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Physicochemical modeling of the Baltic Sea water-sediment column:

I. Reference ion-association models of normative seawater and of Baltic sea brackish waters at salinities 1 - 40‰, 1 bar total pressure and 0 to 30 °C temperature (system Na-Mg-Ca-K-Sr-Li-Rb-Cl-S-C-Br-F-B-N-Si-P-H-O)

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Summary

Computer thermodynamic modeling by means of dual minimization of total Gibbs free energy (IPM algorithm and SELEKTOR++ software, Karpov et al. , 1993; Karpov, 1981) offers new possibilities to quantify the chemical processes that occur in stratified brackish basins such as the Baltic Sea. Unlike many widespread model codes, the dual minimization method treats pH, Eh or partial pressures of gases as functions of P,T and bulk chemical composition rather than as control variables of aqueous system. This leads to more consistent and sensitive models of speciation, mineral solubilities, redox changes etc. in geochemical systems.

This publication presents: the ion-association model of aqueous electrolyte in the system Na-Mg-Ca-K-Sr-Li-Rb-Cl-S-C-Br-F-B-N-Si-P-H-O of major components of seawater, including both sulfate and chloride ion pairing, with parameters of modified Debye-Hueckel equation to calculate free activity coefficients; corresponding set of the apparent partial molal Gibbs free energies of formation of aqueous species, gases and minerals (based upon the SUPCRT92 dataset (Johnson et al., 1992) and association constants from Millero and Schreiber, (1982)), tabulated for P = 1 bar and T from 1 to 30 °C; reference bulk chemical compositions of normative seasalt; air; average Baltic river salt and organic matter; extended linear mixing equations to specify the models of normative marine and brackish water bodies at chlorinity range 0.1 - 19 ‰. The thermodynamic models of metastable normative seawater, as well as Baltic brackish waters were calculated. Thermodynamic values for some carbonate, bicarbonate and borate ion pairs were corrected for better agreement with normative seawater carbonate system parameters. Comparisons of calculated and reference total and mean activity coefficients, association constants, solubilities of atmospheric gases as well as their temperature and salinity dependencies show good agreement, and therefore - internal consistency and validity of the model at salinities 1 to 40 ‰. The calculated limit solubilities of carbonates (including Mg-calcite), quartz, and phosphates also show good agreement with literature data.

A series of equilibria was calculated representing the main water layers of the generalized Baltic Sea water-sediment profile (Gotland Deep). They show good agreement with known profiles of pH, dissolved O_2, H_2S, P, CO_2 etc. across the main halocline and chemocline. This set of thermodynamic models therefore provides a basis for further modeling of Fe, Mn, nutrients and heavy metals cycling in sea-, lake- and porewaters, authigenic mineral precipitation and dissolution, with various environmental and ore-formation implications.

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Introduction

Chemical models of seawater based on thermodynamic equilibrium between aqueous species, gases and minerals originate from the classic work of Garrels and Thompson (1962). Since then such models have been applied to the solubility of minerals in seawater and brines (e.g. Harvie et al., 1984), the formation of ferromanganese nodules (Gramm-Osipov et al., 1989; Gramm-Osipov, 1992), hydrothermal processes in mid-ocean ridges (Grichuk et al., 1985; Wells and Ghiorso, 1991), mass transfer between porewater and sediment (von Breymann et al., 1990; Boudreau and Canfield, 1993), trace element behaviour in stagnant Black Sea waters (Landing and Lewis, 1991), and chemical evolution of the ocean and atmosphere (Drozdovskaya, 1990).

We consider that computer thermodynamic modeling will be valuable in quantifying the chemical factors that control suspended particles dissolution, Fe-Mn-oxyhydroxides precipitation, redox cycling and trace metals behaviour in stratified brackish water-sediment column, and early diagenetic processes in the Baltic Sea, where much relevant chemical data are now available (e.g., Kremling, 1983; Dyrssen and Kremling, 1990; Suess and Djafari, 1977; Heuser, 1988; Ingri et al., 1991; Brügmann et al., 1992; Belmans et al., 1993). Such studies will also have important environmental implications (cf. Hallberg, 1991).

It is clear that the above processes cannot be described in full with "complete equilibrium" models because of kinetic and dynamic factors (see Balzer, 1982; Boudreau and Canfield, 1993). Nevertheless, the calculations of equilibria still do provide a limiting approximation, a reference model that allows one to judge on the degree of metastability in the aqueous system in question. Then, if necessary, additional restrictions according to the principles of local and partial equilibrium should be imposed on the physicochemical model to account for the kinetic or dynamic geochemical observations.

The aim of this text is to present a reference system and dataset for thermodynamic modeling of estuarine geochemical environments such as the Baltic Sea. This includes:

A) An ion-association model of aqueous electrolyte in the system Na-Mg-Ca-K-Sr-Li-Rb -Cl-S-C-Br-F-N-B-P-H-O[1] with parameters for the modified Debye-Hückel equation to calculate activity coefficients of aqueous species at the effective ionic strength < 0.8 molal.

B) Set of standard thermodynamical parameters (apparent partial molal Gibbs free energy of formation, entropy and stoichiometry) for aqueous species, gases and minerals that may appear in equilibrium state, tabulated for pressure 1 bar and temperatures 1 to 30 ° C.

C) Reference bulk chemical compositions of normal sea salt; average river salt; average air; reactive organic matter etc. to specify models of normal and brackish water bodies (by mixing normal sea and river salts) in the salinity range 1 to 40 ‰ , open or closed to the atmosphere, as well as different redox conditions in seawater and porewater.

D) Limiting solubilities of stable or metastable minerals or solid solutions in normative and brackish seawater to assess the nature of thermodynamic control on concentrations of dissolved metals in water bodies.

E) Comparison of calculated activities, activity coefficients of electrolytes, association

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[1] Since Ar does not react with other components in seawater, it was not included, but its mole fraction was added to that of N_2 in the model air composition.

constants, mineral solubilities and other properties of standard seawater with experimental values and those calculated from other models.

The reference normative model mentioned in (A) includes major elements only with dissolved concentrations more than 0.001 mmol kg^{-1}. Their contents and interaction *define* all the important chemical potentials. Provided that this system is calculated correctly (i.e. reproduces the known activities of electrolytes, main experimental association constants, solubilities of gases and mineral solubilities), all the minor and trace elements added would only *follow* the interactions of major species reflected by the pH, Eh, effective ionic strength, alkalinity etc. The extensions of the model to minor elements and heavy metals (i.e., addition of their aqueous species, minerals or solid solutions, adsorbed and organic complexes), and to wider temperature-pressure ranges as found in the marine environment will be reported in subsequent papers.

The aqueous chemical models available in the literature can be classified in two groups. The *ion-association models* (Truesdell and Jones, 1969; Dyrssen and Wedborg, 1974; Dickson and Whitfield, 1981; Millero and Schreiber, 1982; Byrne et al., 1988) account for the measured total activity coefficients of major ions through consideration of ion pairs (or complexes) with free-species activity coefficients calculated from the Debye-Hueckel equation or its modifications. This leads to a set of association constants (K_A, thermodynamic, or K^*, stoichiometric) and set of ion-size parameters for free species (cf. Kielland, 1937). It is generally accepted that models from this group yield reliable estimates of ion activity coefficients and solubility of minerals for major and minor components at low ionic strength (up to 1 mole).

The specific interaction models are based on calculation of ion activity coefficients by equations that involve empirical coefficients for various kinds of interactions between ions rather than on considerations of ion pairs (cf. Pitzer, 1973,1991; Whitfield, 1975a; Harvie et al., 1984; Greenberg and Møller, 1989). At present, such models can be applied to brines up to 6 mole ionic strength in the temperature range between 0 and 250 °C for major ions (Na^+, K^+, Mg^{+2}, Ca^{+2}, Cl^-, OH^-, SO_4^{-2}, CO_3^{-2}). Models of this group are sometimes difficult to use for minor and trace ions and for reduced species because of the lack of appropriate values of specific interaction parameters.

Therefore, models combining both approaches have been suggested recently (Whitfield, 1975b; Millero and Schreiber, 1982; Millero and Hawke, 1992). They include expressions for association constants of ion pairs together with empirical equations for activity coefficients of aqueous species as functions of ionic strength derived from Pitzer's interaction parameters.

Methods, software and data sources for thermodynamic modeling

In practical terms, sophisticated software and extensive databases are needed for geochemical calculations and retrieval of data related to aqueous thermodynamic models. Both kinds of aqueous models have been implemented since 1973 in computer codes and databases to allow equilibria calculations to be performed, and to test mineral solubilities and saturation indexes (see Nordstrom et al., 1979; Bassett and Melchior, 1990). The codes most widespread in hydrogeochemistry, such as WATEQ4F (Ball and Nordstrom, 1991), PHREEQE (Parkhurst et al., 1980), SOLMINEQ.88 (Kharaka et al., 1988) imply the choice of some linearly independent chemical reactions between solids, gases and aqueous species with experimentally or theoretically derived equilibrium constants. It is then possible to calculate an equilibrium speciation by solving the system of (non-linear) mass-action and mass-balance equations (cf. Crerar, 1975; Reed, 1982; Nordstrom and Munoz, 1986).

This approach is closer to the experimental data which are usually converted to the stability constants of specific reactions (Nordstrom et al., 1990) but it is strictly limited to the list of available reactions (usually one per component) in the database. An uncertainty always exists therefore in that some important reactions may be missing and some inconsistencies remain hidden. To account for all mathematically possible reactions within a given set of components would result in too large set of equations for big systems. For such calculations, the analytical pH and Eh values with list of stable mineral phases should normally be prescribed as input, together with temperature, pressure and composition. Usually only saturation indexes of minerals are calculated. Another problem appears when redox processes are modeled - such tasks may result in convergence faults.

Recently, two advances were made in this field that allow the ion-association thermodynamic model of seawater to be applied once again.

First, the alternative approach for model calculations is now implemented in the SELEKTOR program package (Karpov, 1981; Karpov et al., 1993). It starts from the formulation of thermodynamic equilibrium through mathematical concepts of convex programming. Conditions of equilibrium state are derived from the Kuhn-Tucker duality theorem applied to minimization of total Gibbs free energy of a multiphase-multiaggregate system (including aqueous and other non-ideal solutions). In this context, the efficient and reliable *Interior Points Method* (IPM) minimization algorithms have been developed.

If the appropriate thermodynamic properties of components that may appear in the equilibrium state are available, the dual minimization approach requires much less and gives much more than "reaction-based" techniques. For IPM, no explicit reaction or a priori knowledge of pH, Eh and stable phase assemblage are needed, since a feasible initial approximation can always be computed automatically from T, P, bulk chemical composition of system and standard state Gibbs potentials for all virtual components.

Three kinds of results are always computed: direct X (mole quantities of all valid components and phases present at equilibrium), dual u (chemical potentials of stoichiometric units), and set of Kuhn-Tucker criteria F_α for phase stabilities. Since iterative equations are solved with respect to the u vector, the performance of IPM program is high and depends little on the quantity of species combined from the stoichiometric units. The dual solution values permit the retrieval or matching of the (unknown) thermodynamic parameters for any stable or metastable substance if its quantity in the system is known from the experimental data. Some sought-for quantities of components may be fixed in advance by one- or two-side restrictions thus allowing for calculation of partial equilibrium states and modeling of kinetically dependent processes.

A new SELEKTOR++ program (Kulik et al., 1992; Karpov et al., 1993) provides many facilities and powerful tools for system definition, operation with a built-in thermodynamic database, specification of non-ideal solution models, computation of input data objects and equlibrium states, storage and retrieval of results. This means that the principal attention in geochemical applications should be paid to the proper choice of model structure, thermodynamic data and equations for activity coefficients. These comprise the *reference multisystem,* the frame in which a variety of specific processes and systems can be simulated. The most serious concern usually is how to provide a reasonable consistency of the apparent Gibbs free energy of formation values for all components in the system. Formerly, the absence of internally consistent thermodynamic datasets suitable for geochemical applications was regarded as the main disadvantage of the minimization techniques .

Second, a comprehensive thermodynamic dataset on aqueous electrolyte species was recently published (Helgeson et al., 1981; Tanger and Helgeson, 1988; Shock and Helgeson, 1988; Shock et al., 1989; Shock and Helgeson, 1990). It is based upon the Helgeson-Kirkham-Flowers equation of state (HKF-EOS) that can be used to predict the partial molal properties (entropy, enthalpy, volume, Gibbs free energy of formation, heat capacity etc.) of many individual inorganic and organic ions, complexes and neutral species at temperatures 0 to 1000 °C and pressures up to 5 kbar. Helgeson and co-workers estimated the parameters of HKF-EOS for ca. 300 aqueous species and collected them in the database included into SUPCRT92 program package (Johnson et al.,1992) together with algorithms for calculation of thermodynamic properties by HKF-EOS at any given TP.

Extensive internally consistent thermodynamic datasets for inorganic and organic gases, liquids and minerals (Reid et al., 1977; Helgeson et al., 1978; Berman, 1988; Holland and Powell, 1990; Cox et al., 1989; Grenthe et al., 1992) are also now available. Taken together, they comprise a base which is quite sufficient for application of powerful minimization algorithms for thermodynamic modeling in aqueous systems.

We performed an adaptation of algorithms and HKF-EOS parameters dataset of SUPCRT92 for use in the SELEKTOR++ program environment. The references to sources of data on aqueous complexes and minerals added to SELEKTOR++ database are included in the tables. More detailed critical evaluation of thermodynamic data with regard to the normative seawater model will be published elsewhere (Karpov and Kulik, 1994, in prep).

Problem statement

We have tried to develop the ion-association models of normal and estuarine seawater combining the advantages of both the HKF-EOS thermodynamic dataset for aqueous species and the dual minimization IPM algorithm and SELEKTOR++ program. This text describes first the metastable equilibrium thermodynamic model of normative major-element seawater of 35.174 ‰ salinity at 25 °C and 1 bar. Metastable means that the seawater is oversaturated with respect to calcite, aragonite, dolomite and phosphate minerals. Those elements were included whose concentrations exceed or may reach 1 ppm (except Ar and iodine).

The extensive checking of this model is possible by comparisons with other chemical models of standard seawater (Dyrssen and Wedborg, 1974; Johnson and Pytkowicz, 1978,1979; Nordstrom et al., 1979; Millero and Schreiber, 1982; Ball and Nordstrom, 1991). Then the model is to be extended at wider temperature range (1-30 °C). Mixing with riverwater, redox changes caused by C_{org} decomposition, and solubilities of marine minerals and solid solutions can be studied as well. The extension of model to Al, Fe, Mn, Co, Ni, Cr, V, Ba, Cu, Zn, Cd, Pb, Hg, I, As, Se, organic ligands and adsorbed surface complexes on Fe and Mn (hydr)oxides is anticipated.

The ion-association aqueous model is adopted in this study because we rely on the reference thermodynamic dataset for aqueous ions and complexes produced by Helgeson and coworkers. They used the modified Debye-Hueckel equation to calculate the activity coefficients of electrolytes, free ions and complexes when extrapolating their properties to infinite dilution in order to derive the parameters of HKF-EOS (Helgeson et al., 1981; Shock and Helgeson, 1988). Another reason is that seawater model can also be used for studies of the anoxic environments, but less is known on specific-interaction parameters for reduced ions (Plummer and Parkhurst, 1990). The ion-association aqueous model provides direct links to the surface-complexation models for adsorbed species (cf. Dzombak and Morel, 1990; Stumm, 1992). Finally, for trace elements and heavy metals, more data on aqueous association are normally available than on specific interaction (cf. Millero and Hawke, 1992).

There is an important difference between aqueous association models of seawater available from WATEQ4F, SOLMNEQ.88 and other "reaction-based" programs, and our model calculated by the dual minimization IPM algorithm.

In the first case, the speciation is defined by T, P, analytical concentrations of ionic components, analytical (or guessed) pH and Eh and (possibly) prescribed set of stable mineral phases. The frame data include a set of linearly independent reactions and their equilibrium constants together with equations for calculation of free activity coefficients with corresponding ion-size parameters. Since each species in the aqueous phase is normally related to others by only one reaction, and no proton balance calculated, some thermodynamic inconsistencies may be totally hidden.

In the second case, both the phase and component composition at equilibrium state are functions of T,P and bulk chemical composition of the system expressed through mole quantities of stoichiometric units. The frame ("multisystem") consists of the list of components (grouped to phases) that may appear at equilibrium, their Gibbs free energies of formation at given T,P and standard state, and equations with parameters for calculation of activity coefficients for solution species. The pH, Eh and set of stable phases do not define the result but, on the contrary, are themselves functions of the equilibrium state. Since the problem is solved first with respect to chemical potentials of stoichiometric units, any inconsistency between thermodynamic parameters of valid components would affect the equilibrium state and therefore reveal itself.

The strategy of studies

For the above reasons, *the following strategy have been used in this study.*

1. Most consistent chemical compositions of normative seawater (Dyrssen and Wedborg, 1974; Millero, 1978; Nordstrom et al., 1979) were examined and their N, C, H and O contents balanced after calculations of equilibria open to the model air. Bulk compositions of 3517.44 g salts and 96482 g H2O were then calculated (with or without 1000 kg of normative model air).

2. Set of aqueous species (ions, complexes, ion pairs), gases in gas phase, end-members in solid solutions and minerals was constructed. For each component, the stoichiometry and appropriate parameters for calculation of apparent Gibbs free energy of formation at given TP were retrieved from the databases. For non-ideal solution components, corresponding ion-size parameters and other coefficients were provided.

3. Metastable equilibrium state of seawater open to the model air was calculated at ambient conditions without precipitation of minerals like calcite, aragonite, dolomite, magnesite, phosphates etc.

4. Parameters of carbonate system, speciation, total and mean activity coefficients, and thermodynamic and stoichiometric association constants were calculated and compared to the reference values.

5. In order to achieve correct values of pH, carbonate and borate alkalinity, and better agreement with reference constants and activity coefficients, the ΔG_f° values for some carbonate, bicarbonate and borate complexes were adjusted in the range ± 1 kJ (at 25 °C corresponding to ± 0.2 of pK_A). No adjustments of ΔG_f° values for ions and gases were made.

6. The items 3, 4 and 5 were repeated for different seawater compositions, open and closed to the air, trying to achieve better agreement with reference values for seawater while keeping minor adjustment of ΔG_f° values for carbonate and bicarbonate complexes. The resulting model was then used to check the stability of reduced species, mineral solubilities and salinity dependencies.

7. Thermodynamic constants of components were calculated for temperatures of 1, 5, 10, 15, 20, 25, 30 °C at pressure 1 bar either with SUPCRT92 routines and from heat capacity dependence or (for some ion pairs) from dissociation constants of SOLMINEQ.88 database (Kharaka et al., 1988).

8. The sequence of equilibrium states of normative seawater at different temperatures were computed and temperature dependencies of carbonate system values and other parameters calculated and compared to reference data.

9. Average chemical composition of river input into the Baltic Sea was estimated from data of Blazhchishin (1978) and Ahl (1988) and from a conservative mixing model (Millero, 1978) based on chemical determinations of Kremling (1969, 1970, 1972). The compositions of Baltic brackish waters were then calculated for different salinities using modified linear mixing model.

10. A series of equilibrium states was calculated representing the typical water bodies of the Baltic Sea, and their dependencies on temperature, salinity, $P(CO_2)$, and redox conditions were investigated.

Part 1. Thermodynamic model of normative seawater

Normative bulk composition of seawater

We used three compositions of major components of normal seawater (Table 1) recalculated to concentration (mole (kg seawater)$^{-1}$) units of total dissolved elements. The composition A was taken from (Millero, 1978, Table VIII), B - from (Dyrssen and Wedborg, 1974, Table II) and C from (Nordstrom et al., 1979). The values for N, H and O were derived from the model calculations of equilibria in the "open" system with large excess of air. The elements were included with concentrations exceeding 1 mg kg^{-1} or 0.01 mmol kg^{-1}. Phosphorus was included in order to complete the list of major nutrients (C, N, Si, P). Argon was not included due to its unreactivity, although the partial pressure of Ar was added to that of N_2 in the model air.

Obviously, all three normative compositions show little difference. Composition (C) is quite similar to (B) (though no reference is given to the sources of data on seawater composition in Nordstrom et al., 1979). Both can be traced to the composition of Lyman and Fleming (1940). Slightly higher Na and lower Mg content in the (A) composition of Millero (1978) traces to Riley and Tondagai, (1967) as seen in the book (Millero and Sohn, 1992, Table 2.1). Since the Na content is determined by difference (cation-anion balance), its value is not so well established as for Cl and other major elements. The differences of 0.61 mmol kg^{-1} (0.13%) for Na and -0.334 mmol kg^{-1} (-0.63%) for Mg are small and can not affect the calculation of speciation, when pH is taken from the analytical value.

These differences become significant when pH is treated as function of equilibrium state (and therefore of bulk composition). We found it easy to match the parameters of carbonate, bicarbonate and borate ion pairs with Ca^{+2}, Mg^{+2} and Na^{+} in the cases of (B) and (C) compositions in order to obtain the correct pH, carbonate and borate alkalinity values at a $P(CO_2)$ fixed by a large quantity of model air. Unfortunately, it appears impossible to do this in the case of composition (A) because of the higher Na content. Total dissolved carbonate obtained in all runs exceed 0.26 mmol kg^{-1} (normal values near 0.21) and total bicarbonate at given pH is lower (1.83 against 1.88-1.89 mmol kg^{-1}). This is not surprizing because the pH in our model is a dependent parameter that reflects delicate acid-base balance in the whole system. This may also suggest that more precise determinations of Na and Mg to chlorinity ratios are needed for normative seawater.

Regarding this problem, we constructed the model composition of normative seawater from the (B) and (C) compositions (Table 1). This gives a sum of total dissolved solids (TDS) as 35.1744‰ due to amounts of H and O added to balance the composition with respect to the model of closed seawater (without air).

Thermodynamic dataset on aqueous species, gases and minerals

The data on partial molal properties of aqueous ions and some complexes with parameters of HKF-EOS from the SUPCRT92 database (Johnson, Oelkers and Helgeson, 1992 and papers cited therein) offer a good framework for the thermodynamic model of seawater. From the viewpoint of ion-association approach, this database contains values for all important

Table 1

Comparison of bulk normative element compositions of major component seawater dissolved matter (see text for explanations)

Element	Atomic mass, g (1969)	Composition mmol/(kg seawater) A	B	C	Model mmol/kg	Model mg/kg
Na	22.9898	468.99	468.38	468.3816	468.3816	10768
Mg	24.305	52.816	53.15	53.14956	53.15	1292
Ca	40.08	10.28	10.29	10.2869	10.29	413
K	39.0983	10.21	10.21	10.2076	10.21	399
Sr	87.62	0.09	0.093	0.0929	0.093	8.15
Li	6.941			0.0261	0.026	0.18
Rb	85.4678			0.00137	0.014	0.118
Cl	35.453	545.586	545.87	545.8776	545.88	19354
S	32.06	28.24	28.23	28.233	28.23	905.06
C	12.01115	2.09	2.11	2.022	2.1112	25.356
Br	79.904	0.84	0.84	0.8423	0.84	67.29
B	10.811	0.41	0.412	0.4117	0.412	4.46
F	18.9984	0.07	0.0734	0.07316	0.0734	1.394
N	14.0067	0.803	0.804	0.804	0.801	11.25
Si	28.0855			0.07123	0.1	2.81
P	30.9738			0.00063	0.0006	0.0186
H	1.00794	1.331	1.328	1.359	1.327	1.338
O	15.9994	120.27	120.205	120.21	120.2	1923.1
TDS, g/kg		35.1708	35	35		35.1744

Formulae:

Dry air	$(N_2)_{0.79016}\ (O_2)_{0.209476}\ (CO_2)_{0.00034}$
Model air for checks of carbonate system	$(N_2)_{0.79016}\ (O_2)_{0.189}\ (CO_2)_{0.000472}$
C_{org} (ocean, Redfield ratio)	$C_{1.06}\ H_{2.63}\ O_{1.1}\ N_{0.16}\ P_{0.01}$

associates of Ca^{+2} except borate complexes; MgCO3°, $MgHCO3^{+}$, MgF^{+} ion pairs are included, but not MgSO4° and MgCl2°; there are also some K, Na and Sr ion pairs. The dataset provides values for ion pairing between Cl^{-} and Na^{+}, Mg^{+2}, Ca^{+2}, K^{+}, Li^{+}, Rb^{+}. A simple ion-association model may be constructed that accounts for interactions between all main cations and anions (Table 2). In this table, ions considered as "reference" with respect to their partial molal ΔG_f° (the apparent Gibbs free energy of formation at standard state and ambient conditions) values are marked with "*" and complexes available in SUPCRT92 dataset with "+".

ΔG_f° values for those complexes and ion pairs not included into the SUPCRT92 database but necessary for ion-association model were calculated at 25 °C from ΔG_f° values for ions and thermodynamic association constants from the tabulations of Millero and Schreiber (1982), Kharaka et al. (1988), Nordstrom et al. (1990), Ball and Nordstrom (1991). ΔG_f° of phosphate ion-pairs were estimated using K_A values from compilation (Vieillard and Tardy, 1984). Since K_A values are model-dependent, and all models mentioned do not account for ion pairing between Cl^{-} and Na^{+}, K^{+}, Ca^{+2} and Mg^{+2}, the obtained ΔG_f° values were treated only as first approximations. It should be noted in advance, however, that the calculated degree of Cl^{-} pairing at 25 °C in seawater is about 10% for Mg, 5% for Sr, 3% for Ca and Na, 2% for Rb, <1% for K and Li, i.e. not large. For Mg, Ca, K and Sr it is less than sulfate pairing. 96% Cl and 95% Na exist as free ions at the ionic strength of normative seawater.

Nevertheless, we included the Cl^{-} -cation pairing into the model because it affects the proton balance and because the model based on HKF-EOS parameters may be used in principle for elevated temperatures and pressures (up to 350-400 °C and 2 Kbar) where Cl^{-}-cation complexation becomes very significant (cf. Majer and Stulick, 1982; Ruaya, 1988). Such conditions exist, for example, in the hydrothermal cells at mid-ocean ridges (cf. Grichuk et al., 1985; Thompson, 1983; Seyfried and Ding, 1993).

The ΔG_f° values for $NO3^{-}$ and HNO3° species were corrected after Karpov (1981). Without this correction, the control calculations give pH = 1.5 - 2.5 that are quite unrealistic for most of natural waters.

First runs of the model (from a total of 120) showed that ΔG_f° values for some carbonate, bicarbonate, borate and phosphate ion pairs need to be matched for a correct representation of pH and alkalinity, and for a closer agreement with experimentally-derived stoichiometric association constants. This was achieved in a series of subsequent runs by varying the ΔG_f° values . Table 2 represents "corrected" values from the last run accepted for further modeling, together with reported values for K_A that we feel are closer to those of the consistent set mapped to the set of ΔG_f° values for ions and neutral species. In fact, it is possible to fit the ΔG_f° for all ion-pairs in our model to carefully chosen values of K* solving the inverse task of thermodynamic modeling (Karpov and Lashkevich, 1981). The fact that corrections were not large (in the range of 0.2 pK_A) suggests that ion-association approach can be applied to the thermodynamic models of seawater based on existing datasets of partial molal properties of aqueous species. At present, they are at least as internally consistent as sets of reaction equilibrium constants.

The values for gases were taken from SUPCRT92 database (they are all very close to the reference values of CODATA (Cox et al., 1989)). The ΔG_f° values for carbonates, sulfates

Table 2

Thermodynamic data for aqueous species (major elements), reference state (molal), T = 25°C, P = 1 bar, and ion size parameters for calculation of activity coefficients

Element		Species	ΔG_f° J/mole	log K_t (molal)	Ref.	ΔG_f°corr. J/mole	$å_j$,b 10^{-8}cm	Ref. $å_j$,b
B	*	B(OH)3°	-968763		1		0.064	s
		B(OH)4-	-1153220	-9.237	1,7		5.0	x
	+	BF4-	-1486994		1		3.5	p
Ca	*	Ca+2	-552790		1		6; 6.1	kc
		CaB(OH)4+	-1716214	1.8	2	-1716684	4.5	p
	+	CaCO3°	-1099764	3.327	1	-1099550	-0.34	r
	+	CaCl+	-680109		1		4.5	p
	+	CaCl2°	-811696		1		0.064	s
	+	CaF+	-838393	1.3	1,2	-841930	4.5	p
		CaH2PO4+	-1691960	1.407	3	-1691075	4.5	p
	+	CaHCO3+	-1145704		1		3.5	q
		CaHPO4°	-1658280	2.741	3	-1657427	0.064	s
		CaNH3+2	-578900		8		4	p
		CaOH+	-717043	1.22	9		3.5	q
		CaPO4-	-1609200	6.46	3,2	-1608454	3.5	q
		CaS2O3°	-1082940		8		0.064	s
	+	CaSO4°	-1309300	2.3	1,2,5	-1309990	0	s
K	*	K+	-282461.8		1		3; 3.1	kc
	+	KBr°	-376601.8		1		0.064	s
	+	KCl°	-405220		1		0.064	s
		KHPO4-	-1378740	0.29	3,5	-1373165	4	p
	+	KHSO4°	-1031565		1		0.064	s
		KS2O3-	-806940		8		3.5	q
	+	KSO4-	-1031942		1	-1031829	3.5	q
Li	*	Li+	-292600		1		6	k
	+	LiCl°	-415262		1		0.064	s
		LiOH°	-450778.7		4		0.064	s
		LiSO4-	-1041400	0.77	2	-1041454	3.5	q
Mg	*	Mg+2	-453985		1		8; 8.1	kc
		MgB(OH)4+	-1617110	1.57	2	-1617183	4.5	p
	+	MgCO3°	-998972		1	-998272	-0.34	r
	+	MgCl+	-584505		1		4.5	p
		MgCl2°	-714000			-713996	0.064	s
	+	MgF+	-743455	1.9	1,2	-746402	4.5	p
	+	MgHCO3+	-1046840		1		3.5	q
		MgH2PO4+	-1590641	1.508	3	-1592850	4.5	p
		MgHPO4°	-1560670	2.909	3,2	-1559730	0.064	s
		MgOH+	-623826	2.20	9		3.5	q
		MgPO4-	-1511200	6.586	3	-1510348	4	p
		MgS2O3°	-984960		8		0.064	s
		MgSO4°	-1211055	2.21	2	-1211272	0	s

Table 2, continued

Element	Species	ΔG_f° J/mole	log K_t (molal)	Ref.	ΔG_f°corr. J/mole	$\mathring{a}_j$,b 10^{-8}cm	Ref. $\mathring{a}_j$,b
N	+ HNO3°	-103470		1,4	-38107.9	0.064	s
	+ NO2-	-32216.8		1		3	k
	+ NO3-	-110905		1,4	-46024	3	k
	* NH4+	-79454.2		1		2.5	k
	NH4SO4-	-829400				4.5	p
	* N2°	18187.8		1		0.131	s
	* NH3°	-26706.5		1		0	s
Na	* Na+	-261881		1		5; 4.6	k
	NaB(OH)4°	-1416287	0.22	2	-1417087	0.064	s
	+ NaBr°	-358192		1		0.064	s
	NaCO3-	-795686	1.02	2	-795252	3.5	q
	+ NaCl°	-388735		1		0.064	s
	NaHCO3°	-847736	-0.19	2	-848780	0.064	s
	NaHPO4-	-1352673	0.29	5	-1352673	4.5	p
	+ NaHSiO3°	-1285074		1		0.064	s
	NaS2O3-	-784670		8		4.5	p
	NaSO4-	-1010335	0.7	5	-1010279	3.5	q
	NaHS°		-0.83	10	-245108	0.064	s
P	* H2PO4-	-1130265		1		4	k
	+ H3PO4°	-1142650		1		0.064	s
	* HPO4-2	-1089137		1		4	k
	* PO4-3	-1018804		1		4	k
Rb	* Rb+	-283675.2		1		2.5	k
	+ RbBr°	-380785.8		1		0.064	s
	+ RbCl°	-409488.1		1		0.064	s
	+ RbF°	-570906.8		1		0.064	s
	RbSO4-	-1031559	0.6	2		3.5	s
S	HS2O3-	-523628				4	p
	* S2O3-2	-522582		1		4	k
	+ S2O4-2	-600404		1		5	k
	+ HSO3-	-527728		1		4	k
	+ S2O5-2	-790776		1		4	p
	* SO3-2	-486599		1		4.5	k
	+ S2O6-2	-966504		1		4	p
	+ S3O6-2	-958136		1		4	p
	+ S4O6-2	-1040561		1		4	p
	+ S5O6-2	-958136		1		4	p
	+ HSO4-	-755756		1		3.5	q
	* SO4-2	-744459		1		4	k
S-2	* H2S°	-27919.8		1		0.0197	s
	* HS-	11966.24	-6.987	1,6	12035	3.5	k
	HS4-	29081	-7	6		3.5	q
	HS5-	30871	-6.1	6		3.5	q

Table 2, continued

Element	Species	ΔG_f° J/mole	log K_t (molal)	Ref.	ΔG_f°corr. J/mole	$\mathring{a}_j$,b 10^{-8}cm	Ref. $\mathring{a}_j$,b
	S-2	91945.6	14;18.7	6,11	118774	5	k
	* S2-2	79496		1		6.5	b
	+ S3-2	73638.4		1		8	b
	+ S4-2	69036		1		10	b
	+ S5-2	65688.8		1		12	b
	S6-2	62341.6		extr		14	b
Si	+ HSiO3-	-1013783		1		4.5	p
	+ SiF6-2	-2199530		1		4.5	p
	* SiO2°	-833410.9		1		0.064	s
Sr	* Sr+2	-563836		1		5; 5.2	kc
	+ SrCO3°	-1108174		1	-1107687	-0.34	r
	+ SrCl+	-693707.2		1		4.5	p
	+ SrF+	-846381.3		1		4.5	p
	SrHCO3+	-1157534	1.184	5	-1157511	3.5	p
	SrOH+	-725110	0.7		-725129	3.5	p
	SrS2O3°	-1094540		8		0.064	s
	SrSO4°	-1321408		2		0	s
Br	* Br-	-104056.1		1		3	k
	+ BrO-	-33472		1		3.5	q
C	* CO3-2	-527983		1		4.5	k
	* HCO3-	-586940		1		4.1	k
	H2CO3@	-623222		4		0.13	s
	* CH4°	-34451.1		1		0.129	s
	* CO2°	-385974		1		0.0946	s
Cl	* Cl-	-131290		1		3; 3.1	kc
	HCl°	-128430		4		0.064	s
F	* F-	-281750.6		1		3.5	k
	+ HF°	-299834		1		0.064	s
H,O	* H2°	4236		1		0.03	s
	* O2°	16543.5		1		0.121	s
	* OH-	-157297		1		3.5	k
	* H+	0		1,c		9	k
	* H2O°	-237183		1			

Notes:

K - stability constants;

ΔG_f° - apparent partial molal Gibbs free energy of formation from elements;

å - ion-size parameter (eqn.1);

b - coefficient for neutral species (eqn. 5).

References to thermodynamic data in table 2:

1 - SUPCRT92 database (Johnson, Oelkers and Helgeson, 1992);

2 - K from (Millero and Schreiber, 1982, table 3);

3 - K from (Vieillard and Tardy,1984);

4 - Karpov, 1981;

5 - K from the WATEQ4F database (Ball and Nordstrom, 1991);

6 - K from (Morse and others, 1987);

7 - Hershey et al., 1986;

8 - MINEQL-PSI database (cited from (Pearson, Berner, Hummel, 1992);

9 - K from (Arnorsson et al., 1982);

10 - K from (Kharaka et al., 1988);

11 - K from (Schoonen and Barnes, 1989).

References to ion-size parameters and coefficients for neutral species:

k - Kielland (1937) cited from (Nordstrom, Munoz, 1986);

p - set to values 4-4.5;

q- set to value 3.5;

b - from (Ball, Nordstrom, 1991);

x - calculated from activity coefficient 0.633 (Millero, Schreiber, 1982, table 11);

s - for dissolved gases values of solting-out coefficients from (Millero,Schreiber, 1982, Table 13); for other neutral species set to 0.09 (the mean value for dissolved gases);

r - calculated from the value 0.6 of activity coefficient (Millero, Schreiber, 1982, Table 15).

Table 3

Thermodynamic data for gases and minerals
(standard state, T = 25 °C, P = 1 bar)

Phase	Name, formula	log K	ΔG_f° J/mole	Ref.	ΔG_f°corr. J/mole
GAS	CH4		-50835.6	1	
GAS	CO2		-394360	1	
GAS	H2S		-33400	1	
Apatites:					
APATC	apcl Ca5(PO4)3Cl		-6217420	2	
APATF	apf Ca5(PO4)3F		-6443050	2	
APATO	apoh Ca5(PO4)3(OH)		-6297700	2	
CAPCM	cfap-mar (marine apatite) Ca9.54Na.33Mg.13(PO4)4.8 (CO3)1.2F2.48(OH).37		-12294500	3,c	-12294600
CAPCF	cfap carbonate-F-apatite Ca10(PO4)5(CO3)1.45F2.1	-107.6	-12615750	4,5	-12608700
Other Ca-phosphates					
CAPB	brushite CaHPO4(H2O)2	-6.6	-2154750	3,5	-2153366
CAPM	monetite CaHPO4	-6.9	-1681300	3,5	-1679916
CAPW	whitlockite_h Ca3(PO4)2		-3875650	3	-3851624
CAPW	whitlockite_l Ca3(PO4)2	-28.9	-3884820	3,5	-3860794
CAP8	octacalciumphosphate Ca8H2(PO4)6(H2O)5	-93.8	-12261200	5	-12258200
Carbonates:					
CRBC	aragonite CaCO3	-8.32	-1128150	7,8	
CRBC	calcite CaCO3	-8.48	-1129070	7,8	
CRBDM	dolomite_disordered CaMg(CO3)2		-2158450	1	
CRBM	magnesite MgCO3		-1028686	9,1	-1027830
CRBSR	strontianite	-9.27	-1144660	10	
Metastable "marine" carbonates					
CRBC	cal_mar CaCO3	< -7.749		swa	> -1124521
CRBM	mgs_mar MgCO3			swa	> -1017252
CRBDM	dol_mar CaMg(CO3)2	< -14.72		swa	< -2146024
"Defective marine" Mg-calcite solid solution					
CRBC	cal_def CaCO3	-8.327	-1128300	11	
CRBC	dol_dhalf Ca.5Mg.5CO3	-7.8	-1075890	11	
C	carbon		0		
C_ORG	org_matter Redfield		-272490	red	

Table 3, continued

Phase	Name, formula	log K	ΔG_f° J/mole	Ref.	ΔG_f°corr. J/mole
GYPAN	anhydrite CaSO4		-1321830	1,7	
GYPS	gypsum CaSO4(H2O)2		-1797361	7	
HALCF	fluorite CaF2		-1176350	12	
MGOB	brucite Mg(OH)2		-835319	6	
	Mg phosphates				
MGHP	MgHPO4	-5.82	-1577300	3,5	-1576500
MGHPN	newberryite MgHPO4(H2O)3	-5.83	-2288900	3,5	-2288050
MGPF	faringtonite Mg3(PO4)2	-23.3	-3538800	3,5	-3536500
MGPB	bibierrite Mg3(PO4)2(H2O)8	-25.2	-5443400	3,5	-5440900
SIO2	quartz SiO2		-856170	12,1	
SIO2A	sio2_amorphous		-848900	1	
SRSO	celestite SrSO4		-1345670	12	

References to table 3:

1 - SUPCRT92 database (Johnson, Oelkers and Helgeson, 1992);
2 - Zhu and Sveriensky, 1991;
3 - ΔG_f° or K from (Vieillard and Tardy,1984);
4 - Jahnke, 1984;
5 - Gusev et al., 1989;
6 - Karpov, 1992 (personal data);
7 - CODATA tables (Garvin et al., 1987);
8 - Plummer and Busenberg, 1982;
9 - Kittrick and Perya, 1986;
10 - Busenberg and Plummer, 1987;
11 - K_t from (Busenberg and Plummer, 1989);
12 - from MINEQL-PSI database as calculated in (Pearson et al., 1992).

c - $(OH)_{0.37}$ was added to the formula to obtain charge balance;
swa - calculated metastable values from ion-activity products in aerated seawater ($p(CO_2) = 0.000343$ bar);
red - calculated from dual solution of model for completely reduced seawater (cf. Karpov et al., 1993).

When necessary, ΔG_f° values were recalculated using K_t values or known ΔG_f° of aqueous ions to match values of aqueous ions from SUPCRT92 database.

and other minerals of interest for modeling seawater environments were taken from sources listed under Table 3. Some values were estimated or recalculated using more appropriate stability constants or adjusted to values for ions from SUPCRT92 dataset.

Ion-association model of seawater

The ion-association model of aqueous solution has been extensively used to derive the speciation of ions and metals in natural waters (Dyrssen and Wedborg, 1974; Johnson and Pytkowicz, 1979; Turner et al., 1981; Millero and Schreiber, 1982; Millero and Hawke, 1992). It also has been implemented in many widespread computer programs such as WATEQF, SOLMNEQ, MINEQL, EQ3/6, PHREEQE, and the model of standard seawater has been used to compare these programs (Nordstrom et al., 1979). The derivation of parameters for HKF-EOS to compute partial molal properties of aqueous ions and complexes has been performed by extrapolation to infinite dilution using the modified Debye-Hückel equation (Helgeson et al., 1981; Shock and Helgeson, 1988). Equations of this type are used in the ion-association approach to calculate the free activity coefficients of aqueous species.

The ion-association aqueous model consists of:

1) The appropriate set of free ions and complexes sufficient to account for the ionic interactions that should be modeled;

2) A set of the apparent standard values of Gibbs free energies of formation ΔG_f° at given T and P (or complementary set of stability constants) for all species;

3) A set of parameters to calculate individual activity coefficients of free ions, complexes and ion pairs as functions of ionic strength[1] with modified Debye-Hückel equation (Table 2).

We have added several complexes to the original dataset of SUPCRT92 database in order to give a better account of speciation of the major elements in seawater; a few of ΔG_f° values have been corrected. More details are discussed by Karpov and Kulik (1994, in prep.).

Calculation of free activity coefficients

The activity coefficients γ_j of j-th charged aqueous species (ions and complexes) were calculated from Debye-Hückel equations modified by Helgeson et al. (1981):

$$\log \gamma_j = -\frac{A_\gamma z_j^2 I^{1/2}}{1 + \mathring{a}_j B_\gamma I^{1/2}} + \Gamma_\gamma + b_\gamma I, \qquad (1)$$

where z_j stands for charge of j-th species, $\mathring{a}_j$ - ion size parameter (in 10^{-8} cm, listed in table

---

[1] In the present version of SELEKTOR++ program, the equations following are stored in the database record together with species-dependent parameters. Current activity coefficients of aqueous species are automatically calculated at each iteration using current values of the effective ionic strength.

1 for charged species), $\Gamma_\gamma = \log(1 + 0.0180153\, m_\gamma)$ - mole fraction to molality conversion factor, b_γ - extended term coefficient, m_γ -sum of molalities of all dissolved species (for seawater, b_γ was assumed to be equal to that of $b_{NaCl} = 0.064$),

$$I = \frac{1}{2}\sum_j z_j^2 x_j \text{ -} \tag{2}$$

effective ionic strength, x_j - molality of charged ions and complexes, and A_γ, B_γ represent the Debye-Hückel parameters:

$$A_\gamma = \frac{1.82483 \cdot 10^6\ \rho^{1/2}}{(\varepsilon T)^{3/2}}, \quad B_\gamma = \frac{50.2916\ \rho^{1/2}}{(\varepsilon T)^{1/2}}, \tag{3}$$

where T is temperature in °K, ρ is the density, and ε for dielectric constant of water. Both latter values are calculated within the SUPCRT92 routines or may be estimated for standard pressure and temperature below 100 °C with equations given in Nordstrom et al. (1990); the first coefficient in the equation for ε was adjusted from 2727.586:

$$\rho = 1 - \frac{(T_c - 3.9863)^2 (T_c + 288.9414)}{508929.2 (T_c + 68.12963)} + 0.011445 e^{-374.3/T_c}, \tag{4}$$

$$\varepsilon = 2727.428 + 0.6224107 T - 466.9151 \ln T - 52000.87/T$$

T_c - temperature in °C. At ambient conditions, $A_\gamma = 0.5109$, and $B_\gamma = 0.3287$.

We assumed the value of extended term parameter $b_\gamma = 0.064$ (as for NaCl electrolyte, see Table 5 from (Helgeson et al., 1981)). NaCl is the dominant electrolyte in seawater. This value can therefore be accepted as approximation of ionic medium impact. The corresponding value of "distance of closed approach" $å_k$ (ibid., table 2) equals 3.72. Nevertheless, we took the Kielland`s values of $å_j$ for better approximation of the mean and total activity coefficients, and assumed values between 3.5 and 4.5 for charged ion pairs and complexes (the values were chosen following the estimates of Millero and Schreiber (1982), Table 15). Alternatively, instead of using one common b_γ parameter, it would be promising to treat it as individual-ion value b_j as suggested by Truesdell and Jones (1974), with $å_j$ and b_j values determined for each ion by fitting the equation to measured activities of pure electrolytes. This has been carried out by Parkhurst (1990) using data on mean activity coefficients to derive both parameters for a number of individual ions. When applied to seawater, this approach would probably give better values for total activity coefficients, but there is no direct way to assess the validity of $å_j$ and b_j coefficients in mixed salt solutions such as seawater.

The activity coefficients for dissolved gases and neutral species were calculated from the equation

$$\log \gamma_j = k_j I, \tag{5}$$

where k_j is the "salting-out" coefficient (Millero and Schreiber, 1982). We used values for dissolved gases from (ibid., Table 13) and assigned value of k=0.064 equal to the b_γ parameter of equation (1) for other neutral species. The b_γ parameter can be treated as unified salting-out coefficient for all ionic forms in the media of a dominant electrolyte (NaCl in our case; see Helgeson et al., 1981). For carbonate ion pairs, we used value of k = -0.34 following the estimations of (Reardon and Langmuir, 1976) corrected by (Millero and Schreiber, 1982).

Control runs of the model showed that the change in b_γ parameter between 0.064 and 0.074 has very little influence on the resulting activities of aqueous species; only activity coefficients are affected. The same applies for the activity coefficient of water. The runs with $\gamma_{(H_2O)} = 0.983$ and 1 showed almost no difference. We assumed therefore that the activity coefficient of water is 1. It was found, however, that changes in activity coefficient of CO_3^{-2} ion strongly affect pH, carbonate system parameters, and stability of carbonate, hydrocarbonate and borate ion pairs. Zero k_j values for neutral species (Table 2) indicate that corresponding activity coefficients were set to 1 in the computations.

Comparison of calculated parameters with reference data

Tables 4 and 5 present the thermodynamic model of seawater calculated from the data of Tables 1-3 without precipitation of mineral phases. Calculations were performed by means of IPM algorithm (Karpov et al., 1993) implemented in SELEKTOR++ program together with thermodynamic and composition databases where all input data were stored.

The following values were computed for the equilibrium state (index i refers to chemical elements, j - to dependent components, k - to phases (a refers to aqueous, g - to gas phases), r - to reactions):
G_X - total conventional Gibbs free energy of the system at equilibrium state (J);
M_i - total molality of dissolved element in aqueous solution, moles (kg $H_2O)^{-1}$;
C_i - total concentration of dissolved element, mg (kg of solution)$^{-1}$;
u_i - chemical potentials of element (independent component), J mole^{-1};
m_j - molality of aqueous species, c_j - concentration of aqueous species;
x_j - mole quantity, a_j - activity of any component (direct solution),
μ_j - chemical potential of component (J mole^{-1}),
γ_j - activity (fugacity) coefficient of the component (molal scale for aqueous species, mole fraction scale for others),
p_j - equilibrium partial pressure for gases, bar;
X_k - mole quantity of phase in the system at equilibrium state,
F_k - Kuhn-Tucker criterion of phase stability (see Karpov et al., 1993a, Karpov, 1981).

For an aqueous solution only:

I - effective ionic strength (molal) at equilibrium state; pH = -log a_{H+};
Eh - was calculated from the chemical potential of oxygen (Karpov,1981).

Table 4

Results of calculation of ion-association model of normative seawater by means of the dual Gibbs free energy minimization (SELEKTOR++ program environment, version 2.03; at PC 386/87, 40 Mhz, time of calculation was 2.4 min). Input data from Tables 1-3, P=1 bar, T= 25 °C.
Composition: 3517.44 g of seasalt + 96483 g H_2O = 100 kg of seawater.

Total system parameters:
Minimum apparent total Gibbs potential G(X)= -1.295901e+09 J.
Aqueous solution:
pH = -log(a(H+)) = 8.1511; Eh = 0.736 (at H_2O scale);
effective ionic strength I = 0.64844 molal.

Values for chemical elements (independent components)

Independent component	Input chem. composition (moles)	Deviations of mass balance	U-Chemical potential (J/mole)	Total dissoved forms:	
				molality	mg/kg soln
Na	46.83688	3.7574e-07	-335681	0.485466	10768
Mg	5.314855	2.9486e-07	-606669	0.0550887	1291.81
Ca	1.028972	2.0879e-08	-709882.5	0.0106653	412.423
K	1.020972	7.3600e-09	-365912	0.0105824	399.194
Sr	0.0092997	8.6675e-10	-733012	0.0000964	8.14866
Li	0.0025999	2.7578e-11	-390474	0.0000269	0.180466
Cl	54.58651	3.7644e-06	-62803	0.5657912	19353.1
S	2.822923	9.1263e-08	-608407	0.0292597	905.054
C	0.2111142	1.1548e-08	-409020.6	0.0021882	25.358
Br	0.0839977	6.0628e-11	-51557.5	0.0008706	67.1194
F	0.0073398	2.2095e-10	-236933	0.0000761	1.39448
B	0.0411989	1.6043e-09	-629265	0.000427	4.45413
N	0.0800938	6.5788e-09	-297	0.0008302	11.2188
Si	0.0099997	1.9135e-10	-852092	0.0001036	2.80855
P	0.00006	2.4984e-12	-864146	6.219e-07	0.018584
Rb	0.00014	3.5699e-12	-389312.5	1.451e-06	0.119655
H	10711.33	7.8235e-04	-117536	0.0033665	3.27386
O	5367.619	3.9172e-04	-2162	0.1255799	1938.5
Charge	0	-2.9465e-06	71059		

Aqueous phase:
Total moles 5463.78; total grams 99999.99;
Kuhn-Tucker stability criterion (Karpov,1981): $F_\alpha = 0.0004127 < 0.01$.

Equilibrium partial pressures of gases (bar):

p(CO2) = 0.0004721 log p(CO2) = -3.326
p(H2O) = 0.03034 log p(H2O) = -1.518
p(H2) = 0 log p(H2) = -41.183
p(N2) = 0.7869 log p(N2) = -0.104
p(O2) = 0.1748 log p(O2) = -0.7575

Table 5

Results of calculation of ion-association model of normative seawater: Direct solution - values for aqueous species (those with molalities < 1e-13 were excluded)

Phase	Name of species	x_j - molality	Concen-tration, mg/kg	Activity coef-ficient	log acti-vity	Chemical potential (J/moles)
Aqu	B(OH)3°	0.000329	19.621	1.1	-3.441	-988357
	B(OH)4-	0.00004	3.0216	0.7174	-4.545	-1179114
	Ca+2	0.009218	356.44	0.2532	-2.632	-567764
	CaB(OH)4+	7.2e-06	0.8263	0.6999	-5.298	-1746879
	CaCO3°	0.000048	4.6724	0.602	-4.535	-1125388
	CaCl+	0.000238	17.346	0.6999	-3.778	-701627
	CaCl2°	0.00006	6.4744	1.1	-4.177	-835489
	CaF+	1.66e-06	0.0946	0.6999	-5.935	-875757
	CaH2PO4+	2.53e-10	0.00003	0.6999	-9.752	-1746688
	CaHCO3+	0.000039	3.7846	0.6595	-4.592	-1171865
	CaHPO4°	2.846e-08	0.00374	1.1	-7.504	-1700211
	CaOH+	8.04e-08	0.00443	0.6595	-7.275	-758521
	CaPO4-	1.734e-08	0.00226	0.6595	-7.942	-1653735
	CaSO4°	0.001053	138.32	1	-2.978	-1326936
	CO2°	0.000014	0.57932	1.152	-4.804	-413344
	N2°	0.000413	11.163	1.216	-3.299	-594
	O2°	0.000181	5.5808	1.198	-3.664	-4324
	K+	0.010322	389.37	0.6409	-2.179	-294853
	KBr°	6.167e-08	0.00708	1.1	-7.168	-417469
	KCl°	0.000068	4.9043	1.1	-4.125	-428715
	KHPO4-	4.72e-10	0.00006	0.6807	-9.493	-1427300
	KHSO4°	7.46e-13	9.8e-08	1.1	-12.086	-1100501
	KSO4-	0.000192	25.051	0.6595	-3.897	-1054025
	Li+	0.000026	0.17605	0.7479	-4.706	-319414
	LiCl°	1.949e-07	0.00797	1.1	-6.669	-453277
	LiOH°	3.5e-11	8.1e-07	1.1	-10.414	-510171
	LiSO4-	4.64e-07	0.04613	0.6595	-6.514	-1078586
	Mg+2	0.042754	1002.6	0.3231	-1.860	-464550
	MgB(OH)4+	0.000032	3.193	0.6999	-4.649	-1643665
	MgCO3°	0.000106	8.601	0.602	-4.196	-1022175
	MgCl+	0.004913	283.3	0.7302	-2.445	-598413
	MgCl2°	0.00056	51.44	1.1	-3.210	-732275
	MgF+	0.000037	1.54	0.6999	-4.588	-772543
	MgH2PO4+	1.893e-9	0.00022	0.6999	-8.878	-1643474
	MgHCO3+	0.000224	18.427	0.6595	-3.830	-1068651
	MgHPO4°	2.637e-07	0.0306	1.1	-6.537	-1596998
	MgOH+	4.537e-06	0.18084	0.6595	-5.524	-655307
	MgPO4-	1.341e-07	0.01543	0.6807	-7.040	-1550521
	MgSO4°	0.006458	749.94	1	-2.190	-1223722
	NO2-	3.745e-08	0.00166	0.636	-7.623	-75680
	NO3-	4.1e-06	0.24576	0.636	-5.583	-77841

Table 5 - continued

Phase	Name of species	x_j - molality	Concen-tration, mg/kg	Activity coef-ficient	log acti-vity	Chemical potential (J/moles)
Aqu	Na+	0.461252	10231	0.7035	-0.489	-264622
	NaB(OH)4°	0.000019	1.879	1.1	-4.677	-1443736
	NaBr°	7.26e-06	0.721	1.1	-5.097	-387238
	NaCO3-	0.000028	2.2186	0.6595	-4.738	-822246
	NaCl°	0.017453	984.11	1.1	-1.717	-398484
	NaHCO3°	0.000286	23.161	1.1	-3.503	-868723
	NaHPO4-	2.335e-08	0.00268	0.6999	-7.787	-1397069
	NaHSiO3°	0.000019	1.7925	1.1	-4.690	-1311794
	NaSO4-	0.006402	735.32	0.6595	-2.374	-1023794
	H2PO4-	4.3e-09	0.0004	0.6807	-8.533	-1178924
	HPO4-2	1.48e-07	0.0137	0.1712	-7.596	-1132448
	PO4-3	5.403e-11	4.95e-6	0.0172	-12.033	-1085971
	Rb+	1.407e-06	0.116	0.6098	-6.067	-318253
	RbBr°	2.65e-11	4.23e-06	1.1	-10.535	-440870
	RbCl°	3.03e-08	0.00354	1.1	-7.477	-452116
	RbF°	1.8e-10	0.00002	1.1	-9.704	-626243
	RbSO4-	1.37e-08	0.0024	0.6595	-8.044	-1077425
	HSO4-	2.7e-09	0.00025	0.6595	-8.750	-805649
	SO4-2	0.015145	1403.6	0.1712	-2.586	-759172
	HSiO3-	1.98e-06	0.1473	0.6999	-5.858	-1047172
	SiO2°	0.000083	4.8175	1.1	-4.039	-856415
	Sr+2	0.000081	6.884	0.2189	-4.749	-590893
	SrCO3°	1.15e-07	0.01639	0.602	-7.159	-1148517
	SrCl+	5.09e-06	0.6045	0.6999	-5.448	-724756
	SrF+	8.9e-10	0.00009	0.6999	-9.207	-898886
	SrHCO3+	4.03e-07	0.05788	0.6595	-6.575	-1194994
	SrOH+	1.85e-10	0.00002	0.6595	-9.914	-781650
	SrSO4°	9.35e-06	1.6567	1	-5.029	-1350065
	Br-	0.000863	66.555	0.636	-3.260	-122617
	CO3-2	0.000033	1.9025	0.1913	-5.202	-557624
	HCO3-	0.00141	83.032	0.6847	-3.015	-604101
	Cl-	0.541873	18535	0.6409	-0.459	-133862
	HCl°	7.17e-10	0.00003	1.1	-9.103	-180339
	F-	0.000038	0.68838	0.6595	-4.606	-307993
	HF°	2.39e-10	4.6e-06	1.1	-9.580	-354469
	OH-	2.118e-06	0.03475	0.636	-5.871	-190757
	H+	8.664e-09	8.426e-06	0.815	-8.151	-46477
	H2O°	5355.5	96481	1	3.729	-237234

This complete set of parameters of equilibrium state reveals many inconsistencies that exist between input thermodynamic data. It can be used for a straightforward calculation of values and constants for comparisons of model with other models and experimental data. For instance, both thermodynamic K_r and stoichiometric K_r^* stability constants can be derived for any reaction between valid components present in the equilibrium state at given T,P. Mean $\gamma^{\pm}$ and total γ^{T} activity coefficients for any electrolyte can be calculated as well. Any experimentally derived concentration can be used for matching doubtful conventional ΔG_j° value directly through stoichiometry of the aqueous component and corresponding u_i (dual solution) values (Karpov et al., 1993):

$$\Delta G^\circ_j = \mu_j + RT(-\ln \gamma_j + \ln m_j + m_w - 1), \qquad \mu_j = RT \sum_i a_{ij} u_i, \tag{6}$$

where m_w is the molality of water and R the universal gas constant.

Testing the model with carbonate system parameters

The parameters of normative seawater carbonate system are listed in Table 6. The reference values for carbonate alkalinity

$$A_C = [HCO_3^-]_T + 2[CO_3^{-2}]_T \tag{7a}$$

and total alkalinity

$$A_T = [HCO_3^-]_T + 2[CO_3^{-2}]_T + [B(OH)_4^-]_T + [OH^-]_T - [H^+]_T - \Sigma B \tag{7}$$

were taken from (Millero, 1979). Here $[\,i\,]_T = (c_w / 1000)\, \Sigma\, m_{j(i)}$ - total concentration of ion with its ion pairs, c_w - number of grams of water per kilogram of solution. AP = $a(Ca^{+2}) \cdot a(CO_3^{-2})$ denotes ion activity product of Ca^{+2} and CO_3^{-2}, K_t - thermodynamic solubility product of calcite (aragonite), $\Omega = AP / K_t$ - saturation index. The calculated equilibrium data for the normative model of seawater at 25 °C and 1 bar are listed in Tables 4 and 5.

It is clear that agreement between calculated and reference values of carbonate, borate and total alkalinity, pH and $P(CO_2)$ values is quite good. One should keep in mind that our model treats pH and $P(CO_2)$ values as functions of T,P and bulk chemical composition of the system and not as independent parameters. The agreement between all mentioned values therefore suggests that the thermodynamic ion-association model is internally consistent at least with respect to carbonate system. We feel that it might be possible to match the model with greater precision provided that carbonate system parameters were determined with higher accuracy. In particular, the stabilities of the borate species need to be better known.

Saturation indexes for calcite, dolomite and strontianite were calculated both in thermodynamic and concentration scales

$$\Omega = [Ca^{+2}]_T [CO_3^{-2}]_T / K'_T \tag{8}$$

Table 6

Comparison of modeled parameters of the carbonate system with reference data (ambient conditions, salinity 35.17 ‰, effective ionic strength (molal) I = 0.6483)

Parameter (mmol kg^{-1}, m-eqv kg^{-1})	Calculated (Table 4,5)	Reference value (± uncert.)	Difference	Reference
A_T (total alkalinity)	2.4004	2.400	+0.0004	(1)
Total CO_2	2.1112	2.111	+0.0002	(1)
pH (NBS scale)	8.1511	8.151	0	(1)
$[B(OH_4)^-]_T$	0.09455	0.095 (.003)	-0.00045	(1)
A_C (carbonate alkalinity)	2.305	2.305 (.003)	0	(1)
$[HCO_3^-]_T$	1.891	1.890 (.011)	+0.001	(1)
$[CO_3^{-2}]_T$	0.207	0.208 (.005)	-0.001	(1)
$[CO_2^{\circ}]_T$	0.0135	0.0134 (.0002)	+0.0001	(1)
$P(CO_2) \times 10^{-6}$ bar	472.1	472 (7)	+0.1	(1)
$P(O_2)$, bar	0.1748			
$\log(a(Ca^{+2}) * a(CO_3^{-2}))$	-7.834			
$\log([Ca^{+2}] * [CO_3^{-2}])$	-5.672	-5.668	-0.004	(1)
$\log(K_t)$ (calcite)		-8.46(0.03);-8.48		(2);(3)
$\log(\Omega_t)$ (calcite)	0.648; 0.646			
$\log(K^*)$ (calcite)		-6.34(0.01)		(4)
$\log(\Omega^*)$ (calcite)	0.668			
$\log(K_t)$ (aragonite)		-8.32(0.03)		(3)
$\log(\Omega_t)$ (aragonite)	0.486			
$\log(K^*)$ (aragonite)		-6.185(0.01)		(4)
$\log(\Omega^*)$ (aragonite)	0.513			
$\log(a(Sr^{+2})\ a(CO_3^{-2}))$	-9.951			
$\log(K_t)$ (strontianite)		-9.13(0.03);-9.27		(2);(3)
$\log(\Omega_t)$ (strontianite)	-0.821;-0.681			
$\log(a(Mg^{+2})\ a(CO_3^{-2}))$	-7.062			
$\log(a(Ca^{+2})\ a(Mg^{+2}) * a(CO_3^{-2})^2)$	-14.896			
$\log(K_t)$ (dolomite)		-16.54		(5)
$\log(\Omega_t)$ (dolomite)	1.644			

References: (1) Millero 1979; (2) Millero, Milne and Thurmond, 1984; (3) Plummer and Busenberg, 1982; (4) Plummer and Sundquist, 1982; (5) Busenberg and Plummer, 1989.

where K'_T is apparent solubility product of mineral. The saturation indexes for all three minerals show similar values (with difference about 0.02 logarithmic unit) confirming the consistency of related thermodynamic constants and activity coefficients.

Total ion and mean salt activity coefficients

Table 7 presents comparisons of the total activity coefficients of major ions calculated as

$$\gamma_T = \alpha \ \gamma_j, \qquad \alpha = x_j \ / \ x_T \qquad (9),$$

where γ_j is free activity coefficient, x_T - total molality of ion and all its associates, α - fraction of free ion. The calculated values of γ_j for Na^+, Mg^{+2}, Cl^- are lower than both measured and calculated from ion-pairing model of (Millero and Schreiber, 1982). We attribute the lower values of our calculated α due to chloride complexation, since measured and ion-pairing values were usually derived assuming that Cl^- is not associated.

However, the calculated degree of association of alkali and alkali-earth ions is much lower than one would expect from the model of Johnson and Pytkowicz (1978) which also assumes sulfate and chloride pairing. Our calculations yield $\alpha(Cl^-) = 0.9576$ and $\alpha(SO_4^{-2}) = 0.5178$. Since thermodynamic data of Helgeson and coworkers (SUPCRT92 database, Johnson et al., 1992) on NaCl°, $CaCl^+$, $MgCl^+$ etc. are considered highly reliable, we conclude that simultaneous account for Cl^- and SO_4^{-2} ion pairing in the minimization model shows "compensation" effect on α and γ_T values of ions. The degree of such association was obviously overestimated in the earlier models (Elgquist and Wedborg, 1975; Johnson and Pytkowicz, 1978).

γ_T values for Mg^{+2}, Ca^{+2}, Sr^{+2}, HCO_3^-, CO_3^{-2}, HPO_4^{-2} were found to be in good agreement with corresponding "measured" values. For K^+, F^-, SO_4^{-2}, PO_4^{-3}, better agreement was found with values from ion-association model (Millero and Schreiber, 1982). γ_T and α for borate ion are significantly lower than both reference values. This can be traced to the discrepancy between two accepted values of the borate alkalinity (see Millero, 1979, p.1659). It seems that the value of $[B(OH)_4^-]_T = 0.095$ mmol (kg soln)$^{-1}$ accepted from (Lyman, 1957) is too high. In order to balance it, a rather large degree of borate association with Ca, Mg and Na is required. Better agreement would be achieved if the value $[B(OH)_4^-]_T = 0.084$ derived by Hansson (1973) is accepted. This would lead to higher $[CO_3^{-2}]_T = 0.218$ (±0.007) and lower $[HCO_3^-]_T = 1.880$ mmol (kg soln)$^{-1}$ (cf. Table 6) and to a lower degree of bicarbonate and higher - of carbonate association. This is in agreement with the conclusions of Millero (1981) that Hansson's value is more realistic. Higher γ_T for $H_2PO_4^-$ ion may be attributed to the fact that we did not include its ion pairs with K, Na and Sr into the model.

Calculated mean activity coefficients are compared in Table 8. It is interesting that calculated value for NaCl agree better (within 0.004 units) with measured or specific interaction values than with the ion-pairing value. For KCl, agreement is good. For all sulfate salts and $CaCO_3$, higher values were obtained but they are still closer to specific interaction values than to ion-association ones.

Table 7

Comparison of the modeled and reference fractions of free to total ions and total activity coefficients in seawater (ambient conditions)

Ion	Calculated		Millero, Schreiber, 1982				Kester; Johnson, Pytkowicz	
	α, %	γ_T	α, %	γ_T (m)	γ_T (s)	γ_T (i)	γ_T (a)	α, % (b)
Cations								
Na+	95.01	0.668	97.63	0.708	0.708	0.690	0.67	82.97
K+	97.54	0.625	98.01	0.662	0.668	0.615	0.62	78.28
Mg+2	77.36	0.250	89.13	0.257	0.269	0.255	0.33	48.14
Ca+2	86.42	0.219	88.44	0.217	0.241	0.228	0.21	43.54
Sr+2	84.02	0.184	92.01	0.188	0.239	0.231	0.21	
Li+	96.65	0.723						
Rb+	96.95	0.591						
Anions								
Cl-	95.76	0.614	100	0.628	0.628	0.628	0.63	83.31
Br-	99.13	0.630						
F-	49.93	0.329	48.84	0.296	0.519	0.333	0.34	
B(OH)4-	40.82	0.292	53.21	0.360		0.351		
HCO3-	71.94	0.493	79.24	0.532		0.536	0.55	
CO3-2	15.38	0.029	16.04	0.029	0.095	0.029	0.022	
SO4-	51.78	0.089	37.47	0.104	0.103	0.085	0.082	15.91
H2PO4-	66.71	0.454	78.59	0.416	0.456	0.395		
HPO4-2	31.90	0.055	29.68	0.072	0.095	0.072		
PO4-3	0.036	6e-6	0.15	3.7e-5	9e-3	4.2e-5		

Notes:

α - fraction of free ion to its total including all complexes and ion pairs; γ_T - total activity coefficient of ion defined as $\gamma_T = \alpha\ \gamma_F$, where γ_F is a free activity coefficient. Both values were calculated from data of tables 4 and 5.

References:

(a) - Kennish, 1990, p.76; (b) Johnson and Pytkowicz, 1978; (m) - measured, (s) - calculated from specific interaction model, (i) - calculated from ion pairing model (Millero, Schreiber, 1982, tables 20 and 21).

Table 8

Comparison of the modeled and reference mean activity coefficients of electrolytes in seawater (ambient conditions)

Reference: (Millero and Schreiber,1982) table 20

Salt	Mean activity coefficient:			
	calculated	measured	specific interaction	ion-pairing
NaCl	0.671	0.667	0.667	0.658
Na_2SO_4	0.439	0.378	0.373	0.343
KCl	0.641	0.645	0.648	0.621
K_2SO_4	0.413	0.352	0.358	0.318
HCl	0.723	0.627	0.701	0.657
$CaSO_4$	0.208	0.136	0.159	0.139
$SrSO_4$	0.194	0.140	0.157	0.140
$CaCO_3$	0.220	0.086	0.151	0.081

Notes: the mean activity coefficient $\gamma^{\pm}_{MX}$ for electrolyte $M_\nu X_\xi$ is calculated from free activity coefficients by the formula

$$\gamma^{\pm}_{MX} = [(\gamma^F_M)^\nu (\gamma^F_X)^\xi]^{-(\nu+\xi)}$$

Values of free activity coefficients were taken from Table 5.

Thermodynamic and stoichiometric association constants

Reactions and related stability constants are not used explicitly in calculations of equilibria by dual minimization IPM algorithm. We calculated some association constants (Table 9) just in order to compare with values used in marine chemistry for speciation calculations. For the reaction M + L = ML (M denotes metal ion, L - ligand), the thermodynamic association constant is

$$K_A = a(ML) / (a(M) \cdot a(L)) \qquad (10a)$$

and the stoichiometric association constant (cf.Millero and Schreiber, 1982)

$$K^* = [ML] / ([M] \cdot [L]) = K_A (\gamma_M \; \gamma_L) / \; \gamma_{ML}, \qquad (10b)$$

where a(ML), a(M) and a(L) are activities, [ML], [M] and [L] are concentrations, γ_M, γ_L, γ_{ML} are individual (free) activity coefficients of species ML, M and L. Both values were calculated directly from Table 5. Since association constants are model dependent, and no model like ours is available, we included two K_A sets for comparison: the one from Millero and Schreiber (1982) and more recent from the WATEQ4F database (Ball and Nordstrom, 1991). Both models do not account for chloride complexation with major cations. One can not expect an exact matching of reference constants and those calculated from Table 5 because the former contain some unknown inconsistencies different from the inconsistencies between ΔG_f° values for individual species that we accepted as input data (Table 2).

Nevertheless, the agreement is generally satisfactory. Adjustment of ΔG_f° values for borate, carbonate and bicarbonate pairs and complexes in order to match the carbonate system parameters (see above, Tables 2 and 6) resulted in higher values of K_A and K* for borate complexes, higher K* for bicarbonate ion pairs and slightly lower K_A (but the same K*) for carbonate ones. This probably means that total borate is overestimated; Hansson's (1973) value would be more appropriate. K* for $CaH_2PO_4^+$, $CaHPO4^\circ$ are higher because higher K_A values were accepted from (Viellard and Tardy, 1984) and WATEQ4F database to calculate the apparent ΔG_f° values. K_A values for CaF^+ and MgF^+ are lower but K* higher than reference values (Millero and Schreiber, 1982). For $LiSO4^\circ$, $RbSO4^\circ$, and $HSO4^-$ K_A are higher but corresponding K* lower than reference values. In principle, the ΔG_f° values for complexes may be fitted much more precisely to measured concentrations in seawater by solving the inverse two-criterion minimization problem (Karpov et al., 1993) with second criterion being the minimum difference between the calculated and reference concentrations. However, we feel this extra procedure is not well justified for the ion-association model.

Cation speciation

The speciation of cations is calculated from total molality values (Table 4, 5) and molalities of various ion pairs and complexes. The free ion fractions α are given in Table 7. It is clear that a degree of Cl^- pairing is not large - less than 4% except Mg^{+2} (10%). It is of the same magnitude as SO_4^{-2} pairing. Highest complexation occur for Mg^{+2}, mostly with SO_4^{-2}, Cl-, and HCO_3^-. K^+ is affected by SO_4^{-2} and Cl^- pairing only to small degree (< 2.5% total).

Table 9

Comparison of modeled and reference thermodynamic (K_A) and stoichiometric (K^*) association constants

References: (1) - Millero and Schreiber, 1982, table 3 and 16;
(2) WATEQ4F database (Ball and Nordstrom,1991).

Species	log K_A calc.	log K_A ref (1)	log K_A ref (2)	log K^* calc.	log K^* (1) (±)
$CaSO_4$°	2.241	2.28	2.309	0.893	1.03 (0.02)
$CaCO_3$°	3.298	3.2	3.225	2.214	2.1 (0.1)
$CaHCO_3$+	1.055	1.0	1.106	0.493	0.33 (0.05)
CaF+	1.304	1.31	0.94	0.692	0.65 (0.06)
$CaB(OH)_4$+	1.894	1.8		1.318	1.11 (0.02)
CaOH+	1.228	1.3		0.630	0.74 (0.08)
CaH_2PO_4+	1.413	1.0	1.408	0.821	0.24 (0.02)
$CaHPO_4$°	2.724	2.66	2.74	1.335	1.28 (0.03)
$CaPO_4$-	6.723	6.46	6.46	4.559	4.5 (0.1)
$KHPO_4$-	0.282		0.29	0.320	
KSO_4-	0.868	0.88	0.85	0.105	0.26 (0.02)
$MgSO_4$°	2.255	2.21	2.37	1.015	1.01 (0.02)
$MgCO_3$°	2.865	2.9	2.981	1.889	1.94 (0.05)
$MgHCO_3$+	1.044	0.95	1.068	0.587	0.28 (0.08)
MgOH+	2.206	2.2	2.204	1.716	1.70 (0.05)
MgF+	1.877	1.9	1.82	1.374	1.29 (0.02)
$MgB(OH)_4$+	1.769	1.57		1.300	0.93 (0.03)
MgH_2PO_4+	1.515	1.13	1.513	1.030	0.37 (0.02)
$MgHPO_4$°	2.919	2.84	2.87	1.635	1.51 (0.07)
$MgPO_4$-	6.853	5.8	6.59	4.780	3.84 (0.1)
$NaSO_4$-	0.701	0.95	0.70	-0.022	0.30 (0.06)
$NaCO_3$-	0.961	1.02	1.27	0.280	0.42 (0.2)
$NaHCO_3$°	0.003	-0.19	-0.25	-0.340	-0.53 (0.03)
$NaB(OH)_4$°	0.391	0.22		0.060	-0.24 (0.08)
$NaHPO_4$-	0.298	0.80	0.29	-0.45	0.05 (0.02)
$SrSO_4$°	2.306	2.10	2.55	0.897	0.85 (0.1)
$SrCO_3$°	2.874		2.805	1.732	
$SrHCO_3$+	1.189		1.184	0.563	
SrOH+	0.706	0.82		0.048	0.25 (0.09)
$LiSO_4$-	0.778	0.77		0.087	0.26 (0.05)
$RbSO_4$-	0.609	0.60		-0.176	-0.09 (0.05)
HSO_4-	1.988	1.979	1.987	1.329	1.49 (0.01)

Note: numbers in brackets in the last column are estimations of uncertainty intervals for stoichiometric association constants. log K_A values were calculated from log(activity) values from Table 5. log K^* values were calculated from the molality values of Table 5 and converted to concentration scale by subtraction of log(0.96483).

Table 10

Speciation of cations in seawater
calculated from data of tables 4 and 5 (in percent).

Cation Anion	Na+	Mg+	Ca+2	K+	Sr+2	Li+	Rb+	Total molality of anion
SO4-2	1.32	11.70	9.88	1.81	9.70	1.73	0.944	0.02926
Cl-	3.59	10.17	2.29	0.64	5.280	0.72	2.09	0.5658
HCO3-	0.059	0.407	0.366	-	0.418	-	-	0.00196
CO3-	0.0058	0.191	0.450	-	0.144	-	-	2.145e-4
B(OH)4-	0.0041	0.058	0.007	-	-	-	-	9.8e-5
F-	-	0.067	0.0015	-	0.092	-	1.2e-4	7.61e-5
Br-	0.0015	-	-	6e-4	-	-	0.18	8.706e-4
H2PO4-	-	3.4e-6	2.4e-6	-	-	-	-	6.446e-9
HPO4-2	5e-6	4.8e-4	2.7e-4	4.5e-6	-	-	-	4.64e-7
PO4-3	-	2.4e-4	1.6e-4	-	-	-	-	1.515e-7
OH-	-	8.2e-3	7.5e-4	-	1.9e-4	1.3e-4	-	6.7e-6
Total molality of cation	0.4855	0.0551	0.0107	0.0106	9.64e-5	2.7e-5	1.45e-6	

Note: Defis means that corresponded associate was not included into the model.

Reduced sulfur and nitrogen species

Since sulfur exists almost entirely as the SO_4^{-2} species in oxic seawater, we calculated the metastable equilibrium state at TP and composition the same as in Tables 4 and 5 but with addition of 88 g of organic matter with average Redfield C:N:P ratio (Table 1) and without air. Part of resulting printout is presented in Table 11.

This is the case for completely reduced seawater where solid carbon is present as the stable phase. Due to dissolution of C_{org}, the total dissolved inorganic carbon C_T as well as P_T, N_T, and $P(CO_2)$ are higher than in aerated seawater, and pH is lower because of the higher molality of the HCO_3^- ion. Nitrogen is present as NH_4^+ ion. Sulfate ion and its complexes are about half of their concentrations in aerated seawater. The other half is in the form of dissolved H_2S and HS^- ion and, to a lesser extent, as polysulfide and thiosulfate species. As seen from Table 12, the thermodynamic data used here for thiosulfate ion pairs (see Table 2) are not in good agreement with the few values reported by Millero (1986). The match is good for major reduced sulfur species (HS^- and $H_2S°$) and for polysulfides. The speciation of sulfur calculated from the model of completely reduced seawater is given in Table 13. Further extension of the model to include some sulfite and sulfide ion pairs would be appropriate if the related experimental data become available.

Precipitation of minerals and the total equilibrium state

Since it is well known that normative seawater at ambient conditions is oversaturated with respect to calcite, aragonite, dolomite and apatite (Morse and Berner, 1979; Mucci, 1983; Vieillard and Tardy, 1984; Busenberg and Plummer, 1989), it is interesting to include these minerals into the multisystem. In such a way, it is possible to calculate the hypothetical total equilibrium state of seawater with respect to a given mineral. This permits the direct estimation of how much mineral would precipitate and which changes in aqueous speciation would occur. It is an advance of the IPM minimization calculations, since programs like WATEQ4F or PHREEQE normally calculate only saturation indexes (see Table 6). The index shows whether a mineral will dissolve or precipitate at given equilibrium state.

We computed several models that included 100 kg of seawater of 35.17‰ salinity and 1000 kg air with $P(CO_2) = 0.000343$ bar (Tables 14, 15).

Carbonates

A large literature exists on carbonate precipitation and dissolution in seawater (cf. Busenberg and Plummer, 1989). We calculated several simple models in order to show that the developed ion-association aqueous model gives realistic results on carbonate solubility. Calculation of saturation indexes (Table 6) suggests that the normative seawater is oversaturated with respect to aragonite, calcite, dolomite and undersaturated to strontianite. With magnesite, the situation is unclear because its thermodynamic properties are uncertain and range over 4.2 orders of magnitude of the solubility product (cf. Kittrick and Perya, 1986). However, since no precipitation of $MgCO_3$ from normal seawater is reported at

Table 11

Parameters for selected aqueous species from an equilibrium calculation of 100 kg of reduced normative seawater (see tables 1-4), reacted with 88 g of Redfield ratio average organic matter.

Results: pH = 6.8137, Eh = -0.2084, I = 0.6478, minimum total Gibbs potential G(X) = -1.296614 $\cdot 10^6$ kJ, stable excess carbon present(0.015 moles).

Phase	Name of species	x_j - molality	Concentration, mg/kg soln	Activity coefficient	log activity	Chemical potential (J/moles)
Aqu	CaNH3+2	6.08e-08	0.00335	0.1711	-7.983	-624414
	CaS2O3°	2.76e-09	0.00041	1.1	-8.500	-1131408
	CaSO4°	0.000527	69.187	1	-3.278	-1328650
	CH4°	5.93e-08	0.00092	1.212	-7.143	-75174
	CO2°	0.003942	167.23	1.152	-2.343	-399297
	H2°	4.41e-08	0.00009	1.046	-7.336	-37587
	H2S°	0.0073	239.8	1.03	-2.124	-39993
	N2°	0.000416	11.243	1.216	-3.296	-573
	NH3°	5.524e-06	0.0907	1	-5.258	-56667
	KS2O3-	1.38e-09	0.0002	0.6592	-9.040	-858489
	KSO4-	0.000097	12.575	0.6592	-4.196	-1055731
	LiSO4-	2.33e-07	0.02314	0.6592	-6.814	-1080294
	MgS2O3°	2.377e-08	0.00313	1.1	-7.583	-1028190
	MgSO4°	0.003239	375.8	1	-2.490	-1225432
	NaS2O3-	3.2e-08	0.00417	0.6995	-7.650	-828282
	NaSO4-	0.003185	365.52	0.6592	-2.678	-1025525
	NH4+	0.002157	37.507	0.6995	-2.821	-95508
	NH4SO4-	0.000026	2.854	0.6995	-4.741	-856411
	HS2O3-	2.19e-14	2.4e-09	0.6804	-13.827	-602502
	S2O3-2	3.64e-07	0.03933	0.1712	-7.206	-563661
	HSO3-	3.02e-13	2.36e-08	0.6804	-12.687	-600096
	SO3-2	4.3e-13	3.3e-08	0.1913	-13.088	-561255
	HSO4-	2.92e-08	0.00273	0.6592	-7.715	-799745
	SO4-2	0.00753	697.35	0.1712	-2.890	-760903
	SrS2O3°	2.7e-11	5.25e-6	1.1	-10.524	-1154557
	SrSO4°	4.64e-06	0.8219	1	-5.333	-1351800
	HS-	0.007277	231.98	0.6592	-2.319	-1152
	HS4-	4.08e-7	0.0509	0.6592	-6.570	-8370
	HS5-	7.51e-8	0.0117	0.6592	-7.305	-10776

Table 11, continued

Phase	Name of species	x_j - molality	Concentration, mg/kg soln	Activity coefficient	log activity	Chemical potential (J/moles)
Aqu	S-2	1.45e-09	0.00004	0.2111	-9.514	37690
	S2-2	7.77e-08	0.0048	0.2266	-7.755	35284
	S3-2	2.645e-07	0.0245	0.2677	-7.150	32878
	S4-2	4.5e-07	0.0557	0.3813	-6.765	30472
	S5-2	5.77e-07	0.0892	0.435	-6.600	28066
	S6-2	7.6e-07	0.14127	0.4818	-6.435	25660
	CO3-2	0.00002	1.1591	0.1913	-5.417	-558850
	HCO3-	0.01872	1101.3	0.6843	-1.892	-597691

Equilibrium partial pressures of gases (bar)(total gas phase 0.1165 moles):

p(CH4) = 0.0000544 log p(CH4) = -4.264
p(CO2) = 0.13653 log p(CO2) = -0.865
p(H2S) = 0.0700 log p(H2S) = -1.155
p(H2) = 2.6e-7 log p(H2) = -6.585
p(NH3) = 7.97e-8 log p(NH3) = -7.098
p(N2) = 0.7935 log p(N2) = -0.1005
p(O2) = 0 log p(O2) = -69.955

Table 12

Comparison of modeled and reference thermodynamic (K_A) and stoichiometric (K*) association constants for reduced sulfur and nitrogen species
(ref.: Millero, 1986; [1]- Schoonen and Barnes, 1989)

Associate	log Ka calc.	log Ka ref	log K* calc.	log K* ref.
CaS2O3°	1.334	2.28	-0.055	1.03(±0.02)
KS2O3-	0.34			
MgS2O3-	1.48			
NH4SO4-	0.97			
NaS2O3-	0.045			
HS2O3-	0.732			
HSO3-	7.214			
HS-	-7.007	-6.98 (±0.02)	-6.74	-6.524
HS4-	-7.001	-7.0		
HS5-	-6.110	-6.1		
S-2	-14.009	-13.9;-14.6;-18.7[1]		
S2-2	-12.25			
S3-2	-11.64	-12.5		
S4-2	-11.23	-9.52		
S5-2	-11.092	-9.41		
S6-2	-10.925	-9.62		
SrS2O3°	1.432			

Note: values of log K_A were calculated from log(activity) values from Table 11. Values of log K* were calculated from molalities in Table 11 and converted to concentration scale.

Table 13

Speciation of sulfur in the model of reduced normative seawater
(calculated from data of Tables 4 and 11)

Parameter	SO4-2 ligand	S2O3- ligand	HS- H2S	Polysulfides
%Ca-L	3.62	0.68	-	-
%Mg-L	22.18	5.60	-	-
%K-L	0.66	0.33	-	-
%Na-L	21.85	7.56	-	-
%Sr-L	0.032	0.0064	-	-
%NH4-L	0.178	-	-	-
% free anions	51.66	85.84	49.77	-
% of total S	49.91	0.00145	49.96	0.13

Note: concentrations of dissolved SO3-2 species are less than 5e-13 mole (kg H2O)$^{-1}$.

ambient conditions and atmospheric $P(CO_2)$, we recommend for ΔG_f° of "marine" magnesite values greater than -1017000 J $mole^{-1}$ (Table 3). Values down to -2146024 J $mole^{-1}$ are recommended for "marine dolomite" and -1124500 J $mole^{-1}$ for metastable "marine" calcite.

The precipitation of stable pure aragonite (6.2 g) or calcite (7.3 g) results in a pH decrease in 0.25-0.35 units. The seawater seems to be highly oversaturated with respect to "disordered" dolomite. It is known that Mg-calcite precipitate from seawater rather than dolomite. We modeled equilibria between the normative seawater and calcite-dolomite solid solution (Busenberg and Plummer, 1989). The activity coefficients of calcite and dolomite end-members were calculated at each iteration of IPM algorithm by equations:

$$RT \ln \lambda_{dolomite} = (1-w)^2 (A_0 + A_1 (2w-1)), \qquad (11a)$$

$$RT \ln \lambda_{calcite} = w^2 (A_0 + A_1 (4w-3)), \qquad (11b)$$

where λ is the activity coefficient, w is the mole fraction of dolomite end-member $Ca_{0.5}Mg_{0.5}CO_3$, A_0 and A_1 are empirical coefficients kJ $mole^{-1}$, R - universal gas constant, T - temperature (in K). Using log K_t = -8.48 for calcite and -8.27 for "disordered" dolomite with corresponding values of A_0 = 9.86 kJ/mol and A_1 = 3.5 kJ/mol (Busenberg and Plummer, 1989, group I), we obtained at equilibrium the unrealistic values of w = 99.7% with $\lambda_{dolomite}$ up to 120. The group II constants for "defect" marine calcites and dolomites with log K_t between -7.7 and -7.8 yields w = 0.115 to 0.18 and $\lambda_{dolomite}$ = 4.4 to 3.5. The w values (corresponding to mole fraction of $MgCO_3$ from 5.57 to 9%) appear to be realistic for most of the experimental data on Mg-calcite solubility in seawater.

Phosphates

Most Ca and Mg phosphates are weakly soluble. They display unique properties that complicate the determination of their solubility and cause large discrepances in the literature data (Manheim and Gulbrandsen, 1979; Gusev et al., 1989). The thermodynamic values of phosphates are listed in Table 3.

At equilibrium with ideal solution of Cl-,F- and OH-apatite (data from Zhu and Sveriensky, 1991), the total dissolved P concentration decreases by 2-2.5 orders of magnitude. It increases when pH decreases; apatite is almost entirely F-apatite. It is not surprising since mostly carbonate-fluorapatite (francolite) is encountered in marine sediments. It is more soluble than pure F-apatite but, because of its variable composition and ill-defined structure, its thermodynamic properties are not certain. We used data from Janke (1984) on synthetic carbonate-apatite and from Vieillard and Tardy (1984) on "marine" apatite containing Na and Mg. There is evidence that non-apatite amorphous Ca and Mg phosphates precipitate from seawater, and apatite forms later, when Mg-phosphate dissolves (Gulbrandsen et al., 1984). Octacalcium-phosphate $Ca_8H_2(PO_4)_6 \cdot 5H_2O$ is believed to be the most probable precursor of carbonate-apatite (Gusev et al., 1989).

We calculated the solubilities of some Ca and Mg phosphates (Table 15). It is clear that formation of marine apatite precursors is possible only from porewater with high concentrations of biologically-derived phosphate. Formally, P_T concentration in seawater is the

Table 14

Selected parameters of equilibrium solubility of carbonates and apatite in 35.174 ‰ seawater open to the atmospheric air (without Ar), $p(CO_2)$ = 0.000343 bar, T=25 °C, P = 1 bar.

Composition: 100 kg seawater + 1000 kg air.
$G(X)_{min} = -1.344522 \cdot 10^6$ kJ for all runs.

Parameter	Run sw_h1	Run sw_h2	Run sw_h3	Run sw_h4	Run sw_h5	Run sw_h6	Ref.
Precipitated:							
apatite,g	-	0.01	-	-	-	-	(1)
aragonite, g	-	-	6.22	-	-	-	(2)
calcite, g	-	-	-	7.29	-	-	(2)
dolomite, g	-	-	-	-	8.20	-	(3)
Mg-calcite: total, g	-	-	-	-	-	6.698	(4)
mole % CaCO3	-	-	-	-	-	88.50	
mole % Ca0.5Mg0.5CO3	-	-	-	-	-	11.50	
pH	8.2616	8.2615	7.990	7.9115	7.747	7.952	
I, moles	0.6482	0.6482	0.6471	0.6469	0.6467	0.647	
Total molality:							
Ca	412.42	412.38	387.51	383.24	394.57	386.9	
Mg	1291.8	1291.8	1292.0	1292.1	1281.1	1291.0	
C	24.446	24.441	12.407	10.262	6.940	11.324	
P	0.0186	0.00006	0.00012	0.00015	0.0002	0.000134	
F	1.3945	1.3907	1.3908	1.3909	1.3909	1.3908	
F_α criterion	4.13e-4	4.13e-4	4.12e-4	9.96e-10	-3.3e-11	4.1e-4	

Note: F_α is calculated value of a Kuhn-Tucker criterion of aqueous phase stability (Karpov, 1981).

References:

(1) - $\Delta G_f{}^o$ of F-, Cl- and OH- apatite from (Zhu and Sveriensky, 1991), see Table 3;
(2) $\Delta G_f{}^o$ of calcite and aragonite from (Cox et al., 1989);
(3) $\Delta G_f{}^o$ of "disordered" dolomite (Helgeson et al., 1978);
(4) calculated as solid-solution using pKt values 8.327 for "defective" marine calcite and 7.7 for "defective" dolomite by solid-solution model from (Busenberg and Plummer, 1989) with A_0 = 6.29 kJ/mole and A_1 = 1.77 kJ/mole.

Table 15

Solubility of some phosphate minerals in the model normative seawater of 35.174 ‰ salinity at 1 bar and 25 °C, open to air with P(CO$_2$) = 0.000344 bar (thermodynamic data from Table 3).

Mineral	pH	P_total		[H2PO4-]$_T$	[HPO4-2]$_T$	[PO4-3]$_T$
		mg/kg s	molal	molal	molal	molal
No minerals	8.261	0.0186	6.22e-7	4.68e-9	4.34e-7	1.83e-7
F-apatite	8.264	8.7e-5	2.9e-9	2.22e-11	2.05e-9	8.6e-10
carbonate-F-apatite	8.260	3.6e-4	1.2e-8	9.2e-11	8.50e-9	3.56e-9
monetite	8.260	6.1e-3	2.04e-7	1.55e-9	1.43e-7	5.98e-8
whitlockite_l	8.260	2.2e-3	7.5e-8	5.67e-10	5.24e-8	2.2e-8
whitlockite_h	8.254	0.0153	5.11e-7	3.9e-9	3.57e-7	1.5e-7
carbonate-F-apatite marine	8.259	0.0106	3.56e-7	2.7e-9	2.49e-7	1.044e-7
bibierrite	8.230	1.567	5.24e-5	4.34e-7	3.74e-5	1.46e-5
octacalcium-phosphate	8.266	3.297	1.1e-4	9.11e-7	7.85e-5	3.07e-5

Note: concentration of P in seawater ranges between < 10^{-6} - $3.5 \cdot 10^{-6}$ mole$\cdot$kg^{-1} (Bruland, 1983), in porewater of phosphorite sediments - from 0.6 to 20 mg$\cdot$l^{-1} PO$_4^{-3}$ (Gusev et al., 1989).

Table 16

Limit solubilities of minerals, undersaturated in the normative model seawater of 35.174 ‰ salinity at T = 25 °C and P = 1 bar, open to the dry air

Parameter, mmol/kg	alpha-quartz SiO2	amorph. SiO2	strontianite SrCO3	fluorite CaF2	gypsum CaSO4 · 2H2O	celestite SrSO4	"pure" seawater
dissolved mineral	-0.004	-20.9	-0.27	-0.126	-24.49	-0.247	0
$[Si]_T$	0.104	2.187					0.1
$[Sr]_T$			0.361			0.340	0.093
$[C]_T$			2.069				2.012
$[F]_T$				0.3245			0.0734
$[Ca]_T$				10.416	34.30		10.29
$[S]_T$					52.92	52.92	28.23
pH	8.033	8.258	8.258	8.258	8.033	8.033	8.26

Note: the limit solubilities were calculated using thermodynamic data from Table 3 by addition of 100 moles of each mineral to the bulk chemical composition of 100 kg seawater with 1000 kg air.

same as the solubility of whitlockite $Ca_3(PO_4)_2$ or "marine" carbonate-fluorapatite (though it is controlled by biological processes). Anyway, the biological uptake of P from warm aerated seawater seems to be favoured by thermodynamics because of high oversaturation with respect to al" fluorapatite and monetite ($CaHPO_4$).

Minerals undersaturated in normative seawater

Another check of the normative seawater model is to calculate equilibria with solution containing excess weakly soluble minerals such as gypsum, fluorite, celestite. Seawater is normally undersaturated with respect to these minerals. We calculated two models (Table 16): one for solubility of gypsum, celestite and quartz, and another for strontianite, fluorite and amorphous silica. It is obvious that the values obtained are realistic. The normative seawater seems to be saturated with respect to quartz but undersaturated to amorphous SiO_2. The undersaturation to strontianite and celestite is almost equal. The actual processes of dissolution or precipitation of these minerals in the marine environment are controlled by kinetic or dynamic factors, so the numbers in Table 16 are only limiting solubilities.

Part 2. Salinity and temperature dependencies in the normative seawater thermodynamic model

Salinity dependency

We calculated a series of normative seawater models similar to that represented in Tables 4 and 5, but open to the model atmosphere, for salinities from 1 to 45‰ diluted with pure H_2O at T = 25 °C and P = 1 bar. No mineral precipitation was permitted. The composition of a system for different salinities was calculated from the model composition of standard seawater (Table 1) so as to obtain 100 kg of water solution at given salinity and 1000 kg of normative dry air. Steam was excluded from the gas phase.

Some salinity dependencies are plotted in Figs. 1, 2 and 3. The pH value for a system open to the atmosphere steeply decreases at salinity < 10 ‰. Control runs with compositions of 100 kg seawater (of a given salinity) plus 30 g air - almost a closed system - yielded much higher pH values between 8.35 - 8.45. The effective ionic strength *I* appears to be near-linear function of salinity, just as *G(X)* function of minimum total Gibbs free energy. Intercepts of a curve of (log AP) for Ca^{+2} and CO_3^{-2} with lines of (log K_t) of calcite and aragonite (Fig. 2) occur at salinities 15 and 20 ‰, respectively. More dilute seawater is undersaturated with these minerals. The value of F_α - the Kuhn-Tucker criterion of stability of aqueous solution (Karpov, 1981) - is very low at large dilution when no mineral tends to precipitate but becomes 3-5 orders of magnitude higher at higher salinities. As seen from Fig. 1, with dilution, the dissolved carbon escapes into the gas phase in order to maintain the equilibrium relations at fixed $P(CO_2)$ with a corresponding decrease of alkalinity.

Fig. 3 presents a comparison of total activity coefficients of major ions (dots) with reference lines plotted from the calculations of Millero and Schreiber (1982, Table 19). The agreement is good for Na+, K+, Mg^{+2}, Ca^{+2}, SO_4^{-2} and CO_3^{-2}. Our model produces slightly lower

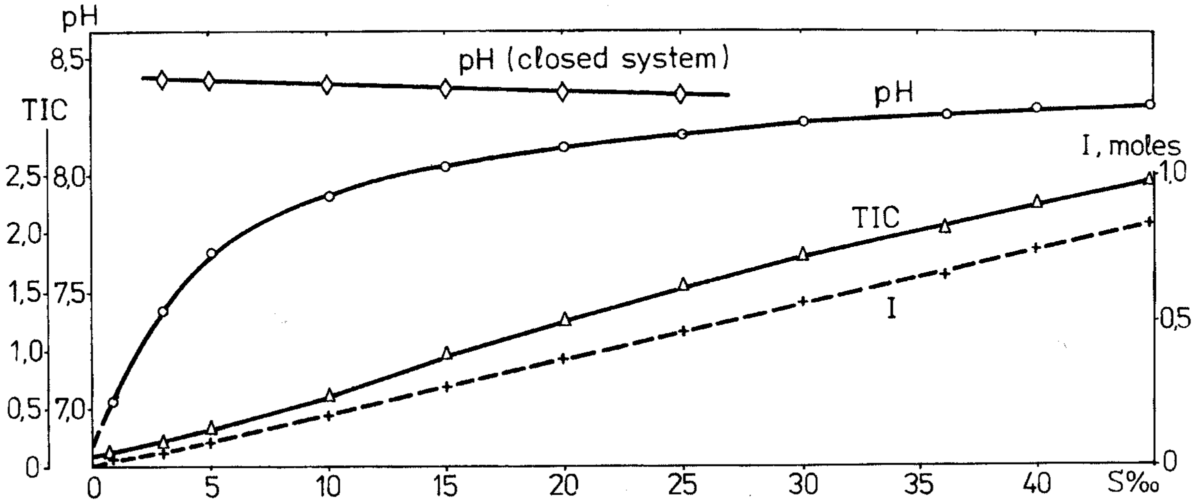


Fig. 1. The salinity dependencies of pH, TIC (dissolved total inorganic carbon), and I (effective molal ionic strength) calculated from the model of normative seawater diluted with pure H_2O and "open" to atmocpheric air. P = 1 bar, T = 25 °C. Composition: 100 kg seawater with 3.51744 kg model seasalt (table 1) plus 1000 kg of dry air. Rhombs represent pH values calculated for "closed" system (the same but without air).

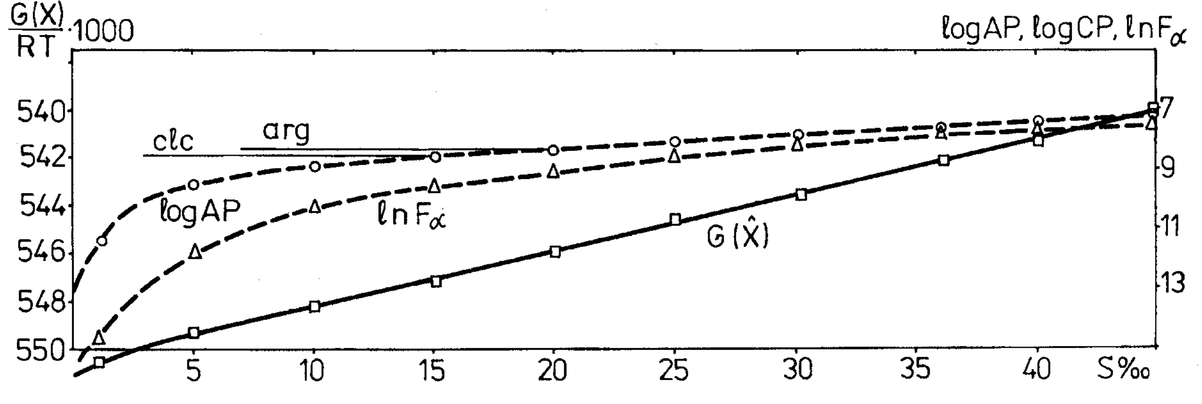


Fig. 2. The salinity dependencies of the total minimum Gibbs free energy of a system G(X), Kuhn-Tucker stability criterion for aqueous phase F_α, and activity product (AP) of Ca^{+2} and CO_3^{-2} ions calculated from the model of normative seawater open to the air at P = 1 bar, T = 25 °C, diluted with pure H_2O. clc and arg are thermodynamic solubility products for calcite and aragonite, respectively (see Table 3). R - universal gas constant.

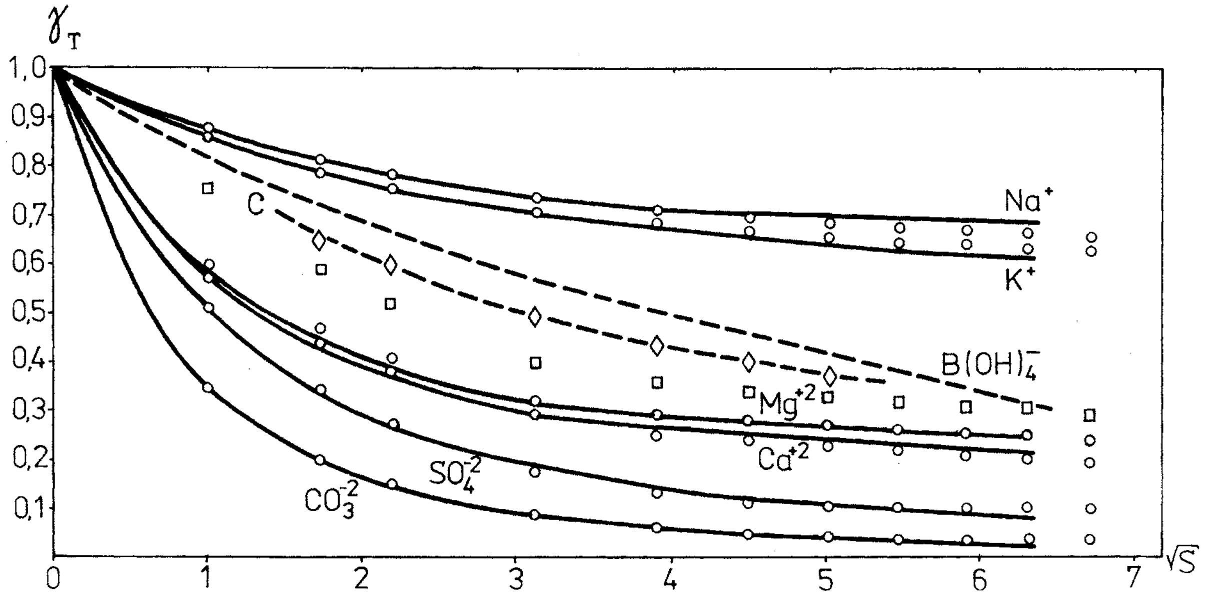


Fig. 3. The salinity dependencies of some total ion activity coefficients (circles and squares) calculated from the model of normative seawater diluted with pure H_2O and open to the air, plotted against tabulations of Millero and Schreiber (1982) (solid lines).
P = 1 bar, T = 25 °C. Rhombs are the calculated total activity coefficients of borate ion in closed (C) system, without 1000 kg of air.

values of γ_T for SO_3^{-2} at salinities between 10 and 20‰ and slightly higher γ_T for Mg^{+2} at salinities 1 to 5 ‰. There are large deviations between γ_T values for $B(OH)_4$- ion calculated for open system (sqares), and reference data (dashed line), except for salinities 35 to 45 ‰.

The reason for this difference is not quite clear. Control runs for an "almost closed" system with only 30 g air to 100 kg of aqueous solution result in γ_T values for borate ion (rhombs in Fig.3) much closer to reference values from Millero and Schreiber (1982). This means that behaviour of dissolved boron in seawater is very sensitive to the exchange between the gas and aqueous phase. The method of calculation used by Millero and Schreiber does not allow one to judge on whether the system is open or closed. We feel that further investigations of borate complexation in seawater with regard to the air-water exchange would clarify the problem. Nevertheless, it is obvious that our ion-association model gives reasonable and accurate estimates of most of chemical parameters of seawater at salinities up to 45 - 50 ‰.

Temperature dependency: thermodynamic data

The thermodynamic database SUPCRT92 and HKF-EOS-based algorithms for calculations of partial molal properties of individual ions and complexes (Helgeson et al.,1981; Shock and Helgeson, 1988; Johnson et al., 1992) provide an excellent framework for thermodynamic calculations of aqueous models in a wide range of temperature and pressure. We calculated ΔG_f° values for ions, gases and some minerals referred in SUPCRT92 database using adjusted version of SUPCRT92 program together with SELEKTOR++ program package. In addition, knowledge of the temperature dependency of the stability of ion pairs and complexes is required for ion-association model of aqueous solution. The task is complicated because we corrected some ΔG_f° (and K_A) values (see Tables 2, 9 and related text).

The SOLMINEQ.88 database (Kharaka et al., 1988) contains data on the temperature dependency of stability for many aqueous species in the form of dissociation constants K_D assigned to temperatures 0, 25, 50, 75, 100, 125, 150, 200, 250, 300 and 350 °C. A number of techniques was used by Kharaka et al. (1988) to retrieve or estimate this dependency from experimental data, literature sources or theoretical considerations. Calculation of dissociation constants over the previously mentioned temperature range is performed in SOLMINEQ.88 using a cubic interpolation subroutine LAGINT.

We collected in Table 17 the log K_A values (converting them from the log K_D values of SOLMINEQ.88 database) for those complexes and ion pairs not available from SUPCRT92 dataset. All the log K_A values were then corrected by addition of differences

$$\Delta(\log K_A) = \log K_A(\text{ours}) - \log K_A(\text{SOLMINEQ}) \qquad \text{at } 25\ ^\circ\text{C} \qquad (12)$$

Since temperature dependencies for major ions and some complexes are incorporated in SUPCRT92 routines and at 0 - 50 °C change of log K_A is almost linear for many complexes, we calculated log K_A values for temperatures 1, 5, 10, 15, 20 and 30 °C assuming linear dependence of log K_A on T. Then, for each T, the ΔG_f° values were calculated using relation

$$\Delta G_f^\circ{}_{MX}(T) = \Delta G_f^\circ{}_M(T) + \Delta G_f^\circ{}_X(T) - 2.303RT \log K_A(T) \qquad (13)$$

where $\Delta G_f^\circ{}_M(T)$ and $\Delta G_f^\circ{}_X(T)$ are values for cation and anion, respectively, calculated previously with SUPCRT92 routines, R - universal gas constant (8.3144 J mol^1 K^{-1}), T in degrees of K. The error of such calculation with respect to cubic interpolation was estimated to be not more than 100 J/mole. The calculated set of ΔG_f° values is presented in table 18.

log K_A values for borate complexes were guessed from 25 °C values found earlier and assumed increase of their stability with temperature. T-dependence of MgCl2° was assumed to be the same as for CaCl2°.

The ΔG_f° values for gases and minerals (table 19) were calculated within SELEKTOR++ program from Majer-Kelley or extended Cp = f(T) equations, except for some Ca and Mg phosphates where neither heat capacity nor entahlpy or entropy is available.

By applying the powerful facilities of HKF-EOS-based routines and cubic interpolation on log K_D data from SOLMINEQ database, it is not difficult to extend this dataset up to 350 °C at pressures along the steam saturation curve. Corrections for larger pressures can also be made, permitting to use the extended dataset, e.g., for modeling chemical processes in subseafloor hydrothermal systems.

Table 17

Temperature dependencies of association constants for species not available from SUPCRT92 database (log K_A values were modified from SOLMINEQ.88 database (Kharaka et al., 1988), see text), and $\Delta G_r°$ values of association reactions for T = 1, 25 and 50 °C.

Species	log K_t = f(T) (°C)			$\Delta G_r°$(T) J/mole			Ref
	1°	25°	50°	1°	25°	50°	
CaB(OH)4+	1.77	1.87	1.97	-9290	-10674	-12188	a
CaOH+	1.2	1.3	1.4	-6298	-7420	-8661	b
CaH2PO4+	1.173	1.405	1.491	-6154	-8020	-9224	b
CaHPO4°	2.544	2.715	2.951	-13352	-15500	-18255	b
CaPO4-	6.3	6.46	6.61	-33066	-36874	-40893	b
KSO4-	0.864	0.86	0.932	-4535	-4908	-5763	b
KHPO4-	0.11	0.29	0.49	-577	-1655	-3031	b
LiOH+	0.25	0.15	0.19	-1312	-856	-1175	b
LiSO4-	0.77	0.77	0.77	-4041	-4395	-4764	b
MgB(OH)4+	1.65	1.748	1.81	-8660	-9978	-11198	a
MgOH+	2.15	2.2	2.3	-11284	-12558	-14229	b
MgCl2°	-0.6	-0.45	-0.3	4199	3710	3094	c
MgSO4°	2.20	2.26	2.34	-11547	-12900	-14477	b
MgH2PO4+	1.3	1.51	1.73	-6823	-8619	-10703	b
MgHPO4°	2.71	2.91	3.14	-14223	-16610	-19426	b
MgPO4-	6.42	6.58	6.81	-33695	-37559	-42131	b
NaB(OH)4°	0.28	0.348	0.44	-1470	-1986	-2722	a
NaCO3-	0.29	0.944	1.43	-1522	-5388	-8847	b
NaHCO3°	-0.139	-0.007	-0.152	730	41	942	b
NaHPO4-	0.1	0.29	0.49	-525	-1655	-3031	
NaSO4-	0.39	0.69	0.98	-2047	-3939	-6063	b
NaHS°	-0.78	-0.83	-0.875	4094	4738	5413	
SrOH+	0.59	0.71	0.85	-3044	-3996	-5259	b
SrCO3°	2.44	2.78	3.15	-12806	-15868	-19488	b
SrHCO3-	0.82	1.18	1.53	-4304	-6735	-9466	
SrSO4°	2.22	2.3	2.375	-11652	-13128	-14693	b

References:

a - assumed linear increase of stability with temperature;

b - recalculated from values of SOLMINEQ.88 database using our values of log K_A at 25 °C assuming the same dependence on temperature;

c - calculated from analogy with $CaCl_2°$;

d - recalculated from the $\Delta G_f°$ values of components.

Table 18

The apparent Gibbs free energy of formation $\Delta G_f{}^\circ(T)$ from elements for aqueous species and gases at temperatures between 1-30 °C at pressure 1 bar at standard state, J -mole.

Values for T = 25°C are also listed in Table 2.

Species	1°C	5°C	10°C	15°C	20°C	25°C	30°C
B(OH)3@	-965098	-965702	-966461	-967224	-967991	-968763	-969540
B(OH)4-	-1150925	-1151283	-1151745	-1152222	-1152714	-1153220	-1153741
BF4-	-1482699	-1483412	-1484304	-1485199	-1486095	-1486994	-1487894
Ca+2	-554108	-553895	-553623	-553351	-553070	-552790	-552506
CaB(OH)4+	-1714323	-1714710	-1715180	-1715668	-1716167	-1716684	-1717216
CaCO3@	-1099206	-1099275	-1099356	-1099429	-1099493	-1099550	-1099598
CaCl+	-680347	-680295	-680237	-680187	-680144	-680109	-680081
CaCl2@	-811253	-811303	-811378	-811470	-811577	-811696	-811828
CaF+	-842959	-842770	-842543	-842328	-842124	-841930	-841747
CaH2PO4+	-1688319	-1688881	-1689514	-1690084	-1690601	-1691075	-1691515
CaHCO3+	-1144313	-1144517	-1144787	-1145074	-1145379	-1145704	-1146049
CaHPO4@	-1657120	-1657175	-1657242	-1657306	-1657368	-1657427	-1657483
CaNH3+2	-577676	-577880	-578135	-578390	-578645	-578900	-579155
CaOH+	-717748	-717596	-717426	-717278	-717151	-717043	-716954
CaPO4-	-1610752	-1610474	-1610033	-1609540	-1609049	-1608468	-1607906
CaS2O3@	-1081768	-1081963	-1082207	-1082452	-1082696	-1082940	-1083184
CaSO4@	-1309391	-1309504	-1309638	-1309763	-1309881	-1309990	-1310090
CH4@	-32648	-32899	-33246	-33623	-34024	-34451	-34903
CO2@	-383418	-383803	-384309	-384840	-385397	-385974	-386572
H2@	18928	18757	18523	18272	18004	17723	17427
H2S@	-25100	-25540	-26108	-26694	-27299	-27920	-28556
N2@	20234	19933	19531	19104	18657	18188	17698
NH3@	-24195	-24605	-25121	-25643	-26171	-26707	-27250
O2@	18903	18552	18083	17594	17079	16544	15987
SO2@	-297491	-298075	-298822	-299585	-300367	-301164	-301981
K+	-280039	-280445	-280949	-281453	-281957	-282462	-282967
KBr@	-371786	-372598	-373606	-374608	-375606	-376602	-377594
KCl@	-400903	-401635	-402543	-403442	-404333	-405220	-406103
KHPO4-	-1370276	-1370809	-1371464	-1372041	-1372652	-1373254	-1373849
KHSO4@	-1026068	-1026967	-1028097	-1029239	-1030395	-1031565	-1032749
KS2O3-	-802450	-803199	-804134	-805069	-806005	-806940	-807875
KSO4-	-1028267	-1028867	-1029614	-1030357	-1031095	-1031829	-1032559
Li+	-292388	-292415	-292454	-292497	-292546	-292600	-292659
LiCl@	-414027	-414221	-414470	-414727	-414991	-415262	-415540
LiOH@	-451090	-451042	-450994	-450926	-450844	-450779	-450798
LiSO4-	-1040123	-1040388	-1040694	-1040970	-1041222	-1041454	-1041671
Mg+2	-457261	-456721	-456043	-455362	-454675	-453985	-453295
MgB(OH)4+	-1616846	-1616886	-1616939	-1617006	-1617087	-1617183	-1617296
MgCO3@	-1000576	-1000206	-999736	-999257	-998769	-998272	-997765
MgCl+	-586756	-586350	-585865	-585392	-584941	-584505	-584084

Table 18, continued

Species	1°C	5°C	10°C	15°C	20°C	25°C	30°C
MgCl2@	-713696	-713814	-713896	-713948	-713984	-713996	-713997
MgF+	-749383	-748863	-748226	-747604	-746996	-746402	-745822
MgH2PO4+	-1592141	-1592290	-1592422	-1592553	-1592739	-1592869	-1593066
MgHCO3+	-1047431	-1047284	-1047134	-1047008	-1046914	-1046840	-1046788
MgHPO4@	-1561144	-1560983	-1560706	-1560403	-1560074	-1559732	-1559382
MgOH+	-625935	-625625	-624209	-624769	-624309	-623840	-623360
MgPO4-	-1514534	-1513939	-1513104	-1512212	-1511271	-1510348	-1509391
MgS2O3@	-985772	-985637	-985467	-985298	-985129	-984960	-984791
MgSO4@	-1211447	-1211425	-1211393	-1211357	-1211317	-1211272	-1211222
HNO3@	-33913	-34598	-35463	-36337	-37218	-38108	-39005
NO2-	-29168	-29690	-30334	-30970	-31598	-32217	-32828
NO3-	-42425	-43034	-43791	-44542	-45286	-46024	-46755
NH4+	-76849	-77274	-77811	-78354	-78901	-79454	-80013
NH4SO4-	-825844	-826437	-827178	-827918	-828659	-829400	-830141
Na+	-260508	-260734	-261019	-261303	-261591	-261881	-262175
NaB(OH)4@	-1412903	-1413577	-1414434	-1415307	-1416179	-1417087	-1418034
NaBr@	-354801	-355362	-356065	-356771	-357480	-358192	-358907
NaCO3-	-790880	-791519	-792557	-793596	-794471	-795252	-795930
NaCl@	-385957	-386415	-386990	-387570	-388151	-388735	-389322
NaHCO3@	-844309	-845180	-846194	-847129	-847990	-848780	-849504
NaHPO4-	-1350693	-1351098	-1351534	-1351947	-1352286	-1352673	-1353057
NaHS@	-242653	-243065	-243589	-244102	-244609	-245108	-245602
NaHSiO3@	-1283085	-1283414	-1283826	-1284240	-1284656	-1285074	-1285493
NaS2O3-	-781344	-781898	-782591	-783284	-783977	-784670	-785363
NaSO4-	-1006248	-1007003	-1007850	-1008672	-1009481	-1010279	-1011070
H2PO4-	-1128057	-1128433	-1128898	-1129358	-1129814	-1130265	-1130718
H3PO4@	-1138939	-1139546	-1140311	-1141077	-1141860	-1142650	-1143452
HPO4-2	-1089660	-1089618	-1089539	-1089430	-1089292	-1089137	-1088967
PO4-3	-1023578	-1022871	-1021934	-1020938	-1019892	-1018804	-1017676
Rb+	-280763	-281250	-281860	-282467	-283072	-283675	-284277
RbBr@	-375246	-376181	-377344	-378500	-379647	-380786	-381916
RbCl@	-404513	-405348	-406395	-407435	-408466	-409488	-410501
RbF@	-567652	-568204	-568890	-569569	-570241	-570907	-571565
RbSO4-	-1027605	-1028318	-1029178	-1030002	-1030794	-1031559	-1032302
HS2O3-	-519640	-520316	-521155	-521986	-522811	-523628	-524438
S2O3-2	-520699	-521059	-521470	-521860	-522232	-522582	-522900
S2O4-2	-597976	-598412	-598934	-599446	-599934	-600404	-600855
HSO3-	-524369	-524929	-525630	-526330	-527029	-527728	-528427
S2O5-2	-788057	-788540	-789126	-789694	-790244	-790776	-791290
SO3-2	-486938	-486932	-486888	-486819	-486722	-486599	-486440
S2O6-2	-963300	-963861	-964547	-965216	-965868	-966504	-967124
S3O6-2	-954640	-955249	-955995	-956724	-957438	-958136	-958819
S4O6-2	-1034298	-1035354	-1036667	-1037973	-1039271	-1040561	-1041844
S5O6-2	-954081	-954763	-955611	-956456	-957298	-958136	-958971
HSO4-	-752760	-753260	-753881	-754504	-755129	-755756	-756384
SO4-2	-743693	-743873	-744066	-744225	-744355	-744459	-744543

Table 18, continued

Species	1°C	5°C	10°C	15°C	20°C	25°C	30°C
S2O8-2	-1109069	-1110078	-1111331	-1112575	-1113810	-1115036	-1116253
HSO5-	-632547	-633358	-634381	-635416	-636461	-637516	-638582
HSiO3-	-1012616	-1012839	-1013091	-1013337	-1013565	-1013783	-1013988
SiF6-2	-2196403	-2196952	-2197622	-2198275	-2198911	-2199530	-2200133
SiO2@	-831151	-831612	-832131	-832595	-833022	-833411	-833775
Sr+2	-564539	-564430	-564288	-564141	-563991	-563836	-563677
SrCO3@	-1106194	-1106557	-1106885	-1107191	-1107478	-1107687	-1107937
SrCl+	-692657	-692824	-693038	-693256	-693479	-693707	-693940
SrF+	-847074	-846949	-846798	-846653	-846514	-846381	-846254
SrHCO3+	-1153373	-1154109	-1154938	-1155771	-1156667	-1157511	-1158363
SrOH+	-724973	-725027	-725051	-725108	-725095	-725129	-725153
SrS2O3@	-1092739	-1093040	-1093415	-1093790	-1094165	-1094540	-1094915
SrSO4@	-1319884	-1320231	-1320578	-1320889	-1321170	-1321423	-1321656
HS-	13762	13462	13093	12733	12380	12035	11698
HS4-	35020	33998	32742	31503	30282	29080	27896
HS5-	37259	36169	34821	33489	32171	30870	29584
S-2	117158	117301	117715	118099	118452	118774	119067
S2-2	80491	80274	80036	79831	79651	79496	79366
S3-2	75504	75149	74730	74341	73979	73638	73316
S4-2	71760	71274	70688	70119	69568	69036	68522
S5-2	69275	68652	67888	67140	66406	65689	64987
S6-2	66763	66004	65068	64146	63237	62342	61459
Br-	-101922	-102303	-102759	-103207	-103638	-104056	-104466
BrO-	-32229	-32466	-32745	-33005	-33254	-33472	-33677
CO3-2	-528849	-528761	-528611	-528431	-528222	-527983	-527720
H2CO3@	-618408	-619233	-620251	-621254	-622244	-623222	-624190
HCO3-	-584530	-584940	-585446	-585948	-586446	-586940	-587431
Cl-	-129792	-130064	-130390	-130700	-131001	-131290	-131570
HCl@	-128318	-128368	-128413	-128438	-128444	-128430	-128396
F-	-281935	-281926	-281901	-281864	-281813	-281751	-281679
HF@	-297637	-297994	-298445	-298445	-299366	-299834	-300307
OH-	-157390	-157402	-157402	-157381	-157344	-157297	-157239
H+	0	0	0	0	0	0	0
H2O@	-235580	-235836	-236163	-236497	-236837	-237183	-237536
Gases:							
CH4	-46400	-47134	-48055	-48979	-49906	-50836	-51768
CO	-132557	-133340	-134320	-135303	-136289	-137277	-138268
CO2	-389266	-390110	-391168	-392229	-393293	-394360	-395430
H2O	-224070	-224815	-225749	-226686	-227626	-228569	-229515
H2S	-28494	-29307	-30326	-31348	-32372	-33400	-34430
NH3	-11559	-12319	-13272	-14228	-15188	-16150	-17116
NO2	58191	57158	55865	54568	53268	51965	50659
SO3	-364999	-366010	-367277	-368548	-369824	-371104	-372388
H2	3108	2594	1949	1302	652	0	-655
N2	4570	3812	2863	1911	957	0	-959
O2	4896	4084	3066	2047	1025	0	-1027

Notes to Table 18:

Calculated by means of SUPCRT92 routines and SELEKTOR++ TPARAM module. Values for aqueous complexes and ion pairs not available in SUPCRT92 were calculated from $\log K_A$ values for 0 and 25 °C adopted from SOLMINEQ.88 database (Kharaka et al., 1988), see Table 17, and $\Delta G_f°(T)$ for ions of Table 18. Values for gases were calculated using standard heat capacity equation with $C_p(T)$ coefficients from SUPCRT92 or (Dorogokupets et al., 1988).

Table 19

The apparent Gibbs free energy of formation from elements $\Delta G_f°(T)$ for minerals at temperatures between 1-30 °C and 1 bar pressure at standard state, J/mole.
Values for 25 °C, names and formulae are listed in Table 3.

Phase	Name	1°C	5°C	10°C	15°C	20°C	30°C	Ref
apatite:								
APATC	apcl	-6208202	-6209685	-6211569	-6213486	-6215437	-6219436	1
APATF	apf	-6434109	-6435548	-6437375	-6439235	-6441127	-6445005	1,2
APATO	apoh	-6288410	-6289920	-6291828	-6293761	-6295719	-6299706	1,2
carbonate-apatite:								
CAPCM	cfap mar	-12294500	-12294500	-12294500	-12294500	-12294500	-12294500	
CAPF	cfap	-12608700	-12608700	-12608700	-12608700	-12608700	-12608700	
other Ca phosphates:								
CAPB	brush	-2150398	-2151096	-2151984	-2152889	-2153811	-2155706	3
CAPM	monet	-1678740	-1679151	-1679673	-1680206	-1680748	-1681862	3
CAPW	whitl_h	-3869868	-3870832	-3872037	-3873241	-3874446	-3876854	3
CAPW	whitl_l	-3879156	-3880100	-3881280	-3882460	-3883640	-3886000	3
CAP8	octacap	-12258200	-12258200	-12258200	-12258200	-12258200	-12258200	
carbonates:								
CRBC	arg	-1126114	-1126442	-1126858	-1127280	-1127710	-1128601	2
CRBC	cal	-1126951	-1127292	-1127726	-1128167	-1128615	-1129532	2
CRBDM	dol dis	-2153643	-2154550	-2155289	-2155680	-2157360	-2159350	4
CRBSR	str	-1142439	-1142780	-1143223	-1143685	-1144164	-1145173	2
Metastable "marine" carbonates								
CRBC	cal_mar	-1122378	-1122724	-1123163	-1123608	-1124061	-1124988	c
CRBM	mgs_mar	-1015749	-1015990	-1016296	-1016608	-1016927	-1017584	c
CRBDM	dol_m	-2141888	-2142556	-2143403	-2144263	-2145137	-2146924	c
Mg-calcite minals								
CRBC	cal_def	-1126181	-1126522	-1126956	-1127397	-1127845	-1128758	c
CRBDM	dol_dh	-1073831	-1074163	-1074585	-1075013	-1075448	-1076338	c

Table 19, continued

Phase	Name	1°C	5°C	10°C	15°C	20°C	30°C	Ref
C	C	130	109	83	56	28	-29	2
GYPAN	anh	-1320121	-1320368	-1320686	-1321012	-1321347	-1322182	2,4
GYPS	gp	-1792824	-1793533	-1794433	-1795350	-1796282	-1798339	2
HALCF	fl	-1172005	-1172400	-1172807	-1175030	-1175487	-1176700	2
MGOB	brc	-833878	-834108	-834401	-834700	-835006	-835638	2
Mg-phosphates								
MGHP	mghp	-1576500	-1576500	-1576500	-1576500	-1576500	-1576500	
MGHPN	newber	-2288050	-2288050	-2288050	-2288050	-2288050	-2288050	
MGPF	farr	-3532166	-3532860	-3533743	-3534644	-3535563	-3537455	3
MGPB	bib	-5440900	-5440900	-5440900	-5440900	-5440900	-5440900	
SIO2	qtz	-855202	-855357	-855555	-855756	-855961	-856382	2
SIO2A	sio2	-847509	-847733	-848018	-848307	-848601	-849204	2
SRSO	cls	-1342702	-1343183	-1343791	-1344409	-1345035	-1346759	2

References for sources of Cp(T) equation coefficients: 1 - (Zhu and Sverjensky, 1991); 2 - (Dorogokupets et al., 1988); 3 - (Viellard and Tardy, 1984); 4 - SUPCRT92 database (Johnson et al., 1992);
c - assumed the same Cp(T) dependence as for stable counterparts.

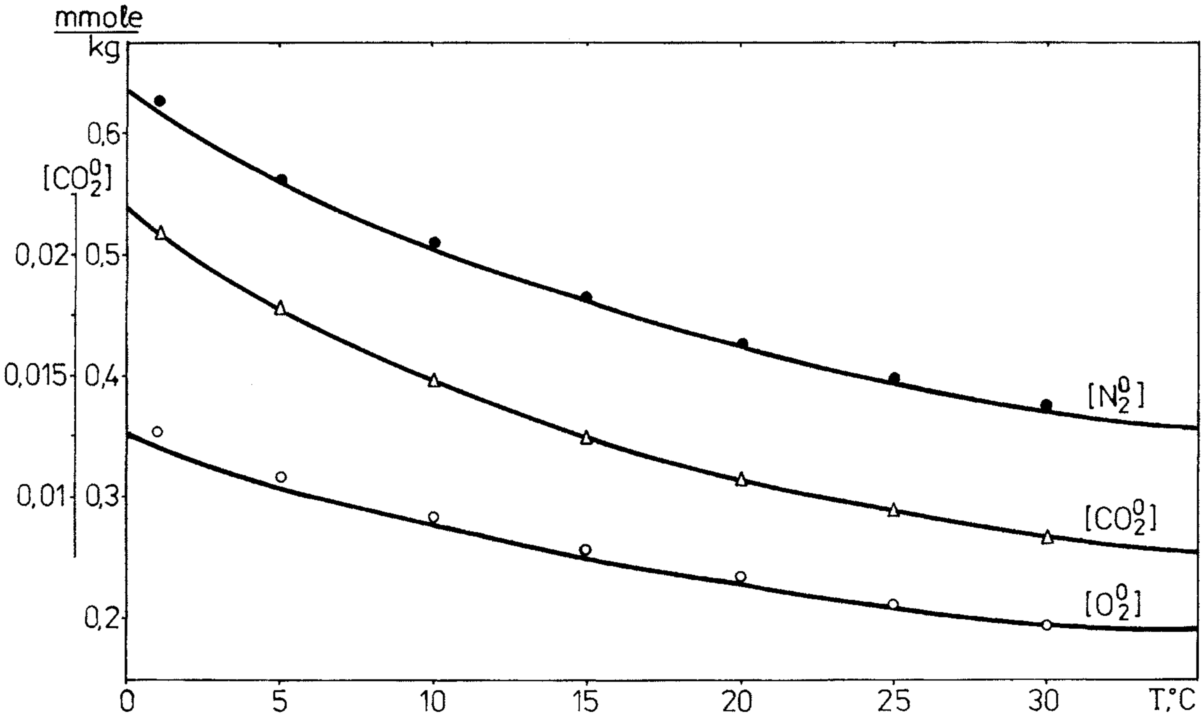


Fig. 4. The solubilities of atmospheric gases versus temperature calculated in a model of normative seawater with salinity 35.1744 ‰ open to the air at P = 1 bar (dots). Solid lines represent tabulated reference solubilities (see text).

Temperature dependencies for normative seawater

We calculated a set of models of normative seawater composition (100 kg seawater of 35.174‰ salinity) open to the air (1000 kg) at temperatures from 1 to 30 °C and 1 bar total pressure. Parameters of carbonate system and concentrations of dissolved gases as most sensitive to temperature changes are plotted at Figs. 4 and 5.

Obviously, the modeling results on O_2 and N_2 solubility (circles) in open seawater are in good agreement with tabulated reference values (solid lines, Popov et al., 1979). The same applies to calculated values of $[B(OH)_4\text{-}]_T$ (Fig. 5a, squares) compared to reference curve plotted from equations for apparent dissociation constant of boric acid (Alekin and Lyakhin, 1984). Behaviour of both thermodynamic and stoichiometric products of Ca^{+2} and CO_3^{-2} ions calculated (Fig. 5b, circles) versus reference ones (lines, Bychkov et al., 1989) is also quite realistic.

Fig. 5c shows the calculated dependencies of total and carbonate alkalinity, $[CO_3^{-2}]_T$, $[HCO_3\text{-}]_T$ and total dissolved carbon versus temperature. The total alkalinity remains nearly the same (about 2.4 meq (kg soln)$^{-1}$) at all temperatures because system is open to the air and decrease in carbonate ion concentration is compensated by increase in bicarbonate. The pH of seawater

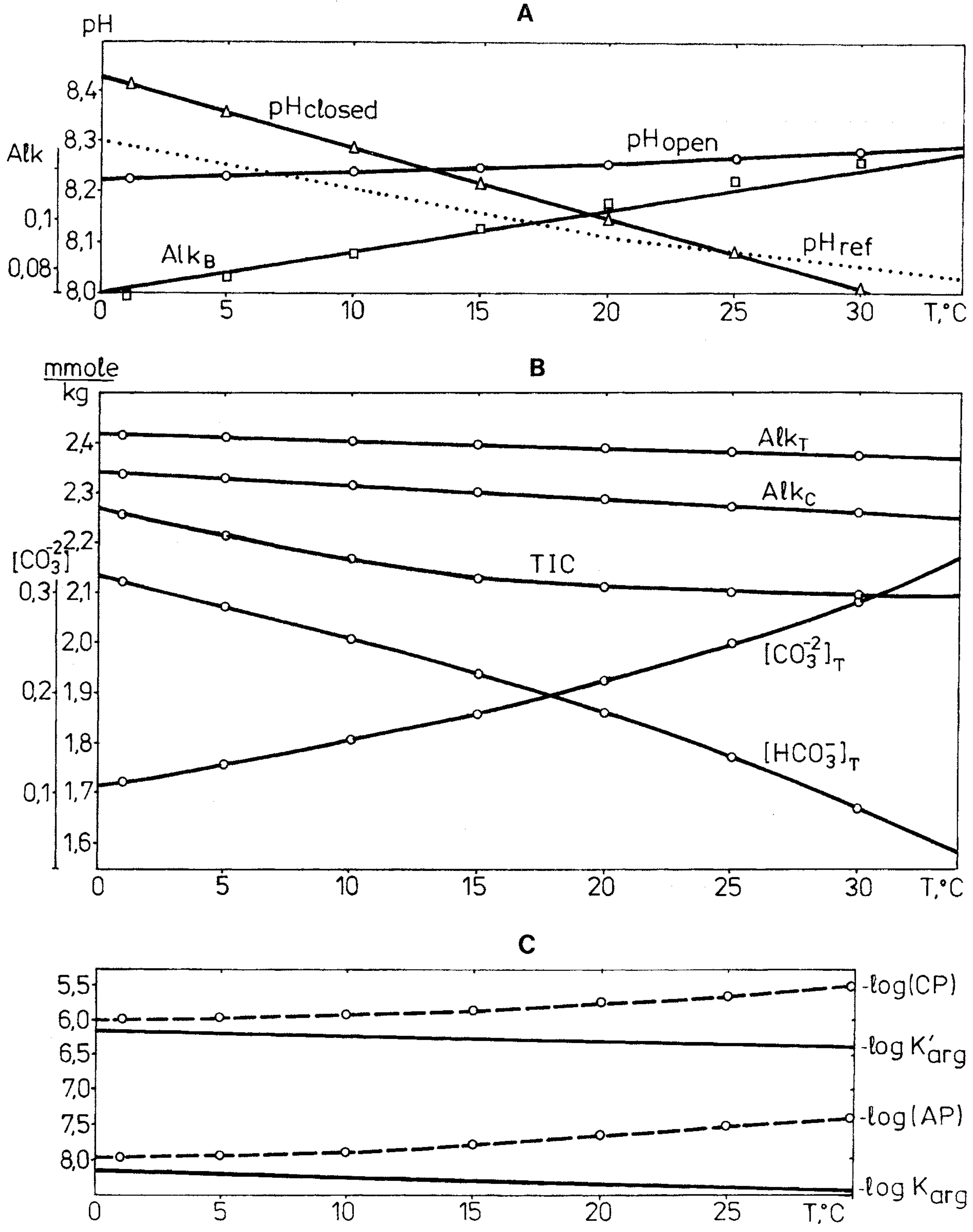


Fig. 5. The temperature dependencies of carbonate system parameters calculated in a model of normative seawater with salinity 35.1744 ‰ open to the air at P = 1 bar.

A - squares denote calculated values of borate alkalinity against reference curve (solid line). pH_{closed} refers to the pH values calculated for a closed system (see text). pH_{ref} (dot line) represents the conventional correction of measured pH on temperature.

B - calculated values of total Alk_T and carbonate alkalinity Alk_C, dissolved total inorganic carbon TIC, total concentrations of carbonate and bicarbonate ions.

C - calculated concentration product (CP) and activity product (AP) of. Ca^{+2} and CO_3^{-2} ions (circles) compared to the temperature dependence of the apparent K' and thermodynamic K solubility products of aragonite (see text).

(open) increases with temperature (fig. 5a, circles). This does not agree with tabulated reference corrections on pH-temperature dependence in seawater (dotted line, see (Alekin and Lyakhin, 1984, Table 7.1) - these corrections suggest that pH becomes lower with temperature.

We suppose that, again, one should consider, which kind of a system - open or closed - is under investigation. To clarify, we calculated a series of equilibria in closed system of 100 kg seawater without air. 0.008 moles CO_2 were added at 25 °C to obtain pH = 8.08 at intercept with reference line (see Fig. 5a). Then equilibria at other temperatures were computed with exactly the same composition. The resulting pH values (triangles on Fig. 5a) reveal the same trend as reference tabulations, but somewhat steeper. Clearly, the tabulations reflect some intermediate situation - a kind of "semi-closed" system.

Conclusions on the normative seawater thermodynamic model

The application of dual minimization algorithms (Karpov, 1981; Karpov et al., 1993) for calculations of aqueous models related to seawater, together with thermodynamic dataset on aqueous species based upon HKF-EOS and correlation algorithms (Helgeson et al.,1981; Shock and Helgeson, 1988; Johnson et al., 1992) show that ion-association approach is efficient for correct representation of chemical properties of seawater and mineral solubilities as well.

Since pH and Eh in minimization problems are not independent factors but rather functions of bulk chemical composition, T and P, it is possible to use well-established parameters of carbonate system etc. for matching the ΔG_f° values of some ion pairs and complexes using simple Debye-Hueckel-type equations for activity coefficients of free species. This procedure also reveals some inconsistencies between accepted acidity constants for boric acid and shows intimate relations between total Na, Mg content and parameters of carbonate-borate system.

The resulting dataset may be used for calculations of equilibria in marine-, brackish- or porewaters at oxic, suboxic and anoxic conditions, including any gases and minerals or solid solutions of interest, at T between 0 and 30 °C and P = 1 bar. The temperature interval can be easily extended up to 150 °C and with less certainty up to 375 °C, and pressure interval up to 1 kbar. New experimental data on mineral solubility or potentiometry may be used for matching ΔG_f° values of aquieous complexes through dual variables (chemical potentials of elements) at elevated temperatures.

The model and dataset can be readily extended by addition of data on thermodynamic properties of trace element compounds, organic species, ion-exchange and adsorption forms etc. to SELEKTOR++ database. Since SUPCRT92 dataset that we rely upon contains data for all ions of interest, only thermodynamic association constants are needed for complexes and ion pairs with their dependencies on T and P. Then ΔG_f° values consistent with values for ions are calculated from common relations. The use of dual variables allows also to derive ΔG_f° values from apparent or stoichiometric constants at given T, P and composition of a system.

Since performance of the IPM dual minimization algorithm depends mainly on the number of independent components (elements) rather than on the number of species, there would be little decrease in speed of computing compared to specific interaction aqueous model based on Pitzer's equations. The latter requires as components only ions and several complexes, but instead calculates at each iteration many sums and products from large set of empirical coefficients for ion-ion interactions. It would be interesting to implement also Pitzer's aqueous model in dual minimization version and compare both models with respect to normative seawater.

Part 3. Thermodynamic model of the Baltic brackish water

A model of the mean normative riverwater inflowing the Baltic Sea

In chemical oceanography, the Baltic Sea is usually considered as the very large estuary - a system of shallower and deeper basins separated by sills and straits. It is connected to the North Sea by an entrance with maximum depth of about 20 m; only episodic inflows of saline waters are possible during winter storms. Because of the large river runoff (2.2 % of the volume of the Baltic Proper per year), a sharp summer thermocline, as well as a halocline, are developed. The halocline is never penetrated by convective water movements. Extensive reviews of hydrochemical investigations in the Baltic have been made by Grasshoff (1975) and Grasshoff and Voipio (1981). The vast data on chemical composition of the Baltic Sea waters have been published by Nehring and Rohde (1966,1967), and Kremling (1969, 1970, 1972). A theoretical analysis of density-salinity relationships and ion concentration anomalies has been performed by Millero (1978).

Millero examined the dependency of ion concentrations (reported by Kremling) on clorinity. The chemical data on Na, Mg, Ca, K, SO_4^{-2}, HCO_3^- (from alkalinity), Br, F, and B were fitted to linear equations and used for esimation of hypothetical composition of the "Baltic river water" extrapolating to zero Cl‰. The composition of brackish water at any given Cl ‰ can then be estimated by means of a conservative linear mixing of average Baltic river water with average seawater:

$$c_i^B = c_i^R + a_i \ c_{Cl}^B \tag{14}$$

where c_i^B is concentration (in g kg^{-1}) of i-th ionic component in Baltic Sea water, c_i^R is the same in average Baltic river vater, c_{Cl}^B is chlorinity of the Baltic Sea water, and

$$a_i = (c_i^S - c_i^R) / \ c_{Cl}^S \tag{15}$$

where $c_{Cl}^S = 19.3744$ ‰ is a chlorinity of normative seawater and c_i^S stands for a concentration of i-th constituent in normative seawater. To apply this linear mixing model of Millero (1978), one should know the c_i^R values representing the composition of "average Baltic river input".

Millero (1978) used for comparison the data on "average world streams" (Livingstone, 1963). Blashchishin (1976) compiled the hydrochemical data on rivers entering the different parts of the Baltic Sea and calculated the composition and runoff for the whole basin. A comparison of these data to the hypothetical composition derived by Millero (1978) from the data of Kremling (1969, 1972) is given in Table 20. It is clear that empirical data of Blazhchishin are closer to Millero's composition than to the world average. This gives strong support for linear mixing model of conservative components. We added some data on Li, Rb and constructed the normative model composition of average river input to the Baltic (Table 20) for subsequent use in thermodynamic modeling. The composition was balanced by control runs of calculation of equilibria of this "river water" with atmosphere at pH = 8. It resulted in total dissolved solids (TDS) 156 mg kg^{-1} (compare to other values). One should take into account the recently documented decrease in total alkalinity and increase in Ca in the Baltic Sea (Ohlson and Anderson, 1990); a possible reason is the shift of the Ca/Alk ratio in rivers due to the increase in acid rain and decay of organic matter.

Linear mixing models of the Baltic brackish waters composition

SELEKTOR++ facilities permit any desired chemical composition to be expressed as a formula of "additional component" with stoichiometric coefficients in moles per unit mass. Any bulk chemical composition of a system can then be specified through numbers of grams of each "additional component". For example, 100 kg of normative seawater were specified as 96482.56 g H_2O plus 3517.44 g of "model seawater salt" (Table 1). For similar fast and convenient calculation of brackish water composition, we found it necessary to extend the linear mixing model and derive appropriate equations.

Assume z to be a weight ratio of normative seawater to river water in the Baltic brackish water. Then Cl content in brackish water is:

$$c_{Cl}^{B} = z\, c_{Cl}^{S} + (1 - z)\, c_{Cl}^{R} . \qquad (16)$$

Since c_{Cl}^{R} is small (< 3.5 mg kg^{-1} or 0.02% of c_{Cl}^{S}), it can be neglected (as it is implicitly assumed in Millero (1978) model). Thus, we can express z ratio as

$$z = c_{Cl}^{B} / 19.374. \qquad (17)$$

Denote c_w^S as mass of pure water of normative seawater in 1 kg of brackish water and c_w^R - mass of pure water of average river water in 1 kg of brackish water; c_s^S and c_s^R - the related masses of normative seawater salt and riverwater salt; and $\sigma = c_s^S / c_s^R$ - ratio of seasalt to riversalt in the brackish water salt. Then it follows:

$c_w^S = 964.8256$ z; $c_s^S = 35.1744$ z; $c_w^R = 999.844$ (1-z); $c_s^R = 0.156$ (1-z);

and

$$c_w^B = c_w^S + c_w^R = 999.844 - 35.0184\, z, \qquad (18)$$
$$c_s^B = c_s^S + c_s^R = 0.156 + 35.0184\, z, \qquad (19)$$
$$\sigma = c_s^S / c_s^R = 225.476923\, z / (1 - z). \qquad (20)$$

Table 20

Chemical composition of "average river water entering the Baltic"
(see text for explanations)

Element	Composition						Ref.
	mg kg^{-1}				Model		
	A	B	C	D	mg kg^{-1}	mmol kg^{-1}	
Na	3.2*	4.1*	6.3	5.1 ± 9.3	3.7	0.16	
Mg	4.1	7.8	4.1	3.0 ± 1.8	4.2	0.17	
Ca	24.5	55.6	15.0	21.0 ± 1.2	22.0	0.55	
K	1.1*	1.5*	2.3	0.0 ± 1.7	0.98	0.025	
Sr					0.09	0.001	G
Li					0.028	0.0004	G
Rb					0.001	0.00001	T
Cl	3.3	4.5	7.8	0	3.54	0.1	
S	2.4	5.3	3.7	1.47 ± 1.5	2.70	0.084	
C	12.84	31.8	11.5	17.0 ± 0.9	16.0	1.333	f
Br				0.0 ± 0.4	0.02	0.00024	T
B				0.14 ± 0.07	0.14	0.013	J
F				0.1 ± 0.03	0.1	0.005	T
N			0.22		14.1	1.02	f
Si	1.87	3.3	6.1		4.0	0.142	
P					0.06	0.002	G
H	1.08	2.7	0.97	1.43	1.345	1.34	f
O	56.53	141.3	61.3	71.7	83.0	5.19	f
TDS, mg/kg	112.7	197.9	120	121 ± 24	156		

Formulae:

C_org (Baltic Sea, normalized to $C_{1.06}$ - Shaffer, 1987)

$$C_{1.06}\,H_{2.9044}\,O_{1.29646}\,N_{0.1174}\,P_{0.008154}$$

References: (A),(B) - recalculated from (Blazhchishin, 1976);
* - because Na+K value is given in the source table, Na and K contents are calculated from their sum using the same weight ratio as in the average world river water (C) recalculated from (Livingstone, 1963);
D - recalculated from "best" values of Millero (1978), table XIII; G - from tables 207, 212 of (Voitkevich et al., 1990); T - Turekian, 1969; f - corrected by calculation of equilibria in riverwater open to the air; J - Ahl and Johnsson (1972) report B content in Swedish rivers 0.013 mg/kg - ten times less than accepted in the model.

Alternatively, using expression (17), the last three equations can be rewritten as functions of chlorinity:

$$c_w^B = c_w^S + c_w^R = 999.844 - 1.8074946\, c_{Cl}^B, \qquad (18a)$$

$$c_s^B = c_s^S + c_s^R = 0.156 + 1.8074946\, c_{Cl}^B, \qquad (19a)$$

$$\sigma = c_s^S / c_s^R = 225.476923\, c_{Cl}^B / (19.374 - c_{Cl}^B). \qquad (20a)$$

It is convenient to use another ratio

$$\theta = c_s^S / c_s^B = 1.815547\, c_{Cl}^B / (0.156 + 1.8074946\, c_{Cl}^B). \qquad (21)$$

The θ ratio is necessary for calculation of c_s^S and c_s^R from given salinity c_s^B or chlorinity c_{Cl}^B of brackish water:

$$c_s^S = \theta\, c_s^B; \qquad c_s^R = c_s^B - c_s^S. \qquad (22)$$

The quantities and ratios used for the calculation of mixed compositions of Baltic waters at chlorinities 0.1 - 17 are listed in Table 21. Some of them are plotted in Fig.6 (circles) against regression lines fitted by Millero (1978). The total alkalinity values plotted as solid circles (Fig.6, A) were calculated from computations of equilibria in Baltic Sea water open to the atmospheric air (see in more detail below). A good match of all calculated values with fitting lines suggest the validity of both linear mixing and thermodynamic models. A small deviation of F- values (Fig. 6, C) at higher chlorinities points to the difference in the bulk chemical composition of normative seawater (see Table 1). It is interesting that calculated A_T values, though higher at low chlorinities, at zero chlorinity are almost the same as reported by Ohlson and Anderson (1990). The corresponding shift in calculated Ca content (if their estimation from 1986 on Ca = 0.878 ± 13 mmol kg^{-1} is used for average river input) is shown on Fig. 6, B as squares and dashed line. It is not quite clear if this value reflect short- or long-term climatic variations or industrial impact.

Thermodynamic models of water bodies in the Baltic Sea water-sediment column

The Baltic Sea shows quite non-uniform distributions of salinity and temperature both in vertical and lateral profiles (cf. Grashoff, 1975; Grasshoff and Voipio, 1981). Above the halocline, two water strata usually exist in a larger part of the basin separated by seasonal thermocline: surface water (S) 20-25 m thick, and "cold winter water" (W at depths 20-25 to 60-80 m). Both have lower salinities (decreasing from 15-25 ‰ in western part to 4-5 ‰ in the Gulf of Bothnia and Gulf of Finland) than underlying "sub-halocline" water. The temperature of S water varies between 0 and 20 °C; in autumn, the thermocline disappears due to cooling and storms, and both S and W strata mix completely. Because of the development of a new thermocline in the spring, the W water body has a uniform temperature 2 - 4 °C during the whole year. At the halocline layer (H), salinity increases by 6 - 12 ‰ and temperature by 1 - 3 °C. In the deeps, beneath the halocline down to 140 - 160 m, the oxic deep water (Do) exist. Due to periodic stagnation in the Landsort or Gotland deeps, the anoxic (sulfidic) deep water (Da) occurs, separated from the Do water by relatively thin layer of a suboxic deep water (Ds), or chemocline, where most processes of geochemical interest proceed. During episodic winter-storm inflows of the North-Sea water, Do and Ds water bodies are destroyed and then form again.

Table 21

Values for calculation of the Baltic Sea water composition from the model compositions of normative seawater (Table 1) and average Baltic riverwater (Table 20), linear mixing model as function of chlorinity (eqs.18a-22). S_sw = 35.1744, S_rw = 0.156 ‰. See text for explanations.

c_{Cl}^B	Ratios			Concentration terms ‰			
‰	z	σ	θ	c_w^B	c_S^B	c_S^S	c_S^R
0.1	0.005162	1.16985	0.539139	999.663	0.33675	0.18156	0.155195
0.5	0.025808	5.97322	0.856594	998.94	1.05975	0.90777	0.151974
1	0.051616	12.2715	0.924651	998.037	1.96349	1.81555	0.147948
2	0.103231	25.9557	0.962902	996.229	3.77099	3.63109	0.139896
3	0.154847	41.3113	0.976366	994.422	5.57848	5.44664	0.131844
4	0.206462	58.6645	0.98324	992.614	7.38598	7.26219	0.123792
5	0.258078	78.4322	0.987411	990.807	9.19347	9.07773	0.11574
6	0.309693	101.156	0.990211	988.999	11.001	10.8933	0.107688
7	0.361309	127.553	0.992221	987.192	12.8085	12.7088	0.099636
8	0.412925	158.591	0.993734	985.384	14.616	14.5244	0.091584
9	0.46454	195.613	0.994914	983.577	16.4235	16.3399	0.083532
10	0.516156	240.534	0.99586	981.769	18.2309	18.1555	0.07548
11	0.567771	296.184	0.996635	979.962	20.0384	19.971	0.067428
12	0.619387	366.927	0.997282	978.154	21.8459	21.7866	0.059376
14	0.722618	587.398	0.9983	974.539	25.4609	25.4177	0.043272
17	0.877465	1614.62	0.999381	969.117	30.8834	30.8643	0.019116

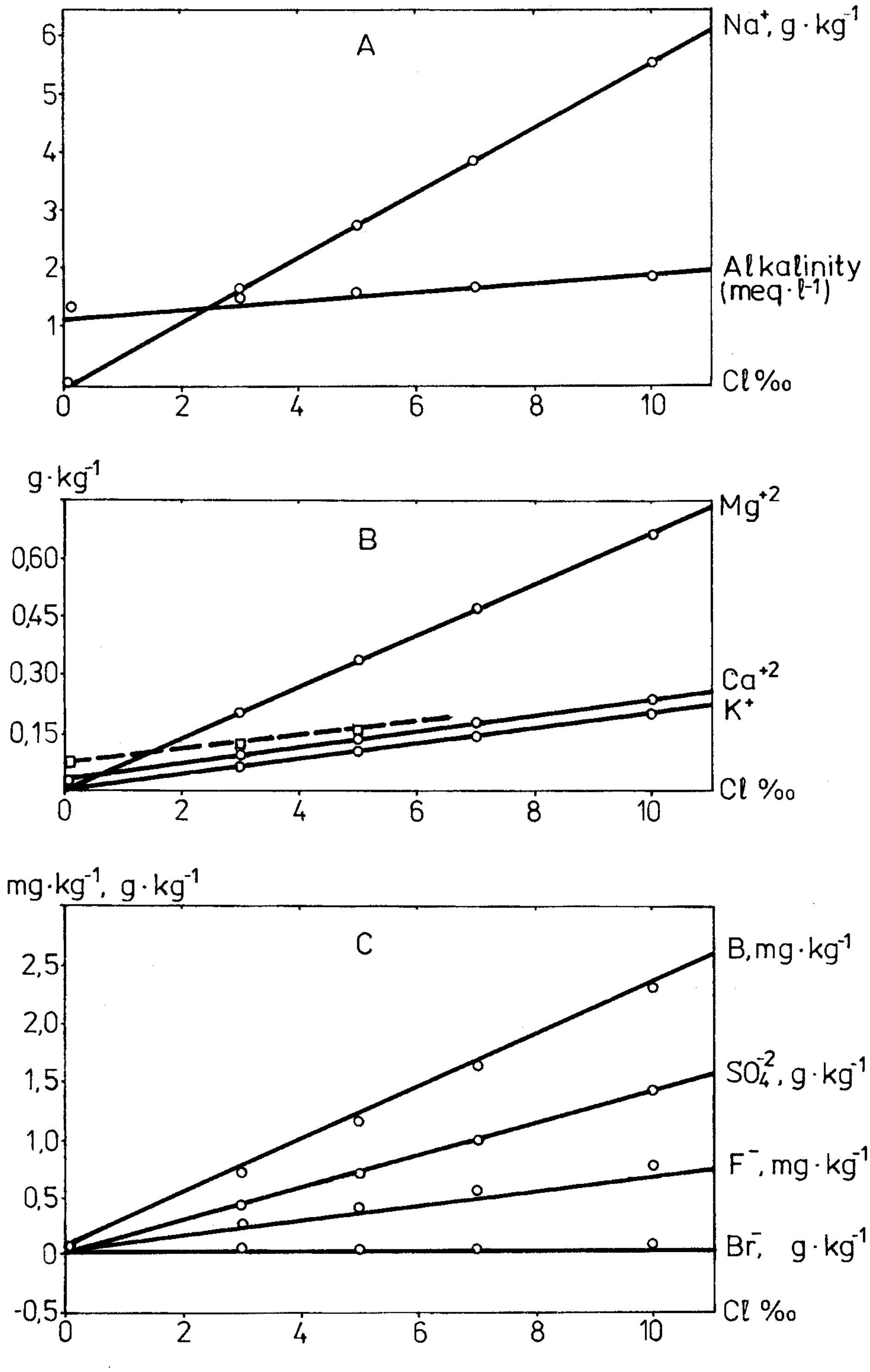


Fig. 6. Comparison of total ionic concentrations in the Baltic Sea water calculated from the linear mixing model of normative seawater and average Baltic riverwater salts (circles), plotted against regression lines from (Millero, 1978). Values of total alkalinity (A) were calculated from the equilibrium models of Baltic seawater at 25 °C and 1 bar total pressure open to the atmospheric air. Squares (B) with dashed line represent Ca^{+2} content if the concentration of Ca^{+2} = 0.878 mmol kg^{-1} is accepted for the average Baltic river water from (Ohlson and Anderson, 1990).

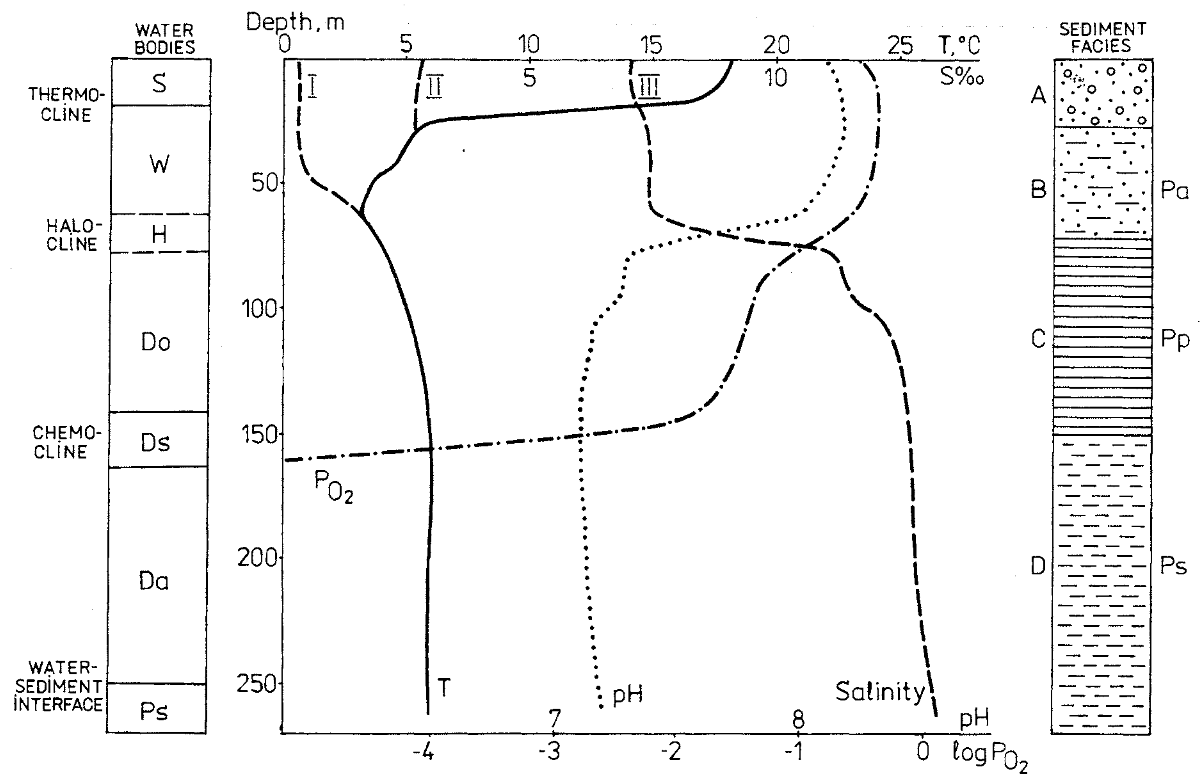


Fig. 7. Generalized Baltic Sea water sediment column for the Gotland Deep (compiled from Grasshoff (1975); Cullenberg (1981); Grasshoff and Voipio (1981); Emelyanov (1986); Dyrssen and Kremling (1990)). Water bodies: S - surface; W - cold winter; H - main halocline; Do - deep oxic; Ds - deep suboxic (unstable chemocline); Da - deep anoxic (unstable); Ps - porewater in sapropelic muds (sediment facies D); Pp - porewater in pelitic muds (facies C); Pa - porewater in aleuritic sediments (facies A and B). Temperature profiles: I -winter; II - spring; III - summer.

Finally, the fresh Holocene sediments contain up to 80 % of porewater, which can be subdivided according to sedimentary facies: shallow-water sand and muddy sand (Pa), intermediate sandy mud (Pp) and deep-water C_{org}-rich Mn-carbonate-sulfidic muds (Ps). The relations between main parameters of all items representing the generalized Baltic Sea water-sediment column, as compiled from profiles at Gotland deep (Grasshoff, 1975, p.474; Kullenberg, 1981, p.140; Grasshoff and Voipio, 1981, p.189; Emelyanov, 1986, p.8-9, 19; Dyrssen and Kremling, 1990), are depicted in Fig.7.

We used this set of profiles in order to compute a series of equilibrium states representing the typical geochemical environments that may be encountered in the Baltic Sea. The following models were calculated for different water bodies.

S - at composition from Cl ‰ = 4 and 7 (salinities 7.393 and 12.81 ‰) - the temperature profile at 1, 5, 10, 15 and 20 °C in a system, open with respect to the atmospheric air (the S_T profile - see Fig. 8).

W - the same system (Cl‰ = 4) at temperature 1 °C, but closed with respect to the atmosphere. H - at temperature 5 °C - the salinity profile (Cl ‰ as shown in Table 21), in closed system, where pH, $P(O_2)$ and $P(CO_2)$ were fixed at typical values by addition of small quantities of the average Baltic C_{org} (Table 20) to the bulk composition (the H_Cl‰ profile; Fig. 9).

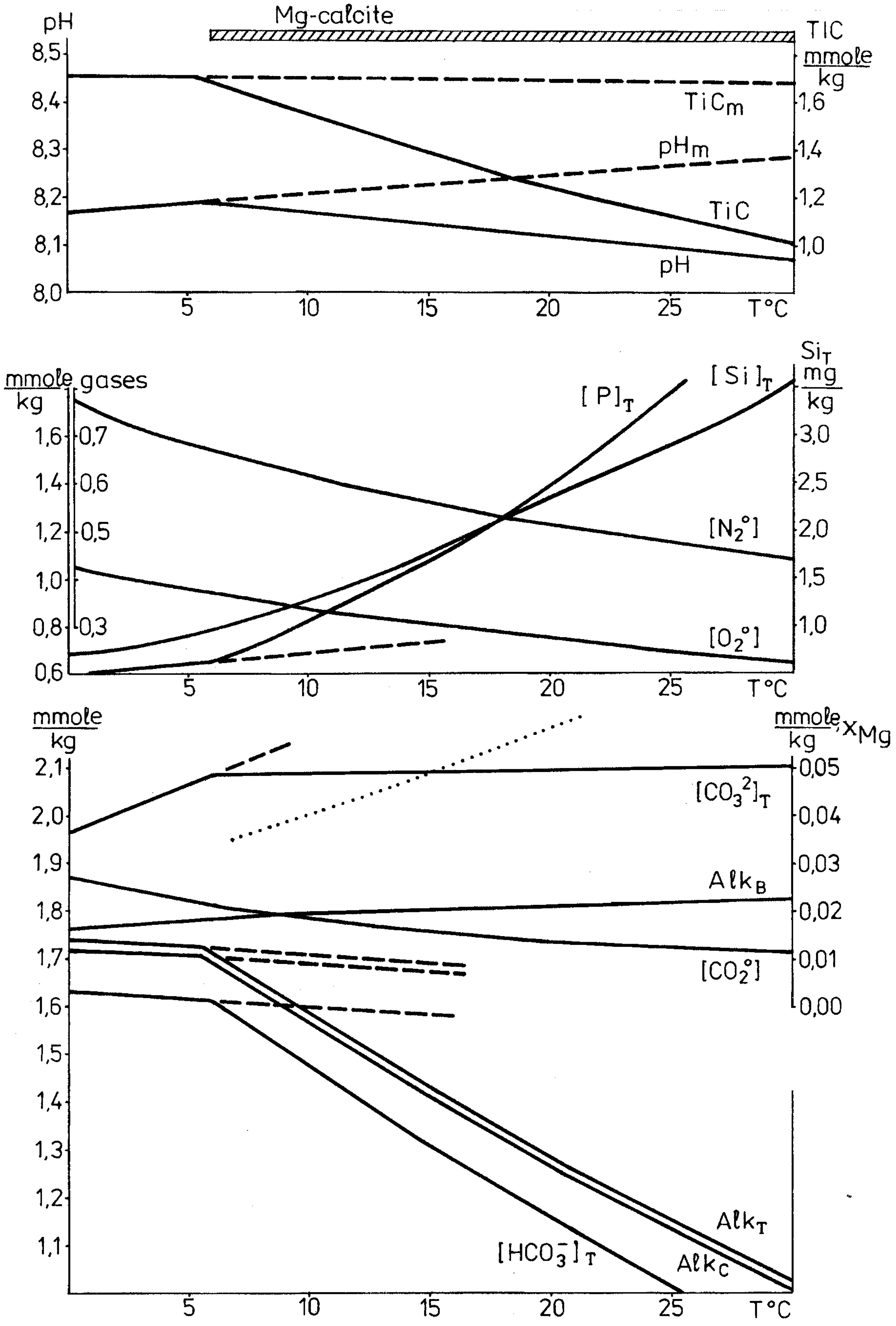
Do, Ds, Da - the closed system at temperature 5 °C and Cl ‰ = 7 (salinity 12.81 ‰), titrated by C_{org} composition from Table 20 until completely reduced state with stable C (the D_.C_{org} profile; Fig. 10, 11).

Pa - the closed system at temperatures 1 and 5 °C and Cl ‰ = 4 and 7 (salinity 7.393 and 12.81 ‰), with excess carbonates, SiO_2, phosphates, titrated by some C_{org} in order to follow the solubility dependencies.

Pp and Ps - the closed system at temperature 5 °C and Cl ‰ = 7 (salinity 12.81 ‰), with excess carbonates, SiO_2, phosphates, sulfur and other minerals, strongly titrated with C_{org} , with stable or metastable C.

In this paper, only major element dependencies are considered; results concerning Fe, Mn, Ba, Zn, and Al aqueous species and minerals will be given in Kulik and Harff (1994, in prep.). Examples of temperature dependency in surface Baltic water of 12.81 ‰ salinity (typical for the South-Western Baltic) are presented in Fig. 8. The system included 100 kg of aqueous solution, 1000 kg of dry air, 0.1 mole SiO_2, and 0.01 mole of composition of carbonate-fluorapatite. The thermodynamic data were used from Tables 2,3, 18 and 19. The Mg-calcite solid solution (see above), quartz and carbonate-fluorapatite were allowed to precipitate in order to follow their solubility. It is clear from Fig. 8a that the aqueous solution becomes (formally) oversaturated with respect to Mg-calcite at this salinity between 5 and 10 °C. Dashed lines show the dependencies of pH, alkalinities, TIC (dissolved total inorganic carbon) and other parameters in the case when no actual precipitation of Mg-calcite would occur. Such a dependency, as well as the N_2 and O_2 solubilities, shows the same trend as discussed for a normative seawater (see Fig. 4, 5). Solid lines show the change of parameters caused by simultaneous precipitation of Mg-calcite. Evidently, this process result in decrease of pH, TIC, total and carbonate alkalinity, total bicarbonate, and Ca with temperature. It also affects the solubility of carbonate-fluorapatite as a result of shifts in chemical potentials of H^+, Ca^{+2}, CO_3^{-2} ions. The solubilities of both carbonate-fluorapatite and quartz increase with temperature, just as mole fraction of Mg in Mg-calcite. Fig. 8,b indicates that Baltic waters with dissolved Si content between 20 and 70 μmole kg^{-1} are undersaturated with respect to quartz.

Fig. 8. Temperature dependencies calculated for the Baltic brackish water of 7 ‰ chlorinity in the system with large excess of model atmospheric air. Solid lines represent parameters of the system with Mg-calcite precipitation allowed, dashed lines - the same system without Mg-calcite precipitation (indexed as m - metastable). Dotted line reflects the mole fraction of Mg in Mg-calcite (x_{Mg}). TIC is total dissolved inorganic carbon, $[P]_T$- total dissolved phosphorus at equilibrium with solid carbonate-fluorapatite, $[Si]_T$- total dissolved silicon at equilibrium with quartz, $[CO_3^{-2}]_T$ - total carbonate, $[HCO_3^-]_T$ - total bicarbonate, Alk_B, Alk_C, and Alk_T - borate, carbonate and total alkalinity. See text for further explanations.



Mg-calcite
pH
8,5
8,4
8,3
8,2
8,1
8,0
TIC
mmole/kg
1,6
1,4
1,2
1,0
TiCm
pHm
TiC
pH
5
10
15
20
25
T°C
mmole/kg
gases
1,6
1,4
1,2
1,0
0,8
0,6
0,7
0,6
0,5
0,3
[P]T
[Si]T
SiT
mg/kg
3,0
2,5
2,0
1,5
1,0
[N2°]
[O2°]
mmole/kg
2,1
2,0
1,9
1,8
1,7
1,6
1,5
1,4
1,3
1,2
1,1
mmole/kg, XMg
0,05
0,04
0,03
0,02
0,01
0,00
[CO3 2]T
AlkB
[CO2°]
AlkT
AlkC
[HCO3-]T

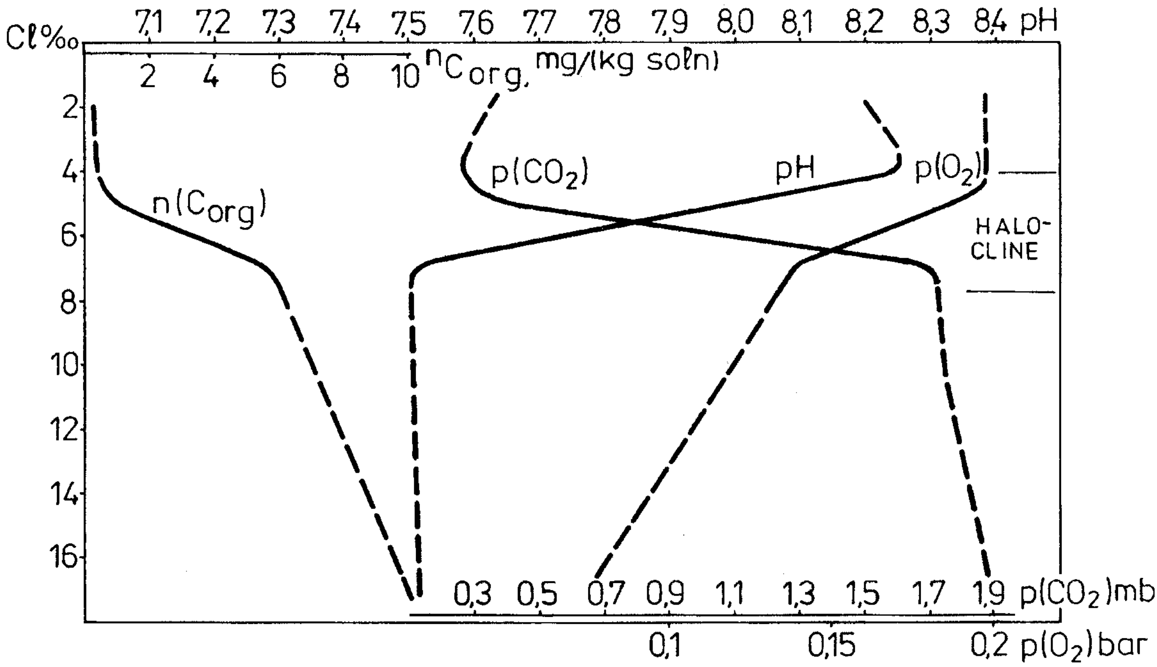


Fig. 9. Behaviour of P(CO_2), P(O_2), and pH in closed Baltic water at T = 5 °C and P=1 bar as functions of chlorinity and titration with C_{org} . Solid lines represent the range of salinity and pH in the Gotland deep halocline (see Fig. 7), dashed lines depict values for other Cl ‰.

In the main halocline (H) water body, the increase in salinity is followed by the drop in pH and P(O_2) reflecting processes of degradation of C_{org} particles produced in upper layers in the deeper water masses (cf. Grasshoff, 1975). The simplest way to reproduce the vertical change in chemical system of halocline layer is therefore to calculate a sequence of equilibria varying both the composition of TDS (expressed through chlorinity - see Table 21) and quantity of oxidized/dissolved organic matter n(C_{org}). For each depth (and salinity), such value of n(C_{org}) may be chosen that results in observed pH and quantity of dissolved oxygen. It is possible to do this because the dual minimization algorithm allows one to treat pH (or P(O_2)) as a function of T,P and composition rather than as independent parameters. Since it is well known that suspended C_{org} from the Baltic contain less N and much less P than the "average ocean" Redfield C_{org}, we used a composition (Table 20) derived from (Shaffer, 1987). The system contained 100 kg of seawater + 4 g air (needed to establish correct initial partial pressures of O_2 and N_2 in closed system at T = 5 °C). The compositions of seawater were calculated for different Cl ‰ values using masses listed in Table 21 and "end-member" model compositions from Tables 1 and 20.

Fig. 9 shows the calculated values of pH, P(O_2) and P(CO_2) as functions of chlorinity and n(C_{org}). Solid lines correspond to the range of salinities for the Gotland Deep halocline (see Fig. 7). Dashed lines follow other salinities. Note that at Cl ‰ > 7, the constant pH = 7.5 was maintained in computations. To achieve this, increasing n(C_{org}) should be added to the system with increasing Cl ‰. The agreement between all values at Cl ‰ between 4 and 8 and corresponding values from Fig.7 is considered as further validation of our model.

The modeling of the chemical system in deep water bodies (Do, Ds and Da) beneath the halocline, as well as in sediment porewaters, in the simplest case requires application of a "process extent" computational scheme (cf. Helgeson, 1969; Karpov, 1981). This scheme is based on the assumption that all irreversible chemical changes in the system are governed by a controlling variable ν called "reaction extent" or "process extent". This approach has proved fruitful in many studies of weathering processes (Kashik, 1990).

In our case, the downward transition from oxic to suboxic and anoxic waters (see Fig. 7) is apparently a result of progressive microbial degradation of organic matter precipitating from surface layers (e.g. Grasshoff, 1975). The halocline makes the system "closed" in the sense that it prevents the supply of oxidants from the above water masses equilibrated to the atmosphere. In fact, only a small part of precipitating C_{org} particles actually dissolves in the water column, as reflected by the very high C_{org} contents (up to 6-8 % in dry weight) in sapropelic muds.

However, it is precisely this quantity of C_{org}, added to the system and then dissolved, that acts like a process extent factor in the deep waters of nearly uniform salinity (12 - 13 ‰), temperature (5 - 6 °C) and pressure. We calculated a series of 25 equilibria in the system of 100 kg Baltic seawater (Cl ‰ = 7) + 4 g air at T = 5 °C and P = 1 bar, adding variable quantities of the Baltic average C_{org}. The most interesting dependencies are plotted at Fig. 10 and 11 against values of $p\nu = -\log(n(C_{org}))$.

The redox transition in this system occurs at $p\nu$ near 1.7744 ($n(C_{org}) = 16.8$ mg kg^{-1}). C_{org} was then added until stable carbon appeared at $p\nu$ near 0.20 ($n(C_{org}) = 0.63$ g kg^{-1}). Note that calculations of redox changes in the system by means of dual minimization algorithm do not require either the Eh or pE to be specified or certain potential-defining redox reactions to be considered, or reactions involving species that are subsequently reduced to be followed. Instead, all changes in activities or concentrations of any species, pH and Eh can be followed immediately as functions of $p\nu$, T and P. Eh values were calculated from the chemical potential of oxygen (Karpov, 1981) and correspond to the reaction

$$\tfrac{1}{2}O_2(g) + 2H^+ + 2e- = H_2O(aq)\,. \qquad (23)$$

At equilibrium with atmosphere and pH = 8.1, Eh = 0.73-0.74 V. The usually measured Eh values in seawater are lower (0.4 V) and related to another reaction (Millero and Sohn, 1992):

$$O_2(g) + 2H^+ + 2e- = H_2O_2.$$

At anoxic conditions, the reaction

$$SO_4^{-2} + 9H^+ + 8e- = HS^- + 4H_2O$$

is recommended. We use the Eh definition (23) because it is valid through all range of stability of water and requires no additional assumptions or species activities.

As seen in Fig. 10, A, pH almost linearly decreases with $p\nu$ until redox transition. This means that, under oxic and suboxic conditions, pH is controlled by the carbonate system. In the reduced part, below $p\nu = 1.7744$, pH increases and the form of pH curve is almost identical to that of $P(NH_3)$ (Fig. 10, C). This suggests that, under reduced conditions, pH is controlled mainly by dissolved ammonia species. At the redox boundary, the pH was calculated to be as low as 6.86 and then increases to 7.2-7.3. Comparison with the generalised profile for Gotland Deep (Fig. 7), as well as literature data (Manheim, 1961; Millero, 1978; Dyrssen and Kremling, 1990), shows good agreement of the calculated pH with measured both in oxic and anoxic deep waters. The higher pH measured for chemocline (7.0 - 7.2) may be explained by the absence of complete redox equilibria between major components of seawater due to mixing of anoxic and oxic waters, precipitation/dissolution of Fe and Mn-rich suspended particles, instability of chemocline etc. A more detailed discussion is given in the next paper (Kulik and Harff, 1994, in prep.).

The behaviour of Eh is typical for weakly-buffered redox transition. Significant amounts of dissolved H_2S (>100 μmole kg^{-1}) appear at pv < 1.5. Since maximum concentrations of $[H_2S]_T > 80$ and $[H_2S°] > 40$ μmole kg^{-1} have been reported for Gotland Deep by Dyrssen and Kremling (1990), we can take this pv = 1.5 value as lowermost for anoxic Baltic water. Lower pv corresponds to porewaters where $[H_2S°]$ as high as 2 mmole kg^{-1} may occur. We are able therefore to adust the schematic diagram of water bodies from Fig. 7 to the redox profile on Fig. 10, B.

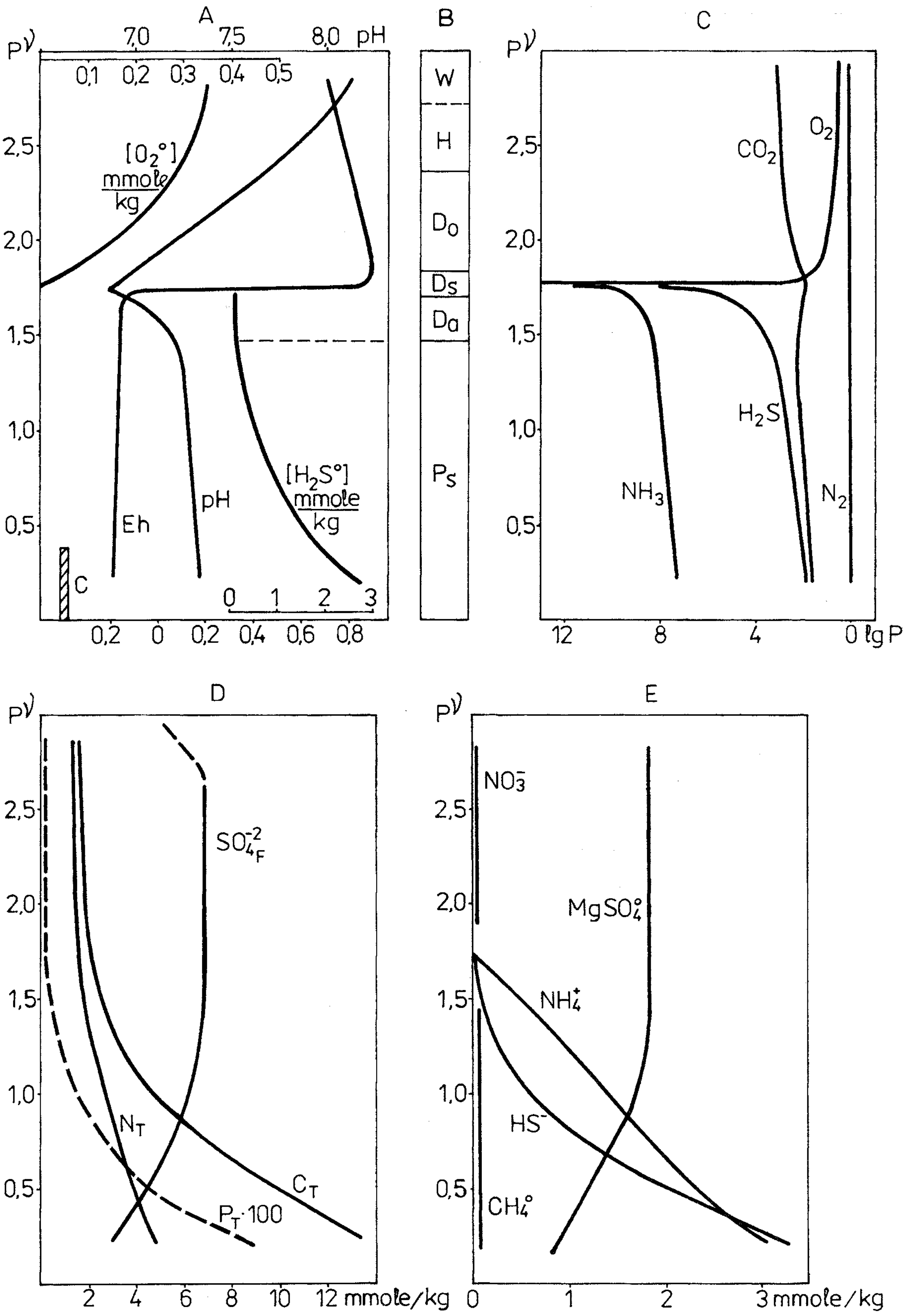
Changes in the equilibrium partial pressures of gases are shown in Fig. 10, C. The behaviour of the curve for $P(CO_2)$ near the redox boundary reflects some delicate rearrangement between activities of carbonate and bicarbonate species that is related to a drop in pH. The $P(N_2)$ line shows no variations even at high amounts of dissolved nitrogen from Corg at low pv.

The behaviour of concentrations of total dissolved N, C, P, S and some of their species (Fig. 10 C, D) is typical for systems governed by C_{org} degradation. $[P]_T$ calculated was 5 μmole kg^{-1} at pv = 1.5 which we assume as lowest for the Da (deep anoxic) water. This is equal to P concentration reported for typical Baltic deep water at pH = 7.0 - 7.3 (cf. Grasshoff, 1975, fig. 15.34). On further reduction (in porewaters), values up to 80 μmole kg^{-1} were calculated, but they are still lower than solubility of octacalciumphosphate. Our calculations confirm the conclusion of Grasshoff (1975) that steep gradients in $[P]_T$ at water-sediment boundary may exist with additional supply of dissolved P into stagnant deep waters.

Unlike P, our simple model gives quite schematic background dependencies for dissolved nitrogen species. The real vertical distribution of nitrate and ammonia in the Gotland Deep and other parts of the Baltic is more complex, and involves denitrification and other effects of biological processes. The near-linear dependence of equilibrium molality of NH_4^+ ion versus pv (Fig. 10, E) is a further evidence of the ammonia control of pH in anoxic waters.

At pv > 1.4 (i.e., in any Baltic deep anoxic water), there is no change in molalities of sulphate ion and its most abundant complex $MgSO_4°$ with respect to their values in oxic water.

Fig. 10. Results of modeling titration of the deep (subhalocline) Baltic water with C_{org} in a closed system at Cl ‰ = 7, T = 5 ° C and P = 1 bar.
$pv = -\log(n(C_{org}))$ in moles kg^{-1}. The redox transition occurs at pv = 1.7744, stable solid carbon appears at pv < 0.4. mmole/kg refer to molalities. N_T, P_T, and C_T - molalities of total dissolved elements. See text for explanations.


A
B
C
D
E
P^{ν}
7,0
7,5
8,0 pH
0,1 0,2 0,3 0,4 0,5
$[O_2°]$ mmole/kg
2,5
2,0
1,5
1,0
0,5
Eh
pH
$[H_2S°]$ mmole/kg
C
0 1 2 3
0,2 0 0,2 0,4 0,6 0,8
W
H
D_o
D_s
D_a
P_s
CO_2
O_2
H_2S
NH_3
N_2
12 8 4 0 lg P
SO_{4F}^{-2}
N_T
C_T
$P_T \cdot 100$
2 4 6 8 10 12 mmole/kg
NO_3^-
$MgSO_4°$
NH_4^+
HS^-
$CH_4°$
0 1 2 3 mmole/kg

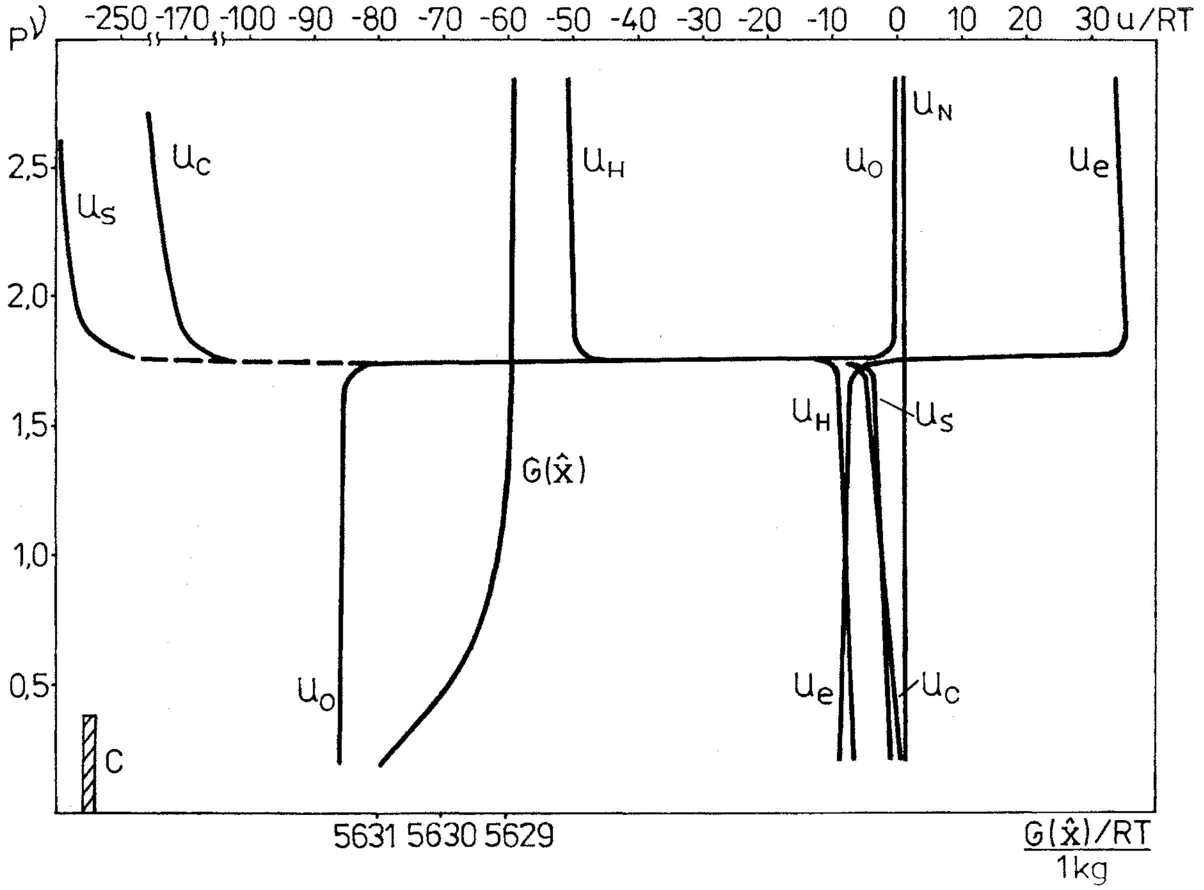


Fig. 11. Behaviour of normalized molal chemical potentials of elements (u/RT, dual solution of convex programming problem), and total normalized minimum Gibbs potential of a system (G(X)/RT), as functions of titration of the deep Baltic water with C_{org} in closed system at Cl ‰ = 7, T = 5 ° C and P = 1 bar. pν = -log(n(C_{org})) in moles kg^{-1}. R is a universal gas constant.

Up to 2-fold depletion in porewater then occurs due to H_2S formation (and HS- with other ionic species). In the case when porewater system is not closed with respect to gases, so that H_2S could escape into the near-bottom water or be consumed by iron sulfide formation, it would cause much stronger depletion both in total dissolved sulfur, sulfate ion and complexes. It may be similar to a case described in (von Breymann et al., 1991). Under these conditions, significant quantities of dissolved methane are also present (Fig. 10, E). The calculations showed that some part of S exists as polysulfides (S_4^{-2}, HS_4^- etc.). Their total molality was not higher than 10^{-7}. Thiosulfates were also present with total molality up to $4{\cdot}10^{-8}$. No significant increase in their concentration was detected under suboxic conditions.

The dual minimization algorithm implemented in SELEKTOR++ program permits the direct calculation of the chemical potentials of independent components (in our case - chemical elements) u_i . Some of them are plotted at Fig. 11, together with the total minimum Gibbs free energy of a system. Note that, in spite of smooth and continuous line of G(X), all potentials except N suffer steep jerks at redox boundary (pv = 1.7744). Potentials of O and e (charge) decrease, of S, C and H increase, and of N remain practically constant. In other parts of the diagram, potentials of O, H, e, and N form vertical lines, whereas potentials of S and C have a negative slope. This slope for carbon can easily be explained by the fact that the system is titrated by C_{org}, and the slope reflects the change of extensive parameter. However, the S potential reflects all (even small) shifts in redox state of the system because sulfur is the main redox buffer in seawater not loaded with Fe and/or Mn.

The diagrams discussed above depict only a small portion of results calculated for the redox profile. Nevertheless, it is evident that the set of thermodynamic data, chemical compositions and equilibria developed here for major component Baltic seawater closely reproduce most of known chemical properties of different water bodies in open and closed systems as functions of salinity, temperature and $n(C_{org})$. The model is very sensitive to changes in composition affecting pH and Eh of seawater. It correctly reproduces solubilities of carbonates, phosphates, sulfates, quartz and even of Mg-calcite regular solid solution.

Concluding remarks

We have attempted to show how it is possible to develop a reference system and thermodynamic dataset for geochemical modeling of estuarine geochemical environments such as the Baltic Sea. The application of new tools for computer thermodynamic modeling such as SELEKTOR++ integrated program implementing the dual minimization IPM algorithm (Karpov et al., 1993) enabled us to build up the ion-association model of normative major component seawater. This model shows good agreement with known parameters of carbonate system, solubility of atmospheric gases, and total ion activity coefficients at P = 1 bar, T between 0 and 30 °C, and salinities between 1 and 40 ‰. It can be readily extended to temperatures up to 370 °C, pressures 1-2 kbar, and to cover many trace elements, organic compounds, and adsorbed forms of interest.

The IPM dual minimization algorithm treats pH, Eh and partial pressures of gases not as independent factors, but rather as functions of T, P and bulk chemical composition of the system. Special attention was therefore paid to the choice of normative bulk composition of seawater, average Baltic riverwater, air and organic matter. We developed the extended linear mixing model of brackish Baltic water that can be used for calculation of its bulk composition as function of chlorinity, sea/riverwater ratio or seasalt/riversalt ratio.

The generalized Baltic Sea water-sediment column (Gotland Deep, Fig. 7) was compiled from literature data. A series of equilibria was calculated representing the main water layers. They show good agreement with known profiles of pH, solubilities of O_2, H_2S, P along redox profile. The set of thermodynamic models constructed for the Baltic sea water bodies therefore provides a comprehensive basis for further modeling of Fe, Mn, heavy metals, and nutrients behaviour in brackish waters, serving as a nucleus for various environmental and mineral-formation implications.

A question may be asked - what new knowledge thermodynamic modeling brings in this situation, if it merely shows the agreement with known parameters of normative seawater and brackish Baltic waters? We think that this agreement itself is a result suggesting that thermodynamic model is internally consistent. If it reproduces accurately the system that can be studied directly (seawater), then it would most probably give correct predictions of conditions existing in environments where it is difficult or impossible to make measurements (diagenetic systems, ancient basins etc.). Predictive abilities are the most valuable outcome from computer modeling.

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