Polarforschung 57 (1/2): 115—121, 1987

The Importance of Biogenic Opal Sediment Input for the Fluorine Chemistry of Antarctic Marine Sediments (Bransfield Strait and Weddell Sea)

By D. Matthies and G. Troll*

Summary: The influence of biogenic opal sediment input (mainly diatom skeletons) on the fluorine budget of marine sediments will be shown for 24 sampling stations of the antarctic regions of Bransfield Strait, Powell Basin, South Orkney Plateau and northwestern Weddell Sea. 4 bulk samples, one from each sedimentation area, contain 9 to 28 wt.-% of biogenic opal, the clay fraction of the 24 samples investigated have 2 to 82 wt.-%. The fluorine concentration in the amorphous biogenic component is 15 ppm. 300 to 800 ppm of fluorine were measured in the clay fractions, 330 to 920 ppm in their lithogenic components. Biogenic opal causes a decrease in fluorine concentration of the sediment by a considerable amount: 6 to 56% relative to the clay fraction, due to the proportions involved. Biogenic opal is therefore taken into account as a "diluting" factor for the fluorine budget in marine sediments.

Zusammenfassung: Der Einfluß des biogenen Opaleintrages (hauptsächlich Diatomeen) auf die Fluorbilanz mariner Sedimente der Antarktis wird für 24 Probenstationen aus Bransfieldstraße, Powellbecken, Süd-Orkney-Plateau und nordwestlichem Weddellmeer dargestellt. In den verschiedenen Sedimentationsgebieten schwankt der Biogenopalgehalt im Gesamtsediment zwischen 9 und 28 Gew.%, in der Tonfraktion zwischen 2 und 82 Gew.%. Die Fluorkonzentration beträgt in der biogenen Opalkomponente 15 ppm. 300—800 ppm Fluor wurden in der Tonfraktion gemessen, 330—920 ppm in der lithischen Komponente. Die biogene Opalkomponente muß daher als „Verdünnungsfaktor" in der Fluorbilanz mariner Sedimente angesehen werden.

1. INTRODUCTION

In this paper the effect of biogenic opal sediment input (mainly diatom skeletons) on the fluorine balance in Antarctic marine sediments of Bransfield Strait and Weddell Sea will be discussed in detail (Fig. 1, Tab. 3). Up to now few data are available dealing with either fluorine concentrations in biogenic opal (KORITNIG 1969, CARPENTER 1969) or the biogenic opal content in Antarctic marine sediments (CHESTER & ELDERFIELD 1968, DEMASTER 1982, DUNBAR 1983).

To establish the influence of biogenic opal sediment input on the fluorine budget of sea sediments it is a priori necessary to know the distribution of this element within the different components of the sediment. During the last 20 years SHISHKINA (1966), HÜBNER (1969), CARPENTER (1968), SHISHKINA et al. (1972), BLANK & KLEMM (1983) investigated the fluorine concentrations in clay minerals and marine sediments almost all of these from low latitudes. The distribution of fluorine in Antarctic sediments was studied in detail by TROLL & MATTHIES (1987). Sediment trap experiments (WEFER et al. 1982) provided information about the production rate of diatoms, its seasonality and the particle flux through the water column.

In this context the following questions are particularly interesting:

a) To what extent does the sediment input of biogenic opal change the fluorine budget?
b) What factors control the biogenic opal sediment input?

* Dr. Dietmar Matthies and Prof. Dr. Georg Troll, Institut für Mineralogie und Petrographie der Universität, Theresienstraße 41, D-8000 München 2

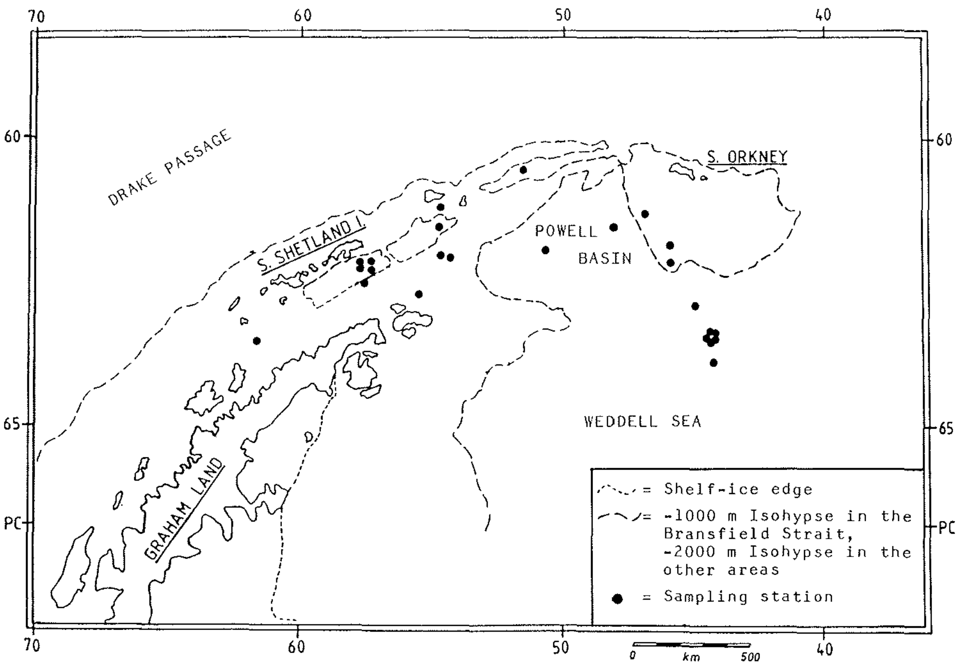

Fig. 1: Area of investigation and geographical position of 24 sampling stations (see Tab. 3).

Abb. 1: Untersuchungsgebiet und Lage der Probenstationen (vgl. Tab. 3).

2. METHODS

The ATTERBERG sedimentation method was used to separate the surface sediments into the grain-size fractions <2, 2-6.3, 6.3-20, 20-63 and >63 μm.

The fluorine analysis was carried out by heating 500 mg of sample to 1200° C for 15 minutes in an inductive furnace. The fluorine liberated was trapped in NaOH-solution. The fluorine concentration in the solution was measured with an ion-selective fluoride electrode, using the standard-addition technique. The fluorine concentration in the sample was calculated using the NERNST equation. The method, reproducibility and accuracy have already been reported in detail by FARZANEH & TROLL (1977), TROLL et al. (1977), MATTHIES (1986), TROLL & MATTHIES (1987).

A wet chemical method was used to separate the amorphous biogenic and volcanic SiO_2 components. This procedure depends on different solubility resistances of the sediment components in a basic enviroment. 1000 mg of sample were left in to 1 l of NaOH-solution (1 molar, 85° C) at constant temperature for 2 hours. The residue (i. e. the lithogenic component) was dried and weighed. This procedure is in accordance with the method described by DUNBAR (1983) and was tested for reproducibility and accuracy by MATTHIES (1986).

3. RESULTS AND DISCUSSION

The sediments are silts with varying proportions of clay (<2 μm) and fine-grained sand (>63 μm). The

Station	Fluorine in ppm			Proportion in wt. %		
	Bulk	LC	AC	LC	BO	VG
Bransfield Str.						
1138—4	420	430	50	69	30	
1141—2	440	440	90	75	24	
1147—6	390	560	60	64	35	
1148—1	440	500	50	54	45	
1149—1	440	470	50	66	33	
1181—2	450	330	100	74	25	1
1182—2	500	810	100	79	20	
1183—4	510	660	330	94	5	
1184—6	410	520	60	65	34	
1186—3	510	580	100	75	24	
1187—1	400	470	100	64	35	
$\bar{x}$	446	525	76	71	28	
s	±43	±128	±24	±10	±10	
n	11	11	10*	11	11	
Powell Basin / Weddell Sea						
1167—5	800	850	380	83	15	
1168—2	790	800	320	92	6	
1169—1	770	570	390	93	5	
1170—1	760	710	390	92	6	
1171—1	800	650	460	94	4	2
1173—6	780	710	410	96	2	
1174—2	630	780	120	84	14	
1179—1	650	730	360	93	5	
1180—4	730	920	480	94	4	
$\bar{x}$	746	747	368	91	7	
s	±64	±105	±105	±5	±5	
n	9	9	9	9	9	
South Orkney Pl.						
1176—4	380	760	20	31	68	
1177—3	300	na	30	17	82	1
1178—4	350	na	80	48	51	
$\bar{x}$	343	—	43	32	67	
s	±40	—	±32	±16	±16	
n	3	—	3	3	3	

* without 1183-4
LC = Lithogenic component
BO = Biogenic opal
na = not analysed
AC = Amorphous component (biogenic opal and volcanic glass)
VG = Volcanic glass

Tab. 1: Fluorine values and weight proportions of biogenic opal and volcanic glass in the clay fraction. Fluorine values are given for the entire clay fraction, their lithogenic and amorphous (biogenic opal and volcanic glass) components. Samples are classified due to their fluorine contents.

Tab. 1: Fluorgehalte und Gewichtsverhältnisse von Biogenopal und vulkanischem Glas in der Tonfraktion. Die Fluorgehalte sind angegeben für die gesamte Tonfraktion (bulk), die lithogene (LC) und amorphe (AC, Biogenopal + vulkanisches Glas) Komponente.

grain-size fraction >6.3 μm consists of the detrital minerals quartz, plagioclase, potassium feldspars, amphiboles, pyroxene, garnet, apatite, glauconite, ore minerals and other heavy minerals (ANGINO & ANDREWS 1968). The clay fraction comprises the clay minerals illite, montmorillonite, smectite, kaolinite, chlorite and mixed layer clay minerals and also detrital quartz and feldspars. Volcanic glasses and diatom skeleton fragments can be found in all grain-size fractions.

As the fluorine distribution in these sediments has already been described in detail (MATTHIES 1986, TROLL & MATTHIES 1987) only the most important facts will be summarised here:

a) Fluorine concentrations in the grain-size fractions are in inverse proportion to grain-size.
b) Between 60 and 87% of the fluorine concentration in the bulk sample derives from the grain-size fractions <6.3 μm.

c) The components apatite, carbonaceous skeletons of marine microorganisms and the carapace of Krill (Euphausia superba), which all contain large amounts of fluorine, have no effect on the fluorine budget of these sediments.

The fluorine distribution in the clay fraction of the sediments allows a classification of the samples into several sample groups which in general correspond with the geographical position of the sampling stations (Tab. 1). The average fluorine concentrations in the lithogenic part of the clay fractions are: 525 ppm (s = +-128 ppm, n = 11) for the Bransfield Strait sediments, 747 ppm (s = +-105 ppm, n = 9) for Powell Basin and Weddell Sea sediments and 760 ppm for the South Orkney Plateau. Higher concentrations in the Powell Basin/Weddell Sea samples are due to a greater amount of illite, reflecting a different source area. The average weight proportions and the fluorine concentrations in the amorphous SiO_2 component (biogenic opal and volcanic glasses) in the clay fraction differ greatly from one sedimentation area to the next. The average contents are: Powell Basin and Weddell Sea 9 wt.% (s = +-5 wt.%, n = 9) with 368 ppm F (s = +-105 ppm, n = 9), Bransfield Strait 29 wt.% (s = +-10 wt.%, n = 11) with 76 ppm F (s = +-24 ppm, n = 10, without station 1183-4) and South Orkney Plateau 68 wt.% (s = +-16 wt.%, n = 3) with 43 ppm F (s = +-32 ppm, n = 3) (Tab. 1).

The amorphous SiO_2 component consists almost exclusively of biogenic opal (mainly diatom skeletons, with occasional sponge needles) with a bulk concentration of 15 ppm F and volcanic glasses with an average bulk concentration of 2125 ppm F (MATTHIES 1986, TROLL & MATTHIES 1987). Thus the average weight proportion of volcanic glasses in the amorphous SiO_2 component can be estimated: 17 wt.% in Powell Basin and Weddell Sea, 3 wt.% in Bransfield Strait and 2 wt.% on South Orkney Plateau. This corresponds to 1—2 wt.% of volcanic glasses in the entire clay fraction of all sedimentation areas investigated. As the fluorine concentration in the various volcanic glasses ranges from 1690 to 3760 ppm F, their proportion in the entire clay fraction can vary +-1 wt.% maximum and is therefore negligible for the fluorine budget in the clay fraction.

The influence of biogenic opal on the fluorine concentration in the entire clay fraction is best seen when the ratio of the weight proportion of biogenic opal is compared to the difference between the fluorine concentration in the lithogenic component (including the volcanic glass fraction) and the entire clay fraction (Tab. 2).

Figure 2 shows the correlation between the weight proportion of biogenic opal and the relative percentual reduction of the fluorine concentration in the entire clay fraction.

In order to find the entire biogenic opal content in the sediments all grain-size fractions of 4 bulk samples were analysed (Fig. 3). It can be deduced that the fluorine concentration in the lithogenic part of the bulk samples is reduced by a considerable amount by biogenic opal, as it is 13% relative (rel.) for 1178-4

Samplegroup	BO	DI		RE	
	(wt. %)	(ppm)	(% rel.)	(ppm)	(% rel.)
Bransfield Str.	32	—100	(= —18)	31	(= —6)
Powell Basin/ Weddell Sea	9	— 44	(= — 6)	49	(= —6)
South Orkney Pl.	67	—433	(= —56)	65	(= —8)

BO = Biogenic opal. DI = Fluorine concentration in the lithogenic component minus fluorine concentration in the entire clay fraction. RE = Decrease of the fluorine concentration in the sample per 10 wt. % of biogenic opal.

Tab. 2: Average biogenic opal content in the clay fraction of different sedimentation areas and the difference between the fluorine content of the lithogenic component and the entire clay fraction. The fluorine concentration in the lithogenic component is relatively lowered by 6—8% per 10 wt. % of biogenic opal.

Tab 2: Durchschnittlicher Gehalt an Biogenopal in der Tonfraktion (BO) und Differenz zwischen Fluorgehalt der lithogenen Komponente und der gesamten Tonfraktion (DI) in den verschiedenen Sedimentationsgebieten. RE = Abnahme der Fluorkonzentration in der Probe je 10 Gew.% Biogenopal.

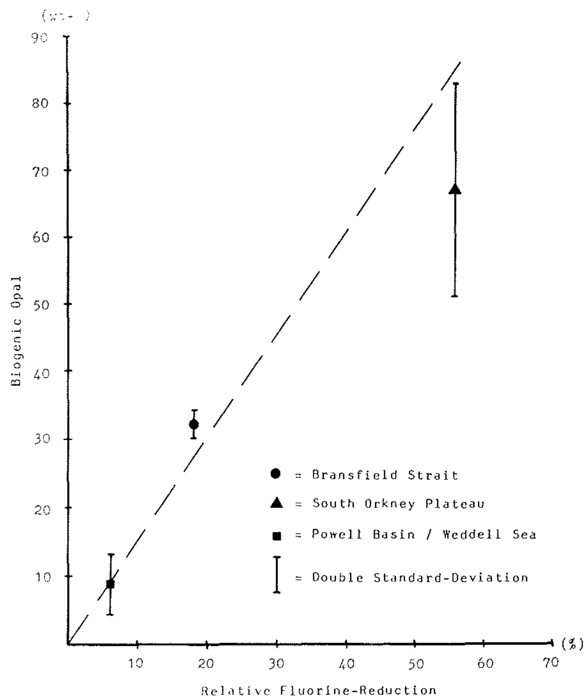

Fig. 2: The relative reduction of the primary fluorine concentrations (= fluorine content of the lithogenic component) as a function of the average biogenic opal proportions in the clay fraction of the different sedimentation areas.

Abb. 2: Relative Reduktion der primären Fluorkonzentration (= Fluorgehalt der lithogenen Komponente) als Funktion der mittleren Biogenopal-Verhältnisse in der Tonfraktion der verschiedenen Sedimentationsgebiete.

(South Orkney Plateau, total biogenic opal: 19 wt.%), 6% rel. for 1180-4 (Powell Basin, biogenic opal: 9 wt.%), 8% rel. for 1182-2 (Bransfield Strait, biogenic opal: 11 wt.%) and 19% rel. for 1184-6 (Bransfield Strait, biogenic opal: 28 wt.%). The data for 1180-4, 1182-2 and 1184-6 are related to the grain-size fractions <63 μm. Because of the small weight proportion of the grain-size fraction >63 μm (15, 13 and 1 wt.%, respectively) and their low opal content, the reduction of the fluorine concentrations will be approximately 1% rel. higher for each bulk sample.

For a sediment input of biogenic opal several criteria must be fulfilled:

a) Diatoms must exist in a sufficient quantity in the upper part of the water column.

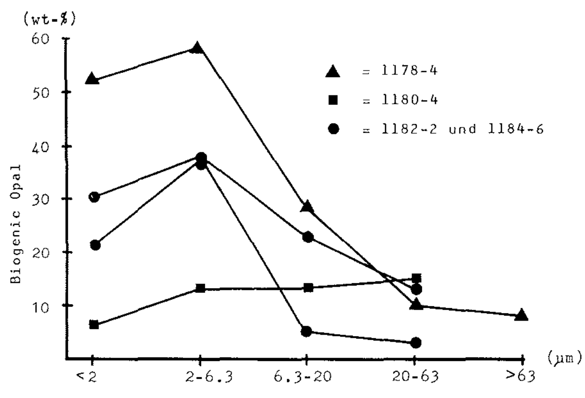

Fig. 3: The biogenic opal content in the grain-size fractions of 4 samples, each from a different sedimentation area.

Abb. 3: Biogenopal je Korngrößenfraktion aus 4 Proben unterschiedlicher Sedimentationsgebiete.

Station	Laditude (S)	Longitude (W)	Water Depth (m)
1138—4	62°16,5'	57°38,6'	1947
1141—2	63°31,8'	61°47,2'	1420
1147—6	61°37,5'	54°51,7'	2240
1148—1	61°13,7'	54°54,3'	64
1149—1	60°35,8'	51°38,1'	3332
1167—5	63°57,5'	44°03,9'	4455
1168—2	63°25,6'	44°34,9'	3879
1169—1	63°24,9'	44°32,7'	3838
1170—4	63°30,9'	44°30,3'	3799
1171—1	63°28,3'	44°30,4'	3817
1173—6	63°00,7'	45°00,5'	3491
1174—2	63°32,5'	44°33,3'	3072
1176—4	62°10,1'	45°53,8'	1481
1177—3	61°56,5'	45°58,0'	469
1178—4	61°24,4'	46°58,9'	486
1179—1	61°36,2'	48°07,7'	3079
1180—4	62°03,0'	50°41,3'	3387
1181—2	62°11,9'	54°26,2'	814
1182—2	62°08,7'	54°45,0'	697
1183—4	62°46,9'	55°25,5'	112
1184—6	61°17,0'	57°20,5'	1821
1186—3	62°20,8'	57°56,4'	1942
1187—1	62°27,5'	57°36,1'	1576
1190—1	60°55,2'	57°05,3'	3305
1191—1	61°01,1'	58°29,5'	5190

Tab. 3: Verifications of 24 sampling stations from RV "Polarstern" cruise in 1983 (ANT-II/3).

Tab. 3: Liste der Proben, ihrer Position und Wassertiefe.

b) As most of the biogenic opal (diatom skeletons) is found in the fine silt fraction, it follows that it must either be broken into smaller pieces or dissolved during transport down through the water column, or both.

In general point a) is fulfilled, otherwise no sediment record of diatom skeletons could be found. WEFER et al. (1982) and GROBE (1986) emphasize the dependence of phytoplankton production on the factors seaice coverage and insolation rate. The appearance of diatoms is therefore correlated with seasonal climatic changes as well as with longer cycles such as glacial/interglacial periods. With respect to the latter, great variations in the biogenic opal content can be expected within sediment cores penetrating several hundred thousand years of sediment.

For point b) Krill swarms are of vital importance. The maximal biogenic opal content is found in the grain-size fraction 2-6.3 μm (Fig. 3). This is in perfect accordance with the findings of GERSONDE (1983, pers. comm.) that Krill breaks the diatom skeletons into pieces of 1-10 μm during consumption. WEFER et al. (1982) and GERSONDE & WEFER (1987) found 50% of biogenic opal in their sediment traps compacted in faecal pellets. The settling velocity of these aggregates is 30 to 200 m/d, depending on their size. The longest time spent in the water column by these faecal pellets at the deepest sampling sta-

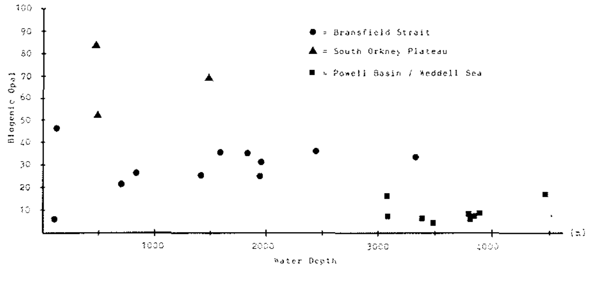

Fig. 4: Biogenic opal content in the clay fraction of 24 samples against depth of the sampling stations.

Abb. 4: Gehalt an Biogenopal in der Tonfraktion in Abhängigkeit von der Wassertiefe.

tion (1167-5, 4455 m) is therefore between 23 to 150 days, i. e. too short for complete dissolution. This explains why there is no obvious relationship between the water depth of the sampling station and the biogenic opal content (Fig. 4).

4. CONCLUSIONS

Because of the very low fluorine concentration in diatom skeletons the biogenic opal content in marine sediments has to be taken into account as a ''diluting'' factor for the fluorine budget of sea sediments. In the sediments investigated the primary fluorine concentrations (= fluorine concentrations in the lithogenic component of the sample) are relatively lowered by 6-19%, depending on the proportion of biogenic opal involved.

Two equally important factors control almost exclusively the fluorine concentrations in these sediments: The fluorine chemistry of the source areas of the lithogenic portion and the abundance of biogenic opal in the sediment. Due to the fact that the production of phytoplankton depends on factors such as seaice coverage and insolation rate, there is a connection between climatic conditions and the fluorine concentrations in these sediments.

References

Angino, E. E. & Andrews, R. S. (1968): Trace element chemistry, heavy minerals, and sediment statistics of Weddell Sea sediments. — J. Sed. Petrol. 38 (2), 634—642.

Blank, P. & Klemm, W. (1983): Zum Fluorgehalt von Kaolinen und Tonen unter besonderer Berücksichtigung der Kaoline des Kemmlitzer Lagerstättenreviers. — Silikattechnik 34 (7), 198—203.

Carpenter, R. (1969): Factors controlling the marine geochemistry of fluorine. — Geochim. Cosmochim. Acta 33, 1153—1167.

Chester, R. & Elderfield, H. (1968): The infrared determination of opal in siliceous deep-sea sediments. — Geochim. Cosmochim. Acta 32, 1128—1140.

Demaster, D. J. (1981): The supply and accumulation of silica in the marine enviroment. — Geochim. Cosmochim. Acta 45 1715—1732.

Dunbar, R. (1983): Manuscript, unpublished.

Farzaneh, A. & Troll, G. (1977): Pyrohydrolysis for the rapid determination of small and large amounts of fluorine in fluorides, silicate minerals and rocks using an ionselective electrode. — Geochem. J. (Japan) 11, 177—181.

Gersonde, R. & Wefer, G. (1987): Sedimentation of biogenic siliceous particles in Antarctic waters (Atlantic sector). — Marine Micropaleontology 11.

Grobe, H. (1986): Spätpleistozäne Sedimentationsprozesse am antarktischen Kontinentalhang vor Kapp Norvegia, östliche Weddell See. — Berichte Polarforsch. 27, 1—122.

Hübner, M. (1969): Geochemische Interpretation von Fluorid/Hydroxid-Austauschversuchen an Tonmineralen. — Ber. Dt. Ges. geol. Wiss. B 14, 5—15.

Koritnig, S. (1951): Ein Beitrag zur Geochemie des Fluors. — Geochim. Cosmochim. Acta 1, 89—116.

Matthies, D. (1986): Der Fluor-Haushalt antarktischer Meeressedimente in Beziehung zu ihren petrographischen Eigenschaften (Bransfield Straße und nordwestliche Weddell See). — Diss. Uni. München, 1—113.

Shishkina, O. V. (1966): Fluorine in oceanic sediments and their pore solutions. — Geochem. Intern. 3, 152—159.

Shishkina, O. V., Baturin, G. N. & Bykova, U. S. (1972): Fluorine in the sediments and ooze water in highly productive parts of the oceans. — Geokkimiya 8, 988—996.

Troll, G., Farzaneh, A. & Cammann, K. (1977): Rapid determination of fluoride in mineral and rock samples using an ion-selective electrode. — Chem. Geol. 20, 295—305.

Troll, G. & Matthies, D. (in preparation): Distribution of fluorine in recent marine sediments related to petrographic composition: Bransfield Strait and Northwestern Weddell Sea, Antarctica.

Weter, G., Suess, E., Balzer, W., Liebzeit, Müller, P. J., Ungerer, A. C. & Zenk, W. (1982): Fluxes of biogenic components from sediment trap deployment in circumpolar waters of the Drake Passage. — Nature 299, 145—147.