt, and inside the sand layers the pebbles, individual shale and fragments are common. The mean grain size (Mz) is 2.93 φ, medium grain size (Md) 3.06 φ and most of them are around 0.1 - 0.125 mm. The sorting is between 0.62 φ and 1.48 φ, i.e., from moderately well sorted to poorly sorted. Dark silt with plant remains is found from 52 cm to 55 cm. The middle part (31 - 21 cm) is mainly composed of dark grey silt and sand. Mz is 3.06 φ, Md= 2.9 φ. The sorting is 3.32 which means to be very poorly sorted. The upper part (0 - 21 cm) mainly consists of blackish silt and clay. Mz is 5.6 φ, Md= 4 φ. The sorting is 5.49, being extremely poorly sorted. From 0 to 4 cm, laminated sediments are composed of mud and silt. The mud layers are formed during winter which lasts as long as 9 months in Arctic, whereas ice thickness is about 1.5 m or 1.6 m, the current is stable, suspended materials are deposited from water and the rate of sedimentation is low. The silt layers are formed in summer when the rate of water flow is changed from slow to fast, more coarse materials are deposited.

Through the above analysis, it can be seen that depositional dynamic condition is different between three sections of the 96-7-1. Materials transferring was stronger and transferring medium was rather simple when the lower part (31 - 71 cm) was deposited. The middle part (21 - 31 cm) is transitional where transgression seems to appear. The upper part (0 - 21 cm) was deposited under an unstable condition when the materials transferring was weaker but the transferring medium was more complicated. It can be inferred that water depth on the borecore 96-7-1 site was becoming deeper from about 31 cm.

3.2 *The geochemical characteristics of total rare-earth elements (ΣREE)*

The analytical results of rare-earth elements were shown in Table 2. Contents of rare-earth elements in the borehole 96-7-1 are lower as compared with the abundance in the earth crust and background values in modern sediments of the world. Total concentrations of rare-earth elements (ΣREE) in the each layer of the borehole are far from the abundance of the crust and the background values in modern sediments, especially, in the layers of 13, 31, 57 cm, ΣREE are 4 ~ 5 times lower than the background except ΣREE of the surface layer (120.3 mg/kg) is similar with Clark value of the abundance in the crust, showing the contents of rare-earth elements in the paleosediments of 96-7-1 borecore are at lower background level of the crust.

Pohob (1973) studied re-distribution of rare-earth elements in sedimentary phases (sea facies, terrestrial facies) under different climatic conditions (moist, dry). The differences among mobility of rare-earth elements from terrestrial rocks to oceans were small, which ranged from −0.3 to 0.2, the average was −0.05 in dry condition. But in moist condition, the mobility of rare-earth elements ranged from −0.1 to 0.6, the average was 0.25. The transportation of heavy REE (HREE) was intensified, e.g., the mobility of Yb was 4 times larger than in dry condition. Most of the rare-earth elements are bound up with suspended sediments (clay and silts), and they are carried and removed by the matter. Transportation of chemical elements depends not only on the properties of elements but also on the physical-chemical and environmental conditions in the surroundings. The energy of transportation is mainly from solar radiation. According to an experiment on chemical dynamics in a laboratory, temperature can affect the rate and direction of chemical reactions in the geochemical system. If temperature rises by ten degrees (10 ℃), then the rate of chemical reaction will increase to 1 time (Nanjing University 1979). It is obvious if climate is warming (temperature rises, precipitation increases), which will lead to strengthening of chemical weathering process in the catchment and multiplying of vegetation. Contents of clay and organic material are increased because contents of clay are in direct proportion with mean annual temperature (Kofuda 1981). Then rare-earth elements are easy to be leached and desorbed from parent rocks and minerals into solution. They will be adsorbed and carried by suspended particles and transported through rivers, deposited and accumulated in basins. The warmer it is, the higher contents of the elements in sediments are. Conversely, the contents are decreased, which is corresponded to environmental and climatic changes.

Total contents of REEs (ΣREE) in 96-7-1 core sediment fluctuated, increasing from lower part to upper part and reflecting climatic and environmental changes in Barrow. Under 31 cm, ΣREE are lower, the average is only 60 mg/kg which is the half of the Clark value of ΣREE in the crust, a quarter of the background value in modern sediments, indicating that it was obviously dry and cold, the mobility of rare-earth elements was too small to be transported from parent rocks. But at 55 cm, ΣREE is as high as 81.4 mg/kg, showing that a moist and warming period probably occurred. From 21 cm to 31 cm, the mean content of ΣREE is increased to 68.06 mg/kg, suggesting that it was transferred warmingly and moistly. From 0 to 21 cm concentrations of ΣREE fluctuated, the average is 95.75 mg/kg. But ΣREE is decreased to 46.9 mg/kg at 13 cm, relatively lower at 4 cm as well, corresponding to dry and cold periods. Up 9 cm layer, Σ

REE fluctuated a litter, it continued to become warm and moist in Barrow region.

3.3 Contents of rare-earth elements (REE)

3.3.1 Sequence of rare-earth elements in the core sediment

From Table 2, it can be seen that contents of rare-earth elements in 96-7-1 borecore follow the order of : Ce> La> Nd> Sm> Yb> Eu> Tb> Lu. The order is similar with the sequence of the abundance of the elements in the earth crust, illustrating that the concentrations of rare-earth elements in the core sediments are controlled by the abundance in the crust.

Table 2. Concentration of REE of 96-7-1 sediment core in Elson Lagoon in Barrow, Alaska(mg/kg)

Depth/cm	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu	ΣREE
96-71-1	36.7	54.1	30.6	5.76	1.28	0.343	2.78	0.366	131.9
96-71-2	32.3	47.1	23.0	5.11	1.17	0.496	2.55	0.368	112.1
96-71-3	27.8	39.6	26.6	4.36	0.939	0.296	2.01	0.287	101.9
96-71-4	25.4	38.6	25.2	4.18	0.898	0.429	2.11	0.258	97.1
96-71-5	27.0	44.3	22.0	4.19	0.962	0.476	2.76	0.289	102.0
96-71-6	26.2	45.1	17.5	3.92	0.978	0.792	2.35	0.290	97.1
96-71-7	24.6	44.7	17.8	3.92	1.14	0.543	3.06	0.335	96.1
96-71-8	27.2	51.3	24.1	4.2	1.15	0.591	2.49	0.322	111.4
96-71-9	31.0	48.5	28.1	4.89	1.14	0.371	2.57	0.346	116.9
96-71-10	20.3	37.7	21.6	3.25	0.840	0.669	1.94	0.301	86.6
96-71-11	16.9	32.1	15.3	2.54	0.752	0.595	1.87	0.243	70.3
96-71-13	11.9	22.1	8.18	1.86	0.62	0.452	1.58	0.241	46.9
96-71-15	17.5	30.3	18.2	2.59	0.785	0.517	2.19	0.267	72.3
96-71-17	26.5	44.9	19.30	3.71	0.827	0.596	1.81	0.277	97.9
96-71-19	19.6	35.5	17.4	2.83	0.782	0.515	1.90	0.231	78.8
96-71-21	14.9	33.6	10.6	2.41	0.683	0.304	1.46	0.175	64.1
96-71-23	15.8	27.8	15.9	2.25	0.697	0.531	1.34	0.202	64.5
96-71-25	15.8	27.0	13.7	2.59	0.734	0.600	1.57	0.283	62.3
96-71-27	17.5	32.0	13.5	2.63	0.797	0.406	1.69	0.214	68.7
96-71-29	19.8	38.8	18.6	3.00	0.892	0.665	1.76	0.182	83.7
96-71-31	15.1	22.0	13.4	2.21	0.623	0.400	0.894	0.153	54.8
96-71-33	16.3	27.0	12.6	2.42	0.693	0.430	1.15	0.170	60.8
96-71-35	15.5	25.2	12.30	2.24	0.573	0.418	1.19	0.184	57.6
96-71-37	16.5	27.2	16.5	2.52	0.643	0.442	0.878	0.154	64.8
96-71-39	15.8	25.4	11.4	2.31	0.632	0.467	1.08	0.094	57.2
96-71-41	17.2	27.6	15.2	2.42	0.68	0.476	1.23	0.207	65.0
96-71-43	14.8	27.0	11.7	2.08	0.615	0.386	1.14	0.158	57.9
96-71-45	13.7	23.7	10.9	1.97	0.679	0.312	1.15	0.142	52.6
96-71-47	14.9	25.7	12.8	2.10	0.600	0.316	0.971	0.122	57.5
96-71-49	14.6	28.8	12.4	2.06	0.638	0.467	1.09	0.185	60.2
96-71-51	16.0	28.5	12.5	2.16	0.689	0.291	1.32	0.137	61.6
96-71-53	22.0	29.4	16.2	3.24	0.887	0.719	1.74	0.266	74.5
96-71-55	22.3	31.4	20.0	4.06	1.02	0.433	1.96	0.260	81.4
96-71-57	12.2	20.6	9.70	2.25	0.585	0.212	0.933	0.111	46.6
96-71-59	14.6	24.3	11.2	2.64	0.624	0.278	1.07	0.155	54.9
96-71-61	15.6	26.7	13.5	2.94	0.766	0.282	1.26	0.150	61.2
96-71-63	15.0	25.5	12.5	2.73	0.720	0.317	1.24	0.159	58.2
96-71-65	13.9	23.2	10.7	2.45	0.692	0.316	1.32	0.150	52.7
96-71-67	16.8	27.8	12.7	2.94	0.757	0.418	2.00	0.267	63.7
96-71-69	16.4	29.4	12.8	3.13	0.762	0.278	1.65	0.194	64.6
96-71-71	20.5	36.7	16.3	3.33	0.781	0.356	1.18	0.155	79.3

3.3.2 Correlation between rare-earth elements and organic matter and clay

It is shown from Fig. 2 that the vertical distribution of rare-earth elements is basically the same as the distributions of organic matter and clay and silts (< 63 μm fraction) in terms of correlation coefficient of 0.90. The research on transportation mechanism shows that rare-earth elements are mostly carried by suspended sediments in an aquatic environment, adsorbed by organic matter and clay and transported with the particulate. Because of the same path followed in the case of transportation, accumulation and deposition, various rare-earth elements have the similar patterns of distributions in the core sediments.

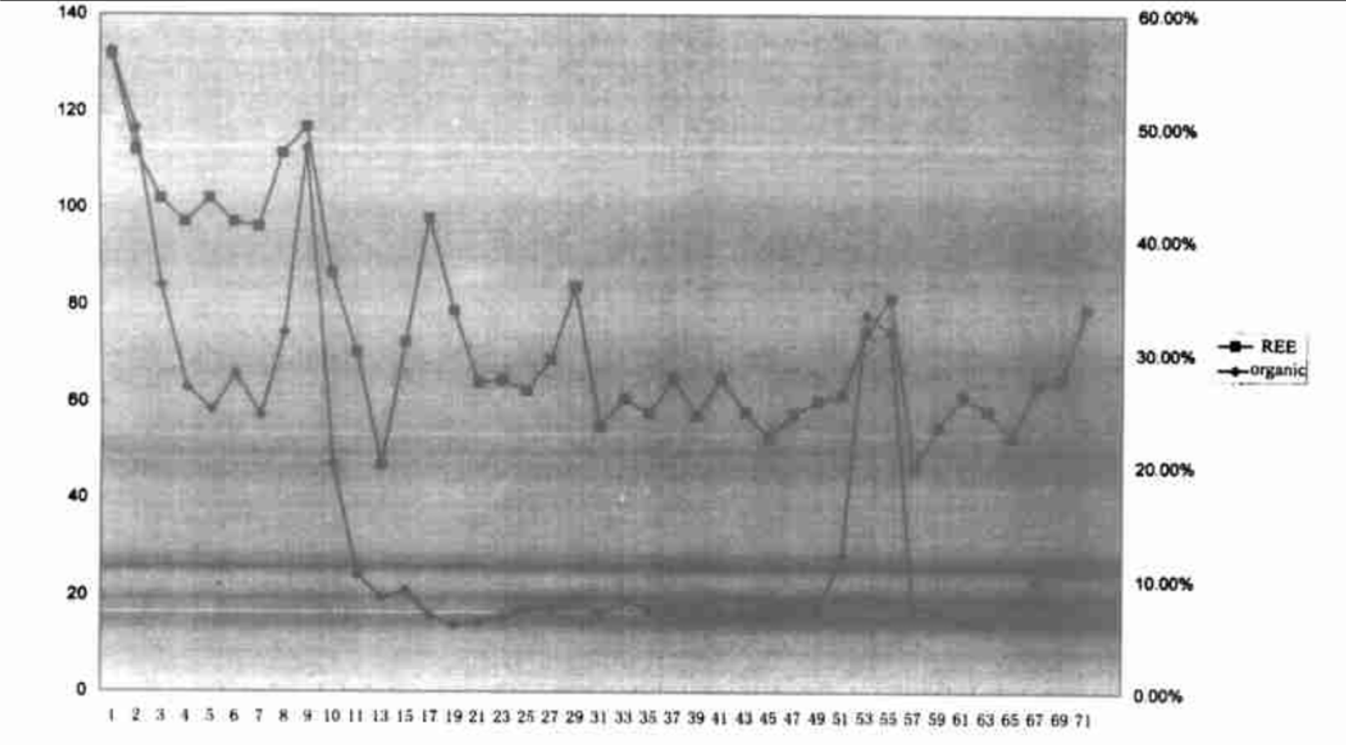

Fig. 2. Variation of ΣREE and < 63 μm fraction (silt and clay) in 96-7-1 sediment core.

3.4 Characteristics of normalized distribution patterns of rare-earth elements

Rare-earth elements La, Ce, Nd, Sm, Eu, Tb, Yb and Lu vary systematically in their chemical properties, therefore, they may exhibit smooth variations of the distributions in sediment samples. Normalization to chondrite meteorites on logarithmic scale of each rare-earth element in the samples compensates for element to element irregularities and reveals the relative variations among neighboring rare-earth elements as a result of geochemical diversities and origin.

The chondrite-normalized distribution patterns of REE in layers with peak and valley values of ΣREE in 96-7-1 sediment core from Elson Lagoon are compared with the chondrite-normalization of American Shale assemblage (Figs. 3 and 4). It is found that the distribution patterns in the layers are similar, the normalized curves tilt to right and belong to the pattern of enrichment of light rare-earth elements. The obliquity of relative contents is negative values, La-Eu section is steep, Eu-Lu section is even, the ration of La/Yb ranges from 4.87 to 9.47 and depletion factors of Eu (δEu) is from 0.73 to 1.12. All these indicate the patterns of rare-earth elements are characterized by light REE (LREE) enrichment and Eu-weakly depletion or normalization which are consistent with

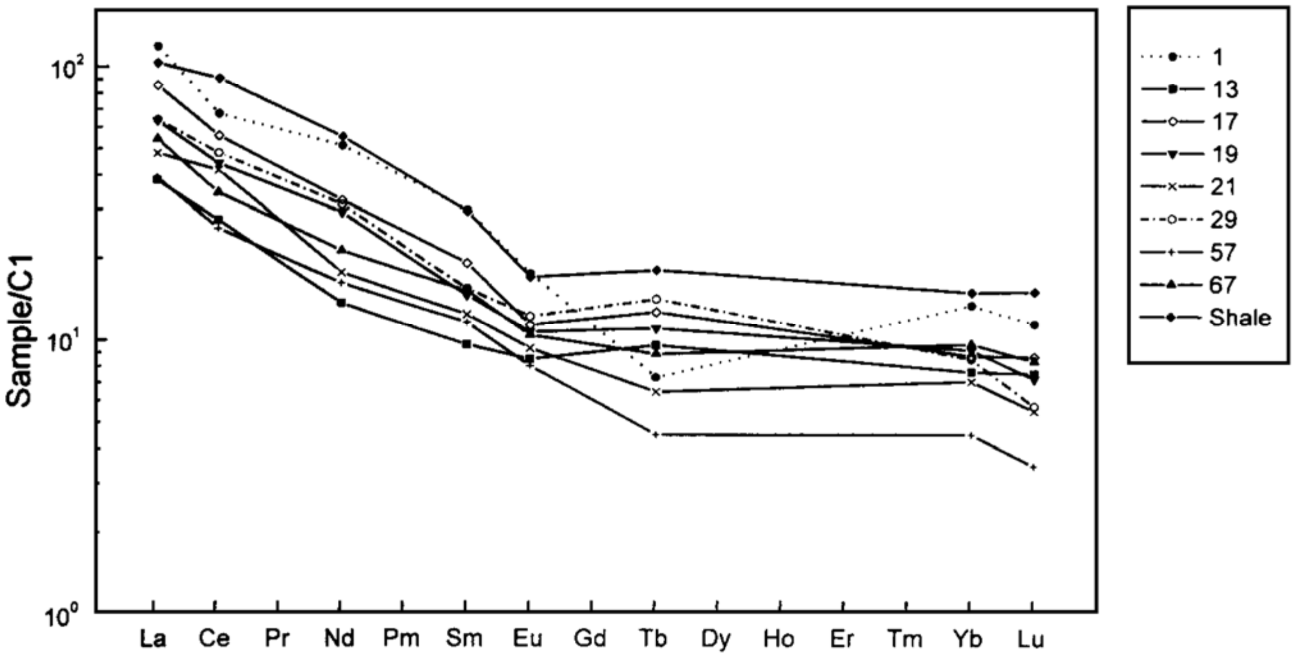

Fig. 3. Chondrite-normalized distribution patterns of REE through borecore 96-7-1.

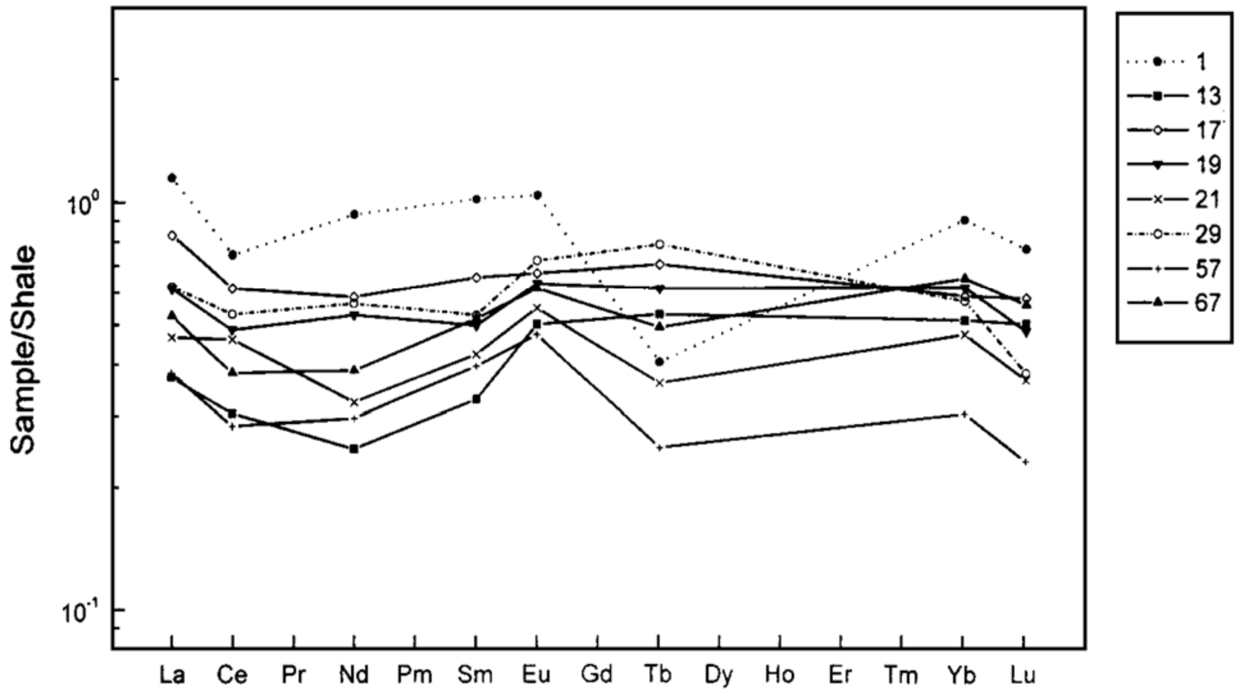

Fig. 4. American Shale-normalized distribution patterns of REE through borecore 96-7-1 in Elson Lagoon in Barrow, Alaska.

their parent materials of sedimentary rocks consisting of perennially frozen but unconsolidated sandy silt and gravels near to surface 2 – 10 m in Barrow and Skull Cliff geological units during Quaternary period 36000 B. P. It is shown that physical weathering is major, chemical and bio-chemical weathering processes are too faint to affect the distribution patterns due to the extreme coldness in Barrow, Arctic Alaska. In long time transportation, the rare-earth elements are mainly adsorbed by suspended sediments, chemical and biological transportation and diagenesis are relatively less. Therefore, the distribution patterns of the elements are different from those of oceanic deposits and carbonates, keeping the characteristics of distribution patterns of their primary terrestrial crust.

3.5 Geochemistry of rare-earth elements and its significance in study of environment change

According to the above-mentioned, Barrow is a background area; the distribution patterns of rare-earth elements keep the characteristics of the elements in their parent rocks in the catchment. The rare-earth elements can be taken as a geochemical indicator along with ^{210}Pb radiation and sedimentology dating to reconstruct paleoclimatic and environmental change history in Barrow (Fig. 5).

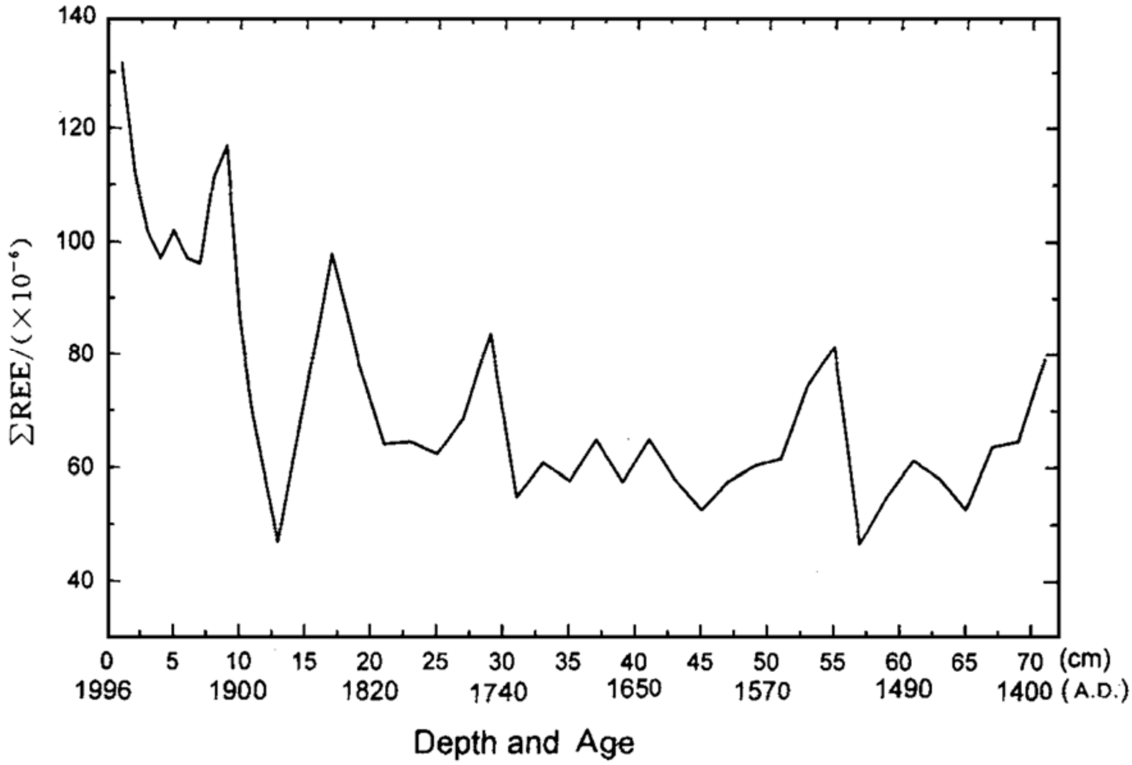

Fig. 5. Vertical distribution of REE through borecore 96-7-1.

3.5.1 below 31 cm (1880s, about 1740 A. D.)

Terrestrial environment with coarse detritus at the site of the borehole is evidenced that chondrite-normalized REE patterns are characterized by terrestrial distribution patterns with light REE enrichment and depleted Ce, δEu> 1 and Eu was close to the normalized pattern, heavy REE depletion, which may be distinguished from that of oceanic deposits, keeps the characteristics of the pattern of sediments as parent rocks. ΣREE is only averaged by 55.2 mg/kg, suggesting that it was comparatively dry and cold in the catchment with strong physical weathering and oxidation condition in the deposit basin. But ΣREE is up to 77.60 mg/kg at 53 – 55 cm layer (about 1540 A. D. or 1550 A. D.) responding to a relatively warming period.

3.5.2 21 – 31 cm (from 1740 A. D. to 1821 A. D.)

The mean concentration of ΣREE increases to 65.2 mg/kg, with contents varying from 46.26 mg/kg to 75.05 mg/kg. But the depletion of heavy rare-earth element Eu decreases to 0.83, suggesting that the environment changed from oxidation to anaerobic condition, Eu ion might be reduced from Eu^{3+} to Eu^{2+}, which causes a strengthening of the mobility of Eu. The strengthening of chemical weathering process and mobility of rare-earth elements correspond to warming and moistening in the environment.

3.5.3 0 - 21 cm (from 1821 A.D. to 1996 A.D.)

The mean concentration of ΣREE increases to 83.13 mg/kg, δEu is lower, being 0.78 and 0.73 respectively. Eu is depleted at large, indicating that the environment has further become moistening and warming. At 17 cm (about 1841 A.D.), ΣREE is 97.9 mg/kg, suggesting that a peak value occurred. It was clearly warming and continued to be warming after 1904 A.D.. However, climatic fluctuations also occurred in the duration. At 13 cm (about 1883 A.D.) and 3 cm (about 1970 A.D.), ΣREE decreased obviously and negative effect existed at the comparatively low temperature stages.

The vertical distribution of chemical elements in the sediment core 96-7-1 is very similar to that in the borecore AB-67 in the Elson Lagoon (Yang *et al*. 1996), which provides sensitive recorders of environmental changes. The paleoenvironmental and climatic changes in Barrow can be reconstructed by taking chemical elements as an indicator, which is similar to or may be comparative with circum-Arctic regions (Overpeck *et al*. 1997). Before 1740 A.D., it was comparatively cold with low sea level in Barrow, which is as same as that in Arctic in a period of the little Ice Age associated with the 17th to 18th century Maunder sunspots minimum period (Overpeck *et al*. 1997). In 1540 A.D. or 1550 A.D., it was more warming, which is similar with the records of Greenland Ice Core (Johnson 1970). Many sites around the Arctic were warming at some time between 1700 A.D. and 1820 A.D.. Barrow began to be warming in 1720 A.D.. After 1820 A.D., warming occurred accompanied with solar irradiant and low volcanic aerosol loading, which probably continued to influence Arctic climate. But the observed colder period was around 1888 A.D. when it was a serious cold winter, heave ice is seen in Arctic ocean and thick, heavy snow covered the Arctic land. The comparatively cold appeared during 1969 A.D. and 1970 A.D. (Overpeck *et al*. 1997, Caleb 1998).

4 Conclusion

(1) As shown in the study, the chemical elements in 96-7-1 borocore in Barrow are generally at the lower background levels.

(2) The chondrite-normalized distribution patterns of rare-earth elements (REE) in the borecore 96-7-1 are characterized by LREE enrichment and HREE weakly depletion, or normally they are consistent with sedimentary parent rocks, REE are mainly affected by machanical-physical processes in the transportation, and effects of chemical and biological transporlation and diagenesis are few. The distribution patterns of REE are different from oceanic deposits and carbonate, suggesting that the vertical distribution of ΣREE in the sediment core reflects strength of chemical weathering in the catchment responded to climatic changes regularity.

(3) Environmental and climatic changes reconstructed with rare-earth elements as an indicator are basically similar in a comparision with circum-Arctic regions.

Acknowledgments This research was supported by National Natural Science Foundation of China(No. 49971078) and Cooperation between North Slope Borough, Alaska, U.S. and Chinese Academy of Sciences, Beijing, China. We thank Dr. T. Albert and C. Brower for many helps in the observation in Barrow.

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