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BIOGEOCHEMISTRY RESEARCH OF FLUORIDE IN ANTARCTIC OCEAN Ⅰ. THE STUDY OF FLUORIDE ANOMALY IN ANTARCTIC KRILL*

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Abstrct The aim of the study is to investigate the existing form and the partitioning pattern of fluoride in krill (Euphusia superba) by analysing the fluoride and other elements in various part of krill, primarily to approach the potential concentrating mechanism and the effect of fluoride in krill on the geochemical characteristics of fluoride in the Antarctic ecoenvironment. The results of the study show that the amount of flouride in various part of krill has a considerable difference. Most of fluoride is concentrated in the carapace, up to 4028 μg/g, and the head and legs, respectively 2724 μg/g and 2828 μg/g. The muscle contains the least flouride with amount of 226 μg/g. The amount of fluoride in whole freeze－dried krill is averagely 1232 μg/g, which indicates that the functional position of fluoride in krill is mainly located at the crust. Only a few of fluoride is found in the chitin of the carapaces (200 μg/g), which exhibits that fluoride in the carapaces exists mostly in the form of the nonchitious constitutent. In addition, the variation and concentration of flouride is related closely to some other elements such as P, Ca. Thus, fluoride in the carapaces is likely to exist as the form of the inorganic salt with P and Ca. It is also estimated from the study that a slightly higher concentration of fluoride in seawater and lower in sediment of the area relative to other oceans is possibly affected by the concentration of fluoride in the huge storage of krill in the area. The bioprocesses and precipitation with relation to the activity of krill should be very important and key sectoin to the geochemical cycling of the fluoride in Antarctic ocean.

Kwy Words Antarctic Krill, Fluoride, Ecoenvironment

Introduction

In 1984 and 1987, China organized the first and third Antarctic expeditions. This paper used the samples and information obtained in the two expeditions to study initially on the problem of fluoride anomaly which is noticed by scientists present in the world.

Krill (Euphansai superba Dana.) as the most of marine biology resource in anatarctic has abundant nutritive value and large reserve (1～2 billion tons). People hope always this resource can be used for human as protein resource. However, high fluoride content in krill is harmful to human health, which brings the difficult to use directly the biology resource.

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Fluoride anomaly in krill was first found by Soevik and Braekkan(1979). Since then, some researcher reported their researches on the change characteristic about fluoride absorbtion process of krill (Adelung, 1987). But many problems is still clear, particularly the concentrating mechanism of fluoride in antactic krill and geobiochemistry process concerning in it.

The aim of the paper is based on further discussion about fluoride distribution in body of krill to reaerch the existing form of fluoride in krill and its geobiochemistry behaviour in enviroment.

Material and Methods

Samples were caught from westnorthern ocean of Antarctic Peninsula (60°～66°S, 52°～68°W), including Bransfield Strait, one of main abundant areas of Antarctic krill.

Krill samples were unfreezed at room temperature and seperated into male, female and immaturity ones. Besides the immaturity krill, the males and females were seperated again into heads (with antennas), abdominal muscle, legs and carapace, then washed and dried. All samples were freezedied at −10℃ and fined to pass 100 mesh.

In addition, some carapace were treated with acid and alkali to make into chitin.

Fluoride content in samples (krill, seawater, sediment and chitin) were determined by fluoride ion selective electrode. Other elements were determined by atomic absorption method.

Results and Discussion

1. Content and Distribution Characteristic of Fluoride in krill

Fluoride content in various part of krill is listed in Table 1. The fluoride content of whole krill is 1102～1432 μg/g, average 1232 μg/g; 3828～4278 μg/g; in carapace, average 4028 μg/g; 2338～3028 μg in head and tail with legs, average 2720 μg/g and 2828 μg/g, and 178～285 μg/g in muscle, average 226 μg/g respectively. The fluoride content in cuticle is higher than other results (see Table 2). Authors thought that the difference is caused mainly by different treatment and determination methods.

Table 1. Fluoride content in various part of krill (μg/g. d. w.).

Station	Sample *	cuticle	head	tail and leg	muscle	whole
61°13. 00 'S		4128	2728	2338	178	1332
56°30. 00 'W		4278	2728	2928	285	1432
	Juv	—	—	—	—	1278
62°25. 62'S		3828	2720	3028	215	1148
54°50. 00'W		3878	2718	3018	225	1102
	Juv	—	—	—	—	1102
Average		4028	2724	2828	226	1232

Table 2. Comparison of fluoride content in krill (μg/g d.w.)

Whole	cuticle	muscle	reference
1058	2594	4.5	Adeling *et al.*, 1986
2040	3330	570	Soevik, *et al.*, 1979
1950		325	Schneppenhein, 1980
7806		60	Szewielow, 1981
1650			Ellingsen, 1982
1009	1958	70	Boone, *et al.*, 1983
1232	4028	226	Present study

The results in Table 1 indicate obviously that the distribution characteristic of fluoride in krill is cuticle > tail with legs > head > muscle and fluoride anomaly in krill has nothing with sexual mature. In other hand, the difference of fluoride content between cuticle composed by chitin and muscle composed by fat and protein is very large, so fluoride content in various part of krill relates only to organism composition. But between immature and mature krill there is no difference obviously.

In seawater, animals have different biological accumulation to fluoride. Even if in normal environment, the fluoride contents in marine animals is very uneven. The results in Table 3 reflect similarly that fluoride content in cuticle or epidermis of some marine animals is more than that of their soft organization, but this difference is obviously less than that of Antarctic krill, both fluoride contents have a great deal of difference. The results in Table 4-5 indicate that there is no distinct anomaly of fluoride content in seawater and plankton which is main food of Antarctic krill. However, why is fluoride content in Antarctic krill more than other animals? Obviously, this is problem to research what cause fluoride anomaly in krill.

Table 3. Fluoride content in some marine animals (μg/g d.w.).

specic	muscle	bone or cuticle	epideris
Gadus morbua (God)	1.0	42.8	13.3
Gadus aeglefinus (Haddock)	3.7	18.2	74.3
Clupea sprattus (Sprat)	2.7	52.5	10.8
Pleuronectes flesus (Flourder)	1.7	19.9	11.6
Portunus depurator (Swimming Crab)	1.6	11.6	
Crangon vulgaris (Shrimp)	1.8	11.5	
Leander serratus (Prawn)	2.1	11.3	

* Schneppengeim 1980

2. Fluoride Composition Form In Krill Cuticle

Adelung (1987) and Buchholz (1983) researched once on the change characteristic of fluoride content in krill during moulting. The results demonstrated that fluoride concentration take place in cuticle, not in other organizations. The fact of high flouride content in cuticle shows that the chitin constitution seems to play an important part in the concentration of fluoride. However the results in Table 4 indicate fluoride content in chitin is not high (200 μg/g), about 4.9 % of total amount. This means that it is impossible for chitin to concentrate fluoride, there must exist other conbination forms in cuticle.

Table 4. Element contents in krill (%).

Sample	Ca	P	Fe	Mn	Mg	K	Na	F
whole	0.91	1.52	41	4.6	0.54	.028	0.53	1226
muscle	0.31	0.93	31	1.7	0.32	0.16	0.26	226
cuticle	3.55	5.59	122	67.8	0.05	0.08	0.03	4078
chitin	0.09	0.35	—	32.9	0.05	0.02	0.03	200
plankton								<0.5

* F, Fe, Mn (μg/g)

As compared with the distribution of other elements in cutile, there are certain relation between fluoride and some elememts, speciallu, Ca and P which are main elements forming krill cuticle. According to the geochemistry behavior of F with Ca and P, it is possible that fluoridein krill is concentrated by the reaction of F whth Ca and P, and existing of Fe and Mn adantage to the reaction. In the enviroment, fluoride exist in the form of $Ca_5(PO_4)_3F$ with Ca and P. This is result that $Ca_5(PO_4)_3Ca_5(PO_4)_3OH$ is replaced by fluoride in alkaline enviromnent (seawater medium). The reaction is

$$Ca_5(PO_4)_3OH + F^- = Ca_5(PO_4)_3F + OH^- \qquad \text{(Reaction 1)}$$

Ksp of $Ca_5(PO_4)_3OH$ is low as 2×10^{-5}, but Ksp of $Ca_5(PO_4)_3F$ is lower than the former. This is the most steady and important mineral form of fluoride combining with Ca and P.

Basing on the results, the reaction(1) may be the fluoride concentrating pattern of krill for hardening of cuticle organism, the fluoride in cuticle would exist in the form of inorganic matter. In Antarctic, as an unique biological environment of high latitude and low temperature, there are very strongly restriction for any animals living there. Thus these animals would adjust self physiological mechanism to fit this environment. Growing period for krill is mainly in the short summer (Jan. to Mar.) of one year. During the period, the biological action of krill is very strong, and the characteristics resperents high frequent moulting cycle (10~14 days, Buchholz, 1983). According to the biological habits of krill, after moulting, krill concentrate rapidly fluoride (38 hours) to harden its culticle and began quickly to food so as to accelarate grow.

3. Geobiochemistry Characteristic of Fluoride Accumulation in Krill

The concentration of fluoride in krill has not only a high ratio but also rapid rate. It generally reaches the equilibrium within 36 hours after moulting (Schenppengeim, 1980).

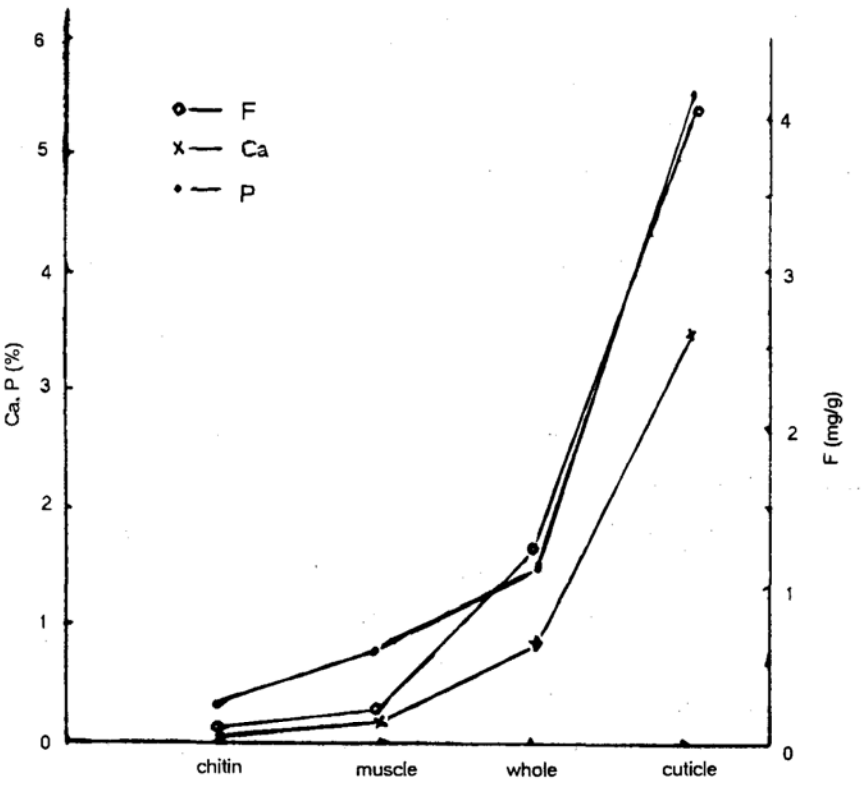

Fig. 1 The relation between fluoride, calcium and phosphorous.

Physiological observations show that the mouth of krill is not hard enough for eating in this stage. This indicates that the concentrating fluoride in krill mainly come from seawater.

In general, fluoride is considered as a major constituent and conservative element in seawater. Although the anomaly of F^-/CI^- ratio in the seawater have been reported, the full evidence for fluoride as a distinct bioelement is still not available. The fluoride content in ocean is 1. 3mg/kg averagely. The content of 1. 25mg/kg is measured in surface seawater of Southern ocean. But in case of high density enrichment of krill and largely rapid absorbtion to fluoride, whether krill concentrating fluoride influence the geochemistry balance fluoride and exist some relationship between both?

The experiment results (Buchholz, 1983) domonstrated that about 90% fluoride in cuticle will come back to seawater with cuticle during moulting. Therefore, the transportation and conversion of this part of fluoride in seawater will be an important link to fluoride cycle in Southern ocean. After moulting, if the remains of fluoride in cuticle could be quickly mineralized and dissolved in form of fluoride ion, the balance of fluoride between krill and seawater would be quickly reached. However, the results in Table 5 seem to show this process can't take place.

Table 5. Fluoride content in the seawater and sediment ($\mu g/g$).

Sample	Deepth	amount of sample	total	ion	particulate	F/Cl
seawater	surface	40	1.41	1.25	0.16	7.50×10^{-5}
	1000m	12	1.60	—	—	7.61×10^{-5}
sediment		45	289			

The change characteristic of fluoride content distribution in seawater and sediment (Table. 5) show that the fluoride content in seawater of research region is higher than that of other ocean (average 1.3 mg/g). On vertical section, the distribution of fluoride content and F^-/Cl^- ratio in surface is higher than that in deeper. It deserves attention that results determinated by different treatment methods (filtered and unfiltered) show that flouride content in filtered seawater isn' t high, and is lower than the average value of ocean seawater. The difference between filtered and unfiltered up to 0.16μg/g. This result also indicates that particulate matter in seawater of research zone makes contribution to fluoride, which is possible reason causing fluoride anomaly in seawater. In vertical water column, fluoride in surface sea water (0~50m) is lower than that in deeper water. Obviously, the fluoride concentration in krill would be a potential reason of fluoride decreasing in surface, while fluoride increasing in the deeper water layers results from the decomposition of krill wreckage(rekcids) in the bottom. The informations show that the particle matter in the water colum of Bransfild Strait are mainly constituted by the biogenic constituent and the change is very strong in different months and different water layers. No matter what is biogenic is or non—biogenic particule matter, the content and ratio in upper water is higher than that in deeper layer; and the particule matter was transported mainly as krill wreckage (Wefer *et al.*, 1988). Lower fluoride content is sidement of research zone and weaker influence of organism (Cheng *et al.*, 1990) reflect also the tendency of fluoride in krill wreckage return into environment from surface to bottom. However, could the fluoride releasing from krill wreckage balance enough the change of fluoride content in water coloum? If the fluoride in krill (total amount billion) are all put into the water column within 100m in Bransfiled Strait, the fluoride in the seawater may only increase 0.10 μg/g. Obviously, in the light of the reserve of krill in the research region, the increment of fluoride would be smaller. Accordingly, there must exist other resource of fluoride. The research results (Zhang, 1990) indicate that the sediment system not to be mani "sink" of fluoride, but the exact evidence on fluoride variation in the ecologic environment of southern ocean are not obtained yet. It need to research further.

Coclusion

1. Analysis results indicate that the function position of concentrating fluoride in krill is

mainly ctrust. The distribution characteristic of fluoride is cuticle > tail with legs > heads > muscle.

2. Lower fluoride content in chitin (only 200μg/g) indicates that fluoride in cuticle don't exist in the form of chitinous composition.

3. Fluoride in krill has closely relation to Ca and P, it may be existed in the form of inorganic of Ca and P.

4. The high concentrating of fluoride in krill is one of potential reasons causing change of fluoride content in seawater.

5. As main storage of fluoride, krill would affect fluoride geobiochemistry cycle in Southern ocean.

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