Aquatic Geochemistry **1**: 53–88, 1995.

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The Chemistry of the Anoxic Waters in the Framvaren Fjord, Norway

WENSHENG YAO and FRANK J. MILLERO
University of Miami, Rosenstiel School of Marine and Atmospheric Science, 4600 Rickenbacker Causeway, Miami, FL 33149, U.S.A.

(Received: 1 July 1994; accepted: 18 December 1994)

Abstract. In the summer of 1993, a number of chemical parameters (H_2S, O_2, pH, TA, TCO_2, NH_4^+, PO_4^{3-}, SiO_2, Mn^{2+} and Fe^{2+}) were measured in the Framvaren Fjord, a permanently super-anoxic fjord in southern Norway. The extremely steep gradient of sulfide near the interface suggests that other than downward flux of oxygen, three other possible oxidants, particulate manganese and iron oxides, phototrophic sulfur oxidation bacteria and horizontally transported oxygen account for the oxidation of the upward flux of H_2S. Water intrusion through the sill accounts for the temperature inflection above the interface, which, together with internal waves (Stigerbrandt and Molvaer, 1988), may cause fluctuations of the depth of interface. Significant gradients of hydrographic properties and chemical species between 80–100 m suggest that there is a "second interface" at about 90 m that separates the deep and older bottom waters. A stoichiometric model is applied to examine the biogeochemical cycles of S, C, N and P in the Framvaren. High C:S, C:N and C:P ratios are found while the nutrients (N, P) have Redfield ratio. Based on the C:N:P ratio of 155:16:1 in organic matter, about 30% of sulfide produced by sulfate reduction is estimated to be removed by processes such as oxidation, formation of FeS_2, degassing and incorporation into organic matter. The rates of oxidation of H_2S by Mn and Fe oxides in the water near the interface were slightly faster than the observed values in the laboratory, probably due to the presence of bacteria.

Key words: Anoxic waters, the Framvaren fjord.

1. Introduction

The Framvaren, located in southern Norway, is a permanent super-anoxic fjord which has the highest levels of H_2S (6 mM) reported for an open anoxic basin. The fjord has a shallow sill of 2 m that separates the outer Helvikfjord (80 m) from the basin that is 183 m deep (Skei, 1988). The large salinity gradient (Figure 1) accounts for the large pycnocline that separates the surface and deep water. Based on the hydrography, the water masses can be divided into four major layers: the low salinity surface layer (0–2 m) above the sill depth; the intermediate oxygenated layer down to ~18 m; the deep water where steep gradients in the chemistry occur (18–90 m); and the bottom water below 90 m, where changes in salinity and chemistry are small (Skei, 1988a).

Due to the unusual chemical and microbiological properties, the Framvaren has been widely used as a natural laboratory to study anaerobic processes since 1930s (Skei, 1986). Earlier studies on the hydrography, currents, trace metals, isotopes,

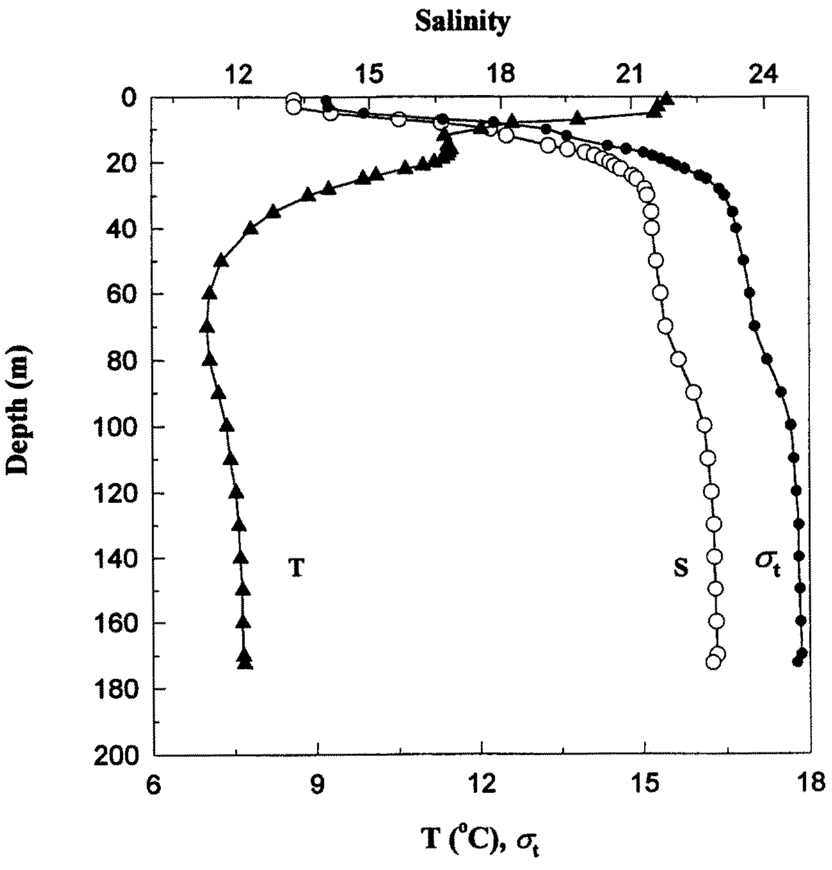

Fig. 1. Temperature, salinity and density profiles for the Framvaren Fjord waters.

microbiology, sedimentation and seismology of the fjord have been reviewed (Skei, 1986; Skei, 1988a). Unlike most other anoxic basins, the O_2/H_2S interface (~18 m) in the Framvaren is at a depth of significant light penetration. Dense populations of photosynthetic bacteria are present at the redox boundary (Skei, 1988). Measurements of ATP indicate that the interface is very active biologically (Sørensen, 1988). This high biological activity can effectively control the biogeochemistry of metals and non-metals (Tebo and Nealson, 1984; McKee and Todd, 1993). The redox-active metals (Fe, Mn and Co) show the characteristic maximum near the interface (Jacobs *et al.*, 1985; Haraldsson and Westerlund, 1988; Landing and Westerlund, 1988). More recently, Millero (1991) studied the oxidation of H_2S with O_2 in the Framvaren. The oxidation rates were found to be greatly enhanced by the high content of Fe and Mn. Only low levels of the intermediates SO_3^{2-} and $S_2O_3^{2-}$ were found near the interface.

The pathways and rates of respiratory processes and nutrients regeneration are important for understanding the global cycles of nitrogen, phosphorus, carbon, oxygen and sulfur. Fjords and basins in which deep water becomes anoxic or approach anoxic conditions due to bottom water stagnation, provide a natural laboratory to investigate these pathways and rates (Smethie, 1987). Much of our understanding of anaerobic microbial decomposition of organic matter has come from studies of these systems (Richards, 1965; Grasshoff, 1975). Dyrssen (1987, 1989) has used a stoichiometric model of the organic matter based on available data to show that more sulfate was reduced than sulfide found in the Framvaren. In June 1993, we had the opportunity to participate in an investigation in the Framvaren Fjord coordinated by Jens Skei at the Norwegian Institute for Water Research. In this paper we report on the measurements of a number of chemical parameters (H_2S, O_2, PO_4^{3-}, NH_4^+, SiO_2, pH, TA, TCO_2, Mn^{2+} and Fe^{2+}) and examine the relationships of these parameters in this unique anoxic basin.

2. Methods

The water samples were collected in 5-L Niskin bottles and 10-L Go-Flo bottles (for Mn and Fe). The sampling resolution with these bottles was relatively poor. For determination of dissolved Mn and Fe across the chemocline, a better sampling resolution (10 cm) was achieved by using a submersible pumping system (supplied and operated by B. Mackee and J. Todd). The temperature and salinity were obtained from a SeaBird CTD sensor. The concentrations of dissolved oxygen were determined by Winkler titrations (Carpenter, 1965). Concentrations of H_2S in the samples were determined spectrophotometrically with the methylene blue technique (Cline, 1969). All the samples were fixed with reagents immediately after they were on board. Three different reagents were used for the appropriate ranges of H_2S. Concentrations of H_2S in the deep-water samples were diluted (after being fixed) with deionized water before determination to a level valid for the calibration ($< 1{,}000\ \mu M$). Samples for pH, total alkalinity (TA), phosphate and ammonia were collected in 130 ml glass bottles with a rubber stopper. Samples for total inorganic carbon (TCO_2) were collected in the same glass bottles with the addition of $HgCl_2$ (enough to precipitate all the H_2S). Samples for silicate were collected in plastic bottles. Samples for dissolved Mn^{2+} and Fe^{2+} were filtered through 0.45 μm Nuclepore filters immediately after collection and fixed with appropriate reagents for colorimetric measurements in hours. A HP 8452A spectrophotometer was used to do the spectral measurements.

The pH and TA were determined within hours after collection. The pH of the water samples was measured at 25°C with an Orion glass electrode and a Ag-AgCl double junction reference electrode calibrated with 0.005 m Tris buffers at different salinities (10–25) on the total pH scale (Dickson, 1993). The samples were kept under a N_2 atmosphere to minimize the oxidation of H_2S. The Nernst response of the electrode pair was examined using seawater buffers (Bis, Tris and 2-Aminopyridine) that cover a pH range from 6.8 to 8.8 (Millero *et al.*, 1993a). The precision of the pH measurements was ±0.005 pH units. The TA of the water samples was determined spectrophotometrically using the bromocresol green indicator at 25°C (Breland and Byrne, 1993). A 100 ml water sample was delivered to the water-jacketed cell by a volume-calibrated pippet. HCl (0.25 m and 1.0 m) was added by Brinkmann 665 Dosimat to bring the final pH of sample within the range of 3.7–4.0. The 0.25 m and 1.0 m HCl solutions were made with Suprapur HCl (30%) in Milli-Q water and standardized using the method of silver chloride gravimetry (Little, 1971) in the laboratory. The acidified sample was purged with N_2 for 5 min. The final pH of the acidified, degassed sample was determined spectrophotometrically after the addition of bromocresol green. The TA of the sample was calculated by the amount of excess acid. The precision of this method for seawater samples was ±2 μM. Laboratory calibrations of the technique agreed to ±2 μM with potentiometric titrations (Millero *et al.*, 1993b).

Since high concentrations of H_2S interfere with the nutrient measurements, it was removed by adding HCl and purging with N_2. The concentrations of silicate in the samples were determined on board ship by a colorimetric technique based on the reaction of the silicate with an acidified molybdate reagent to yield a silicomolybdate complex (Parsons *et al.*, 1984). The precisions were estimated to be ±1 μM at low levels (45 μM) and ±10 μM at high levels (600 μM). The concentrations of phosphate, ammonia and TCO_2 were determined after the samples were returned to the laboratory. The concentrations of phosphate in the samples were determined by a colorimetric technique based on the reaction of the phosphate with an acidified molybdate reagent to form a phosphomolybdate complex, which was then reduced with ascorbic acid to a highly colored blue compound (Parsons *et al.*, 1984). The precisions were estimated to be ±0.03 μM at low levels (0.02 μM) and ±2 μM at high levels (100 μM). After the acidified samples were neutralized the concentrations of ammonia were determined by a colorimetric technique based on the formation of Indophenol Blue (Parsons *et al.*, 1984). The TCO_2 was determined in the laboratory by coulometric analysis using a 5011 coulometer (Johnson *et al.*, 1985). The coulometer was calibrated using standard Na_2CO_3 solutions and Certified Reference Material. The precision of the TCO_2 measurements was ±2 μM.

The concentrations of Mn in filtered samples were determined using a colorimetric method (Brewer and Spencer, 1971). The detection limit was estimated as 0.2 μM. The dissolved Fe^{2+} measurements were made using the Ferrozine technique (Landing and Westerlund, 1988). The detection limit was estimated as 20 nM. The dissolved Mn^{2+} and Fe^{2+} concentrations in the deep samples were determined by direct injection GFASS after the samples were returned to the lab. The detection limit for Mn and Fe in the deep waters were estimated as 20 nM and 5 nM, respectively.

The measurements on the rates of oxidation of hydrogen sulfide by Mn and Fe (hydr)oxides were performed in a 1000 cm^3 Plexiglass vessel at 25°C. MnO_2 was prepared according to the procedures given in Murray (1974). Goethite (αFeOOH) was prepared according to Schwertmann and Cornell (1991). The freshly precipitated hydrous Fe(III) oxide was produced by adding Fe(II) into the water just above the interface and letting it to be oxidized. The synthesized metal oxides were added to the waters near the interface (containing ~25 μM H_2S), which were kept under N_2 atmosphere. The reaction rates were followed by monitoring the decrease of total sulfide concentrations with time ($-d[H_2S]/dt = k\,[MO_X][H_2S]$). The reactions have been found to be first order with respect to both H_2S and metal oxides (Yao and Millero, 1994).

3. Results

The water samples were collected at a central station of the basin during 4–7 June (1993). Table I summarizes the results of all the measured parameters.

3.1. TEMPERATURE AND SALINITY

The maximum temperature occurred at the surface and decreased sharply with depth to 14 m. The temperature slightly increased in the middle of intermediate layer and reached a sub-maximum at 16.5 m (Figure 1). This temperature structure might be due to the intrusion of the surface water of Helvikjord through the sill, which may also contribute to the renewal of the upper 10–20 m waters (Stigebrandt and Molvaer, 1988). There was a steep salinity increase from the surface down to the bottom of the intermediate layer (~20 m) which contributed to the large pycnocline. A secondary halocline was also observed at about 90 m (Figure 1). The salinity in the surface waters was about 13.26 which is much higher than the value found during the 1989 cruise (9.70). Both cruises were at the same time of the year. These results suggest that the local freshwater supply to the Framvaren may vary annually.

3.2. OXYGEN AND HYDROGEN SULFIDE

The dissolved oxygen in the surface water was 283 μM which is close to the saturated value (285 μM). The maximum value 292 μM in the subsurface (6 m) is due to photosynthesis. The oxygen concentration decreased sharply from 15 m and became undetectable below 18 m (Figures 2a and 2b). The H_2S was found to appear at 20 m (0.43 μM) which corresponded to the $\sigma_t = 15.8$ isopycnal surface. The interface at 18 m showed no overlap in the levels of O_2 and H_2S within the sampling scale (1 m). The interface was found to locate at 18 m (σ_t= 16.52) in 1979, at 18 m (σ_t= 15.8–15.9) in 1985 and at 19 m (σ_t = 15.60) in 1989. The oxic/anoxic interface has been relatively stable during the last 20 years based on the depth resolution of the Niskin bottles. Small fluctuations however are expected to occur due to changes in the exchange of water with outside basin and internal waves (Stigebrandt and Molvaer, 1988). The concentrations of H_2S in the bottom water were found to be as high as 5.8 mM which is in reasonable agreement with the recent results of Landing and Westerlund (6.1 mM, 1988) and Millero (5.7 mM, 1991). The sulfide data in the bottom water scattered from 6.4 mM to 8.4 mM in

TABLE I. Data for station F1. Values for all chemical species in μM.

Depth (m)	T (°C)	Salinity	O_2	H_2S	PO_4^{3-}	NH_4^+	SiO_2	pH	TA	TCO_2	Mn	Fe
1	15.44	13.27	283		–	–	–	–	–	–	–	–
2	15.41	13.26	–		0.30	–	–	7.819	914	875	–	0.06
5	15.22	14.12	274		0.40	5.1	–	7.881	990	953	–	–
6	14.75	14.88	292		–	–	–	–	–	–	–	–
10	12.03	17.76	245		–	–	–	7.448	1280	1275	–	0.02
14	11.18	18.83	183		–	–	–	–	–	–	–	–
15	11.42	19.10	154		0.25	5.6	19.0	6.986	1352	1479	2.6	–
15.5	11.36	19.34	113		–	–	–	–	–	–	–	–
16	11.48	19.55	53		0.18	11.0	–	–	–	–	4.8	–
17	11.44	19.95	14		–	–	–	–	–	–	6.8	–
17.5	11.41	20.04	6.6		–	–	–	–	–	–	–	–
18	11.41	20.16	8.3		0.18	8.6	–	–	–	–	8.6	0.06
19	11.33	20.34		0	0.25	–	–	–	–	–	10.7	0.07
20	11.17	20.51		0.43	0.31	11.6	49.5	7.248	1880	1928	13.7	0.07
20.5	11.10	20.57		2.87	0.40	–	–	–	–	–	14.0	0.12
21	10.97	20.62		11.9	1.02	67.2	–	–	–	–	18.0	2.85
21.5	10.81	20.70		97.8	1.33	–	–	–	–	–	16.7	1.70
22	10.65	20.76		182	2.36	55.5	–	–	–	–	16.2	1.55
23	10.37	20.90		194	1.98	65.5	–	–	–	–	15.3	1.58
24	10.12	20.02		–	3.72	–	–	–	–	–	14.6	1.37
25	9.88	21.12		–	–	–	89.7	7.158	2680	2534	–	–
26	9.70	21.20		396	5.11	118	–	–	–	–	12.2	1.03
28	9.25	21.31		–	6.11	–	–	–	–	–	9.5	0.65
30	8.87	21.36		526	9.41	145	102	7.002	3148	2944	8.4	0.52
40	7.82	21.47		1132	15.2	153	136	6.959	4003	3427	5.8	0.12
50	7.27	21.56		1564	20.3	320	171	6.891	5024	4308	3.8	0.08
60	7.05	21.66		1764	25.7	409	210	6.890	6158	5398	2.7	0.06
70	7.00	21.77		2176	37.9	521	266	6.914	7887	6910	2.5	–
80	7.05	22.06		2858	51.7	713	350	6.917	10,118	8798	–	–
90	7.21	22.40		3911	72.2	1140	457	6.904	14,360	12,655	1.1	0.02
100	7.36	22.64		4528	87.0	1281	558	6.898	16,826	14,897	–	–
110	7.43	22.72		4599	91.0	1421	586	6.900	17,660	15,738	0.8	0.03
120	7.53	22.79		4936	97.0	1547	570	6.898	18,368	16,262	0.8	–
130	7.58	22.85		5034	100	1548	611	6.902	19,012	16,874	–	0.02
140	7.61	22.86		5100	101	1629	625	6.902	19,329	17,156	0.6	–
150	7.64	22.88		5106	102	1617	626	6.885	19,510	17,463	–	0.03
160	7.65	22.90		5685	102	1586	640	6.885	19,489	17,000	0.8	–
170	7.66	22.92		5813	101	1646	634	6.885	19,603	17,025	0.5	0.04
175	–	–		5852	100	1549	608	6.868	19,812	17,349	–	–

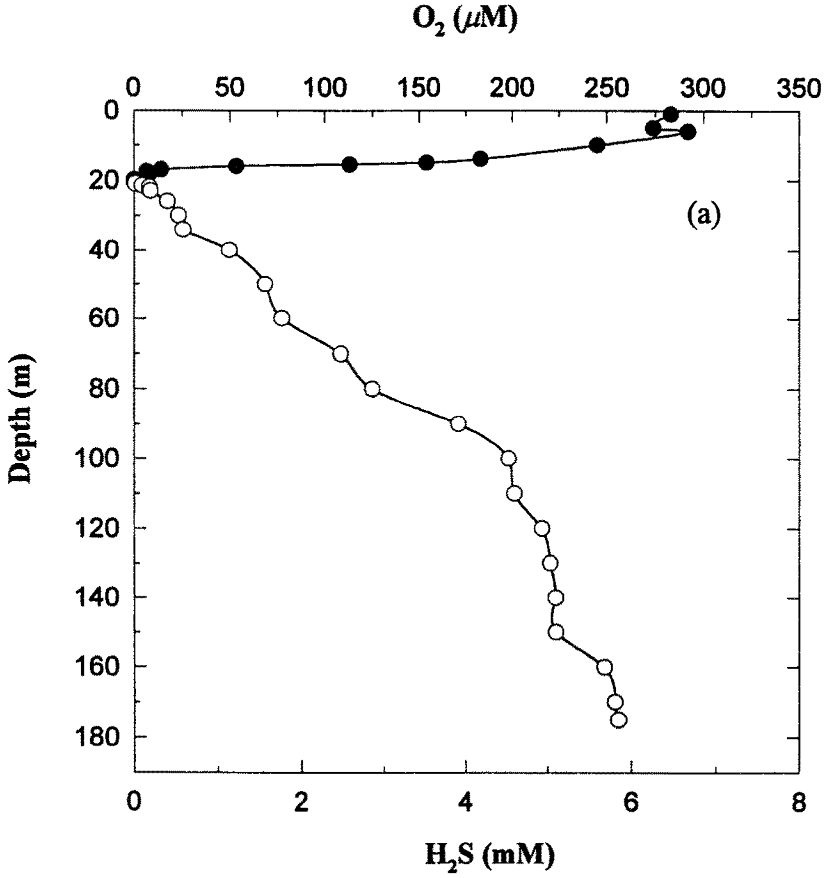

Fig. 2. Depth profiles of O_2 and H_2S. (a) Whole water column.

the earlier investigations performed during 1979 and 1985 (Skei, 1986) reflecting analytical difficulties. It is not possible to detect any sulfide evolution over this time scale. On the contrary, it has been suggested that the bottom water has likely reached a steady state (Dyrssen *et al.*, 1984). As pointed out by Millero (1991), the gradient of H_2S in the bottom water (below 100 m) is much smaller than that in the deep water (20–100 m). He suggested that this may be due to the separation of the older water and more recent anoxic water (Skei, 1983). The distributions of nutrients, TA and TCO_2 (given below) show the same pattern.

3.3. DISSOLVED Mn AND Fe

The dissolved Mn and Fe together with O_2 and H_2S near the interface are shown in Figure 2b. The concentrations of dissolved Mn increased rapidly below 15 m, corresponding to the rapid decrease of O_2 and reached a maximum at 21 m where the concentration of H_2S was 12 μM. The maximum dissolved Mn found in this study,

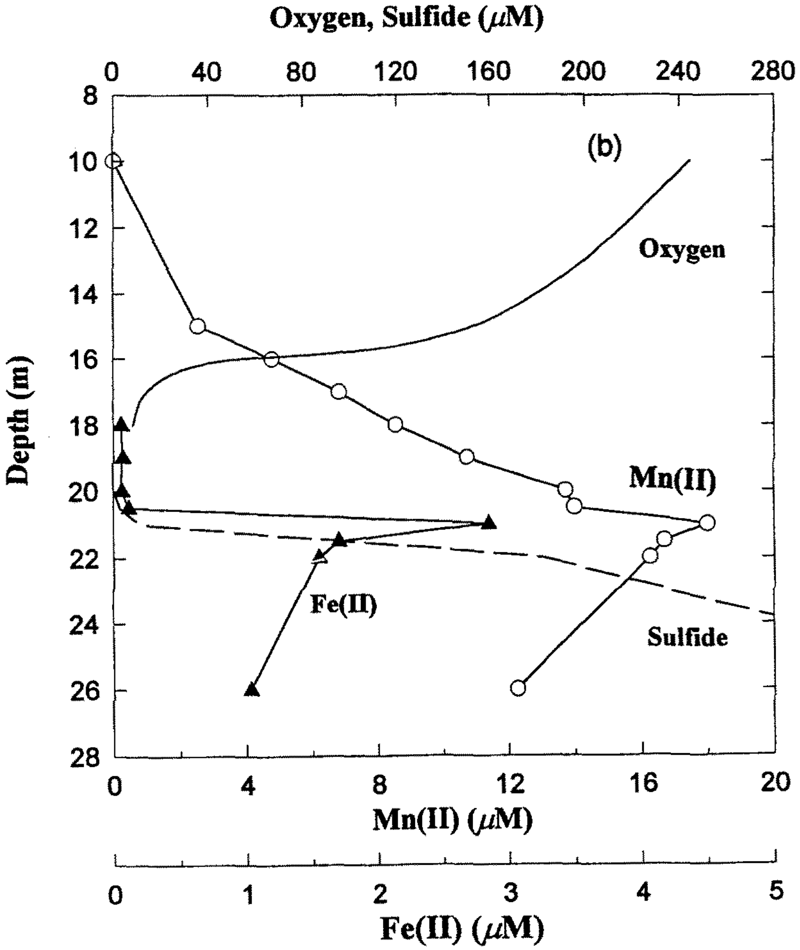

Fig. 2. (b) Near the interface together with dissolved Mn and Fe.

18.0 μM, is higher than previous values of 10.0 μM (Dyrssen *et al.*, 1984), 10.5 μM (Jacobs *et al.*, 1985) and 15.29 μM (Haraldsson and Westerlund, 1988). Our higher value might be due to the better sampling resolution with the submersible pumping system. It might also reflect the continuing accumulation of Mn in the transition zone. The concentrations of dissolved Mn decreased rapidly below the maximum peak at 21 m and reached nearly constant values (less than 1 μM, Table I) below 100 m.

The concentrations of dissolved Fe started increasing just below the O_2/H_2S interface (Figure 2b) to a sharp maximum at 21 m. The maximum value found in this study, 2.85 μM, is higher than earlier values of 2.1 μM (Dyrssen *et al.*, 1984), 2.65 μM (Jacobs *et al.*, 1985), 0.89 μM (Landing and Westerlund, 1988) and 2.0 μM (Haraldsson and Westerlund, 1988). Again, these differences could be caused by various sampling depth and/or fluctuation of Fe(II) concentration with time. The lower value of 0.89 μM (Landing and Westerlund, 1988) found in the winter time might result from the oxidation of Fe(II) near the interface by O_2 due to the enhanced water mixing in this season. The concentrations of dissolved Fe(II) decreased rapidly below the maximum to less than 40 nM in the bottom water (Table I), probably due to the formation of iron sulfide minerals (Skei, 1988b).

3.4. PHOSPHATE, AMMONIA AND SILICATE

The concentration of phosphate in the surface water was about 0.4 μM and reached a minimum (0.18 μM) between 16–18 m, which may be due to the high productivity at this region (Sørensen, 1988) or absorption onto Mn and Fe particles. Maximum values of particulate Mn and Fe are usually found at or above the O_2/H_2S interface (Tebo *et al.*, 1984; Skei, 1986). The PO_4^{3-} increased rapidly below the interface and reached a maximum of 100–102 μM in the bottom water (Figure 3). In the Black Sea, the phosphate profile was characterized with two maxima, in upper and lower boundary of the interface, respectively, and a minimum in the middle (Murray and Izdar, 1989). This unique phosphate distribution was first suggested by Shaffer (1986) to be the result of redox processes involving Fe and Mn that cause the vertical transport of phosphate across the suboxic/anoxic interface. Because of the shallow depth of the interface (~18 m) and the steep chemical gradient across the interface, no such phosphate anomaly is found in the water column of the Framvaren.

Ammonia was present in the oxic euphotic zone at about 5.0 μM (Table I). It increased rapidly below the interface and reached a maximum of 1.6 mM in the bottom waters (Figure 3). Relatively high (~20 μM) silicate was found in the oxic waters and the concentrations increased rapidly below the interface to a maximum of 640 μM in the bottom water (Figure 3). The concentrations of phosphate, ammonium and silicate in the bottom water were all close to the results of earlier studies (Skei, 1986).

3.5. pH, TOTAL ALKALINITY AND TOTAL CARBON DIOXIDE

The distributions of pH, TA and TCO_2 are plotted in Figure 4. The pH in the surface waters was about 7.89 and decreased to a minimum (6.98) at 15 m. The low pH at 15 m is difficult to explain although it agrees with the calculated value using TA and TCO_2. The pH decreased below the interface and was constant below 90 m (about 6.90).

The TA increased with depth from the surface to the interface corresponding with the increase in salinity. The average normalized (to $S = 35$) TA was 2.41 mM in the surface water which is slightly higher than the value in ocean surface water (about 2.35) probably due to the impact of fresh water with high normalized TA. Below the interface the TA increased rapidly due to the bacteria anaerobic respiration of organic matter to bicarbonate and simultaneously reduction of sulfate to hydrogen

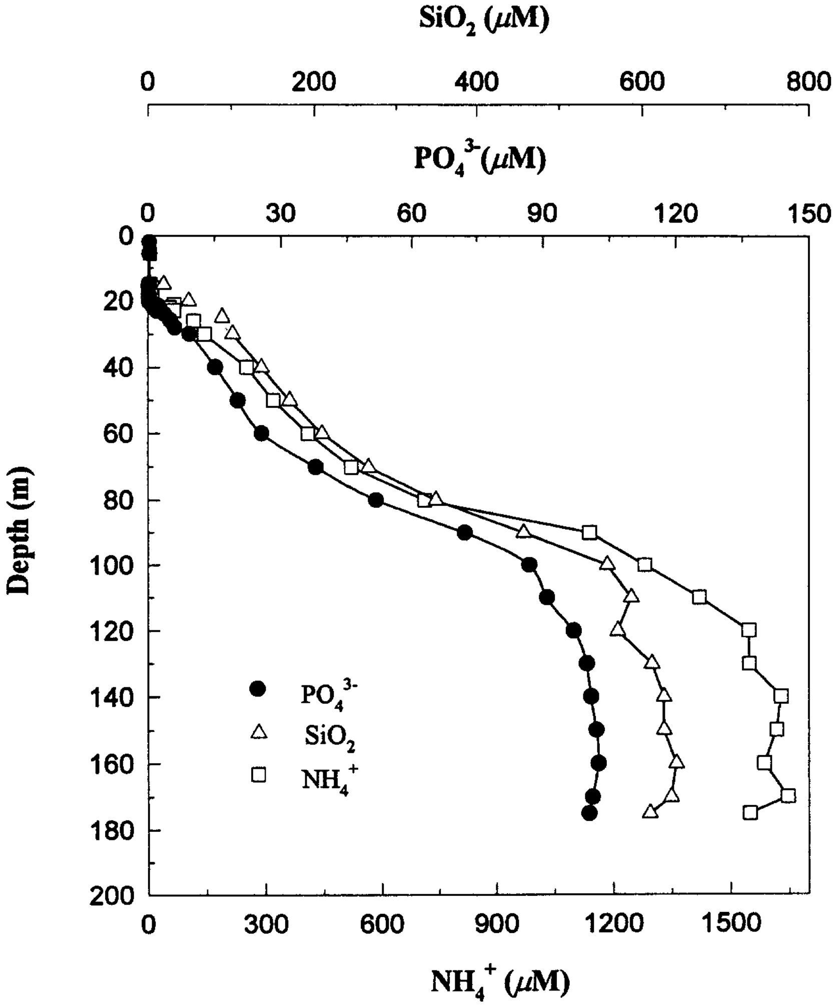

Fig. 3. Profiles of ammonia, phosphate and silicate in the Framvaren.

sulfide. The TA was found to be 19.8 mM in the bottom water which was about 1 mM lower than earlier results (Skei, 1986).

The TCO_2 in the water samples was determined after the poisoned samples were returned to the laboratory. Due to the extremely high TCO_2 in the anoxic water (the pCO_2 in the bottom water was as high as 38,000 μatm), a large amount of CO_2 in samples (about 2 mM in the bottom samples) was lost to the head space in the sample bottles. We thus give the calculated values of TCO_2 in Table I and Figure 4 for the samples below the interface. The values of TCO_2 were calculated based on the pH (25°C), TA and salinity using the carbonate constants given by Roy *et al.* (1993). The TA is defined as (Dickson, 1981):

$$TA = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-]$$

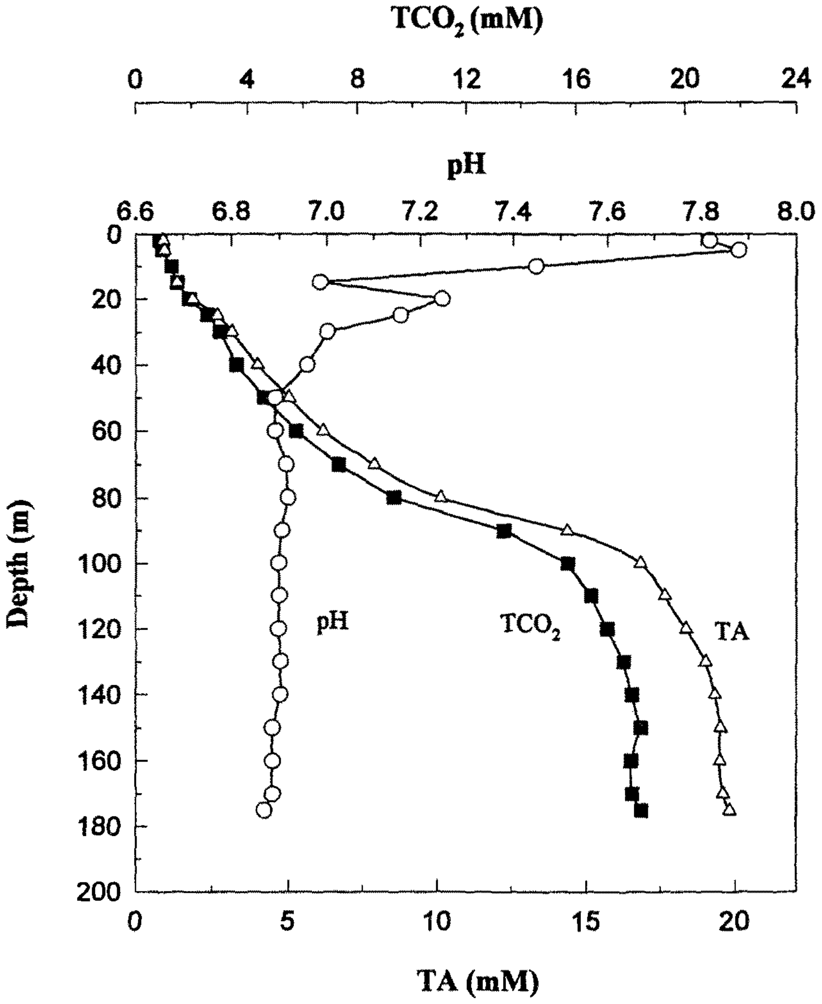

Fig. 4. Profiles of pH, TCO_2 and TA in the Framvaren.

$$+ [HPO_4^{2-}] + 2[PO_4^{3-}] + [HS^-] + [NH_3]$$
$$+ [Si(OH)_3O^-] - [H^+] - [HSO_4^-] - [HF] - [H_3PO_4].$$

To calculate the carbonate alkalinity one has to correct for the contribution of $B(OH)_4^-$, HPO_4^{2-}, PO_4^{3-}, HS^-, NH_3 and $Si(OH)_3O^-$ in the waters. The dissociation constants of acids needed to make these calculations are presented in the Appendix. We recommend the use of these constants for the thermodynamic calculations of carbonate system in anoxic waters. The TCO_2 increased rapidly below the interface due to the oxidation of organic matter to inorganic carbon. The concentration of TCO_2 in the bottom water was 17.3 mM which was 1 mM lower than earlier values (Skei, 1986).

4. Discussion

4.1. HYDROGRAPHIC PROPERTIES AND VENTILATION OF THE FRAMVAREN

In order to explain and understand the measured distributions of different chemical species in the Framvaren, the physical transport parameters and the rate of vertical circulation must be known. The mean local freshwater supply to the Framvaren is only about 1 m^3 s^{-1} (Skei, 1988a). Therefore much of the freshwater stored in the Framvaren probably emanates from outside sources. The water density in the Helvikfjord is normally higher than that in the Framvaren at the corresponding depths. The water exchange between the Framvaren and the Helvikfjord is greatly hampered by the shallow sill (2 m) and channel (500 m long) that separates the two basins. The water exchange between the Framvaren and the Helvikfjord is almost completely barotropic and driven by the fluctuation in the sea-level between the two basins. Model calculations (Stigebrandt and Molvaer, 1988) indicate that most of the seawater entering the Framvaren from the Helvikfjord as a density current may only contribute to the renewal of the upper 10–20 m due to the low density of the inflowing water. Unfortunately, the salinity observations in the Helvikfjord are sparse and it is not possible to estimate the residence time of water at different depths (Stigebrandt and Molvaer, 1988). The renewal of water at great depths may occur only when the Helvikfjord has very dense surface water. This renewal will cause the oxic/anoxic interface to fluctuate. A fish kill took place in the winter 1942 apparently due to extremely high-density water at the sill depth and the resultant raise of the interface (Skei, 1988a).

Salinity increased sharply from the surface to the interface, while the temperature showed an inflection at 14 m (σ_t = 14.19) and reached a sub-maximum at 16.6 m (σ_t = 14.87) (Figure 1). The same temperature structure was observed in previous studies (Figure 5). However, the extent of the increase of temperature has varied. It was most significant in 1984 (ΔT = 4.7°C) . The depth of the temperature inflection varied from 9 m to 14 m (σ_t = 13.2 to 16.0). This "sub-maximum temperature layer" might originate from the warm surface water of the Helvikfjord as discussed above. The extent of the temperature anomaly and the depth of the "sub-maximum temperature layer" depend on the extent of the water exchange and the difference in the hydrographic properties of the two basins. This water intrusion caused the non-linear relationship between temperature and salinity across the interface (Figure 6). This suggests that the horizontal transport might be an important process near the interface which has to be considered in explaining the vertical profiles of chemical species.

In the deep water, the salinity increased slightly from the interface down to 80 m while temperature decreased sharply down to 60 m and was almost constant between 60–80 m. Both temperature and salinity increased from 80–100 m (Figure 1). There was no linear T-S relationship in the deep water (Figure 6). The nature of the curvature in the bottom water (Figure 6) suggested an additional source of heat flow. As discussed earlier, chemical species showed large gradients

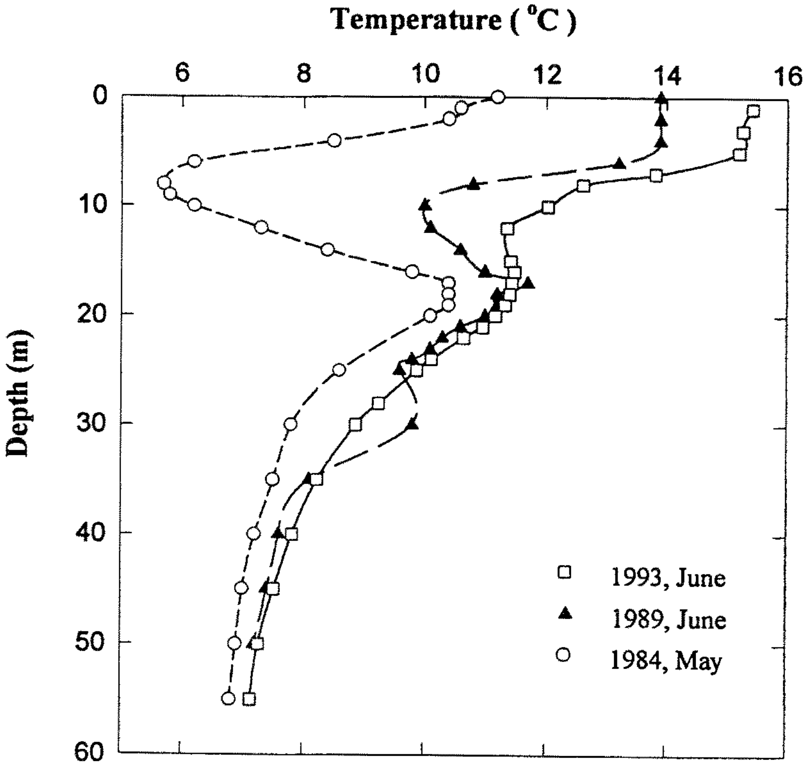

Fig. 5. Profiles of temperature in upper 60 m in recent years.

through the region between 80–100 m (Figures 2–4). The hydrographic properties and the concentrations of chemical species changed very slightly below 100 m. The interface between 80–100 m may reflect the separation between the older and more recent anoxic waters that occurred after a channel was dug in 1850 allowing water to enter from the outside basin. This water input might have caused a certain amount of deep water renewal. The extent of this renewal and its effect on the seawater at the bottom is not known. Skei (1988a) argued that the renewal was likely to be complete based on the fact that only 50% of the sulfate in the bottom water today is reduced. Anderson *et al.* (1988) assumed that a total water exchange took place. This opinion was based on sediment data which showed a dramatic change in color from light-colored to black at a depth corresponding to about 1850. Due to the existence of the chemical gradients at this interface, we feel that the renewal might only be partially complete. One would expect this renewal to continue slowly as the slight step in the hydrographic properties at the top of the bottom layer and be smoothed out by diffusion. Anderson *et al.* (1988) reported the high value of $\delta^{34}S$ for sulfide at 80 m indicating a flux from below. The uniform properties in the bottom layer suggested that it was produced and maintained by convection, probably driven by geothermal heat from the sediments. The temper-

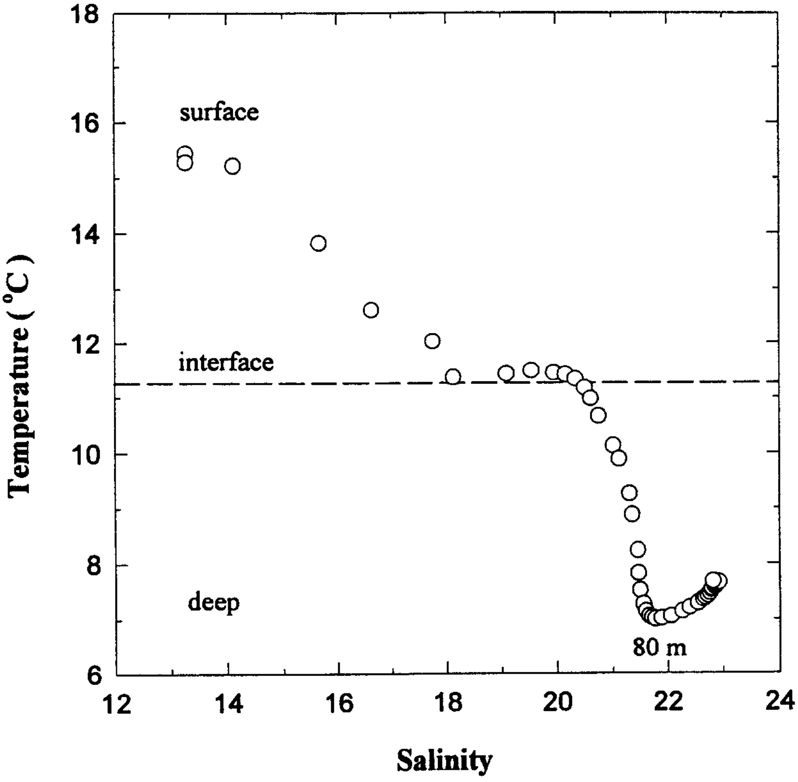

Fig. 6. Temperature–salinity diagram in the water column.

ature and salinity both increased slightly below 80 m, so the vertical transport is possibly controlled by double diffusion. Double diffusion takes place when the gradients of temperature and salinity have the same sign and thus have opposite effects on the density. Murray *et al.* (1991) compared the characteristics of the Black Sea benthic layer with available models to characterize the double diffusion process. No such attempt was made for the Framvaren due to the lack of heat flux measurements.

The strength of the vertical density stratification ($d\rho/dz$) is commonly expressed as the square of the Brunt–Väisäloä frequency, N, defined as

$$N^2 = (-g/\rho)(d\rho/dz). \tag{1}$$

The plots of N^2 below 30 m of waters collected in 1964, 1979 and 1993 are shown in Figure 7. The maximum values of N^2 are all between 80–100 m showing the boundary between deep and bottom water. It also shows that the density stratification in 1964 was more significant than at the present. This evolution of the density structure resulted from the continued diffusion process. The second interface will eventually no longer exist after the renewal of the bottom water is completed. Unfortunately, any change of the exact position of the interface is not possible to

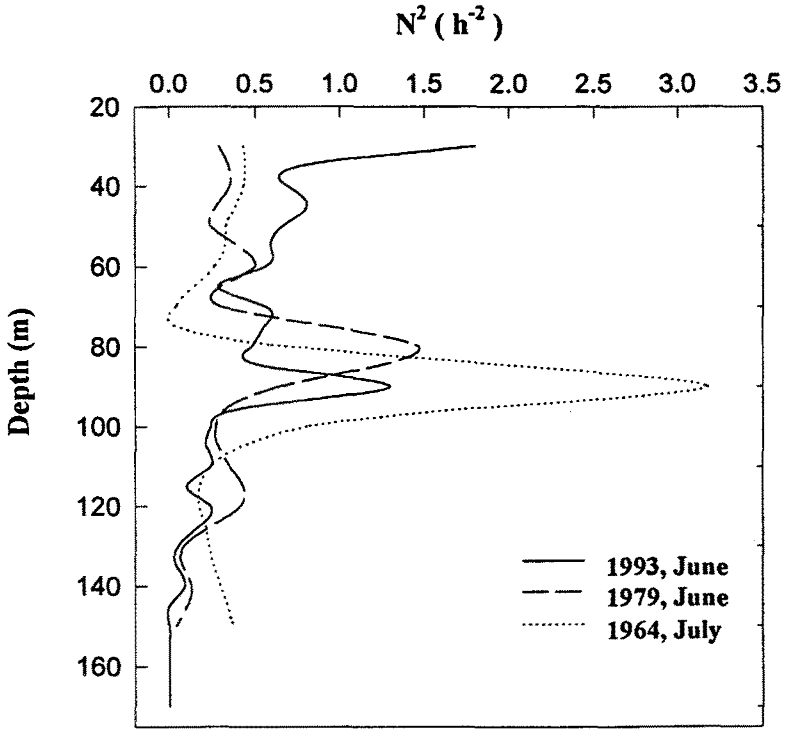

Fig. 7. The Brunt–Väisäloä frequency plotted as N^2 versus depth.

identify due to the non-detailed sampling resolution. The temperature in the bottom water showed a significant decrease of 1.1°C from 1930s to the present (Figure 8). This suggests that the heat flow to the bottom water, most probably geothermal heating from sediments, is decreasing. The salinity in the bottom water also showed a decreasing trend. This decrease in salinity implies that the renewal of the bottom water was with the lighter water above by vertical diffusion. Vertical diffusion might also account for the decrease of temperature in the bottom water.

4.2. BIOGEOCHEMICAL CYCLES OF S, C, N AND P IN THE FRAMVAREN WATER COLUMN

Biogeochemical cycles of C, N, P and S are linked because they are all involved in the photosynthesis and respiration (decay) of plants in a nearly fixed stoichiometric ratio. The decomposition of organic matter and the associated release of nutrients proceeds by aerobic respiration in the presence of oxygen, by denitrification when oxygen is depleted, by sulfate reduction when nitrate and nitrite are depleted and by fermentation when sulfate is depleted. Richards (1965) developed stoichiometric models for these processes using a ratio of C:N:P of 106:16:1, the generally accepted ratio for average plankton material for the world ocean (Redfield *et al.*,

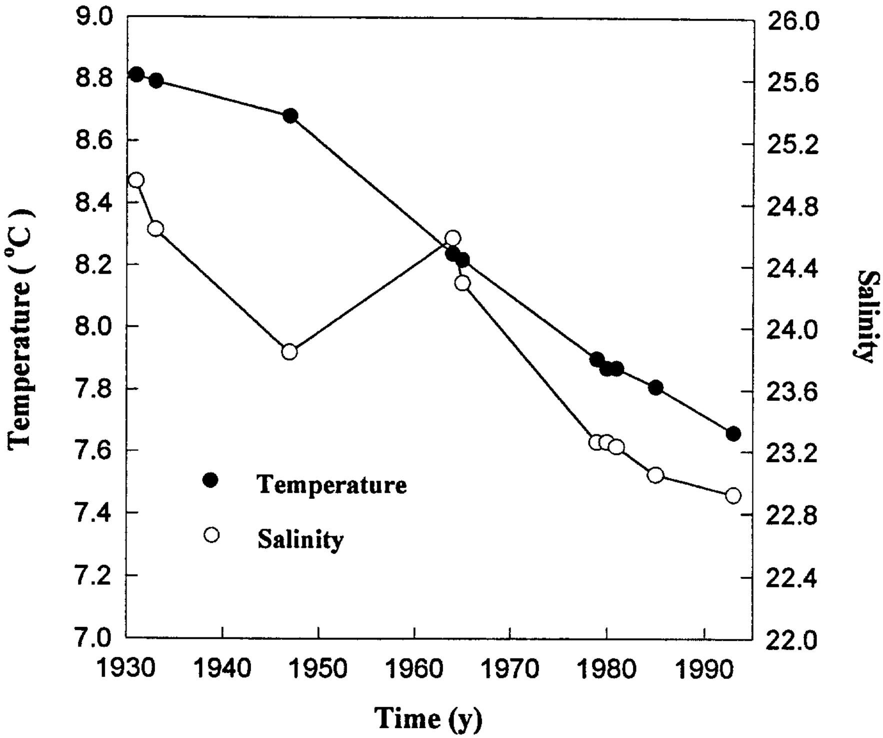

Fig. 8. Temporal changes of temperature and salinity in the bottom waters.

1963). For aerobic respiration:

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 106\ O_2$$
$$= 106\ CO_2 + 16\ NH_3 + H_3PO_4 + 106\ H_2O. \qquad (2)$$

In the presence of dissolved oxygen the ammonia is subsequently oxidized to nitrate by nitrifying bacteria

$$16\ NH_3 + 32\ O_2 = 16\ HNO_3 + 16\ H_2O. \qquad (3)$$

Denitrification can be represented by

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 84.8\ HNO_3$$
$$= 106\ CO_2 + 42.4\ N_2 + 148.4\ H_2O + 16\ NH_3 + H_3PO_4. \qquad (4)$$

The next most available source of free energy for the metabolic oxidation of organic matter in seawater is sulfate

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 53\ SO_4^{2-}$$
$$= 106\ HCO_3^- + 53\ H_2S + 16\ NH_3 + H_3PO_4. \qquad (5)$$

This model can be used to predict the steady-state concentrations of C, N, P and S in anoxic systems. As pointed out by Brewer and Murray (1973), there are some deficiencies in this approach because it does not account for mixing or the rates at which the system is driven to a steady state. According to the model, carbon, nitrogen and phosphate are released in the atomic ratio of 106:16:1. However, there are some processes that can alter this ratio. Under aerobic conditions, the regenerated phosphate can be absorbed on iron and manganese oxyhydroxides. Denitrification, occurring at oxic/anoxic interfaces, can alter the ratio of combined nitrogen (nitrate + nitrite + ammonium) to carbon dioxide and phosphate by producing N_2O and N_2. It is also possible that the organic matter has a C:N:P ratio different than 106:16:1 when lipids rather than carbohydrates are formed or degraded. Phytoplankton can also incorporate C:N:P in ratios different than 106:16:1 depending on the availability of these elements.

4.3. HYDROGEN SULFIDE

At present, it is not possible to establish a complete balance of sulfur in the Framvaren due to the incomplete measurements of sulfur species, especially the particulate sulfur (such as S^0 and FeS_2) and organic sulfur compounds. The ratio of thiols (mercaptants) RSH to H_2S was found to be 0.036 in the Framvaren (Dyrssen, 1989). Mopper and Kieber (1991) reported a significant organic thiols portion (e.g. 10–20%) of the total reduced sulfur near the top of the sulfidic zone in the Black Sea. The difference between the initial sulfate concentration, ($[SO_4]_{init}$), as calculated from salinity, and the measured sulfate concentration is found to be significantly higher (1–3 mM) than the measured sulfide in bottom water (Dyrssen, 1987; Anderson *et al.*, 1988). This discrepancy is explained by the removal of sulfide by oxidation and formation of iron sulfides (FeS and FeS_2) in addition to the degassing of H_2S (Dyrssen, 1987). If the major product of oxidation of H_2S is sulfate (Millero, 1991), the discrepancy may be even higher. The removal of sulfide by formation of iron sulfides is restricted to a continuing supply of iron. At pH = 7.0, about 30% of the total hydrogen sulfide is in $H_2S(aq)$. Degassing might be a pathway for H_2S to escape into upper oxic water and be oxidized. In addition, there is evidence for the early diagenetic incorporation of inorganic sulfur into organic compounds (Aizenshtat *et al.*, 1983; Vairavamurthy et al., 1992; Krein and Aizenshtat, 1994).

Like other anoxic basins, the evolution of anoxic conditions in the Framvaren started from the bottom due to the restricted supply of dissolved oxygen. The hydrogen sulfide concentration is mainly controlled by the supply of organic matter and its encounter with oxygen – either through the injection of fresh seawater over the sill or by vertical exchange through the oxic/anoxic interface. A simple vertical advection/diffusion model is commonly used to examine the flux of chemical species and explain the sequence of redox reactions occurring across the interface (Brewer and Murray, 1973). One difficulty of this approach is that horizontal

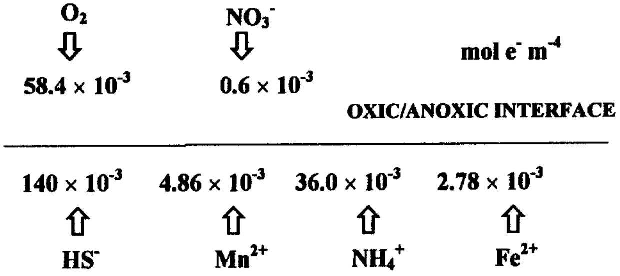

Fig. 9. Electron equivalent gradients (mol e^- m^{-4}) into the oxic/anoxic interface from above and below.

transport might be important because diffusion and mixing are more rapid along, rather than across isopycnal surfaces. As discussed above, the lateral mixing is significant near the interface in the Framvaren. No attempt is made to estimate the vertical advection velocity and eddy diffusion coefficient and create a one-dimensional model for the system. However, one can calculate the vertical molar and electron equivalent gradients across the interface and use them as a qualitative constraint for the proposed reactions (Murray *et al.*, 1994). The vertical electron gradients are obtained by multiplying the vertical molar gradients and the number of electrons required for the appropriate redox reactions, assuming that O_2 and NO_3^- are reduced to H_2O and N_2 and that HS^-, Mn^{2+}, Fe^{2+} and NH_4^+ are oxidized to S^0, $MnO_2(s)$, FeOOH(s) and N_2, respectively. The resulting gradients (in mol e^- m^{-4}) are shown in Figure 9.

It can be seen from Figure 9 that the upward sulfide electron gradient (140×10^{-3} mol e^- m^{-4}) was about three times greater than downward O_2 electron gradient (58.4×10^{-3} mol e^- m^{-4}). Most of the downward oxygen flux in the Black Sea was suggested by Jannasch (1991) to be consumed by heterotrophic aerobic respiration. The sulfide gradients was about 110 times steeper than that of the Black Sea (5.1×10^{-3} mol e^- m^{-4}, assuming SO_4^{2-} as product, Murray *et al.*, 1994) while the O_2 gradients were the same in both basins (52.8×10^{-3} mol e^- m^{-4}, Murray *et al.*, 1994). The extremely steep gradient of sulfide in the Framvaren results from the high content of sulfide in the water column and the shallow depth of the basin. This deficiency of an oxygen gradient suggests that the downward flux of O_2 cannot account for the oxidation of upward sulfide. Three possible alternatives for sulfide oxidation have been proposed (Murray *et al.*, 1994), but none of them are easy to verify. First, oxidized metals such as MnO_2 and FeOOH could serve as oxidants (Millero, 1991). The sharp maximum peaks of Mn(II) and Fe(II) (Figure 2b) just below the interface results from the reductive dissolution of Mn and Fe oxides by sulfide. One difficulty with this metal oxide hypothesis is that the sum of the vertical electron gradients of Mn(II) and Fe(II) are much less than that of sulfide (Figure 9). This problem can be overcome if the particulate oxides are mainly transported horizontally into the intermediate layer through the sill. Luther *et al.*

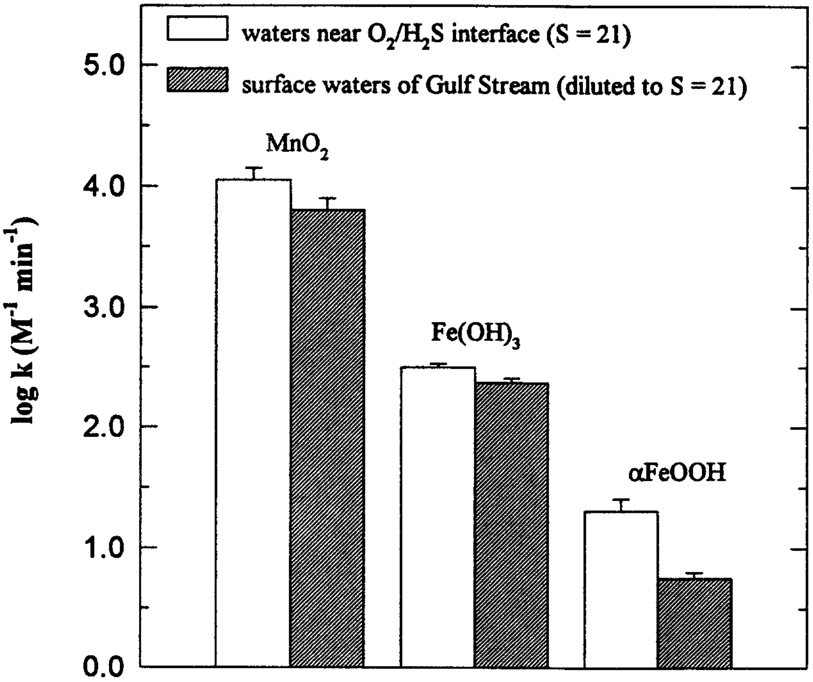

Fig. 10. Rates of H_2S oxidation by Mn(IV) and Fe(III) (hydr) oxides.

(1991) proposed that dissolved Mn(III), which was suggested to be produced by the ligand centered oxidation of Mn(II) carboxylic acid ligand complexes, could react with and oxidize sulfide. A second possible explanation is that photosynthetic sulfide oxidation by phototrophic sulfur bacteria takes place in the chemocline (Jørgensen *et al.*, 1991). Dense populations of the phototrophic bacteria are present at the interface in the Framvaren (Sørensen, 1988). It is not clear whether there are specific species among them that can oxidize sulfide anaerobically. The third alternative process is horizontal ventilation which results from the water intrusion through the sill as discussed earlier. Dissolved oxygen in these ventilating injections could oxidize sulfide. Traces of the oxidation intermediates SO_3^{2-} and $S_2O_3^{2-}$ were found near the anoxic interface (Millero, 1991). Such ventilation could account for the imbalance in the gradients of oxygen and sulfide.

The rates of oxidation of H_2S by Mn(IV) and Fe(III) (hydr)oxides in the water near the interface ($\sim > 21$ m) were determined and compared with the values obtained in the surface waters of Gulf Stream (diluted to $S = 21$ and adjusted to same pH) in the laboratory (Figure 10). It has been shown that PO_4^{3-} (1 μM at 21 m) inhibits the oxidation of H_2S by Mn and Fe (hydr)oxides due to its specific absorption on the oxide surface, while other minor species (such as NH_4^+, SiO_2, Mn^{2+}, Fe^{2+}, humic and fulvic acid) have little effect on the reaction rates (Yao and Millero, 1993; 1994). The higher oxidation rates observed in the field might be related to the extensive microbiological activities near the interface (Sørensen, 1988). Many studies have suggested that high biological activity can effectively control the biogeochemistry of redox-active elements such as Mn, Co and U (Tebo and Nealson, 1984; Burdige and Nealson, 1986; Mckee and Todd, 1993). The rate constant for the H_2S oxidation by MnO_2 (1.12×10^4 M^{-1} min^{-1}) was more than one order of magnitude higher than the value by hydrous Fe(III) oxides (316 M^{-1} min^{-1}). The rate constant for the more crystalline αFeOOH was 20 M^{-1} min^{-1}. Hydrous Fe(III) oxide (derived from hydrolysis and oxidation of Fe(II)) is believed to be the more common Fe oxide phase at O_2/H_2S interface due to the redox cycling of Fe (Crosby *et al.*, 1983). It is not possible to estimate the in situ rates of oxidation of H_2S by Mn(IV) and Fe(III) (hydr)oxides at the interface based on our measurements. Elemental sulfur (S^0) has been found to be the dominant product from the oxidation of H_2S by Mn and Fe (hydr)oxides in laboratory studies (Yao and Millero, 1994).

4.4. CARBONATE SYSTEM

The normalized TA (NTA = TA × 35/S) and normalized TCO_2 ($NTCO_2 = TCO_2 \times 35/S$) in the bottom water of the Framvaren are about twelve times more than in the open ocean, suggesting an enormous production of both TA and TCO_2 from oxidation of organic matter through the reduction of sulfate (equation 5). The value of NTA in the Framvaren surface water was 2.41 mM which is only slightly higher than the typical value of the open ocean (2.35 mM), while the $NTCO_2$ is much higher (2.31 mM) than the value of open ocean (2.05 mM). Much higher values of both NTA (6.34 mM) and $NTCO_2$ (5.80 mM) were found in the surface water of the Black Sea (Goyet *et al.*, 1991). As discussed by Dyrssen (1985, 1986), these high values result from the low salinity and high NTA of the river water mixing with Mediterranean seawater. The lower NTA in the Framvaren surface water indicates that the impact of fresh water is minor. However, the cause of the higher values of $NTCO_2$ in the surface water needs further discussions. Two possible processes, oxidation of organic matter in oxic water and diffusion from below the interface, are proposed below to explain this different distribution of TA and TCO_2 in the surface water of the Framvaren Fjord.

The values of NTA and $NTCO_2$ above the interface are plotted in Figure 11. It can be seen that NTA remained almost constant while $NTCO_2$ increased sharply. A similar result was found in the upper 50 m in the Black Sea (Goyet *et al.*, 1991). This phenomenon might be explained by the aerobic respiration of carbohydrate in the oxic layer

$$CH_2O + O_2 = CO_2 + H_2O \qquad (6)$$

which produces CO_2 and does not affect TA. Owing to the constant flux of organic carbon below 20 m, Naes and Skei (1988) suggested that the mineralization of organic matter in the water column is restricted to the upper 20 m where oxygen is present.

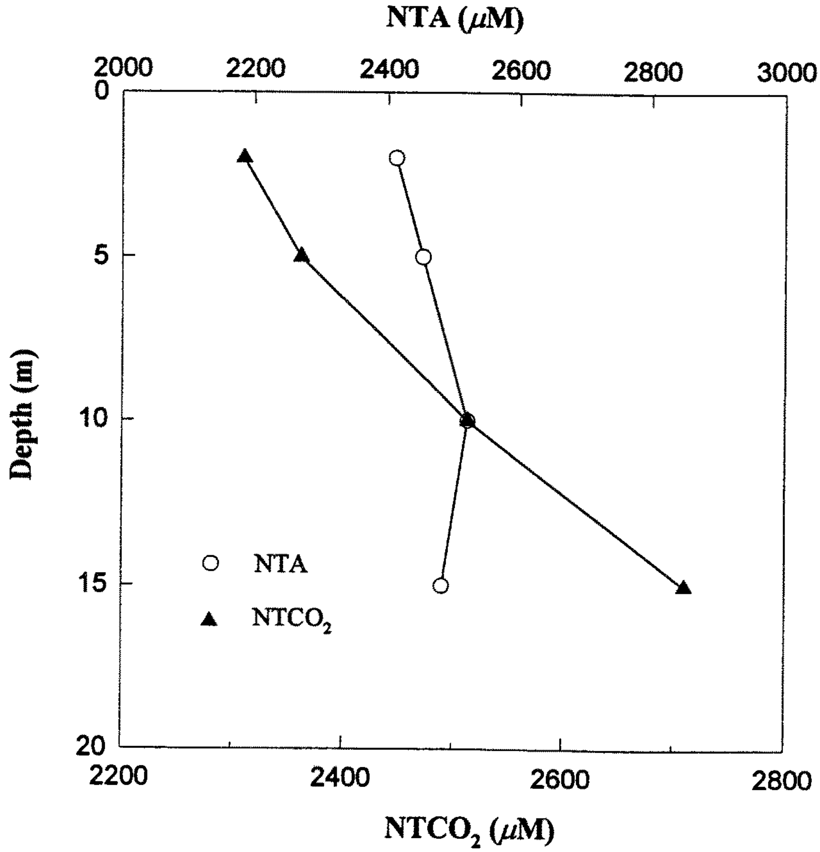

Fig. 11. Profiles of normalized TCO_2 and TA above the interface.

Another possible source of high TCO_2 in the surface is "leaking" from below the interface to the surface layer by upwelling and/or eddy diffusion. By this process, one would expect an increase in TA in the surface layer as well, unless the upwelled sulfide is oxidized by O_2 with SO_4^{2-} as the main product (Millero, 1991; also see discussed below):

$$H_2S + 2O_2 = SO_4^{2-} + 2H^+ \tag{7}$$

which produces H^+ to balance the excess carbonate alkalinity in anoxic water (equation 5)

$$H^+ + HCO_3^- = CO_2 + H_2O. \tag{8}$$

However, this reaction might lead to degassing of CO_2 to the atmosphere.

In the deep water, the build-up of TA and total CO_2 results from the oxidation of organic matter through sulfate reduction. According to equation 5, the relationships between TA and TCO_2 to H_2S concentrations, give slopes of

$$\Delta TA/\Delta H_2S \approx (106 + 16 - 2)/53 = 2.3,$$

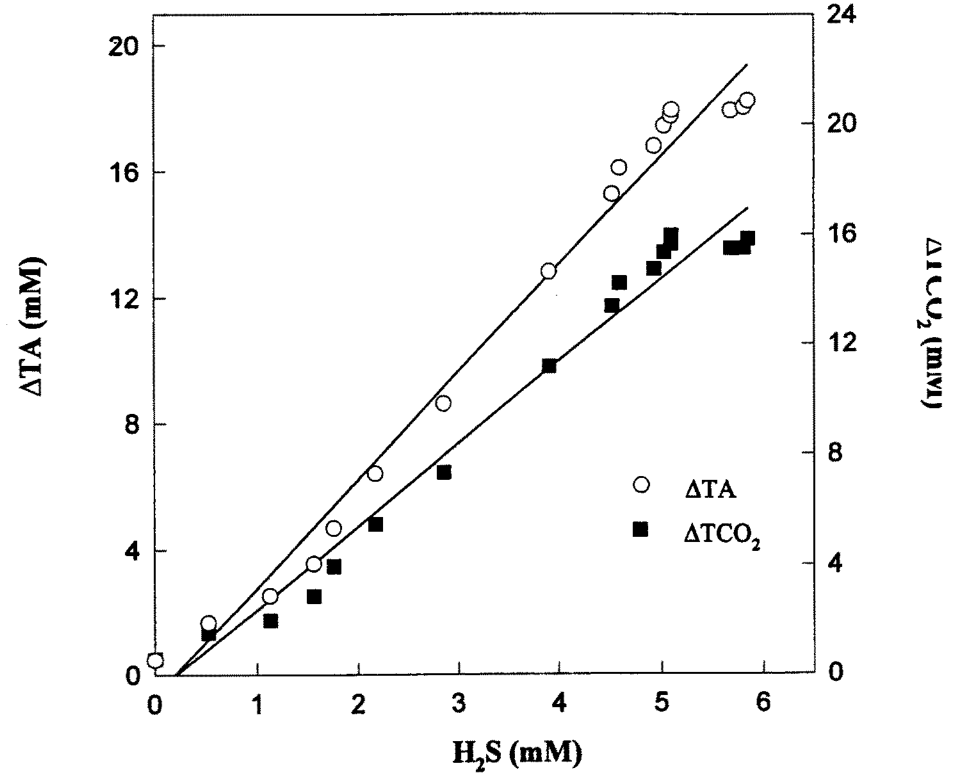

Fig. 12. Plots of concentrations of ΔTCO_2 and ΔTA in anoxic waters versus concentrations of H_2S.

$$\Delta TCO_2/\Delta H_2S \approx 106/53 = 2.0.$$

The relationship between TA and TCO_2 should give a slope of

$$\Delta TA/\Delta TCO_2 \approx (106 + 16 - 2)/106 = 1.13.$$

Our experimental results are shown in Figures 12 and 13. The values of ΔTA and ΔTCO_2 are calculated by correcting for the initial values: $\Delta TA = TA - 2.41*S/35$ and $\Delta TCO_2 = TCO_2 - 2.31*S/35$. The linear correlation between these properties demonstrates that hydrogen sulfide is produced proportionately to the formation of both TCO_2 and TA. However, the ratios of ΔTA to H_2S and ΔTCO_2 to H_2S (for all data 20–175 m) are 3.42 (±0.11) and 3.00 (±0.12), respectively, and are both higher than the model values. Slightly lower values of $\Delta TA/H_2S = 3.12\ (\pm 0.31)$ and $\Delta TCO_2/H_2S = 2.65\ (\pm 0.32)$ are found for the data from 30–80 m probably due to our higher values of H_2S above 90 m. Based on previous data (Skei, 1986), a value of $\Delta TCO_2/\Delta H_2S = 2.54$ was obtained by Dyrssen (1989). Formation of chemogenic calcite was reported by Anderson *et al.* (1987) in the bottom waters of the Framvaren. This process would worsen the fit between our observations and theory. These ratios are also found to be higher than the model

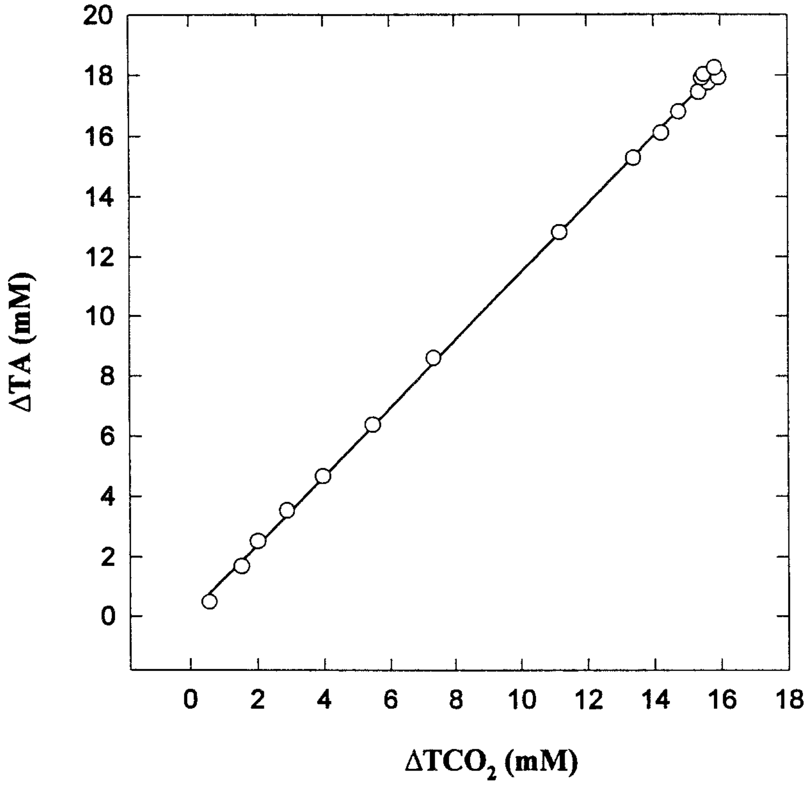

Fig. 13. Plot of ΔTCO_2 versus ΔTA in anoxic waters in the Framvaren.

TABLE II. Stoichiometric ratios in anoxic waters of different basins.

Basin	$\Delta TCO_2:H_2S$	$\Delta TA:H_2S$	$PO_4:H_2S$	$NH_4:H_2S$	$Si:H_2S$	C:N:P
Framvaren[a]	3.00	3.42	0.019	0.30	0.11	155:16:1
Black Sea[b]	2.30	3.05	0.009	0.23	0.61	255:25:1
Cariaco Trench[c]	2.01	2.43	0.018	0.31	0.91	112:17:1
Model value	2.00	2.30	0.019	0.30	–	106:16:1

[a] This study.

[b] The ratios for TCO_2 and TA to H_2S are from Goyet *et al.* (1991), others are calculated based on the data report for 1988 Black Sea Expedition by Friederich *et al.* (1990).

[c] Zhang and Millero (1993), corrections for total sulfur were made to include sulfite and thiosulfate.

values in the Black Sea (Goyet *et al.*, 1991) while they are in good agreement with the theoretical values in the Cariaco Trench (Zhang and Millero, 1993, Table II). The ratio of ΔTA to ΔTCO_2 in anoxic waters of the Framvaren is 1.14 and equal to the model value. The same value of $\Delta TA/\Delta TCO_2$ (1.15) was found by Dyrssen (1989). This ratio is higher (1.32) than the theoretical value (1.14) in the Black

Sea. As suggested earlier by Dyrssen (1985), the differences between the observed ratios and the model values may be attributed to a combination of high values of TA and TCO_2 and the low values of H_2S. One of the possible explanation of low H_2S concentration is that a small fraction of hydrogen sulfide is removed by formation of Fe sulfides (Goyet *et al.*, 1991)

$$2FeOOH + 3H_2S = FeS + FeS_2 + 4H_2O \tag{9}$$

without changing TA and TCO_2. Kemp (1990) suggested that the pyrite flux accounted for the removal of roughly half of the net production of H_2S in the Black Sea and must play a key role in building up the excess TA and TCO_2. However, Goyet *et al.* (1991) argued that the capacity of this reaction must be small due to the low dissolved iron concentrations and cycling rates in the Black Sea.

Inflow of O_2 containing water through the sill may cause the removal of H_2S in the deep waters of the Framvaren, such as the renewal of the bottom waters when the channel was dug in 1850. In order to keep the same deviations in the ratios TA/H_2S and TCO_2/H_2S, the removal process of H_2S should not change the TA. In other words, sulfide should be removed from the water column as FeS_2 (equation 9) and elemental sulfur or polysulfides

$$2H_2S + O_2 = 2S^0 + 2H_2O \tag{10}$$

$$(x - 1)S^0 + HS^- = HS_x^- \tag{11}$$

again, without altering both TA and TCO_2. If the product in equation 10 is SO_4^{2-} instead of S^0 (equation 7), the alkalinity will be lowered. Millero (1991) found that the main reaction product between H_2S and O_2 was SO_4^{2-} when O_2 was in excess. As shown by Anderson *et al.* (1988) the reaction causes the formation of SO_4^{2-} with a low isotope ratio. However, elemental sulfur or polysulfides might be the major product of oxidation of sulfide when the concentration ratio of O_2 to H_2S is much lower than 1 (Chen and Morris, 1972), which is the case when O_2 containing waters are introduced into the super-anoxic water. Experimental errors in the measurements of TA and H_2S, and the presence of organic acids which are not taken into account in this simple chemical theory, are also likely to contribute to the difference.

The calculated pCO_2 in the surface water in June 1993 is 250 μatm. This low pCO_2 is mainly due to the low temperature (15.41°C) and low CO_2 content (875 μM, due to low salinity) in the surface water. If the pCO_2 in the atmosphere is assumed to be 350 μatm, the surface water of Framvaren serves a sink of CO_2 for the atmosphere.

4.5. NUTRIENTS (N, P, SI)

As discussed above, the cycles of nutrients are controlled by biological processes either aerobically or anaerobically. Nitrogen transformations are always complicated at oxic/anoxic interfaces due to its many oxidation states. Unfortunately, no

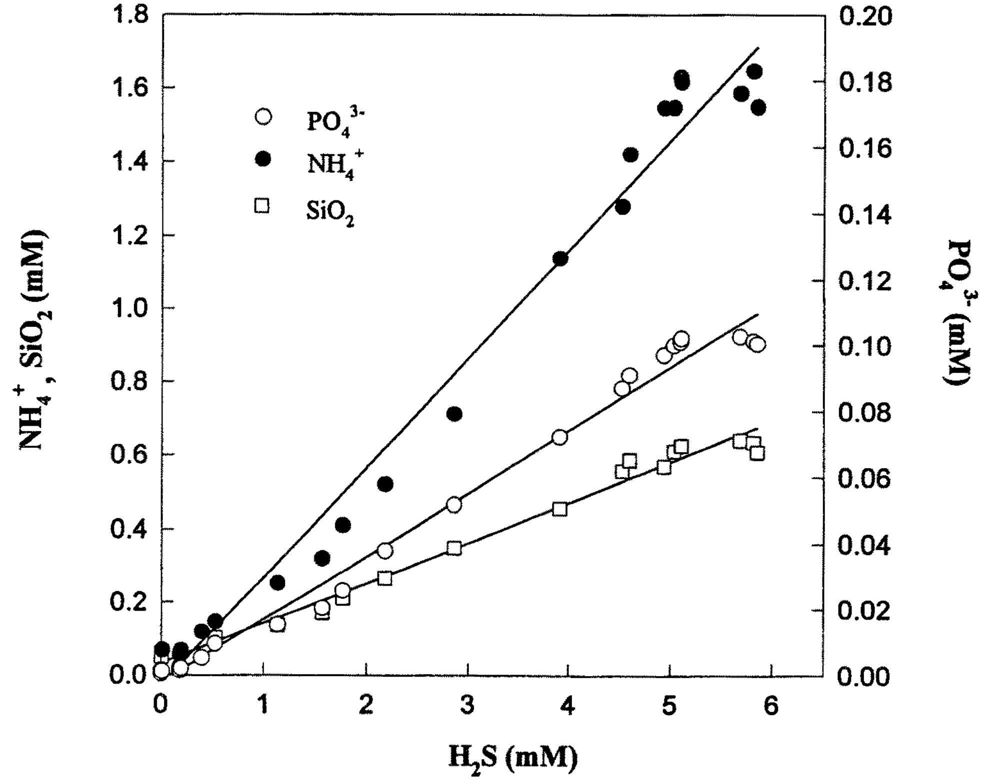

Fig. 14. Plots of concentrations of ammonia, phosphate and silicate versus concentrations of H_2S.

extensive measurements of NO_3^- and NO_2^- have been made in the Framvaren. One measurement of NO_3^- made in 1981 (Skei, 1986) showed that the concentrations of NO_3^- were very low (< 0.5 μM) from surface down to 15 m, which was close to the concentrations of PO_4^{3-} (about 0.3 μM). Low primary production in the upper part of euphotic zone (Sørensen, 1988) might be due to the limiting concentration of NO_3^-. Ammonium was present in the upper euphotic zone at the level of μM indicating that ammonium diffused from below the interface was not completely oxidized.

Ammonium started increasing below the interface due to the anaerobic decomposition of organic matter. Based on equation 5, a plot of NH_4^+ versus H_2S should give a slope of 0.30. Our experimental result gives the same value 0.30 (±0.01) for all data from 20–175 m (Figure 14). A lower value of $NH_4^+/H_2S = 0.25$ (±0.02) is found for data from 30–80 m. The ratio of NH_4^+ to H_2S in Cariaco Trench (0.31, Zhang and Millero, 1993) agreed with the model value while it is lower (0.23) in the Black Sea (Table II). Due to the possible removal of H_2S as discussed earlier, the real ratio of NH_4^+ to H_2S must be lower than the model value. One explanation for this is that the C:N ratio in organic matter is higher than 106:16. The detailed discussion will be given below.

Compared with nitrogen, phosphorus transformations are simple in terms of redox chemistry because of its single oxidation state. However, phosphate can absorb onto particles such as reactive Fe and Mn oxyhydroxides, which results in a lower recycling efficiency than C and N, especially in upper oxidizing sediments (Martens, 1993). The adsorption process is much less important under anoxic conditions (Krom and Berner, 1981). The rapid increase of concentrations of phosphate below the interface also resulted from the anaerobic respiration of organic matter. Based on equation 5, the ratio of PO_4^{3-} to H_2S should be 0.019. Our experimental result gives exactly the same value 0.0191 (±0.0004) for all data from 20–175 m (Figure 14). Similar value of 0.0188 (±0.0021) is found for 30–80 m. The ratio of PO_4^{3-} to H_2S in Cariaco Trench (0.018, Zhang and Millero, 1993) agreed fairly well with the predicted value while it was only half of the model value (0.009) in the Black Sea (Table II). This low recycling efficiency of PO_4^{3-} in the Black Sea might partially due to the removal of PO_4^{3-} by absorption onto particles. Again, the good agreement between the measured ratio of PO_4^{3-} to H_2S in the Framvaren with the model value might be incidental when we consider the possible removal of H_2S produced by sulfate reduction. Possible explanations will be presented below.

The linear correlation between sulfide and silicate in the anoxic waters of the Framvaren gives a slope of 0.11 (±0.01) (Figure 14) indicating that silicate is also released proportionately to the production of hydrogen sulfide. There is no theoretical ratio of Si to H_2S from the oxidation of biogenic organic matter because it depends on the relative abundance of siliceous phytoplankton (e.g. diatoms). The ratios are 0.61 and 0.91 for the Black Sea and Cariaco Trench, respectively. Silicate in the Framvaren is relatively low with respect to the sulfide level. At present little is known about the effect of anoxic environments on the solubilization of silicate.

4.6. CARBON:NITROGEN:PHOSPHORUS RATIO

The classical work of Redfield has introduced the concept of nearly parallel C, N and P circulations in aquatic ecosystem. Nutrients are taken up by phytoplankton and released during organic matter degradation according to a simple and constant stoichiometry. In the more recent GEOSECS study, the slope of a plot of nitrate concentration versus phosphate concentration for much of the word ocean is about 16:1 (Craig *et al.*, 1981; Spencer *et al.*, 1982). These data strongly suggest that in the ocean today nitrogen and phosphorus are incorporated into living plankton and released from decomposing plankton in the Redfield ratio. However, the ratio of C:P in marine detritus has been suggested by Peng and Broecker (1987) to be 127 instead of 106. Based on chemical data from isopycnal surfaces of the Atlantic and Indian oceans, Takahashi *et al.* (1985) yielded a C:N:P ratio of 103:16:1 if the carbon value was represented by the observed increase in the TCO_2 concentration, and a ratio of 140:16:1 if the carbon value was assumed to be represented by the

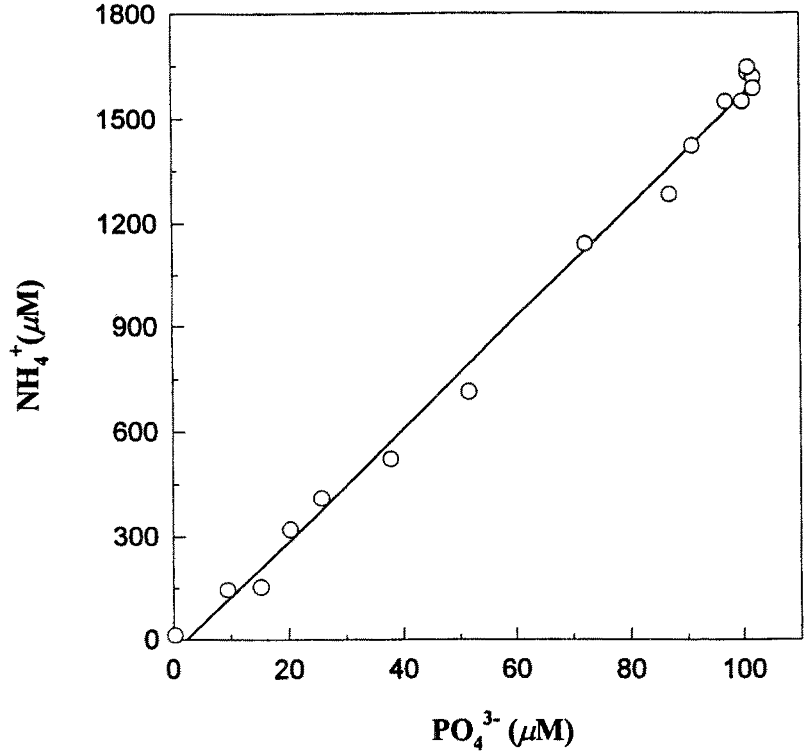

Fig. 15. Plot of concentrations of ammonia versus concentrations of phosphate in anoxic waters.

oxygen utilization minus the oxygen used for oxidation of NH_3 with two moles of O_2 per nitrogen atom. Heckey *et al.* (1993) has concluded that the Redfield ratio is the exception rather than a rule in lake particles. The C:P and N:P ratios are more variable for lake particles but generally higher than the Redfield ratio of 106:16:1. Terrestrial soils and vegetation are rich in C and N (Wetzel, 1975) with high C:N, C:P and N:P ratios. One could expect that C, N and P in those marine environments such as basins and fjords, which are influenced by the terrestrial input might not have Redfield behavior.

No major rivers enter the Framvaren and the overall freshwater input through five small streams has been estimated to be ~1–2 m^3 sec^{-1} (Skei, 1988a). The major input of terrestrial origin organic matter is tree leaves which have high C:N and C:P ratios. Part of these tree leaves are difficult to decompose. The C:N:P ratio of bacteria is unknown and the bacteria might contribute significantly to the carbon flux. The linear correlation between concentrations of NH_4^+ and concentrations of PO_4^{3-} for samples collected below the oxic layer (Figure 15) shows a slope N:P of 16.0 (±0.3) which is the same as the Redfield ratio. A lower value of N:P = 14.0 (±1.0) is found for 30–80 m. A plot of concentrations of TCO_2 versus NH_4^+ in the deep anoxic waters gives a slope C:N of 9.6 (±0.2) (Figure 16) which is

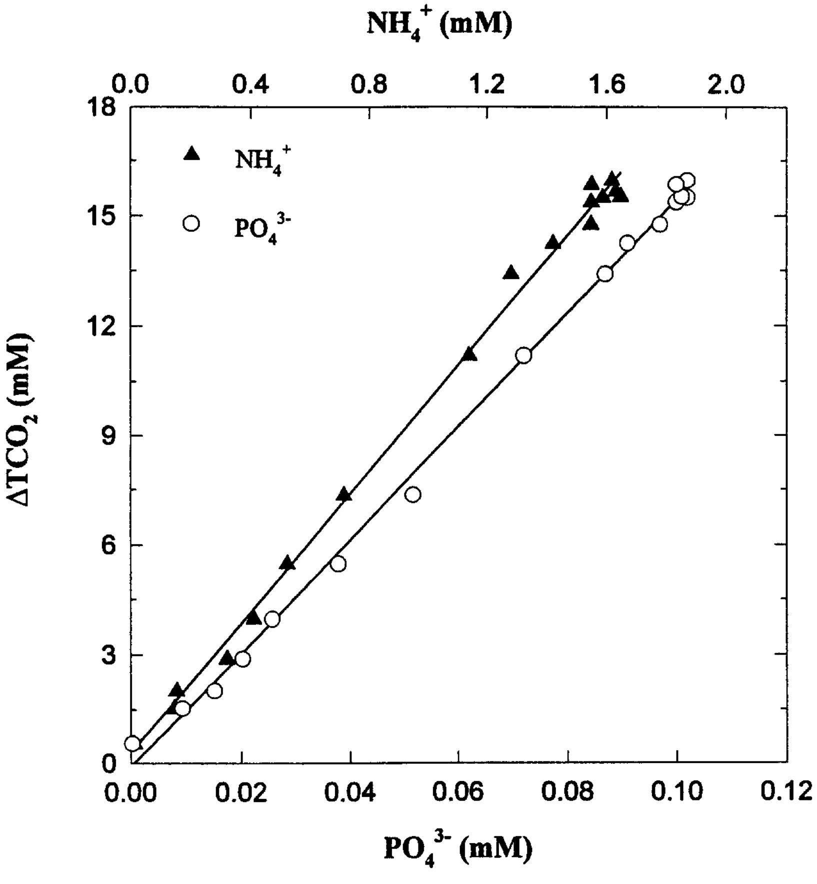

Fig. 16. Plots of concentrations of ΔTCO_2 versus concentrations of ammonia and phosphate in anoxic waters.

higher than the Redfield value of 6.6. A similar value of C:N = 10.0 (±0.6) is found for 30–80 m. On the basis of measurements of organic carbon and nitrogen in the suspended material collected from sediment traps, Naes and Skei (1988) reported an average C:N ratio to be 8 in the sedimenting material. The particulate C/N ratios in the surface waters were found to be about 10 in June 1993 (McKee, 1993). A plot of concentrations of TCO_2 versus PO_4^{3-} in the anoxic waters (20–175 m) of the Framvaren shows a slope C:P of 155 (±2) (Figure 16) which is much higher than the Redfield ratio of 106, and also higher than the value of 127 for ocean waters suggested by Peng and Broecker (1987). These results indicate that the nutrients (N, P) show Redfield behavior in the Framvaren while ratios of C:N and C:P are higher. Dyrssen (1989) suggested that the excess of carbohydrates could easily be explained by the addition of tree leaves and other terrestrial matter. It has also been proposed that phytoplankton can incorporate C:N:P in ratios different than 106:16:1 depending on the availability of these elements (Smethie, 1987). The high C:N and C:P ratios might result from the excess supply of inorganic carbon compared to N and P.

As discussed above, the C:N:P ratios show slight differences between the deep water and the older bottom water (below 90 m). Future work with better sampling resolution is needed to elucidate these differences. If we assume the C:N:P ratio of the organic matter in the Framvaren to be 155:16:1 based on the average value for all the data (20–175 m), equation 5 can be rewritten as

$$\begin{aligned}&(CH_2O)_{155}(NH_3)_{16}(H_3PO_4) + 77.5\ SO_4^{2-}\\&\quad = 155\ HCO_3^- + 77.5\ H_2S + 16\ NH_3 + H_3PO_4.\end{aligned} \tag{12}$$

The increase of C:N and C:P ratios does not change the value of 2.0 for $\Delta TCO_2/\Delta H_2S$, while the ratio of $\Delta TA/\Delta H_2S$ decreases slightly from 2.3 to 2.2. The ratios of NH_4^+ and PO_4^{3-} to H_2S both decrease from 0.30 to 0.20 and 0.019 to 0.013, respectively. We further assume that total inorganic carbon, ammonia and phosphate in the anoxic waters of the Framvaren are produced only through the decomposition of organic matter based on equation 12 and there are no significant removals for them. This assumption is supported, but not proved, by the fact that the correlations between C, N and P are better than the correlations between C, N, P with H_2S (Figures 12, 14, 15 and 16). In order to rebalance the measured NH_4^+/H_2S and PO_4^{3-}/H_2S ratios (0.30 and 0.019, respectively) to the new model values (0.20 and 0.013, respectively), the initially formed H_2S should equal to

$$[H_2S]_{\text{init.}} = (77.5/53) \times [H_2S]_{\text{meas.}}.$$

In other words, about 30% of the H_2S produced from sulfate reduction has been removed which corresponds to 2.8 mM SO_4^{2-} anomalies in the bottom water. This is equal to the estimate (about 3 mM in the bottom water) made by Dyrssen (1987) and Anderson *et al.* (1988) by calculating the SO_4^{2-} balance. As discussed above, the removal of sulfide includes the processes such as oxidation, formation of FeS_2, degassing and incorporation into organic matter. Partial renewal of the bottom water due to the excavation of the sill in 1850's and the following modifications, if not complete, accounts for most of the sulfide removal.

If we take the initially formed H_2S ($[H_2S]_{\text{init.}}$) instead of the measured values, the ratios of $TCO_2/[H_2S]_{\text{init.}}$ and $TA/[H_2S]_{\text{init.}}$ are 2.04 and 2.33, respectively, which are close to the model values (2.0 and 2.2, respectively) predicted by equation 12.

C:N ratio is 10 in the Black Sea which is the same value as in the Framvaren. The extremely high value of C:P ratio may be due to the anomalous behavior of phosphate as discussed earlier. Higher C:N and C:P ratios in the Black Sea may also result from the large influence from terrestrial inputs. The C:N:P ratio in the Cariaco Trench, which is a typical open ocean with little terrestrial input, is found to be 107:15:1 (Table II) and agrees well with the Redfield value.

Whether the C:N:P ratio of marine organism, i.e. the Redfield ratio, has changed over time with changing ocean chemistry is still a major problem concerned with aspects of the global cycles of these elements. A shift to higher Redfield ratios, by allowing more carbon to be taken up for the same amount of nutrients, can affect the atmospheric CO_2. Due to the terrestrial and anthropogenic fluxes, higher C:N and C:P ratios are likely to be developed in basins, fjords and more importantly, in the coastal zone. That is one of the reasons why the coastal area requires more attention than ever when we study the global budget of CO_2.

5. Conclusion

The water intrusion through the sill has an important effect on the chemical processes at the interface. More transect stations are needed to study the horizontal gradients of hydrographic properties and chemical species in order to completely understand the physical and chemical cycles in both surface and bottom waters. Transformations of nitrogen near the interface require further investigations. The simple stoichiometric oxidation model provides a useful understanding of the biogeochemical cycles of C, N, P and S even though there are some defects with the model. Measurements on the rates of H_2S oxidation by chemical and biological processes in the chemocline, and a complete accurate analysis of sulfur species, both inorganic and organic, in water column as well as sediments should be done in order to elucidate the sulfur budget and its evolution in this super-anoxic basin.

Acknowledgements

The authors thank Dr. Skei for coordinating the field operations during this investigation; Dr. Mckee for letting us use the hydrographic data; Dr. Todd for sampling assistance and Mr. Sørensen for oxygen analysis. The paper was enhanced by the constructive remarks of Dr. Dyrssen and Dr. Skei. This work was supported by the Oceanographic Section of the National Science Foundation (OCE9201739).

Appendix

ACIDITY CONSTANTS FOR THERMODYNAMIC CALCULATIONS

The constants as a function of temperature and salinity were selected from the following papers and refitted if necessary on the pH of seawater scale.

The carbonic acid constants of Roy *et al.* (1993) (S = 5 to 45) converted to the seawater scale have been fitted to the equations (mol $\{\text{kgsoln}\}^{-1}$)

$$\begin{aligned}\ln K_1 &= 3.17537 - 2329.138/T - 1.59702 \ln T \\ &+ (-0.210502 - 5.79495/T)\, S^{0.5} + 0.0872208\, S - 0.00684651\, S^{1.5}\end{aligned}$$

$$\begin{aligned}\ln K_2 &= -8.19754 - 3403.878/T - 0.352253 \ln T \\ &+ (-0.0888846 - 25.9532/T)\, S^{0.5} + 0.1106658\, S - 0.00840155\, S^{1.5}\end{aligned}$$

with standard errors of 0.0035 in pK_1 and 0.0030 in pK_2. Using the pure water values (Millero, 1979)

$$\ln K_1^0 = 290.9097 - 14554.21/T - 45.0575 \ln T$$

$$\ln K_2^0 = 207.6548 - 11843.79/T - 33.6485 \ln T$$

the fits have also been forced to the infinite dilution values

$$\begin{aligned}\ln K_1 = {} & \ln K_1^0 + (-229.2858 + 9748.6609/T + 34.62250 \ln T)\, S^{0.5} \\ & + (54.56216 - 2325.8857/T - 8.24864 \ln T)\, S \\ & + (-3.99995 + 171.6195/T + 0.608360 \ln T)\, S^{1.5} \\ & - 0.00263720\, S^2 \end{aligned} \qquad \text{(a)}$$

$$\begin{aligned}\ln K_2 = {} & \ln K_2^0 + (-164.7153 + 6418.2879/T + 25.48351 \ln T)\, S^{0.5} \\ & + (38.07286 - 1493.2431/T - 5.918760 \ln T)\, S \\ & + (-2.701481) + 108.02891/T + 0.429120 \ln T\, S^{1.5} \\ & - 0.00610290\, S^2 \end{aligned} \qquad \text{(b)}$$

with standard errors of 0.0090 in pK_1 and 0.015 in pK_2.

The combined results of Hansson (1973), Culberson and Pytkowicz (1973) and Dickson and Riley (1979a) on the dissociation of water in seawater have been fitted to the equation (mol $\{\text{kgsoln}\}^{-1}$)

$$\begin{aligned}\ln K_W = {} & 148.9802 - 13847.26/T - 23.6521 \ln T \\ & + (-5.977 + 118.67/T + 1.0495 \ln T)\, S^{0.5} - 0.01615\, S \end{aligned}$$

with a standard error of 0.01 in $\ln K_W$.

The dissociation constant of boric acid in seawater was selected from Dickson (1990)

$$\begin{aligned}\ln K = {} & (-8966.90 - 2890.51\, S^{0.5} - 77.942 + 1.726\, S^{1.5} - 0.0993\, S^2)/T \\ & + (148.0248 + 137.194\, S^{0.5} + 1.62247\, S) \\ & + (-24.4344 - 25.085\, S^{0.5} - 0.2472\, S) \ln T \\ & + 0.053105\, S^{0.5}\, T \end{aligned} \qquad \text{(c)}$$

where the standard error is 0.0042 in $\ln K_B$.

Fits of the combined results of Dickson and Riley (1979b) and Johansson and Wedborg (1979) on the dissociation constants of phosphoric acid in seawater, forcing the fits through the infinite dilution values (Bates and Acree, 1943), are given by (mol $\{\text{kgsoln}\}^{-1}$)

$$\begin{aligned}\ln K_1 &= 115.54 - 4576.752/T - 18.453 \ln T + (0.6971 - 106.736/T)\, S^{0.5} \\ &\quad + (-0.01844 - 0.65643/T)\, S \qquad \text{(d)}\end{aligned}$$

$$\begin{aligned}\ln K_2 &= 172.1033 - 8814.715/T - 27.927 \ln T \\ &\quad + (1.3566 - 160.340/T)\, S^{0.5} \\ &\quad + (-0.05778 + 0.37335/T)\, S \qquad \text{(e)}\end{aligned}$$

$$\begin{aligned}\ln K_3 &= -18.126 - 3070.75/T + (2.81197 + 17.27039/T)\, S^{0.5} \\ &\quad + (-0.09984 - 44.99486/T)\, S \qquad \text{(f)}\end{aligned}$$

where the standard errors are 0.09, 0.03 and 0.2, respectively, in pK_1, pK_2 and pK_3.

The dissociation constant of hydrogen sulfide in seawater was selected from Millero *et al.* (1988) (mol $\{\text{kgsoln}\}^{-1}$)

$$\ln K_{1S} = 225.838 - 13{,}275.3/T - 34.6435 \ln T + 0.3449\, S^{0.5} - 0.0274\, S$$

where the standard error is 0.076 in $\ln K_{1S}$.

Fit of the combined results of Khoo *et al.* (1977) and Johansson and Wedborg (1980) on the dissociation of ammonium in seawater, forcing the fit through the infinite dilution values (Bates and Pinching, 1949), is given by (mol $\{\text{kgsoln}\}^{-1}$)

$$\begin{aligned}\ln K &= -0.25444 - 6285.33/T + 0.0001635\, T \\ &\quad + (0.46532 - 123.7184/T)\, S^{0.5} + (-0.01992 + 3.17556/T)\, S\end{aligned}$$

where the standard error is 0.01 in pK.

The dissociation constant of silicic acid has not been measured in seawater. Busey and Mesmer (1977) studied the ionization equilibria of silicic acid in sodium chloride solutions ($I = 0$–5 m) from 60 to 300°C and fitted the dissociation constant to a Pitzer type equation. The data below 100°C from Busey and Mesmer (1977) along with the results of Ingri (1959) in 0.5 m NaCl at 25°C were fitted to the equation (mol $\{\text{kgsoln}\}^{-1}$)

$$\begin{aligned}\ln K &= 117.40 - 8904.2/T - 19.334 \ln T + (3.5913 - 458.79/T)\, I^{0.5} \\ &\quad + (-1.5998 + 188.74/T)\, I + (0.07871 - 12.1652/T)\, I^2\end{aligned}$$

where the standard error is 0.02 in pK.

The solubility of calcium carbonate as aragonite and calcite in seawater from 0 to 40°C and $S = 5$ to 35 was chosen from Mucci (1983). His results can be represented by the equations (mol $\{\text{kgsoln}\}^{-1}$)

$$\begin{aligned}\log K_{\mathrm{Cal}} &= -171.9065 - 0.077993\,T + 2839.319/T + 71.595\log T\\ &\quad + (-0.77712 + 0.0028426\,T + 178.34/T)\,S^{0.5}\\ &\quad - 0.07711\,S + 0.0041249\,S^{1.5} \qquad \text{(g)}\\ \log K_{\mathrm{Arg}} &= -171.945 - 0.077993\,T + 2903.293/T + 71.595\log T\\ &\quad + (-0.068393 + 0.0017276\,T + 88.135/T)\,S^{0.5}\\ &\quad - 0.10018\,S + 0.0059415\,S^{1.5}. \qquad \text{(h)}\end{aligned}$$

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