Marine Sulfur Chemistry

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Abstract Investigations of anoxic basin waters like the Black Sea and the Norwegian fjord Framvaren as well as studies of the inorganic sulfide chemistry have resulted in considerable knowledge of marine sulfur chemistry. This article summarizes much of the more important findings and points out some of the future work that should be carried out.

Sulfur is an essential element for the marine life. Since sulfate is one of the major constituents of seawater it never becomes a limiting element in oxygen-containing waters unlike the case with nitrate, phosphate and silica in the photosynthesis zone.

In anoxic waters, however, sulfate is used by sulfur-bacteria to oxidize organic matter which has decended into stagnant water from the production layer. Such waters may be depleted of sulfate and this is particulary the case with pore waters in organic-rich sediments. The purpose of this paper is to give an overview of marine sulfur chemistry with special reference to anoxic basins and point out problems that should be further investigated.

Assimilatory sulfate reduction

In the productive, euphotic zone assimilatory sulfate reduction proceeds in phytoplankton by sulfate activation through the formation of adenosine-5´-phosphosulfate (APS) by ATP-sulfurylase and transfer to the 3´-phosphate (PAPS) by APS-kinase. Reduction of the acivated sulfate group is performed by reductases. In this way, essential sulfur-containing compounds are formed (see Table 1).

The biochemistry of sulfur has been treated by Huxable (1986). Cysteine, $HSCH_2CH(NH_3^+)COO^-$, is the key compound for the biosynthesis of other thiols. These thiols may bind such metal ions as Cd^{2+} and Hg^{2+}. At the same time plankton assimilate phosphate, which explains the simultaneous depletion of cadmium and phosphate in surface waters together with the release upon decay below the

Table 1. Some naturally occurring biochemical substances containing sulfur

Compound	General structure	Examples
Thiols (mercaptans)	RSH	*l*-Cysteine, coenzyme A, glutathione
Sulfides (thioethers), thiazole	RSK	*l*-Methionine, thiamine (aneurin)
Disulfides, methylsulfonium compounds	$RSSR_1$, $(CH_3)_2S^+R^-$	*l*-Cystine, *S*-Adenosyl-*l*-methionine, dimethyl-*l*-propiothetin (dimethylsulfonio-propionate)
Sulfoxides	$RSOR_1$	Allinin, allicin
Sulfonic acids	$R\text{-}C\text{-}SO_3^-$	Glucose-*l*-sulfonate, cysteic acid, taurine, methyltaurine
Sulfate esters	$R\text{-}OSO_3^-$	Phenolsulfates, polysaccharide sulfates, APS, PAPS
Sulfamates	$R_2NSO_3^-$	Aryl sulfamates, mustard oil, glycosides

euphotic zone. Compounds containing -SeH groups also bind cadmium and mercury. Since selenium is a microelement the removal of Se(VI) and Se(IV) in surface waters is observable. Mature pilot whales which feed on squids have a high mercury level according to Julshamn *et al.* (1987). The Faroe Islands depend to a very large extent on marine food, part of which consists of meat from the pilot whale.

Cysteine is oxidized to the disulfide cystine, $(\text{-SCH}_2\text{CH(NH}_3^+)\text{COO}^-)_2$. Thus it plays an important role in redox reactions in the organisms. The disulfide bridge is responsible for the formation and maintenance of secondary structures in proteins.Little cystine is present in the cells, but the tissue concentration of cysteine is 10-100 μM. Glutathione is the most abundant of the non-protein thiols with a tissue concentration of 0.5-10 mM. Adenosylmethionine is the most important methylating agent and acts in a myriad of transmethylation reactions.

Ferredoxins are low-molecular weight iron-sulfur proteins which transfer electrons from one enzyme system to another. Molybdoferredoxin in the enzyme system nitrogenase is responsible for biological nitrogen fixation. Nitrate reductase also contains molybdenum. In nitrogenase molybdenum is bound to a cluster with 6-8 iron and sulfur.

Thiamine, which contains a thiazole group in the form of a pyrophosphate, is the coenzyme of decarboxylases. Taurine, $NH_3^+CH_2CH_2SO_3^-$, is formed by degradation of cysteine. Among its actions can be mentioned the osmolar and electrophysiological effects. Polysaccharide sulfates are found in algae, where they act as cell-wall components. The zwitterion $(CH_3)_2S^+CH_2CH_2COO^-$ is the precurser to

dimethylsulfide.

Metal stability constants

In spite of the work by Wasastjerna (1923) most compiled constants for the protonization of the sulfide ion ($H^+ + S^{2-} \Leftrightarrow HS^-$) are in the range of log K_1 = 12 to 15. From a plot of the dissociation constants for H_2S_n Dyrssen and Kremling (1990) found a value of log K_1 = 16.52 ± 0.94, which is not too far from the value of 16.2 found by Wasastjerna. This means that the values of the solubility products, K_{s0}, have to be recalculated according to Tables 2a and 2b with the value of K_1 that each author has used.

Only a few equilibrium constants have been determined for the formation of $M(SH)_2$ ($M^{2+} + 2SH^- \Leftrightarrow M(SH)_2$, namely for iron(II) log β_2 = 6.2, for zinc 12.9, for cadmium 13.8 and for mercury 37.7. As judged by the constants for mercaptoethanol, $HOCH_2CH_2SH$, in Table 3 taken from Martell and Hancock (1996) the complexes MSH^+ for Mn, Fe, Co and Ni should be rather weak. Zn^{2+} ,

Table 2a. Average values of the solubility constant K_1K_{s0} calculated from compiled data of the values of K_{s0} and K_1.
$K_{s0} = [M^{2+}] [S^{2-}]$; $K_1 = [HS^-] / [H^+] [S^{2-}]$; $K_1K_{s0} = [M^{2+}] [HS^-] / [H^+]$

M^{2+}	log K_1K_{s0}
Mn^{2+}	0.17 ± 0.28 (green), 3.34 ± 0.19 (pink)
Fe^{2+}	-4.16 ± 0.49
Co^{2+}	-7.44 ± 0.12 (α), 11.07 ± 1.72 (β)
Ni^{2+}	-5.6 (α), -11.1 (β), -12.8 (γ)
Cu^{2+}	-22.30 ± 0.19
Zn^{2+}	-10.93 ± 0.25 (α), -8.95 ± 0.32 (β)
Cd^{2+}	-13.39 ± 0.68
Hg^{2+}	-38.9 ± 0.4 (black), -39.5 ± 0.4 (red)
Sn^{2+}	-11.95 ± 0.10
Pb^{2+}	-13.97 ± 0.57

Table 2b. Average values of the solubility constant K_1K_{s0} calculated from compiled data of the values of K_{s0} and K_1.
$K_{s0} = [M^+]^2 [S^{2-}]$; $K_1 = [HS^-] / [H^+] [S^{2-}]$; $K_1K_{s0} = [M^+] [HS^-] / [H^+]$

M^+	log K_1K_{s0}
Cu^+	-34.65 ± 0.57
Ag^+	-35.94 ± 0.81
Tl^+	-7.22 ± 0.40

Table 3. Formation constants (log K_1) for metal complexes with mercaptoethanol according to Martell and Hancock (1996).

Mn(II)	1.8	Cu(I)	16.7
Fe(II)	2.5	Ag(I)	13.4
Co(II)	(3.2)	CH_3Hg^+	15.9
Ni(II)	3.9	H^+	9.72
Cu(II)	8.1		
Zn(II)	5.7		
Cd(II)	6.1		
Hg(II)	25.0		
Pb(II)	6.6		

Table 4. Recalculation of vertical profiles of filtered ferrozine Fe (II) from the anoxic water of Framvaren (Landing and Westerlund, 1988) using $K_1 = 10^{2.5}$ and pH = 7. The concentrations of iron and sulfide are given in mol/L.
Log K_s = log S + 7 - log ($[SH^-]^{-1}$ + 316 + $10^{6.2}$ $[SH^-]$)

Depth (m)	log S + 7	$[SH^-]^{-1}$	$10^{6.2}[SH^-]$	log K_s
20	-0.081	200000 (uncertain)	7.92	(-5.38)
22	0.53	62500	23.4	-4.27
24	0.91	25000	63.4	-3.49
26	0.89	16260	97.2	-3.33
30	0.95	6173	256	-2.88
40	0.82	3984	397	-2.85
50	0.44	2941	537	-3.14
90	-0.29	597	2647	-3.56
110	-0.57	403	3918	-4.24
170	-0.59	331	4780	-4.32

Mean value of log K_s = -3.56 ± 0.49

Cd^{2+} and Hg^{2+} form negatively charged complexes with SH^-, but Fe^{2+} does not seem to do so.

Iron(II) has been determined in the Norwegian fjord Framvaren where the sulfide concentration increases to 7-8 mM below the chemolcline (depth at 20 m were the basin water becomes anoxic (sulfidic)). The solubility constant K_1K_{s0} = K_s for the equilibrium

$$FeS(s) + H^+ \Leftrightarrow Fe^{2+} + SH^-$$
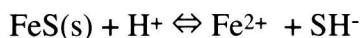
is calculated from the total dissolved iron(II) S

$$S = [Fe^{2+}] + [FeSH^+] + [Fe(SH)_2] = [Fe^{2+}](1 + K_1[SH^-] + \beta_2[SH^-]^2)$$

=

$$K_s[H^+]([SH^-]^{-1} + K_1 + \beta_2[SH^-])$$

Table 4 presents the calculation of log K_s for $K_1 = 10^{2.5}$ = 316 and $[H^+]$ = 10^{-7}

using determinations by Landing and Westerlund (1988). The value of log K_s = -3.56 ± 0.49 corresponds to amorphous FeS (*cf.* Table 2a). Thus in spite of the fact that Skei (1988) has demonstrated the presence of framboidal pyrite this compound does not determine the concentration of dissolved iron in the sulfidic water below the chemocline. At the Gotland Deep in the Baltic Sea (see Dyrssen and Kremling, 1990) the concentration of iron(II) was 1.9 µM for a total concentration of sulfide of 83.2 to 91.2 µM and the pH = 7.11. Thus
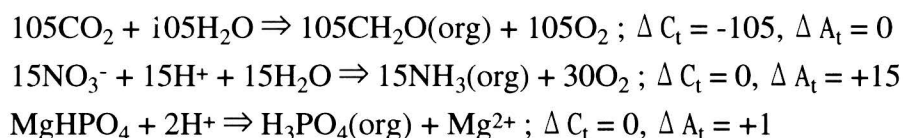
$$\log K_s = -5.72 + 7.11 - \log (22936 + 316 + 69.1) = -2.98$$

This value is in the same range as the value of -3.56 ± 0.49 obtained in Framvaren.

The low pH of anoxic water

There seems to be a general agreement to use the Hansson (1973) scale for the determination of pH in seawater. The scale is based on the titration of TRIS, $C(NH_2)(CH_2OH)_3$, in synthetic seawater with hydrochloric acid. In the new edition of Methods of Seawater Analysis (Grasshoff *et al.*, 1999, Ch. 7 by Wedborg *et al.*) this scale is used.

It has been shown by Dyrssen (1977, 1992) that pH is mainly dependent on the difference between the alkalinity (A_t) and the total dissolved inorganic carbon (C_t). These concentrations are shifted upon the formation of phytoplankton
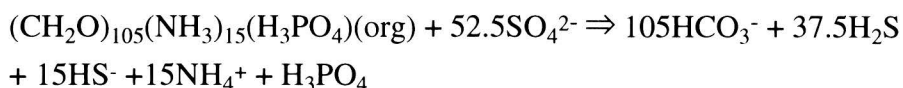
$$105CO_2 + 105H_2O \Rightarrow 105CH_2O(org) + 105O_2 \; ; \; \Delta C_t = -105, \; \Delta A_t = 0$$
$$15NO_3^- + 15H^+ + 15H_2O \Rightarrow 15NH_3(org) + 30O_2 \; ; \; \Delta C_t = 0, \; \Delta A_t = +15$$
$$MgHPO_4 + 2H^+ \Rightarrow H_3PO_4(org) + Mg^{2+} \; ; \; \Delta C_t = 0, \; \Delta A_t = +1$$

Thus the production of phytoplankton with the stoichiometric composition $(CH_2O)_{105}(NH_3)_{15}(H_3PO_4)$ will cause the following skifts:

$$\Delta A_t = +16, \; \Delta C_t = -105, \; \Delta (A_t - C_t) = +121, \; \Delta O_2 = +135,$$
$$\Delta [NO_3^-] = -15$$

If the nitrate concentrations drops from 10 µmol per kg seawater to zero because of the production of phytoplankton then $\Delta (A_t - C_t)$ will increase by (121/15)10 = 80.7 µM. Since $\Delta (A_t - C_t)$ is about 450-460 µM per pH unit Δ pH will be about +0.18. Furthermore, if the concentration of oxygen drops from 300 µmol per kg seawater upon decomposition of organic matter $\Delta (A_t - C_t)$ will decrease (121/135)300 = 269 µM and pH will drop by 269/455 = 0.59. Thus when the water becomes anoxic the pH is lowered considerably.

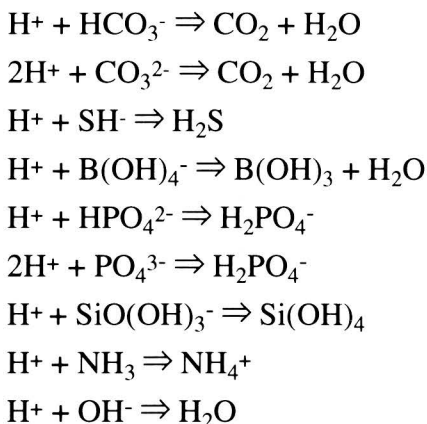In sulfidic (anoxic) seawater the oxidation of organic matter will take place by the following reaction:

$$(CH_2O)_{105}(NH_3)_{15}(H_3PO_4)(org) + 52.5SO_4^{2-} \Rightarrow 105HCO_3^- + 37.5H_2S$$
$$+ 15HS^- + 15NH_4^+ + H_3PO_4$$

Since the constants for the protonization of HCO_3^- and SH^- are not very different a titration of HCO_3^- will include SH^- and correspond to $\Delta C_t = 120$. ΔA_t is 118 (H_3PO_4 lowers the alkalinity by two units). Thus $\Delta (A_t - C_t)$ will be practicalyy zero and the pH of anoxic water will be low and almost independent of how much organic matter has been decomposed.

Acid titration of anoxic waters

The following reactions will occur upon titration of sulfidic (anoxic) seawater with hydrochloric acid:

$$H^+ + HCO_3^- \Rightarrow CO_2 + H_2O$$
$$2H^+ + CO_3^{2-} \Rightarrow CO_2 + H_2O$$
$$H^+ + SH^- \Rightarrow H_2S$$
$$H^+ + B(OH)_4^- \Rightarrow B(OH)_3 + H_2O$$
$$H^+ + HPO_4^{2-} \Rightarrow H_2PO_4^-$$
$$2H^+ + PO_4^{3-} \Rightarrow H_2PO_4^-$$
$$H^+ + SiO(OH)_3^- \Rightarrow Si(OH)_4$$
$$H^+ + NH_3 \Rightarrow NH_4^+$$
$$H^+ + OH^- \Rightarrow H_2O$$

At pH 7 the main bases are HCO_3^- and SH^-. In order to evaluate the alkalinity from the equivalence point the amount of acid added (H_t) has to equal the initial alkalinity (*i.e.* bases with a protonization constant $\geq 10^{4.5}$). Since the acid added will to some extent form excess H^+, HSO_4^- and HF

$$H_t = [H^+] + [HSO_4^-] + [HF] - A_t$$

In order to determine $C_t = [CO_2] + [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$ one has to know the initial total concentrations of sulfide (*i.e.* $[H_2S] + [HS^-]$), borate (calculated from the salinity), phosphate, silicate and ammonia and their protonization constants while $[OH^-]$ is calculated from the ionization product, the value of which ($pK_w = 13.31$) includes $MgOH^+$.

Thus the treatments given by Johansson and Wedborg (1982) and in the new edition of Methods of Seawater Analysis (Grasshoff *et al.*, 1999; Ch. 8 by Ander-

son *et al.*) have to be supplemented by the equations

$$S_t = [H_2S] + [HS^-] = [HS^-](1 + [H^+]K_1)$$

where

$$K_1 = [H_2S]/[H^+][HS^-]$$

The values for log K_1 can be taken from Almgren *et al.* (1976) for different salinities and temperatures. This is also the case for the titration of pore waters (Haraldsson *et al.*, 1997).

Sulfur analysis of anoxic waters

In the new edition of Methods of Seawater Analysis (Grasshoff *et al.*, 1999) chapters 5 and 6 by Fonselius *et al.* and Dyrssen *et al.* treat the determination of hydrogen sulfide, thiosulfate and sulfur.

The colorimetric analysis by the formation of methylene blue from dimethyl-p-phenylenediamine using a separate solution of iron(III) chloride in 6 M HCl as a catalyst is recommended for low concentrations of hydrogen sulfide (up to 0.3 mM). This method is similar to Cline´s method which uses a mixed diamine-iron(III) chloride solution. Cline´s method is recommended for the concentration range of 0.2 to 1 mM hydrogen sulfide. Preservation of samples may be obtained by adding zinc acetate, which forms ZnS. Samples with high concentrations of hydrogen sulfide may be diluted if the sulfide is protected against oxidation as ZnS.

Sulfur (S^0) can be determined by extraction with chloroform and measuring S^0 by UV spectrophotometry at 270 nm. In order to protect the sulfide from oxidation the sulfur can be coprecipitated by using zinc acetate. In another method S^0 is extracted with carbon sulfide which is evaporated. The S^0 is redissolved in a cyanide solution. After cyanolysis the SCN^- is determined by adding iron(III) chloride and measuring the iron complex at 460 nm.

Thiosulfate which is an intermediate oxidation product of sulfide is determined by an iodometric titration to tetrathionate. Again sulfide is protected as ZnS.
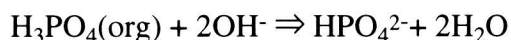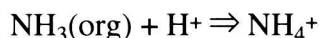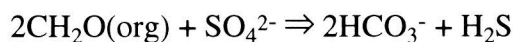

Isotopic shifts

Sulfate reduction with isotopic shifts occurs not only in organic-rich sediments (*cf.* Habicht and Canfield, 1997), but also in stagnant basin waters like the Norwegian fjord Framvaren and the Black Sea. Isotopic fractionation takes place during the bacterial reduction of sulfate. In general the fractionation drops from 40 to

20 ‰ with an increase of the rate of sulfate reduction (Habicht and Canfield, 1997). For the super-anoxic fjord Framvaren where the sulfide concentration increases to 7 mM in the bottom water at 150-180 m a plot of $\delta^{34}S$ against the amount of HCO_3^- produced showed a constant fractionation of 40 ‰ (Anderson et al., 1988). In the bottom water the isotope fractionation produced sulfate with $\delta^{34}S$ close to +30 ‰ and sulfide with $\delta^{34}S$ close to -11 ‰. Close to the chemocline the hydrogen sulfide has a $\delta^{34}S$ content close to -20 ‰. Seawater contains sulfate with 20 ‰ $\delta^{34}S$, but in Framvaren some sulfate had only 14.8 ‰ $\delta^{34}S$, which indicates a formation from hydrogen sulfide. Thus our results for Framvaren show that some sulfate in the depth range of 8 to 50 m around the chemocline at 18 to 20 m is formed by the oxidation of hydrogen sulfide. Since the reaction is $2O_2 + H_2S \Rightarrow H_2SO_4$ the alkalinity should decrease.

Release rates

For anoxic fjords with stagnant basin water the decomposition of organic matter mainly produced by phytoplankton takes place on the bottom. The reactions are

$$2CH_2O(org) + SO_4^{2-} \Rightarrow 2HCO_3^- + H_2S$$
$$NH_3(org) + H^+ \Rightarrow NH_4^+$$
$$H_3PO_4(org) + 2OH^- \Rightarrow HPO_4^{2-} + 2H_2O$$

Our first investigation of release rates took place in Byfjorden (Almgren et al., 1975). A calculation by Dyrssen and Svensson (1982) of the concentration profile of hydrogen sulfide from the chemocline at 20 m down to the bottom at 48 m gave a release rate of 4.9 to 5.8 mmol m^{-2} d^{-1}. This agreed with a benthic chamber investigation (Dyrssen and Hallberg, 1979) that gave a release rate of 6.4 mmol m^{-2} d^{-1}. The corresponding release rates of carbonate, ammonium and phosphate in Byfjorden were 11.8, 0.98 and 0.15 mmol m^{-2} d^{-1}. In Framvaren (Dyrssen et al., 1996) the mineralization took place according to the following reaction:

$$(CH_2O)_{148}(NH_3)_{15}MHPO_4(org) + 74SO_4^{2-} \Rightarrow 148HCO_3^- + 15NH_4^+ + 15HS^- + 59H_2S + MHPO_4$$
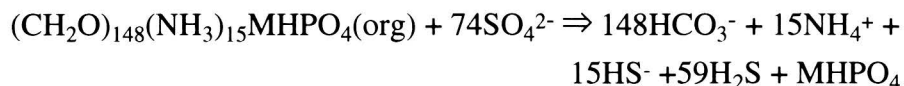
The calculated release rate for carbonate in Framvaren was 1.8 to 2.5 mmol m^{-2} d^{-1} which is considerably lower than in Byfjorden, but Byfjorden was fertilized by nutrients from the city of Uddevalla.

The runoff of 1 m^3 s^{-1} to Framvaren contains dissolved silica with a mean con-

centration of 31.2 ± 12.2 mmol m^{-3} (Dyrssen, 1998) corresponding to a silica input of 31.2 mmol s^{-1}. Plankton (*e.g.* marine diatoms) form biogenic opal. Part of this opal finds its way to the bottom of the fjord. A silica release rate of of 0.43 ± 0.08 mmol m^{-2} d^{-1} was found by Rutgers van der Loeff *et al.* (1984) with anoxic benthic flux chambers. Using a release rate of 0.43 mmol m^{-2} d^{-1} a simple silica balance calculation (Dyrssen *et al.*, 1997) and an area of 1.39×10^6 m^3 at the depth of 100 m the flux of dissolved silica corresponds to 6.8 ± 1.3 mmol s^{-1}. The supply of dissolved silica by the runoff (31.2 ± 12.2 mmol s^{-1}) is large enough to cover this release of Si(OH)$_4$ from the bottom. The release may be mediated by the bacterial decomposition of the organic tissue of the diatoms, but is most likely an inorganic process.

Some sulfide reactions

At the end of May 1995 we measured the freons in Framvaren (Dr. Toste Tanhua, personal communication) and in the beginning of June, 1993 Shapiro *et al.* (1997) determined both CFC-11 [CCl$_3$F] and CFC-12 [CCl$_2$F$_2$]. Because of the rapid decay of CFC-11 below the chemocline at 20 m according to Shapiro *et al.* (1997) (see Table 5) the ratio of CFC-11 to CFC-12 drops considerably from the surface value of 2.034 ± 0.096. However, Table 5 shows that the decay of CFC-11 takes place at 15-18 m, *i.e.* in oxic water above the chemocline at 20 m. As pointed out

Table 5. Ratios of CFC-11 to CFC-12 in Framvaren in June 1993 by Shapiro *et al.* (1997) and in May 1995 by Dr. Toste Tanhua (personal communication)

Depth (m)	Tanhua	Shapiro *et al.*
1	-	2.025
5	-	1.957
10	-	2.119
15	-	0.800
18	-	0.927
19	1.442	-
20	0.780	0.641
21	0.802	-
22	-	0.086
23	0.655	-
24	-	0.0093, 0.0219
25	0.337	-
26	-	0.0094
27.5	0.0331	-
30	0.233	0.0124

above the isotope shifts indicate an oxidation of hydrogen sulfide above the chemocline. To my knowledge the reaction between freons and hydrogen sulfide has not been investigated.

Likewise Dyrssen (1998) showed that molybdenum which is conservative in ocean water is not conservative in the water above the chemoclines in Framvaren as well as in the Black Sea. One guess is that it is removed by reduction of MoO_4^- to Mo(IV) and formation of $MoS_2(s)$.

Thus besides the reduction of nitrate, iron(III) and Mn(IV) there are other reactions. One important reaction at the chemocline is denitrification. According to Yao and Millero (1995) it seems as if the alkalinity is not affected. Dyrssen *et al.* (1996) suggested that the following reaction would explain this

$$2\ NH_3(org) + 3NH_4^+ + 3NO_3^- \Rightarrow 4N_2(g) + 9H_2O$$
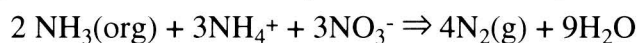
Thus oxygen and hydrogen sulfide may not be involved in denitrification.

Conclusions. Future work

Plankton assimilate and reduce sulfate and selenate. Most likely the food chain plankton-squids-pilot whales-Faroese man is very short. Thus a study of the uptake of mercury and the formation of compounds containing -SH and -SeH groups would reveal an important route for the transfer of sulfide metals into living organisms.

Denitrification is an important process which is favored in the transition zone between oxic and anoxic layers (*e.g.* bottom water containing some oxygen and organic-rich sediments). Especially favorable conditions are present at the chemocline (redoxcline, pycnocline) in basins with permanently sulfidic (anoxic) water. Such conditions are present in the Norwegian fjord Framvaren and the Black Sea where it might be possible to establish the stoichiometry of the process.

Elemental sulfur is mostly studied by microbiologists at the chemocline, but qualitative observations in Framvaren (Dyrssen *et al.*, 1996) show the presence of S^0 well below the chemolcline. Coprecipitation of S^0 with ZnS and chloroform extraction should enable a quantitative determination. Below the chemocline S^0 is most likely a measure of the entrainment of oxic water below the chemocline ($O_2 + 2H_2S \Rightarrow 2S^0 + 2H_2O$).

Freons are used as tracers for studies of vertical circulation in the ocean. However, in sulfidic seawater CFC-11 is certainly not stable. The reaction between

H_2S and CCl_3F should be investigated.

The mineralization of organic matter may take place in other parts than on the bottom of anoxic basins. Together with microbiologists it should be possible to find out where the mineralization takes place and the rate of the process.

The production of biogenic opal should be measured and correlated with the supply of $Si(OH)_4$. By the use of sediment traps the downward flux of biogenic opal could be measured. Experiments with benthic flux chambers should give reliable values of the release rate. Thus the vertical advection of $Si(OH)_4$ could be obtained.

Dyrssen (1999) has compared the Black Sea with Framvaren, and pointed out investigations that should be made in the future.

Coprecipitation of trace metals such as Co, Ni, Cu and Zn with FeS has been suggested (*e.g.* Dyrssen and Kremling, 1990) to explain the determinations of trace metals in particles. However, reliable values for the formation of most MSH+ and $M(SH)_2$ complexes have not been determined. As shown above for iron(II) these complexes influence the solubility of MS.

References

Almgren, T., Danielsson, L.-G., Dyrssen, D., Johansson, T. and Nyquist, G. 1975. Release of inorganic matter from sediments in a stagnant basin. *Thalassia Jugoslavica* **11**:19-29.

Almgren, T. Dyrssen, D., Elgquist, B. and Johansson, O. 1976. Dissociation of hydrogen sulphide in seawater and comparison of pH scales. *Mar. Chem.* **4**:289-297.

Dyrssen, D. 1977. The chemistry of plankton production and decomposition in seawater. In Ocean Sound Scattering Prediction ed. by N.R. Andersen and B.J. Zahuranec, p.65-84, Plenum Press, New York, 859 pp.

Dyrssen, D. and Hallberg, R. 1979. Anoxic sediment reactions - a comparison between box experiments and a fjord investigation. *Chem. Geol.* **24**: 151-159.

Dyrssen. D. and Svensson, T. 1982. On the calculation of release rates from stagnant basin sediments. *Chem. Geol.* **36**: 349-351.

Dyrssen D. and Kremling, K. 1990. Increasing hydrogen sulfide concentration and trace metal behavior in anoxic Baltic waters. *Mar. Chem.* **30**:193-204.

Dyrssen, D. 1992. Processes that determine the pH of seawater. *Vatten* **48**:246-

250.

Dyrssen, D., Hall, P.O.J., Haraldsson, C., Chierici, M., Skei, J. and Östlund, H.G. 1996. Time dependence of organic matter decay and mixing processes in Framvaren, a permanently anoxic fjord in South Norway. *Aquatic Geochemistry* **2**:111-123.

Dyrssen, D. 1998. The source of silica and trace metals in particulate matter in Framvaren Fjord. *Aquatic Geochemistry* **3**:329-343.

Dyrssen, D. 1999. Framvaren and the Black Sea - similarities and differences. *Aquatic Geochemistry* **4**:1-15.

Grasshoff, K., Kremling, K. and Ehrhardt, M. (editors) 1999, Wiley-VCH, pp. Chapter 5. Determination of hydrogen sulfide by S. Fonselius, D. Dyrssen and B. Yhlen. Chapter 6. Determination of thiosulphate and sulphur by D. Dyrssen, S. Fonselius and B. Yhlen. Chapter 7. Determination of pH by M. Wedborg, D.R. Turner, L.G. Anderson and D. Dyrssen. Chapter 8. Determination of alkalinity and total dissolved inorganic carbon by L.G. Anderson, D.R. Turner, M. Wedborg and D. Dyrssen.

Habicht, K.S. and Canfield, D.E. 1997. Sulfur isotope fractionation during bacterial sulfate reduction in organic-rich sediments. *Geochim. Cosmochim. Acta* **61**:5351-5361.

Hansson, I. A new set of pH scales and standard buffers for sea water. *Deep-Sea Res.* **20**:479-491.

Haraldsson, C., Anderson, L.G., Hassellöv, M., Hulth, S. And Olsson, K. 1997. Rapid, high-precision potentiometric titration of alkalinity in ocean and sediment pore waters. *Deep-Sea Res.* **I, 44**: 2031-2044.

Huxtable, R.J. 1986. Biochemistry of Sulfur. Plenum Press, New York, 445 pp.

Johansson, O. and Wedborg, M. 1982. On the evaluation of potentiometric titrations of seawater with hydrochloric acid. *Oceanologica Acta* **5**: 209-218.

Julshamn, K., Andersen, A., Ringdal, O. and Moerkoere, J. 1987. Trace elements intake in the Faroe Islands. II. Intake of mercury and other elements by consumption of pilot whales (Globicephalus Meleanus). *Sci. Total Environ.* **65**:63-68 (Part I p. 53-62).

Landing. W.M. and Westerlund, S. 1988. The solution chemistry of iron(II) in Framvaren. *Mar. Chem.* **23**: 329-343.

Martell, A.E. and Hancock, R.D. 1996. Metal Complexes in Aqueous solutions.

Plenum Press, New York, 253 pp.

Rutgers van der Loeff, M.M., Anderson, L.G., Hall, P.O.J., Iverfeldt, Å., Josefson, A.B.,Sundby, B. and Westerlund, S.F.S. 1984. The asphyxiation technique: An approach to distinguishing between molecular diffusion and biological mediated transport at the sediment-water interface. *Limnol. Oceanogr.* **26**: 675-686.

Shapiro, S.D., Schlosser, P., Smethie Jr., W.M. and Stute, M. 1997. The use of ^{3}H and tritiogenic ^{3}He to determine CFC degradation and vertical mixing rates in Framvaren Fjord, Norway. *Mar. Chem.* **59**: 141-157.

Skei, J. 1988. Formation of framboidal iron sulfide in the water of a permanently anoxic fjord - Framvaren, South Norway. *Mar. Chem.* **23**: 345-352.

Yao, W. And Millero, F.J. 1995. The chemistry of anoxic waters in the Framvaren fjord. *Aquatic Geochemistry* **1**: 53-88.