

# Calcium carbonate saturometry by alkalinity difference measurement

Calcium carbonate  
Saturometry  
Sediment/water interface  
Redox turn over  
Carbonate de calcium  
Degré de saturation  
Interface eau-sédiment  
Transition d'oxydo-réduction

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## ABSTRACT

A new technique to obtain the degree of saturation with respect to calcite and other calcium carbonate modifications is described and quantitatively evaluated. Exploitation of the alkalinity difference before and after equilibration with calcite as a direct measureable quantity obviates the need for laboratory based solubility products. The method has been applied to an *in situ* bell jar experiment covering a whole redox turn over at the sediment/water interface. Kinetic effects caused temporary undersaturation, and the subsequent rise in pH and saturation degree during anoxic conditions was attributed to iron sulfide precipitation and the dissolution of a carbonate phase more soluble than calcite. Results obtained from alkalinity difference measurements are compared with saturation calculations from pH-alkalinity data.

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## RÉSUMÉ

Détermination du degré de saturation en carbonate de calcium par la mesure de la différence d'alcalinité.

Une méthode nouvelle donnant accès au degré de saturation de la calcite et à d'autres modifications du carbonate de calcium est présentée. Par la prise en compte de la différence de l'alcalinité — paramètre directement mesurable — il n'est plus nécessaire de se référer aux déterminations expérimentales de la solubilité. La méthode d'équilibrage en ce qui concerne la calcite est appliquée à une expérience *in situ* en « cloche ». Par cette expérience, il est possible de simuler la transition d'oxydo-réduction à l'interface eau-sédiment. En raison d'effets cinétiques, le système devient en premier lieu sous-saturé, et il est possible d'expliquer l'accroissement postérieur du pH et du degré de saturation par la précipitation du sulfure de fer et par la dissolution de la phase carbonate. Les résultats obtenus par cette nouvelle méthode sont comparés avec le calcul de la saturation, utilisant les données de pH et l'alcalinité.

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## INTRODUCTION

The increasing anthropogenic injection of fossil fuel carbon dioxide into the atmosphere has stimulated efforts to clarify how far the present oceans can absorb the surplus *via* dissolutions of carbonates (Andersen, Malahoff, 1977). In addition to the problem of transfer

and dissolution kinetics there is the question of the degree of saturation of different marine environments with respect to calcium carbonates. Several approaches to the determination of the saturation state of the oceans have been used. From shipboard measurements of pH and titration alkalinity (TA) [or another pair of the parameters pH, TA,  $\sum \text{CO}_2$  and  $p\text{CO}_2$  (Park, 1969)]

the concentration of carbonate ion can be calculated applying a suitable set of apparent dissociation constants  $K_i^a(S, T, p)$  for carbonic and boric acid. Multiplication by the calcium concentration yields the ionic concentration product (ICP) from which the saturation state  $\Omega$  can be derived by comparison with the apparent solubility product  $SP^a(S, T, p)$ :

$$\Omega = c_{Ca} \cdot c_{CO_3} / SP^a = ICP / SP^a$$

When activity coefficients  $\gamma_i(S, T, p)$  of all involved species are known the more classical approach *via* thermodynamic equilibrium constants  $K_i^0(T, p)$  can be used (Berner, 1971). A more direct way of estimating the saturation state, the *in situ* calcium carbonate saturometry, was developed by Weyl (1961) and later used in a refined form (e.g. Ben-Yaakov, Kaplan, 1969, 1971). These authors determined the *in situ* change of pH upon addition of calcite to seawater. A pH decrease, for example, indicates precipitation on the added calcite and hence achievement of equilibrium from supersaturation. However, intercomparison of  $\Omega$  estimates from different techniques is often difficult because of (i) the dependance of the calculated profile on the set of equilibrium constants chosen and (ii) unsatisfactory agreement between saturometer-based and shipboard analysis-based saturation profiles (Ingle *et al.*, 1973; Ben-Yaakov *et al.*, 1974; Skirrow, 1975).

It is of interest, therefore, to evaluate a further method of saturation determination which makes use of another directly measureable quantity that is accessible when calcium carbonate is equilibrated with seawater. The alkalinity change before and after addition of calcite to a seawater sample was first related to the  $CaCO_3$ -saturation state by Wattenberg and Timmermann (1936). In a more theoretical sense Pytkowicz (1965, 1968) used the quantity  $\Delta S$ , the number of moles of calcium carbonate which have to dissolve or precipitate in order to achieve saturation. Semiquantitatively, as a measure of deviation from saturation, Wefer (1976) recorded an annual cycle of the alkalinity changes upon equilibration with calcite in the Kiel Bight shallow water environment. Applying the same method of equilibration at room temperature to some Baltic seawater profiles Suess and Wefer found poor agreement with saturation values calculated from pH and alkalinity data (pers. comm.). Possibly this may be due to the fact that they did not relate the shipboard-obtained alkalinity changes to the *in situ* (S, T, p)-conditions. Because it is not possible for practical reasons to equilibrate each seawater sample at its *in situ* temperature each equilibration must be made at a certain (e.g. room) temperature with a consequent deviation from the *in situ* saturation state.

In the following study the shipboard measured alkalinity changes are quantitatively related to the *in situ* saturation state of shallow waters of varying salinities. The number of moles dissolved or precipitated during equilibration of the seawater sample with calcite reflects the distance from equilibrium. Comparison of the stoichiometric solubility product obtained at equilibrium with the *in situ* ionic concentration product yields the saturation of the sample with respect to the employed calcite. The method is then applied to samples

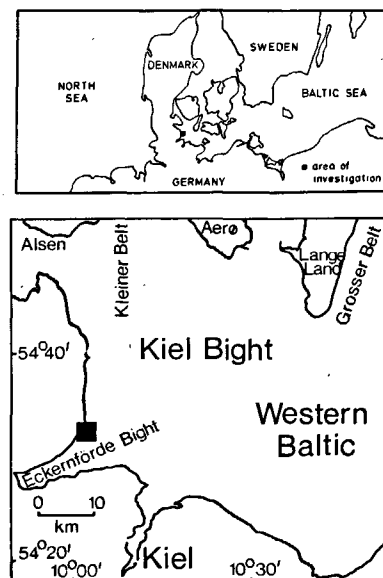
extracted from an *in situ* bell jar experiment in which remineralisation of organic matter and calcium carbonate dissolution was followed during a whole redox turnover. Finally, values of the degree of saturation derived from alkalinity changes are compared with convenient pH-carbonate alkalinity calculations using different sets of equilibrium constants.

## MATERIALS AND METHODS

### Research area

A bell jar system was set up in a restricted sea area in the Kiel Bight, Western Baltic, at a water depth of 20 m (Fig. 1). Situated in the transition between North Sea and the Baltic Sea the Kiel Bight is known for frequent, short-term significant salinity fluctuations. The sediment underlying the bell jar system was a fine muddy sand with a carbonate content of 0.2% dw in the upper 2 cm and a fifth of that in the layers below. Wefer and Lutze (1978) estimated that only 1% of the foraminiferal carbonate produced is accumulated in those sediments.

Figure 1  
The area under investigation: Kiel Bight, Western Baltic Sea.



### Experimental system

To simulate the transition from oxic to anoxic conditions an *in situ* bell jar system enclosing 2 094 l seawater over 3.14 m<sup>2</sup> sediment has been applied (Balzer, 1978). The processes were followed by automatic probes for Eh, pH, temperature and oxygen together with a remote controlled stirrer (Dieckmann *et al.*, 1976). Once a week SCUBA-divers took water samples from inside by means of 300 ml air tight glass syringes.

### pH

The pH-probe consists of a normal glass electrode (Fa. Ingold) and an Ag/AgCl-reference electrode with solidified electrolyte and ceramic diaphragm which is pressure independant down to 250 m and hydrogen sulfide resistant (Lazaran-Electrode, Fa. Beckmann).

To check the probe against drift the pH of syringe samples was measured once a week using a standard combination electrode (Fa. Ingold). Both systems were standardized against at least two NBS-low ionic strength buffers.

### Alkalinity

The titration alkalinity (TA) was determined by standard acid addition according to Anderson and Robinson (1946). In order to obtain carbonate alkalinity (CA) those protolytic species had to be subtracted from TA (Gieskes, 1974) which contributes significantly to the total alkalinity: borate alkalinity was calculated from chlorinity data and the boron/chlorinity ratio of Kremling (1972) making use of  $K'_B$  (Cl, T) according to Edmond and Gieskes (1970); the sulfide contribution was estimated from total sulfide and the dissociation constants  $K'_1$  ( $H_2S$ ) and  $K'_2$  ( $H_2S$ ) as a function of ionic strength according to Skopintsev (1957; cited in Richards, 1975).

### Calcium

Calcium was titrated complexometrically with EGTA using GHA as indicator (Tsunogai *et al.*, 1968). Replicate analyses yielded a coefficient of variation of 0.13%.

### Other components

Chloride was titrated argentometrically (Grasshoff, 1976). Hydrogen sulphide was determined spectrophotometrically with the methylene-blue-method or iodometrically titrated in case of higher concentrations (Fonselius, 1976).

### Saturometry

Immediately after recovery, water from the air tight syringes was poured into 50 ml glass bottles. After addition of approximately 4 g of reagent grade "marble powder" (Fa. Merck) the bottles were carefully stoppered, attention being paid to the exclusion of gas bubbles and maintained at  $22 \pm 2^\circ C$  for 24 hours. To ensure good seawater-calcite contact the bottles were regularly shaken. Subsequently the solutions were filtered through 0.45  $\mu m$  Nucleopore filters and the alkalinity was determined as in the original sample analyzed at once. The Merck marble powder was X-ray pure calcite with a mean particle size of 60  $\mu m$ .

### CALCULATIONS

The main problems associated with the quantitative evaluation of the primary data are: (i) achievement of saturation is accompanied by pH changes so that carbonate ion concentration is changed not only as a result of increase or loss in total carbon dioxide but also because of the simultaneous pH-dependant internal distribution among the different inorganic carbonate

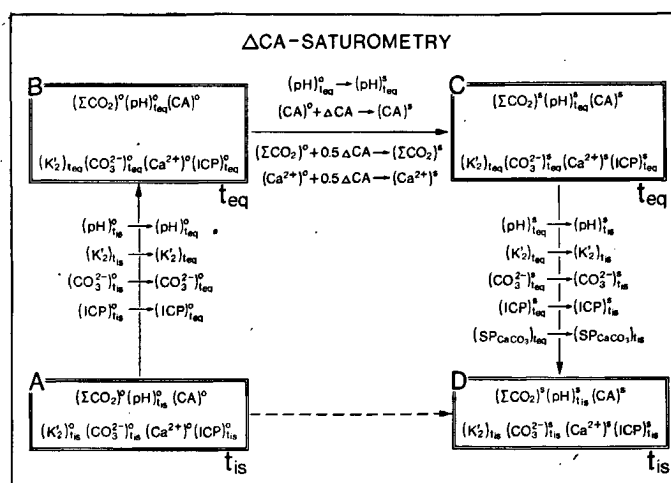


Figure 2

Alkalinity difference based saturometry: Simulation of in situ equilibration (A to D) by a cyclic process: A over B and C to D.

species, (ii) for practical reasons it is necessary to equilibrate the sample at a temperature generally different from the *in situ* value. These problems can be catered for by considering a cyclic process (Fig. 2) which enables the equilibrium conditions at the *in situ* temperature ( $t_{is}$ ) to be calculated from the observed, shipboard-determined saturation conditions at the (higher) temperature ( $t_{eq} = 22^\circ C$ ).

The cycle comprises the following steps (Fig. 2) where the subscripts ( $_{t_{is}}$ ) and ( $_{t_{eq}}$ ) refer respectively to *in situ* and shipboard equilibration temperature and the super-scripts ( $^0$ ) and ( $^s$ ) indicate respectively the value of a property before and after achievement of saturation. A: For *in situ* conditions of temperature ( $t_{is}$ ) and salinity the ionic concentration product is completely described when  $(pH)^0$ ,  $(\Sigma CO_2)^0$  and  $(Ca^{2+})^0$  are known. A to B: At constant  $\Sigma CO_2$  temperature is raised to  $t_{eq}$  with the accompaniment of the temperature dependant changes in pH,  $(CO_3^{2-})$  and (ICP). B: At  $t_{eq}$   $(CO_3^{2-})^0$  and  $(ICP)^0$  can be obtained from  $(\Sigma CO_2)^0$  and  $(pH)_{t_{eq}}^0$ . B to C: At constant  $t_{eq}$  the sample is equilibrated with calcite. Gain or loss of alkalinity consequent on the dissolution or precipitation of  $CaCO_3$  results in changes of CA,  $\Sigma CO_2$ ,  $Ca^{2+}$  and also pH. C: At  $t_{eq}$  the ionic concentration product after saturation  $(ICP)^s$  can be derived from  $(CA)^s$ ,  $(\Sigma CO_2)^s$  and  $(Ca^{2+})^s$ . C to D: By means of known temperature coefficients for the solubility product of calcite the  $(ICP)^s$  can be converted from  $t_{eq}$  to the *in situ* temperature. D: The degree of saturation  $\Omega$  is equal to the ratio of  $(ICP)_{t_{is}}^0$  in step A and  $(ICP)_{t_{is}}^s$  in step D.

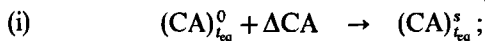
A computer program written for this cyclic process proceeds in the following way:

(a) The measured quantities:  $t_{eq}$ ,  $\Delta t = t_{eq} - t_{is}$ , pH, carbonate alkalinity (CA), alkalinity change ( $\Delta CA$ ), and calcium concentration constitute the data input.

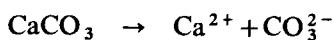
(b) From  $(pH)_{t_{eq}}$  and CA, and the  $K'_1$ ,  $K'_2$  (S, T)-polynomials of Mehrbach *et al.* (1973) the total carbon dioxide is calculated. Interconversion of the components of the carbon dioxide system is handled within the mathematical framework represented extensively in Skirrow (1975). Total carbon dioxide is a temperature

independent quantity and permits computation of carbonate ion concentration at  $t_{is}$  after conversion of pH,  $K'_1$ , and  $K'_2$  to *in situ* conditions. Multiplication with calcium concentration yields the *in situ* ionic concentration product before saturation  $(ICP)_{t_{is}}^0$ .

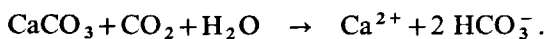
(c) When equilibrated with calcite at  $t_{eq}$  the following changes of parameters take place in the test solution (for simplicity we consider only undersaturated seawater with dissolution and alkalinity increase ( $\Delta CA$ ) upon addition of calcite; achievement of equilibrium from supersaturation would change signs only):



(ii) Increase of alkalinity by  $\Delta CA$  means dissolution of  $0.5 \Delta CA$  moles  $CaCO_3$  according to:



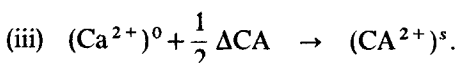
or



Hence



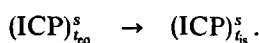
and



Without taking notice of the pH changes accompanying the saturation step the equilibrium concentration of carbonate ion at  $t_{eq}$  can be calculated from  $(\sum CO_2)^s$  and  $(CA)^s$ . From  $(CO_3^{2-})^s$  and  $(Ca^{2+})^s$  the ionic concentration product  $(ICP)^s$  at  $t_{eq}$  can be computed.

(d) In order to obtain the saturation state at *in situ* temperature the  $(ICP)^s$ , being equal to the respective solubility product ( $SP_{calc}$ ), has to be converted from  $t_{eq}$  to  $t_{is}$  by means of the temperature coefficient ( $\gamma$ ) of the latter product.

The most reliable determinations for  $\gamma$  seem to be those of Ingle *et al.* (1973) because in these equilibrium was approached from both under- and supersaturation and because particular care was taken to eliminate sources of possible uncertainties in previous investigations. Assuming the coefficient to be independent of salinity the value of  $\gamma = 0.0108 \cdot 10^{-7} / ^\circ C$  has been used for the conversion:



(e) The saturation state equals the ratio of  $(ICP)_{t_{is}}^0$  (calculated in b) and  $(ICP)_{t_{is}}^s$  (calculated in d):

$$\Omega = (ICP)_{t_{is}}^0 / (ICP)_{t_{is}}^s.$$

#### APPLICATION TO AN *IN SITU* EXPERIMENT

The saturometry method using alkalinity difference measurements has been applied to a bell jar experiment

that lasted over 99 days from May to September. Due to microbial degradation of organic matter the oxygen content decreased systematically and was completely exhausted at the 57th day of the experiment. Subsequent sulphate reduction yielded hydrogen sulfide concentrations up to  $54 \mu g \cdot dm^{-3}$ . During low oxygen concentrations from the 45th to 57th day denitrification occurred (Balzer, 1978).

As parameters describing the carbonate system: carbonate alkalinity and pH are given in Fig. 3. Immediately after enclosure of the water mass the pH dropped from its initial value of 8.30 at a slowly decreasing rate until it was stabilized at  $pH = 7.49$ . The simultaneous increase in alkalinity shows dissolution of calcium carbonate working against the pH-lowering due to  $CO_2$  input from degrading organic matter. Due to a technical defect between the 28th and 43rd day of experiment (a sampling valve had not been closed properly) a partial water exchange with surrounding waters of higher salinity took place so that data from this period do not represent closed system conditions. Except for a prolongation of the oxic phase there was no significant effect on the  $CO_2$  system and the results after the 43rd day are completely uninfluenced by this event. In contrast to the commonly observed behaviour of pH to further decrease or stabilize during continuing decay of organic matter pH increased after commencing denitrification and sulphate reduction. After a stabilization period at 7.75 the pH dropped slightly again at the end of the experiment. The pH change is connected with a significant increase in alkalinity indicating intensive carbonate dissolution.

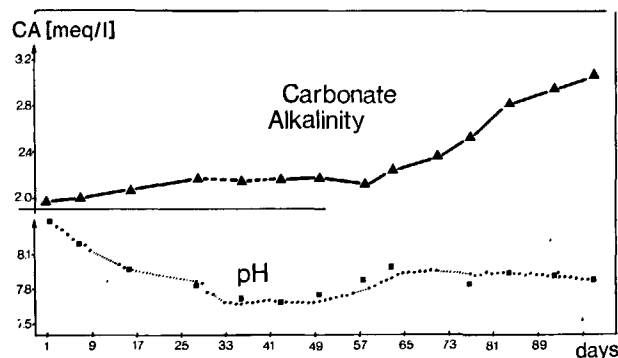


Figure 3

*In situ bell jar experiment (May to September 1976): Changes of carbonate alkalinity (triangles; broken line: see text) and pH during a whole redox turn over (squares represent shipboard pH measurements, large dots: *in situ* probe measurements of pH and the dotted line connects probe data during breakdown of power supply).*

To elucidate how far this behaviour is a direct consequence of varying degrees of saturation, the saturation state with respect to calcite has been calculated by different methods (Table and Fig. 4). Computations from pH and alkalinity data yielded considerable but nearly constant deviations when using apparent dissociation constants and solubility products of Edmond and Gieskes (1970) in the first case compared with results using the respective constants of Mehrbach *et al.* (1973) and Ingle *et al.* (1973). The latter saturation states were about 20% higher.

Also shown in Figure 4 are the alkalinity differences obtained from shipboard equilibration with calcite and

Table

In situ bell jar experiment (May to September 1976): Chlorinity  $Cl$  (‰), temperature  $T$  (°C), pH, carbonate alkalinity  $CA$  (meq.  $dm^{-3}$ ), alkalinity difference  $\Delta CA$  (meq.  $dm^{-3}$ ), calcium concentration  $Ca^{2+}$  ( $mM \cdot kg^{-1}$ ), saturation state  $\Omega$  (in per-cent) from pH-alkalinity data using apparent constants of Mehrbach *et al.* (1973) and Ingle *et al.* (1973);  $\Omega$  (MI), using apparent constants of Edmond and Gieskes (1970);  $\Omega$  (EG) and alkalinity difference based saturation state  $\Omega$  (CA).

Day	Cl	T	pH	CA	$\Delta CA$	$Ca^{2+}$	$\Omega$ (MI)	$\Omega$ (EG)	$\Omega$ (CA)
01	9.74	8.0	8.30	1.93	0.01	5.474	171.1	136.8	(71.5)
07	9.76	8.1	8.00	1.97	0.11	5.521	92.3	75.4	(41.7)
16	9.77	9.2	7.77	2.05	0.05	5.539	60.8	50.0	55.6
24	9.76 <sup>a</sup>	10.0 <sup>a</sup>	7.70	2.11	0.02	5.594	56.2	46.1	66.7
28	9.81	10.1	7.67	2.15	0.00	5.586	53.7	44.1	73.7
36	10.63	10.1	7.48	2.13	0.20	6.021	37.7	30.8	30.2
43	11.30	10.1	7.50	2.14	0.07	6.280	41.6	33.5	57.1
50	11.43	10.4	7.50	2.15	0.07	6.326	42.7	34.6	57.8
58	11.47	10.7	7.60 <sup>a</sup>	2.10	0.09	6.370	53.3	43.2	51.2
63	11.34	10.8	7.70	2.21	0.05	6.309	69.9	56.3	63.4
71	11.46	12.4	7.76	2.32	0.015	6.376	90.7	72.9	78.5
77	11.46 <sup>a</sup>	13.3	7.74	2.49	0.02	6.440	97.9	78.5	78.5
84	11.46	13.2	7.74	2.75	-0.105	6.453	107.8	86.6	130.4
92	11.46	13.7	7.71	2.89	-0.08	6.520	109.4	87.9	117.5
99	11.38	15.0	7.68	2.98	-0.11	6.538	111.9	89.7	132.2

(<sup>a</sup>) Interpolated from probe measurements

their conversion to *in situ* degrees of saturation. Especially in the first measurements there is considerable scatter in the  $\Delta CA$  data probably arising from insufficient amount of calcite (Chave and Suess, 1967) added to reach equilibrium. From the ionic concentration product after equilibration it is concluded that the first two runs had not reached true equilibrium.

The course of the saturation state experiment is divisible into two distinct periods: in the first of these the rapid input of  $CO_2$  from decaying organic matter is not matched by a corresponding dissolution of calcium carbonate and led to undersaturation with respect to calcite; the second period is characterized by the stepwise overcoming of the undersaturation by the dissolution of calcium carbonate. Although this tendency is reflected in all three curves, the saturation state calculated according to Edmond and Gieskes (1970) remained in the undersaturated region until the end of the experiment; however, both the pH-alkalinity based computations according to Mehrbach *et al.* (1973) and Ingle *et al.* (1973) and the independent alkalinity difference based calculations indicate a transgression of the 100% saturation level nearly at the same day.

## DISCUSSION

### Estimation of saturation states

The fact that the same set of pH-alkalinity data yields slight under- or supersaturation depending on the choice of apparent equilibrium constants reflects the present unsatisfactory state with regard to knowledge of these constants. The apparent dissociation constants according to Mehrbach *et al.* (1973) are probably to be preferred since Takahashi *et al.* (1976) found them to be internally consistent with GEOSECS data. However, estimates of the saturation state from pH-alkalinity data depend also on a proper value for the solubility product; at present there is still some dispute over the best value to use (Takahashi, 1975; Skirrow, 1975; Berner, 1976).

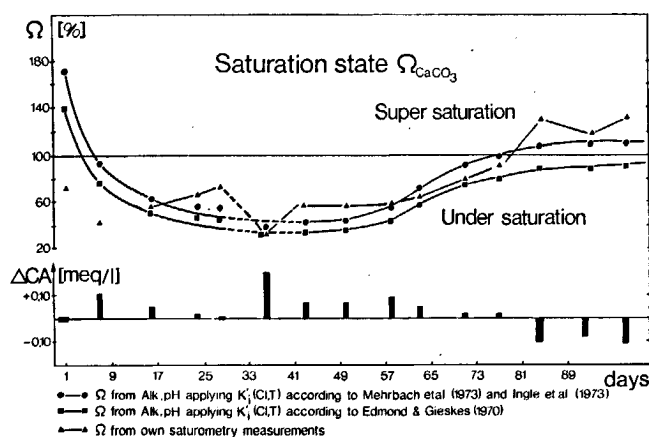


Figure 4

In situ bell jar experiment (May to September 1976): Measured alkalinity differences ( $\Delta CA$ ) and degrees of saturation  $\Omega$  (%) calculated by different methods: (a) and (b) from pH-alkalinity data; (c) using the alkalinity difference measurement. Broken line: see text.

In a qualitative way at least the saturometry technique is to be able to decide between the different pH/alkalinity computations about the real saturation state. Results obtained from computations using apparent equilibrium constants according to Mehrbach *et al.* (1973) and Ingle *et al.* (1973) are consistent with the saturometry data leading to supersaturation in the last part of the experiment; for this stage of the experiment the degree of saturation calculated *via* pH/alkalinity data was  $\Omega$  (MI)=110%, whereas the saturometry-based value was ca.  $\Omega$  (CA)=125%. For pH/alkalinity based determinations of  $\Omega$ , the principal experimental factor likely to influence the accuracy (if common shipboard accuracy is accepted (Grasshoff, 1976)) is the pH determination; for the *in situ*-pH-saturometry determinations again the precision of the pH measurements is critical (Ben-Yaakov, Kaplan, 1969). However, the alkalinity difference saturometry is affected mainly by the determination of the alkalinity difference; replicate analyses showed this quantity to be reproducible to within  $0.02 \text{ meq. } dm^{-3}$ . In addition to the influence of the

added amount of calcite on the achievement of equilibrium (see above), it is essential to allow sufficient time for the achievement of equilibrium. The experience of the present investigation suggests that at least 10 hours are necessary and that the period of 20 minutes employed by Ben-Yaakov *et al.* (1974) is insufficient for equilibrium to be attained. Such lengthy equilibration times entail the risk of interference by bacterial CO<sub>2</sub> production and for this reason poisoning with HgCl<sub>2</sub> is recommended.

Because the ionic concentration product (ICP)<sup>s</sup> calculated for 100% saturation corresponds to the solubility product, a comparison may be made with literature values (which include determinations at lower salinities): from the last eight values of the experiment (salinity of 20.69‰) a mean solubility product of  $p(\text{ICP})^s = 6.584$  is obtained for 22°C. This agrees reasonably well with the respective value  $pK'_{\text{calc}} = 6.563$  of Ingle *et al.* (1973); the value  $pK' = 6.451$  calculated from the data of Edmond and Gieskes (1970) is considerably lower.

The main limitation of the saturometry technique (as well as all other determinations of calcite solubility) probably lies in the uncertainty associated with achievement of "true" equilibrium. There is a strong interference of Mg<sup>2+</sup> ions of seawater with homogeneous nucleation of carbonates (Pytkowicz, 1968; Katz, 1973). This holds especially for calcite if equilibrium is approached from supersaturation: precipitation of magnesian calcites may occur leading to incorrectly high values for calcite solubility (Berner, 1975). Thorstenson and Plummer (1977) found that a Mg-calcite with about 4 Mol-% magnesium carbonate represents the most stable phase in seawater; thus low-magnesian calcites may precipitate on calcite grains. If equilibrium is approached from undersaturation, adsorption of dissolution-inhibiting trace species may cause the rate of equilibration to decrease considerably (Berner, 1976). Since results of solubility controlling surface coatings or precipitates on calcite are not unequivocal until now equilibration with pure calcite should be used further and be supplemented by simultaneous equilibration with aragonite where compositional changes due to surface reactions are less pronounced (Berner, 1976).

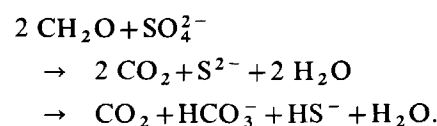
An advantage of all saturometry techniques is that they achieve their object without the necessity to refer to solubility products which are laboratory determined and generally relate to very limited (oceanic) conditions. Thus saturometry-based methods are particularly advantageous for studies of estuaries and brackish semi-enclosed seas (e.g. Baltic Sea) where wide ranges of salinities and anomalies in the cation and anion chlorinity ratios (Kremling, 1972; Grasshoff, 1975) occur; under these conditions the application of constants derived for oceanic environments appears to be especially inadvisable. One factor which should be considered is the possibility that certain constituents (e.g. dissolved organics or certain inorganic ions) may be involved with unknown influence on solubility behaviour *via* surface reactions [e.g. Moeller and Parekh (1975) report a 30% increase in solubility in the presence of 1 μM · dm<sup>-3</sup> HPO<sub>4</sub><sup>2-</sup>]. If this were to be so, saturometry based direct measurements may attribute a more real saturation state to the sample in the sense

of its ability to attack *in situ* calcium carbonates or to precipitate certain amounts from the dissolved phase. Possibly the "artificial" character of the marble-calcite so far employed can be overcome by using instead various naturally occurring biogenic calcium carbonates indigenous to the investigated area.

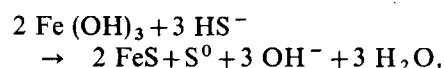
#### CaCO<sub>3</sub>-saturation during the experiment

The course of the degree of saturation during the experiment (Fig. 4) followed the expected pattern only during the first stage: starting from supersaturation which usually prevails in the Kiel Bight (Wefer, 1976) at the season chosen the seawater enclosed in the bell jar suffered rapid oxygen consumption and hence, an increase of P<sub>CO<sub>2</sub></sub> and lowering of the saturation state. However, instead of being stabilized at or near the 100% level the system quickly showed marked undersaturation. The most probable reason seems to be the inability of carbonate dissolution (due to lack of active surfaces) to compensate so fast for the increase of P<sub>CO<sub>2</sub></sub> and the lowering of carbonate ion concentration.

The progressive overcoming of this kinetic hindrance and the stepwise approach to eventual equilibrium is probably assisted by the bacterial degradation of organic coatings; this period of spontaneous rise of saturation is associated with sulphate reduction. pH changes under these anoxic conditions are unlikely to be governed solely by the carbon dioxide system (Skirrow, 1975). Unlike the degradation of organic debris by dissolved oxygen which leads more or less directly to CO<sub>2</sub> generation, sulphate reduction results in the replacement of anions of a strong acid by those of a weak acid; these anions subsequently hydrolyze consuming protons and thus partly compensate for the introduction of acid carbon dioxide. Schematically this can be represented by:



Although being a source of excess alkalinity (Knull, Richards, 1969; Berner *et al.*, 1970; Almgren *et al.*, 1975) the process of anoxic decomposition of organic matter seems to have little influence on pH (Ben-Yaakov, 1973). The latter author calculated the equilibrium pH during this process for a closed system and found that pH should be lowered to pH 6.9 and be well buffered there because weak acids and bases so produced enter the solution in constant proportion. If contact with sediments is admitted, the pH may be shifted by additional reactions which are essential for the sediment/water system of the present study: precipitation of sulphides, carbonate and silicate reactions, the latter being of minor importance here. Ben-Yaakov (1973) concluded that removal of sulphides from solution represented schematically by



has the effect of increasing the pH, the maximum pH to be expected at about 8.3 but probably controlled by

calcium carbonate precipitation. In the system investigated here the solubility product of iron sulphide is exceeded soon after commencing sulphate reduction.

Finally, it might be noted that the observed pH rise cannot be attributed solely to reaction of sulphides with iron oxides since some contribution derives from the dissolution of calcium carbonate as the undersaturation of the bottom water is overcome; this uptake is reflected in both the alkalinity and the calcium concentration (Table). The slight decrease in its slope towards the end of the experiment as well as the more or less stabilization of the saturation state above the 100% level may indicate approach of equilibrium with a phase more soluble than calcite. This may well be aragonite which is known to be present in the sediments of this area (Wefer, pers. comm.).

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