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ANOMALY OF FLUORINE IN A SEDIMENTARY SYSTEM, WESTERN ANTARCTIC OCEAN

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Abstract Fluorine content in bulk sediment and its pore water in Western Antarctic Ocean is 200~395 μg /g and 1.18~1.92 μg / ml respectively, far below the average reported previously in the world oceans (540 μg / g and 2.7μg / ml, respectively). This study also shows that the distribution of fluorine in the sediments of the area is mainly controlled by the chemical composition of the material from the surrounding islands, and the element seems to be mostly incorporated in the hornblende, thus the correlation between the element and the hornblende amount in the sediments can be expressed statistically as following: F=217+ln Vh. The low concentration of fluorine in the pore water is largely due to the weak weathering process on the islands and the precipitation of the element with calcium. It can be indicated well by the lower value of anion-exchangeable (HCO_3^-) F^- in the studied area, which is only about one tenth of that in Pacific Ocean and a quarter in South China sea and a half in the sea east of Zhejiang . In addition, the decomposition of the organic matter in the sediment will probabally provide fluorine to the pore water, which can be easily captured by the solid phase. Therefore, the possible mechanism of the element's transition and redistribution in the sedimentary system can be preliminarily described as:

$$F_{-Org} \xrightarrow{\text{Early diagenetic decomposition}} F_{-\text{pore water}} \xrightarrow{\text{Calcium compounds}} F_{-\text{solid phase}}$$

Key words fluorine, sediment, western Antarctic ocean.

1. Introduction

The abundant biomass in the Antarctic Ocean has inspired long-term biological and ecological researches. Although these researches involved the high content of fluorine in Antarctic Krill to some extent, the geochemical behavior of fluorine, which may have a great and sensitive influence on the ecosystem in the Antarctic Ocean, has not got the proper observation.

Having analysed florine contents in sediments and their pore water as well as sea water obtained during the First China Antarctic Ocean Expedition, compared F content with that of the sediments from other oceans and the original rocks, the authors found the geochemical anomaly of fluorine in the sedimentary system of the study area. Here some controlling factors concerned are discussed.

2. Materials and Methods

The samples were collected during the First Chinese. Antarctic Ocean Expedition from January to February, 1985; the locations were given in Fig. 1. The surface sediments, upper-10cm thick, were taken by means of grabber, and the box samples were sectioned in sequences of 0—2, 2—5, 5—10, 15—20, and 20-bottom (in centimeter).

After sampling, a part of subsample was placed into plastic containner and others were centrifugalized (4000 r/ min.) to seperate pore water. The pore water then was filtered through 0.45 μm aperture Nuclipore filter. The obtained solution was acidified to pH 2 with hydrochloric acid. The sea water, which was not filtered, was placed directly into acid-cleaned polythylene bottles and acidified to pH 2. All of the samples were reserved in the sealed and ice-cold conditions and unoccupied space at the top of containner was flushed with nitrogen gas.

Fluorine content was determined with fluorine selective ion electrode (Tan, 1982). The F

content in sediment samples was calibrated with the samples of GSD (Table 1). The concentration of Ca^{2+} in pore water was determined on Y-2 flame atomic absorption spectrometer. Organic carbon in sediments was measured using K_2CrO_4–H_2SO_4 method. The mineral data were provided by the geological department of our institute.

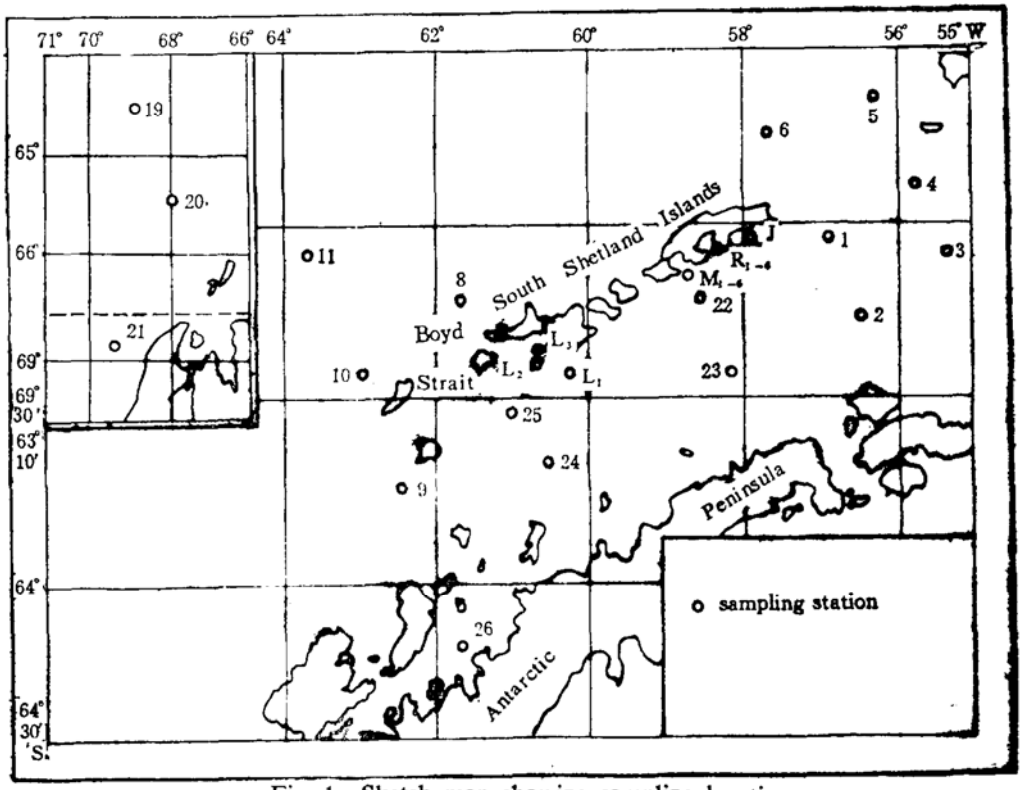

Fig. 1. Sketch map showing sampling locations.

Table 1. Fluorine content in sediment (in ppm) examined with standard sampies (GSD).

Standard samples	GSD—1	GSD—2	GSD—6
Usable value	870±35	345±14	690±23
Medium (one third)	829—937	310—371	635—721
Our method	900	310	625

3. Results

1. Lower fluorine content in the sediments

The results simply reveal the content and distribution of fluorine in sediments (Table 2). It could be seen that the maxmum F content is 395 μg/g(in dry sample)and the minimum only 200μg/g.

According to the data summerised by Carpenter (Carpenter, 1969), fluorine content in recent ocean sediments ranges from 450 to 1100 μg/g. The investigation carried out by Shishkina (Shishkina, 1981) indicated that the fluorine content in various sediments of ocean basins were almost the same. It is about 540μg/g in deep ocean sediments in average and varies in 310 to 710 μg/g (Table 3). Analysis carried out by the authors by the same analytical procedure, in a sedimentary column on the continental shelf of East China Sea (121°59′39″E, 28°35′2″N) also indicates that the fluorine content ranges in 660—940 μg/g Table 4 in the sediments down to 700 m depth.

From the comparison of the different results above, we suggest that the fluorine contents in the sediments of the studied area is usually lower than that in other oceans. Is there a lower fluorine zone in the sedimentary system in the sea area?

Table 2. Distribution of fluorine contentin sediments and their overlying waters.

Area	Adjacent to South Shetland Is.										
stations	M1	M2	M3	M5	M6	R1	R2	R4	J1	L1	L3
pore water	1.56	1.58	1.84	1.52	1.44	1.80	1.48	1.84	1.78	1.78	1.84
sediments	287	335	265	170	336	205	258	—	270	250	230
Area	Adjacent to South Shetland Is.					Northeastern area					
stations	L5	S8	S10	S25	av.	S3	S4	S5	S6	av.	
pore water	1.92	1.40	1.70	1.78	1.68	1.38	1.38	1.44	1.85	1.51	
sediments	220	310	330	370	274	200	230	270	—	233	
Area	Southwestern area							Deep sea			
stations	S2	S23	S24	S9	S20	S21	av.	S11	S19	av.	
pore water	1.91	1.70	—	1.44	1.70	1.18	1.59	1.58	1.64	1.61	
sediments	270	350	375	305	260	330	315	360	395	378	

Table 3. Average fluorine content in sediments and pore waters of oceans.

area	sediment type	in sediment(μg/g)	in pore water(μg/ml)
Pacific	red ooze	540(8)	2.7(11)
Atlantic			1.6(4)
average		540(8)	2.4(15)
range		310—710	1.1—4.0
Pacific	carbonaceous	510(6)	3.5(5)
Atlantic	and clay—	540(1)	
Indian	carbonaceous	540(2)	2.0(1)
average	sediment	520(9)	3.2(6)
range		370—620	2.0—4.8
Pacific	clay	600(1)	5.2(1)
Indian	sediment	580(1)	2.3(2)
average		590(2)	3.3(3)
range		580—600	2.0—5.2
the average			
in ocean sed.		540(19)	2.7(24)
range		310—710	1.1—5.2
Black Sea	oceanic ooze	550(19)	1.0(28)
range	and carbonaceous	300—710	0.0—1.8
Baltic Sea	oceanic clay	380(1)	2.4(2)
range	sediment		2.3—2.5

Table 4. The fluorine content in sedimentary column of quaternary off Zhejiang coast.

depth(m)	0—0.2	1.6—1.7	5.5—5.6	14—14.1	19—19.1	25—25.1
content(ppm)	705	700	710	915	745	830
depth(m)	30—35	45—45.1	50—60	70—80	80—100	190—200
content(ppm)	940	660	690	795	675	745

2. The lower fluxes between sediments and their overlying waters

It has been well known that the fluorine concentration in sea water is about 1.3 μg/g. the typical fluorine distribution in pore water of surface sediments in the studied sea area is shown in Fig. 2. Form the figure, the concentration approaches to that of the average of the oceans,though it gets slightly increased with the depth. In Table 3, except the Black Sea, fluorine concentration in pore waters of oceanic sediments is higher than 2.0 μg/g and some of them are even higher than 3.2 μg/ml. But the determined result (Table 2) show that in the surface water, the fluorine concentration is lower than 2.0 ppm, which means a lower gradient of fluorine concentration across the interface between pore water and their overlying water than that in other oceans .

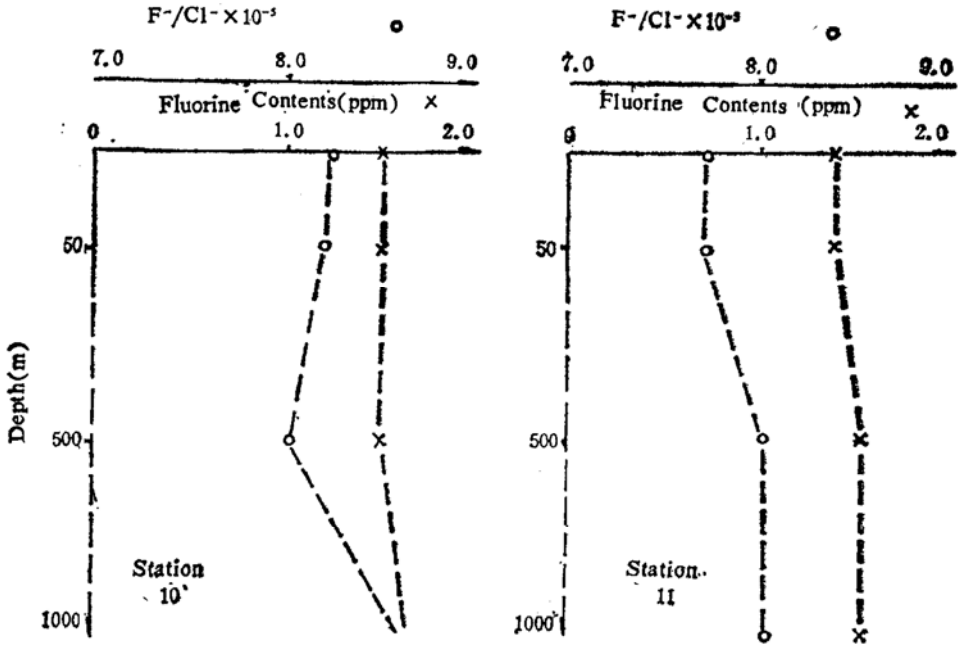

Fig. 2. The vertical distribution of fluorine in deep ocean of the studied area.

According to Fick's first law, the diffusion flux:

$$F = -\phi^2 D_s^i (\partial C_i / \partial x) \cdot \cdot$$

where: ϕ—Porosity of the sediment; D_s^i —Diffusion coefficient (Yuan, 1974); $\partial C_i / \partial x$ — Concentration gradient of the element.

Furthermore, D_s^i will decrease with the drop of temperature. The temperature of Antarctic bottom current is lower than zero centigrade, so the diffusion flux of fluorine from the sediments up to overlying water would be much less than that in other oceans. Besides, the information preliminarily shows that there exists a fluorine gradient from overlying water to sediment in Maxwell

bay and Adimiralty bay in Antarctic summer (Fig. 3).

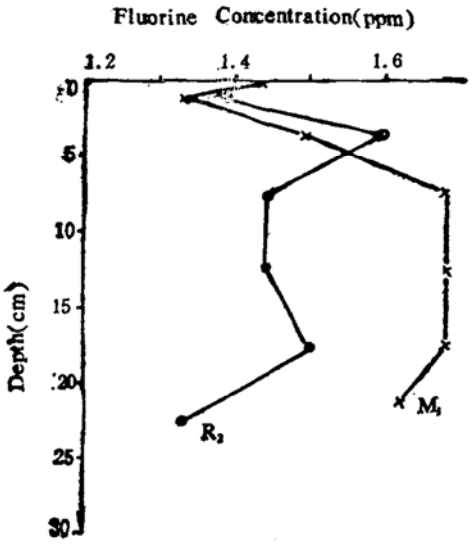

Fig. 3. Vertical distribution of fluorine in pore water.

To estimate the fluxes:

$F_m = 0.75^2 \times 6.67 \times 10^{-6} \times 0.11/2 = 2.1 \times 10^{-7}$ ($\mu g / cm^2/s$)

$F_R = 0.69^2 \times 6.67 \times 10^{-6} \times 0.06 / 2 = 9.5 \times 10^{-8}$ ($\mu g / cm^2/s$)

The behaviors of elements in surface sediment should be an important factor in the buget of ocean. According to Broecker's model, if the fluorine diffusing up from sediment to overlying water was considered, the lower flux of fluorine would greatly affect the geochemical cycle of fluorine in the sedimentary system of Antarctic ocean.

There is no annual fluvial input in Antarctic ocean. How could the consumed part of fluorine in biologic process be compensated ? Whether the Antarctic ocean is in unstable state for fluorine, or the geochemical cycle is different from that in other oceans ? Because of the important influence of fluorine on the Antarctic krill and the role of the krill in Antarctic ecosystem, it is necessary to reveal the cause of the anomaly.

4. Discussion

Analysis of the result preliminarily reveals a low fluorine phenomenon in the sedimentary system. In the following, we would further discuss the main controlling factors on the phenomenon with further understanding of the geochemical behaviors of fluorine in the ocean.

1. The source of materials and sedimentary environment

The main characteristics of sedimentary environment or sedimentation in Antarctic ocean are the weathering process might be dominated by physical factors; there are neither fluvial input annually, nor wave-prevailing coastal zone and glaciers deliver unsorted materials directly into deep continental shelf (Anderson *et al.*, 1983), where the effects on the distribution of elements in sediments.

It is shown in table 2 that there is a tendency of decreasing fluorine content in sediments

from southwest to northeast in the studied sea area. According to other authors (Edwards and Goodell, 1969; Weaver *et al.*, 1980; Andrew, *et al.*, 1980), the northeastern part of the area, Elephant Island and the islands nearby are mainly composed of a series of metamorphic rocks; the middle part, the South Shetland Islands of a series of intermediate-basic rocks, and the western part, the west coast of Antarctic Peninsula of intermediate-acidic rocks.

Table 5. Average content and range of fluorine(μg/g) in different rocks.

type	number	range	average
Olivine	4	12—21	16
Gabbro	5	300—480	390
Kimberlite	1	250	
Diorite	6	390—1940	673
Alkaline rocks	31	220—12400	1957
Granite	14	520—4550	1322
Rhylite	8	260—1080	645
Andesite	4	210—505	361
Basalt	12	180—540	402

The volatiles, such as fluorine and others, tend to be concentrated in later magma, and when metamorphism take place the rock trends to loss their volatiles. It could be seen in table 5, that the fluorine tends to be higher with increasing acidity of rocks (Liu *et al.*, 1984). So the dis tribution of fluorine should be mainly controlled by the bed rock cmpositions on the islands nearby, under the particular conditions of sedimentation in Antarctic ocean. This could be confirmed by the correspondence of distribution of major elements (Cheng *et al.*, 1988) and the distribution pattern of rare earth elements (Ma *et al.*, 1988) in the sediments with those in the rocks on nearby islands.

2. Main fluorine-bearing minerals

Fulorine tends to be incorporated into apatite, topaz, biotite, hornblende, etc, in addition to fluorite (CaF_2), depending to its geochemical characteristics (Liu *et al.* 1984). Determination of minerals in the studied area indicates that there are few apatite and biotite found, which range in 0.0–2.4%and 0.0–4.9% respectively; and topaz was rarely found. On the contrary, hornblende was found in a high percentage, up to 30.1%. Comparing the fluorine content in rather possible F-rich minerals with that in the sediments (Fig.4), we find that the fluorine-bearing mineral in the sediments is mainly hornblende [$F_7=(Si_4O_{11})_2F_2$]. The statistical relation between F content and amount of hornblende among clastic minerals could be expressed as:

$$F=217+36 \ln H.$$

Where: F–Fluorine content in ppm; H–Hornblende in %.

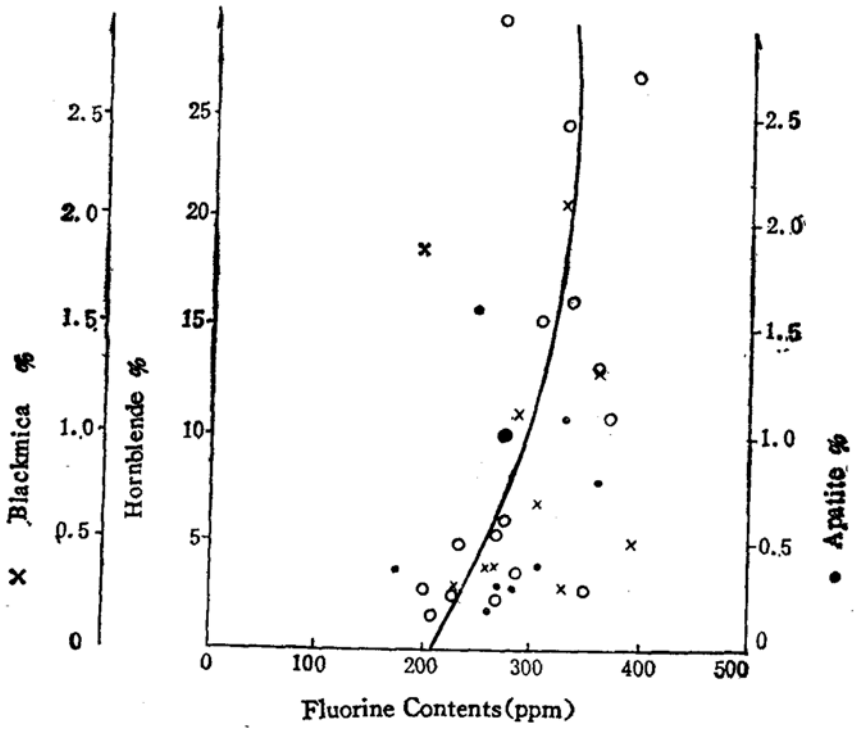

Fig. 4. The relationship between fluorine and hornblende, biotite and apatite.

The linear correlation coefficient $r=0.59$ ($N=18$) $>r_{\alpha}=0.47$ ($\alpha=0.05$). From above discussion we considered that though the hornblende is not a fluorine-rich mineral, it is a dominant mineral in the sediments, and hence contributes more significant distribution of fluorine.

From the minerological viewpoint, we could get the two points; the rare existence of the fluorine-rich minerals, such as apatite, biotite, topza etc., might result in the lower fluorine content in the sediments, and the existence of hornblende in such a high percentage indicate the weak chemical weathering, but the chance of fluorine entering the pore water in physical process would be very small. It may be a possible cause for lower concentration of fluorine in the pore water of studied area.

3. The transition and mechanism distribution of soiid-liquid phases in the sedimentary system

The solubility product of calcium fluoride is very low:

$CaF_2 \rightleftharpoons Ca^{2+}+2F^-$, $K_{sp}=4\times 10^{-11}$

This low solubility product makes theoretically almost all of the fluorine to be accumulated in solid phases. The analytical result indicates that average concentration of calcium in pore wate in the studied area is $362\pm 24.6\ \mu g/g$. Dividing the studied area into three zones as listed in table 2, and their solubility products may be estimated to be:

$L_1=[F^-]^2[Ca^{2+}]=(1.5/19\times 10^{-3})^2\times(362/40\times 10^{-3})=5.7\times 10^{-11}$(Northeastern area);

$L_2=(1.67.10^{-3})^2\times(362/30\times 10^{-3}) =7.1.10^{-11}$(Nearby South Shetland Islands);

$L_3=(1.59/19\times 10^{-3})^2\ (362/40\times 10^{-3}) = 6.3\times 10^{-11}$ (The continental shelf of Antarctic Peninsula)

The estimated result implies that F^- concentration in pore water may be basically controlled by the law of solubility product related with Ca^{2+}, and the fluorine in liquid phase could chiefly

form calcisalt and deposit in solid phase into sediments. There is some change of fluorine in pore water with the change of sedimentary organic matters, Analysed the relation between the organic matters and the fluorine content in sediments, we found there is indeed a clearly positive correlation between them. Their statistical equation may be expressed as:

$F=168+229\times C$, $r=0.63>r_{\alpha}=0.42$ ($N=22$, $\alpha=0.05$)

Here we selecte two profiles to try to discuss the mechanism (Fig. 5).

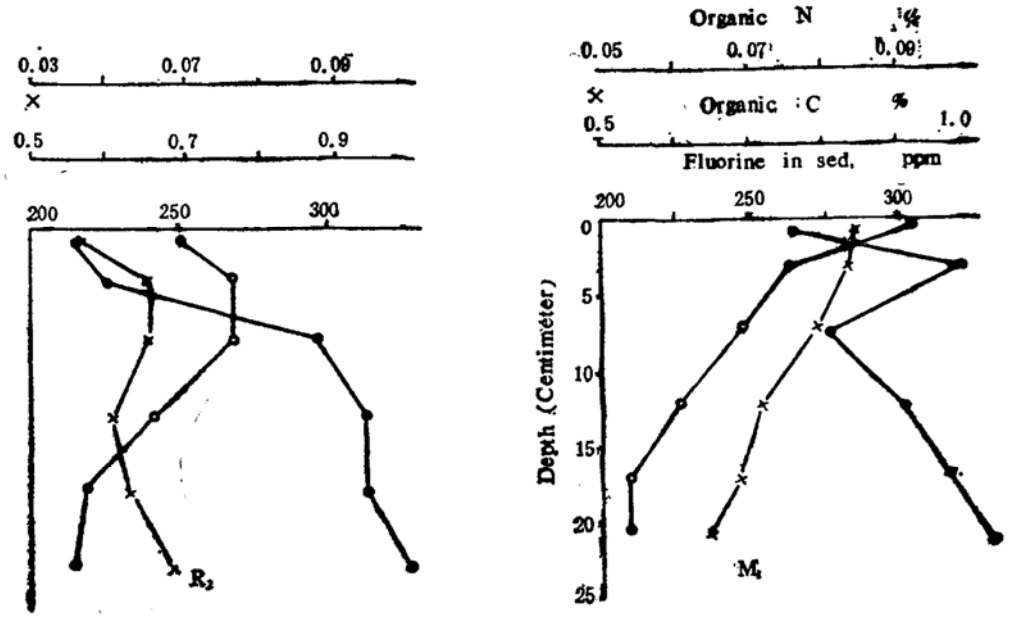

Fig. 5. Relationship between fluroine and organic matter on the profiles across sediments.

Fig. 5 directly shows the accumulating process of fluorine with the decomposition of deposited organic matters in sediments. The fluorine concentrations in pore water (Fig.3) is sharply found near the surface of sediments on the whole profile, and a concentration peak appears with the increasing depth . This evidence could indicate the release of fluorine from the deposited organic matters, which had accumulated fluorine onto the bottom, and the fluorine released might be captured by solid phases in sediments.

From above discussion, we preliminarily describe the distribution and transition mechanism for solid-liquid phases as:

$$\text{Organic matter (fluorine)} \xrightarrow[\text{Dceomposition}]{\text{Early diagenesis}} \text{Pote water} \xrightarrow[\text{Calcicompounds}]{\text{Mostly formed}} \text{Solid phase}$$

5. Conclusion

The analysis of anomalous phenomena of fluorine content preliminarily indicates that the lower fluorine anomalies are basically controlled by the internal causes of the sedimentary system So some balance models for fluorine in oceans calculated by normal conception might be unsui table, that is, the balance model for fluorine in studied area might be different from that in other oceans. The mechanism for formation of the low fluorine anomalies would be discussed in our other article and further works.

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