AN EXPERIMENTAL INVESTIGATION OF "CALCITE AND ARAGONITE PRECIPITATION RATES IN SEAWATER AS A FUNCTION OF SALINITY" AND ITS APPLICATIONS TO SOME GEOLOGICAL PROBLEMS

by
Shaojun Zhong
Department of Geological Sciences
McGill University, Montreal
Quebec, Canada
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Calcite & Aragonite Precipitation Rates as a Function of Salinity

ABSTRACT

The precipitation rates of calcite and aragonite in artificial seawater at various salinites (i.e., S = 5, 15, 25, 35, and 44) were quantitatively determined by using a constant disequilibrium (chemo-stat) seeded-precipitation technique. The experiments were conducted at 25°C and 1 atm total pressure (with P_{CO_2}= 0.3 %) over a wide range of saturation states ($2.6 < SI_C < 17$).

The precipitation rate data, obtained under similar experimental conditions, were fitted to an empirical rate law of the following form: Log(Rate) = n Log(SI-1) + Log(k), where n is the empirical reaction order and k is the rate constant. Calcite and aragonite precipitation rates in seawater are independent of the salinity over the range investigated. This study confirms previous findings (Burton and Walter, 1987) that above a given saturation state with respect to calcite (SI_C > 2.6), aragonite precipitates faster than calcite at 25°C.

In contrast to what was once believed (e.g., Folk, 1974), results from this study, as well as some previous ones (e.g., Badiozamani et al., 1977; Walter, 1986), demonstrate that variations in salinity (or ionic strength) do not have a significant kinetic effect on the precipitation rates of calcite or aragonite. The results are discussed in the context of a number of geological environments where salinity happens to be one of the most obvious variable parameters, which might be controlling carbonate precipitation.

RESUMÉ

Les vitesses de précipitation de la calcite et de l'aragonite dans des solutions d'eau de mer artificielle de diverses salinités (i.e., 5, 15, 25, 35, 44) ont été déterminées de façon quantitative à l'aide d'une technique (chemo-stat) d'ensemencement, sous des conditions de déséquilibre constant. Les travaux ont été exécutés à 25°C sous une pression totale d'une atmosphère (et une P_{CO_2} = 0.3%) et couvrant une large gamme de saturations ($2.6 < SI_C < 17$).

Les données de vitesse de précipitation obtenues dans des conditions expérimentales semblables ont été adaptées à une loi cinétique empirique de la forme suivante: Log(Vitesse) = n Log(SI-1) + Log(k), où n et k représentent, respectivement, l'ordre empirique et la constante de vitesse de la réaction. Les vitesses de précipitation de la calcite et de l'aragonite sont pratiquement indépendantes de la salinité, à l'intérieur de la gamme étudiée. Cette étude confirme les résultats d'une étude précédente (Burton and Walter, 1987) qui indiquait qu'en deça d'une valeur donnée de l'indice de saturation de la calcite (i.e., $SI_C > 2.6$), l'aragonite précipite plus rapidement que la calcite à 25°C.

Contrairement à ce que l'on croyait jadis (e.g., Folk, 1974), les résultats de cette étude ainsi que ceux de certaines autres (e.g., Badiozamani et al., 1977; Walter, 1986) démontrent que les variations de la salinité (ou la force ionique) n'influencent guère les vitesses de précipitation de la calcite et de l'aragonite. Les résultats sont discutés dans le contexte de plusieurs environnements géologiques où la salinité est l'un des paramètres variables qui semble le plus susceptible d'être responsable du contrôle de la précipitation des carbonates.

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CHAPTER I

INTRODUCTION

I.1 General considerations

Carbonate sediments and rocks formed a large part of the sediments and sedimentary rocks in the geological history. The study of carbonates is very important because they possess an extremely sensitive record of past life and conditions on the Earth and are generally good reservoirs for base metals and hydrocarbons (James and Choquette, 1983a).

Carbonate sediments and rocks are subject to chemical alternation during both their initial formation and their later diagenesis. Because of the deepening of our understanding of these alternation processes and the availability of more and more sophisticated analytical methods, primary petrological descriptive studies were replaced by combined petrographic and geochemical investigations. Geochemical tracers, such as isotopes and trace elements, are called upon to give quantitative and/or semi-quantitative interpretations and predictions of the conditions of the formation and diagenesis of these sediments and rocks.

Although the dominant source of calcium carbonate in marine sediments is biogenic, inorganic precipitation of calcite and aragonite has also been recognized as an important factor in controlling the formation as well as the early diagenesis of carbonate sediments. It is fairly well-known that the rock-water interactions are the primary driving force in carbonate diagenesis (James and Choquette, 1983a) and probably responsible for part of the carbonate origin. In other words, it is the interaction between rock and its surrounding fluids that controls the mineralogy and the change of texture and structure of the carbonates during their precipitation and diagenesis. As a result, reaction kinetics of carbonates with their surrounding fluids (e.g., seawater, pore water, deep subsurface fluids) have become a major focus of study in recent decades (e.g., Bricker, 1971; Bathurst, 1975; Morse and Berner, 1979; Berner, 1980; James and Choquette, 1983a, b; 1984; Walter, 1986; and others).

It has been realized that for many geochemical systems, kinetics is of paramount importance in determining their fate and evolution (Lasaga, 1981). Some of the reaction rates are so slow that thermodynamic equilibrium is rarely achieved. This is especially true of the carbonate-water reactions. Well established facts supporting this conclusion include: (1) Surface seawater is supersaturated with respect to a number of carbonate minerals, such as dolomite, calcite and aragonite, but there is little evidence suggesting that this supersaturation is relieved by simple inorganic precipitation; (2) Calcite is more stable than aragonite in seawater, whereas inorganic precipitation of aragonite is more common in tropical surface seawater than that of calcite or Mg-calcite; (3) Dolomite is the most stable carbonate mineral at the surface of the Earth, however, dolomitization rarely occurs in this environment today.

Carbonate sediments are mainly composed of calcite (or Mg-calcite) and aragonite. Because of the relative simplicity of carbonate sediments in terms of their chemical composition, one alternative approach to understanding the relative rates of carbonate formation and diagenetic reactions is the direct rate determination through well-controlled laboratory modeling of natural systems. This approach has proven quite successful. Carbonate mineral reaction kinetics are especially amenable to laboratory study (Morse, 1983). Many studies have been conducted on carbonate-solution (mostly seawater and fresh water) interactions and very fruitful results have come out in the last decade. Results related to this study will be reviewed in the next section and in Chapter II. Briefly, it has been demonstrated that there are many factors which may influence the reaction kinetics of calcite and aragonite (particularly their precipitation and dissolution rates). These factors include: (1) Mg/Ca concentration ratio of the solution (e.g., Berner, 1967, 1975; Chen et al., 1979; Mucci and Morse, 1983); (2) the presence of orthophosphate ions (e.g., Berner and Morse, 1974; Walter and Hanor, 1979; Walter, 1986; Mucci 1986); (3) sulphate concentration of the fluids (e.g., Sjöberg, 1978; Walter, 1986; Mucci et al., 1988); (4) organic coating on carbonate particles (e.g., Berner et al., 1978; Sjöberg, 1978); (5) temperature of the environment (Burton and Walker, 1987; Mucci, 1987); (6)

pressure (Acker et al., 1987); (7) salinity (Folk, 1974; Badiozamani et al., 1977; Chen et al., 1979; Kazmlerczak et al., 1982; Walter, 1986); etc..

Among all the factors mentioned above, salinity is one of the least well studied and understood variables.

I.2 Previous studies:

Carbonate minerals are usually surrounded by seawater and/or seawater related pore waters at the time of their formation and diagenesis. The chemical composition of seawater is best described by its salinity. The relative constancy of composition of seawater in terms of its major elements permits the use of the term "salinity" to describe the concentration of "sea salt" in a sample of seawater. Salinity is a term widely used in the oceanography and sedimentary geology communities. It was originally defined as the weight of inorganic salts in one kilogram of seawater, when all bromides and iodides are replaced by an equivalent quantity of chlorides, and all carbonates are replaced by an equivalent quantity of oxides (Knudsen, 1899; after Wilson, 1975). This definition was, however, soon found to be impractical because of the difficulties encountered in salinity determination. In practice, salinity is most often derived from the chlorinity, specific density or conductivity of the seawater sample. There is a linear correlation between salinity and chlorinity, which is given by the following formula (UNESCO, 1981):

$$S = 1.80655\ Cl \qquad \text{I.1}$$

where S is salinity and Cl is chlorinity.

Since salinity is not defined as a ratio, it should not bear any units (i.e., per mil) as it did in the recent past (e.g., Morse et al., 1984; Fofonoff, 1985).

It has long been realized and it is now well understood that salinity has a strong influence on the thermodynamic behaviour of all species in a solution, such as varying the activities of anions and cations and further, changing the solubilities of solids. The possible influence of salinity on the kinetics of carbonate-solution interactions has been suggested by several geological observations, although little was known about the mechanism behind the effect. For example, James and Choquette (1983b) summarized that aragonite is more common in waters of slightly elevated salinity than in normal seawater. Likewise, Folk (1974) proposed that dissolved Na^+ may act as an inhibitor for calcite precipitation. Further more, it has been repeatedly suggested that salinity could be one of the controlling factors in the process of dolomite formation (e.g., Hanshaw et al., 1971; Folk and Land, 1975), which is mainly a matter of formation kinetics (Morrow, 1982).

A number of laboratory investigations have been made on the possible kinetic influence of salinity on the evolution of carbonate minerals. The results remain incomplete and sometimes controversial.

Badiozamani et al. (1977) studied the influence of salinity on carbonate cementation experimentally and revealed that: (a) cement grain size increases with increasing temperature and NaCl content of solution; (b) cements formed in freshwater and NaCl solutions are calcitic, euhedral, bladed to equant, three sided pyramids, whereas sea water experiments produced pseudohexagonal aragonite whiskers. While the first observation indicates that high salinity inhibits nucleation and enhances crystallization rate, the second seems to suggest that the increase in salinity alone does not have any effect on the mineralogy as well as crystallization habit of the precipitates.

Chen et al. (1979) conducted a laboratory study on the spontaneous nucleation and precipitation rates of carbonate minerals in $CaCl_2$-$MgCl_2$ solutions. Despite of the fact that their experiments were not well controlled, their results suggested that in solutions with a Mg/Ca molar ratio of 5, no change in the mineralogy and nucleation or precipitation rates of the carbonate minerals (i.e., Mg-calcite and aragonite) was brought about by an addition of 3.5 weight per cent of NaCl (equivalent to seawater). Whereas, when up to 13 weight per cent of NaCl were added, the nucleation and precipitation rates of aragonite were increased while that of Mg-calcite were significantly reduced.

Kazmlerczak et al. (1982) found that increasing ionic strength (by adding NaCl) over the range of 0.002 m to 0.200 m had no effect on calcite growth rates in $CaCl_2$ solutions. A recent well-controlled laboratory study by Walter (1986) indicated that calcite growth rates did not change significantly when a certain amount of NaCl was added to the medium to make the ionic strength of the solution equivalent to that of normal seawater (ionic strength = 0.7 m). These results are in agreement with those of Chen et al. (1979) but conflict with Folk's (1974) suggestion.

Apart from the above studies, salinity has not received the attention it deserved. Furthermore, most of the previous experiments were conducted in solutions which differed significantly in composition from seawater. As is the case for other processes (e.g., inhibition, incorporation; Mucci, 1986; Mucci et al., 1988), these results may not be directly applicable to seawater. Consequently, an investigation of the influence of seawater salinity was desirable.

I.3 Objective of this study:

The purpose of this research project was to utilize a well-controlled laboratory experimental approach to investigate the precipitation rates of calcite and aragonite in seawater at various salinities in order to quantify the kinetic effect of salinity of seawater on these rates. The influence of salinity on the composition of the seeded overgrowths (or precipitates) will be the subject of a forthcoming paper.

CHAPTER II

FUNDAMENTAL THERMODYNAMIC AND KINETIC CONSIDERATIONS

II.1 The thermodynamics of the calcium carbonate-seawater system:

The calcium carbonate-seawater system can generally be characterized by the following reactions:

$$CO_{2(g)} + H_2O = H_2CO_3^*{}_{(aq)} \tag{2.1}$$

$$H_2CO_3^*{}_{(aq)} = H^+ + HCO_3^- \tag{2.2}$$

$$HCO_3^- = H^+ + CO_3^{2-} \tag{2.3}$$

$$Ca^{2+} + CO_3^{2-} = CaCO_{3\,(s)} \tag{2.4}$$

where $H_2CO_3^*$ represents the sum of the undissociated CO_2 species (i.e., CO_2 and H_2CO_3) in solution; the subscript "g" indicates the gas phase; "s" refers to a solid; and "aq" marks species in the aqueous phase.

Under equilibrium conditions, the activity of each species can be related to each other according to the following set of thermodynamic constants:

$$K^o_o = (H_2CO_3^*)/f_{CO_2} = [H_2CO_3^*]\gamma_{H_2CO_3^*}/P_{CO_2} \tag{II.1}$$

$$\begin{aligned} K^o_1 &= (H^+)(HCO_3^-)/(H_2CO_3^*) \\ &= (H^+)[HCO_3^-]\gamma_{HCO_3^-}/[H_2CO_3^*]\gamma_{H_2CO_3^*} \end{aligned} \tag{II.2}$$

$$\begin{aligned} K^o_2 &= (H^+)(CO_3^{2-})/(HCO_3^-) \\ &= (H^+)[CO_3^{2-}]\gamma_{CO_3^{2-}}/[HCO_3^-]\gamma_{HCO_3^-} \end{aligned} \tag{II.3}$$

$$K^o sp_c = (Ca^{2+})(CO_3^{2-}) = [Ca^{2+}][CO_3^{2-}]\gamma_{Ca^{2+}}\gamma_{CO_3^{2-}} \tag{II.4}$$

where K^o_o, K^o_1, K^o_2, and $K^o sp$ are thermodynamic equilibrium constants: K^o_o is the solubility of carbon dioxide; K^o_1 and K^o_2 are, respectively, the first and second dissociation constants of carbonic acid in solution; and K^o_{sp} is the thermodynamic equilibrium solubility product of calcium carbonate. The subscript "c" denotes calcite; a subscript "a" will be used in the same manner to denote aragonite. (i), [i], and γ_i are the activity, concentration and activity coefficient of species i in solution, respectively. f_{CO_2} is the fugacity and P_{CO_2} is the partial pressure of carbon dioxide. In eqn II.1, f_{CO_2} is assumed to be equivalent to P_{CO_2}.

To obtain or use these constants, the activity coefficients of the ions involved in each reaction must be known. In dilute solutions (where ionic strength is less than 0.1 m) activity coefficients of ions are generally determined from an extended form of the Debye-Hückel limiting law (Davies, 1962):

$$\log \gamma_i = -0.509\, Z_i^2 \left(1/(1 + I^{1/2}) - 0.3\, I \right) \qquad \text{II.5}$$

where Zi is the charge of ion i and I is the ionic strength, which is defined as:

$$I = 1/2 \sum Z_i^2 [i] \qquad \text{II.6}$$

In more concentrated solutions such as seawater, activity coefficients can be estimated using ion-pairing (e.g., Millero and Schreiber, 1982) or specific interaction (e.g., Pitzer, 1973; Harvie et al., 1984) models.

Although considerable advances have been made in recent years in the interpretation of ionic interactions in multi-component electrolyte solutions (e.g., see Millero and Schreiber, 1982, for detail), problems still persist. This is especially true when high ionic strength solutions such as seawater are involved and when the solution conditions deviate from 25°C and 1 atm. (or the standard conditions). In order to bypass this difficulty, apparent and stoichiometric constants are used in some cases in place of the thermodynamic constants. The apparent or stoichiometric constants are analogous to the thermodynamic constants but defined in terms of the total ionic concentrations (stoichiometric constants) or in terms of both total ionic concentrations and activities (apparent constants). For the calcium carbonate-seawater system:

$$K'_o = [H_2CO_3^*] / P_{CO_2} \qquad \text{II.7}$$

$$K'_1 = (H^+) [HCO_3^-] / [H_2CO_3^*] \qquad \text{II.8}$$

$$K'_2 = (H^+) [CO_3^{2-}] / [HCO_3^-] \qquad \text{II.9}$$

$$\text{and} \quad K^*sp_c = [Ca^{2+}] [CO_3^{2-}] \qquad \text{II.10}$$

where for constants, superscript "'" represents apparent constants and superscript "*" marks a stoichiometric constant.

A comparison between the thermodynamic constants and the apparent or stoichiometric constants reveals that the apparent and stoichiometric constants are simply thermodynamic constants exclusive of the activity coefficients of all (for stoichiometric) or part (for apparent) of the ions involved in each reaction. As activity coefficients are affected by changes in solution composition (e.g., Davies, 1962; Millero and Schreiber, 1982), unlike thermodynamic constants, apparent and stoichiometric constants are not only a function of temperature, pressure, but also of the solution composition.

Most studies in oceanography make use of apparent or stoichiometric constants. These constants are well suited to seawater because of the relative constancy in concentration of its major elements. The composition of the major elements largely determines the activity coefficients. A list of the major components of seawater and their concentrations at salinity 35 is given in Table II.1.

Apparent and stoichiometric constants were also used in this study since they are well established in seawater-like solutions (to be fully discussed later).

Two parameters which are quite useful in characterizing the carbonate-seawater system are total alkalinity (or titration alkalinity) and carbonate alkalinity. The total alkalinity (A_t) is defined as the equivalent sum of bases that are titratable with strong acid (such as HCl) (Stumm and Morgan, 1981). The carbonate alkalinity (A_c) is termed as the equivalent sum of carbonate bases (i.e. HCO_3^- and CO_3^{2-}).

In seawater:

$$A_t = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [H_3SiO_4^-] + [\text{organic anions}] + [OH^-] - [H^+] + \ldots\ldots. \qquad \text{II.11}$$

Since the concentrations of many of these species are negligible in most surface seawaters (e.g., see Table II.1) and our artificial solutions (see Section III.3), the major contributors to the alkalinity are carbonic and boric acid species. As a result, the total alkalinity can be simplified into the following form:

$$A_t \cong [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] \qquad \text{II.12}$$

Table II.1 Major Constituents and Their Concentrations in Normal Seawater (S = 35.00)

Species	gram/kg sw	mole/kg sw
Na^+	10.7822	0.46900
Mg^{2+}	1.2837	0.05282
Ca^{2+}	0.4121	0.01028
K^+	0.3991	0.01021
Sr^{2+}	0.0079	0.00009
Cl^-	19.3529	0.54587
SO_4^{2-}	2.7124	0.02824
HCO_3^-	0.1135	0.00186
Br^-	0.0672	0.00084
T_B	0.0254	0.00041
F^-	0.0013	0.00007

$T_B = [B(OH)_3] + [B(OH)_4^-]$

Sources: Kester et al. (1967) and Millero (1974)

By definition:

$$A_c = [HCO_3^-] + 2\,[CO_3^{2-}] \qquad \text{II.13}$$

Thus, $A_t \cong A_c + [B(OH)_4^-]$ II.14

It must be pointed out that titration alkalinity is independent of P_{CO_2}, as carbon dioxide does not directly affect the charge balance of the solution. In other words, the reaction between CO_2 and seawater does not change the concentration of total titratable bases in the solution.

The first dissociation of boric acid is represented by:

$$B(OH)_3 + H_2O = B(OH)_4^- + H^+ \qquad 2.5$$

At equilibrium:

$$K'_B = (H^+)[B(OH)_4^-]/[B(OH)_3] \qquad \text{II.15}$$

where K'_B is the first apparent dissociation constant of boric acid in solution.

The second dissociation reaction of boric acid, for which the equilibrium constant is more than three orders of magnitude smaller than the first one (CRC Handbook, 1975, p.D-130), can be ignored for most practical purposes:

$$pK^o_{B1} = 9.14,\ \text{while}\ pK^o_{B2} = 12.74$$

Given the above considerations, the following equation is obtained:

$$[B(OH)_4^-] = T_B / ((H^+)/K'_B + 1) \qquad \text{II.16}$$

where T_B is the total boric acid concentration in seawater. It is more or less conservative in seawater and can be obtained from the following relation (Culkin, 1965):

$$T_B = 0.00001174\ S \qquad \text{II.17}$$

The degree of saturation of calcium carbonate in seawater is characterized by the saturation state (or saturation index, SI). For calcite:

$$SI_c = (Ca^{2+})(CO_3{}^{2-})/K^{o}sp_c = [Ca^{2+}][CO_3{}^{2-}]/K^{*}sp_c \qquad II.18$$

When $SI_c < 1$, the solution is undersaturated with respect to calcite and the dissolution of solid calcite, if present, should occur. When $SI_c = 1$, the system is at equilibrium. While if $SI_c > 1$, the solution is supersaturated. Under conditions of supersaturation, precipitation of calcite will occur, provided seeds are present in the solution or the supersaturation is high enough to induce spontaneous nucleation.

A similar parameter (i.e., SI_a) and scenario can apply to aragonite.

The calcium concentration in solution can be analyzed directly (to be fully discussed later), while the carbonate concentration in solution cannot. Given that carbonic and boric acid species in solution are in equilibrium, it can be obtained indirectly from any two of the four following measureable parameters: pH, A_t, Pco_2, and ΣCO_2. ΣCO_2 is the sum of all the dissolved carbonate species, and is defined as:

$$\Sigma CO_2 = [H_2CO_3{}^{*}] + [HCO_3{}^{-}] + [CO_3{}^{2-}] \qquad II.19$$

The combination of parameters for which the analytical equipment is most readily available and perhaps the most frequently used combination is the pH-A_t pair of the solution (e.g., Millero, 1979; Morse and Berner, 1979; Mucci, 1986; 1987; Burton and Walter, 1987). A consideration of eqns. II.9, II.13, II.14, and II.16 results in the following relationship:

$$[CO_3{}^{2-}] = \frac{A_t - T_B / ((H^+)/K'_B + 1)}{(H^+)/K'_2 + 2} = \frac{A_C}{(H^+)/K'_2 + 2} \qquad \text{II.20}$$

This equation gives the formula for calculating the concentration of carbonate ions in solution from the directly measured data (i.e., A_t and pH).

The solution pH is a very important parameter in terms of defining the thermodynamic characteristics of the carbonic acid system. The relative abundance of different species of carbonic acid in solution is a function of the pH of the solution. This relation is clearly shown by a Bjerrum diagram (Figure II.1). For most of the waters on the surface of the Earth, their pH is mainly controlled by the carbonic acid system.

II.2 The kinetics of the calcium carbonate precipitation reations.

As mentioned in Chapter I, the calcium carbonate precipitation processes in seawater are basically kinetically dominated. It is often more appropriate to treat the system by a kinetic approach.

The main difference between a thermodynamic approach and a kinetic one is that while thermodynamics identify a point toward

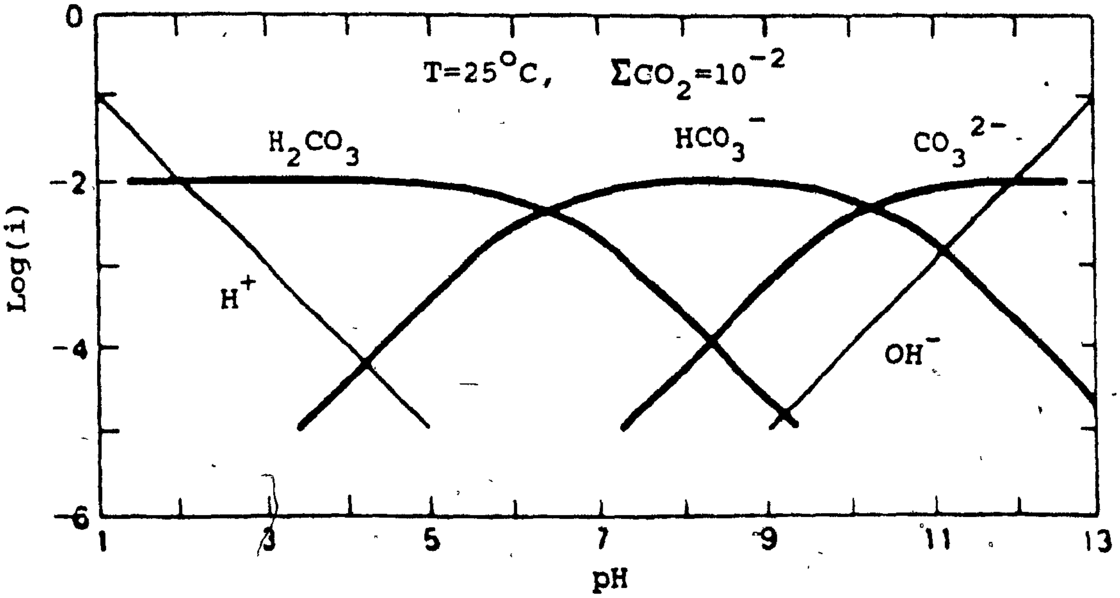


Figure II.1 Bjerrum Plot of Carbonate-Water System

(From Drever, 1982)

which the reactions progress, kinetics focus on finding the reaction path and therefore, the reaction mechanisms and their rates. Thus, a kinetic study will give much more insight into the development of a reaction than thermodynamics do. In fact, thermodynamic equilibrium of a reaction can be treated as a specific case in the field of kinetic study. For example, the thermodynamic equilibrium, from a kinetic point of view, is the state at which the forward and backward reaction rates (assuming the stoichiometry of the reactions are the same) are equal to each other so that no net change occurs.

A basic idea in the study of reaction kinetics (e.g., inhibition and/or catalysis mechanisms) is that under a given set of conditions, one mechanism will be slower than others. The slowest mechanism is generally called the rate controlling mechanism. The rate controlling mechanism for solid-solution (i.e., dissolution and precipitation) reactions is generally one of the two following types: (1) diffusion control (or transport control), where the diffusion to or from the surface of the solid controls the rate of the reaction, and (2) surface reaction control, where reactions occurring on the surface of the solid (e.g., dehydration, segregation, etc.) determine the rate. Different mechanisms dominate the reaction kinetics under different conditions.

Extensive studies have demonstrated that in highly under-saturated solutions, the rate of calcite dissolution is controlled by diffusion processes between the mineral surface and the bulk solution. On the other hand, closer to equilibrium the rate is limited by surface reaction processes (Berner and Morse, 1974; Plummer and Wigey, 1976; Plummer et al., 1978, 1979; Richard and Sjöbery, 1983; Morse, 1983). It has been confirmed that above a pH of 4, the dissolution of calcite is controlled largely by surface reactions (Reddy and Nancollas, 1971; Nancollas and Reddy, 1971; Berner and Morse, 1974; Plummer and Wigley, 1976; Sjöberg, 1976; Sjöberg and Richard, 1984; Plummer et al., 1978; Morse, 1983).

The kinetics of calcite precipitation received less attention than that of its dissolution reactions. It is generaly agreed that the precipitation reaction of calcite is mainly controlled by surface reactions, although the mechanism(s) of the reactions are poorly defined (Plummer et al., 1978). Even less research has been done on the aragonite precipitation kinetics (Berner, 1975; Berner et al., 1978; Walter, 1986; Burton and Walter, 1987; Mucci et al., 1988). Fortunately, all these studies have indicated that the aragonite precipitation is most likely a surface-reaction dominated process which is comparable to the calcite precipitation process.

The prediction of the rates of surface reactions is very complex since it requires knowledge of reaction mechanisms and their individual rates. The surface reactions are further complicated by, firstly, the ionic concentration differences between bulk solution and mineral surface; and secondly, the influences of "foreign ions" in seawater on the dissolution and precipitation of calcium carbonate. "Foreign ions" in this study refers to those ions which are present in the solution but are not the major participants in the overall reaction(s). For example, for reaction 2.4, ions other than Ca^{2+} and $CO_3{}^{2-}$ in seawater are called "foreign ions".

Many rate equations based on kinetic modelling have been used to fit the dissolution and precipitation kinetic data under restricted sets of solution conditions. The most successful and widely accepted model was the Plummer et al. (1978) mechanistic model. This model described three different dissolution mechanisms which occur simultaneously while a single reaction dominates the process under given solution conditions (i.e., pH, Pco_2, and others) (House, 1981a, b; Reddy et al., 1981; House and Tutton, 1982; Morse, 1983; Inskeep and Bloom, 1985; Buhmann and Dreybrodt, 1987). The three reactions describing the mechanisms are:

$$CaCO_{3(s)} + H^+ = Ca^{2+} + HCO_3{}^- \qquad 2.6$$

$$CaCO_{3(s)} + H_2CO_3{}^* = Ca^{2+} + 2HCO_3{}^- \qquad 2.7$$

$$CaCO_{3(s)} + H_2O = Ca^{2+} + HCO_3{}^- + OH^- \qquad 2.8$$

The Plummer et al. (1978) model also proved to be well suited for the precipitation mechanisms of calcium carbonate (Reddy et al., 1981; House, 1981a, b).

A recent paper by Inskeep and Bloom (1985), however, indicated that at pH above 8 and Pco_2 less than 0.01 atm (similar range as used in this study), the Plummer et al. (1978) mechanistic model could not adequately describe their experimental data. Furthermore, the Plummer et al. (1978) model suffers from the fact that parameters such as the solid surface P_{CO_2} and pH values, which are vitally important in the modelling process, cannot be measured directly.

As an alternative, an empirical approach has been used in many carbonate kinetic studies, of both dissolution (Sjöberg, 1976; Morse and Berner, 1979; Walter and Morse, 1985; Walter, 1986) and precipitation reactions (Nancollas and Reddy, 1971; Mucci and Morse, 1983; Inskeep and Bloom, 1986; Mucci, 1986; Burton and Walter, 1987; Mucci et al., 1988). This approach does not attempt to treat data in a manner based on a mechanistic model or a series of elementary reactions (Morse, 1983), but on the overall reaction rate (e.g., reaction 2.4). It treats the reaction rate in terms of an empirical reaction order and rate constant.

The general form of the equations, which have been found to fit most of the surface controlled kinetic data for calcium carbonate, is (Morse, 1983):

for dissolution: $$R = k(1 - SI)^n \qquad \text{II.21}$$

for precipitation: $$R = k(SI - 1)^n \qquad \text{II.22}$$

where n is the empirical reaction order and k is the rate constant.

In logarithmic form these equations become simple and linear:

$$\log R = n \log (1 - SI) + \log k \qquad \text{II.23}$$

$$\log R = n \log (SI - 1) + \log k \qquad \text{II.24}$$

Therefore, it is possible to simply fit data to these linear equations and determine the order of the reaction from the slope and the rate constant from the intercept.

The empirical form for precipitation (i.e., eqn. II.22) shows that the precipitation rate is directly linked to the degree of supersaturation (i.e., (SI-1)) rather than the saturation state (SI) itself. The rationale behind this expression stems from crystal growth theory, the net measured precipitation rate being the difference between the forward reaction (i.e., precipitation) and backward reaction (i.e., dissolution) rates (Lasaga, 1981). For example, at equilibrium, or when the degree of disequilibrium equals zero, the precipitation rate is equal to the dissolution rate. In this case, the net rate (or the measured rate) equals zero. It is the degree of disequilibrium (or the distance from the equilibrium), instead of the saturation state, which controls the measured precipitation rate. When other factors (e.g., T, P, etc.) are kept constant for a series of experiments, the relation between the measured precipitation rate and the corresponding degree of disequilibrium should follow the empirical rate law defined by equation II.22. The same reasoning applies for the dissolution kinetics, or to equation II.21.

The empirical rate law described by equations II.22 or II.24 was used to analyze and fit the rate data obtained in this study.

II.3 The function of salinity:

Salinity, as defined in Chapter I, is a way to express the sum of all the components in natural waters. In seawater, the major constituents which contribute to the salinity are Na^+, Cl^-, Mg^{2+}, Ca^{2+}, $SO_4{}^{2-}$, K^+, and $HCO_3{}^-$ (see Table II.1). A unique and important characteristic of seawater, as mentioned before, is the constancy of the relative concentrations of those major constituents over a wide range of salinity values. Under this special circumstance, the compositional dependence of the stoichiometric and apparent constants of the calcium-carbonic acid-seawater system (i.e., reactions 2.1, 2.2, 2.3, and 2.4) can be simplified to a function of salinity. Also, there is a direct link between salinity and ionic strength in seawater (Millero, 1983, after Mucci, 1983):

$$I = 0.0199201\ S \qquad \text{II.25}$$

A general theory of ionic strength effects on rates of reactions in aqueous solution, called the primary kinetic salt effect, is based on the assumption that reaction rates are proportional to the activity of ions in the activated state. Thus, a reaction rate will be varied by the activity coefficient of the activated complex, which in turn is a function of ionic strength (Bischoff, 1968).

In fact, if the individual behaviour of those ions composing the salinity and ionic strength of seawater is considered, salinity or ionic strength can affect a reaction in two ways. One is thermodynamic and the other is kinetic.

The abundance of each ion changes the ionic strength of a solution. This is called the ionic strength effect. Some ions may exhibit common-ion effect, while some others might form ion-pairs. All these interactions and others can influence the activity coefficient (γ_i) of each ion and thus the rates of the reactions in which these ions are involved. Hence, the thermodynamic influence of salinity on reaction kinetics is by altering the activity coefficients of those substances (ions, complexes, compounds, etc.), which are involved in the reactions, through ionic strength, common-ion, and ion-pair effects.

For calcium carbonate precipitation reactions in seawater, the salinity effects on the activity coefficients of calcium and carbonate ions will alter the saturation state of the solution with respect to solid $CaCO_3$ phases and thereby, the precipitation rates.

It is important to note that the thermodynamic influences of salinity on a dissolution or precipitation reaction is related only to changes in the stoichiometric solubility (in terms of concentrations) of the solid.

The second effect is related to the involvement of some of the foreign ions in the surface reaction processes of the precipitation or dissolution. This involvement may interfere with the surface reaction processes and therefore, the rates of these processes. The interference is either through the adsorption of foreign ions at active growth sites on the solid surface or by forming intermediate compounds with the reactants and/or products to inhibit or catalyse the surface reactions. The occupation of foreign ions at active growth sites on the solid surface may inhibit one of the reactants from approaching the solid surface to form the precipitate.

Fortunately, it is possible to differentiate these two types of effects in the calcium carbonate-seawater system. The stoichiometric solubility products of calcite and aragonite have been determined as a function of salinity (Mucci, 1983). The kinetic data (or precipitation rates) are expressed as a function of the saturation state, which takes into account the variations of stoichiometric solubility caused by the thermodynamic effects of salinity. Precipitation rate variations of calcite (or aragonite) measured in seawater solutions of different salinity but identical saturation state could only be due to the kinetic effects of salinity on the precipitation reactions if all other conditions (i.e., Pco_2, pH, T, ...) were also maintained constant.

As a matter of fact, many previous studies of individual ions in seawater, such as Mg^{2+}, $SO_4{}^{2-}$, $PO_4{}^{3-}$, have demonstrated that these foreign ions exhibit both thermodynamic and kinetic influences on the calcium carbonate precipitation and dissolution reaction rates. The kinetic effects of Mg^{2+}, $SO_4{}^{2-}$, $PO_4{}^{3-}$ are significant and selective with respect to different calcium carbonate minerals (i.e., calcite and aragonite).

The special role of magnesium ions has attracted much of the attention. A quantitative experimental study by Mucci and Morse (1983) demonstrated that the kinetic effect of Mg^{2+} on the calcite precipitation rate is significant. They attributed the inhibition mechanism to the impingement of hydrated Mg^{2+} ions (which has a smaller size, higher charge density, and therefore, a stronger potential of hydration than Ca^{2+} ion) on the crystal lattice of calcite at active growth sites. The amount of Mg^{2+} incorporated in the overgrowth was controlled by the Mg/Ca ratio of solution and was independent of precipitation rate (Mucci and Morse, 1983). Obviously, Mg^{2+} is kinetically involved in the calcite precipitation reactions.

It has been found that the presence of sulphate ions in solution hinders both calcite dissolution and precipitation rates (Sjöberg, 1978). Both calcite and aragonite precipitate at much slower rates in the presence of sulphate (Walter, 1986). A recent study (Mucci et al., 1988) indicates that dissolved sulphate ions inhibit the precipitation rates of both calcite and aragonite to the same degree. The $MgCO_3$ incorporation in calcite is influenced significantly by the presence or absence of the sulphate ions. More $MgCO_3$ is incorporated in calcite precipitated from sulphate-free seawater than from normal seawater, if all the other conditions are kept constant (Mucci et al., 1988). The detailed suphate inhibition mechanism remains unknown.

Phosphate ions strongly impede both the precipitation and dissolution rate of calcite. Studies of the precipitation of calcite from both dilute electrolyte solutions (Reddy, 1977; Sjöberg, 1978) and artificial seawater (Mucci, 1986; Walter, 1986) have shown that micromolar concentrations of phosphate can significantly lower the precipitation rates of both calcite and aragonite. The inhibition mechanism is believed to be related to crystal poisoning by phosphate. The adsorption of the PO_4^{3-} ion at the most energetic sites on the solid surface (such as holes, kinks, steps, etc.) is blamed for the precipitation inhibition (Mucci, 1986). Phosphate appears to be selective in inhibiting aragonite precipitation (Walter, 1986).

The remaining major species in seawater that have not been discussed so far are Na^+, Cl^- and K^+. As mentioned earlier, geologic observations suggested that dissolved Na^+ may act as an inhibitor of the calcite precipitation reactions, while laboratory studies seem to contrast with this suggestion (see Section I.2).

It is quite reasonable to conclude that some of the foreign ions do kinetically inhibit the precipitation rate of calcium carbonate. Previous quantitative studies have provided information for better understanding of the inhibition mechanisms of these individual ions. Nevertheless, the kinetic influence of the change of salinity, which is more closely related to some geological and oceanographic processes (such as evaporation and fresh water dilution of seawater) than the change of concentration of individual ions, on calcium carbonate precipitation rates need to be quantitatively addressed.

A chemo-stat system (Morse, 1974) with a seeded growth technique (Reddy and Nancollas, 1971) was used in this study to systematically investigate the influence of changing salinity on the precipitation rates of calcite and aragonite in seawater solutions at 25°C and one atmospheric total pressure.

CHAPTER III

EXPERIMENTAL PROCEDURES

III.1, Principle of the chemo-stat system:

The chemo-stat system, whose purpose is keeping the solution composition close to constant during a reaction (e.g., precipitation, dissolution, etc.), was first introduced by Morse in 1974 (Morse, 1974) for the experimental study of carbonate mineral kinetics. It is an open system in which the concentrations of all the reactants are kept constant or the system is at a steady state of disequilibrium.

The working principle of the chemo-stat technique and its application to the study of carbonate precipitation comes from the consideration of the following reaction:

$$(1-x-y)Ca^{2+} + xMg^{2+} + ySr^{2+} + CO_3{}^{2-} = Ca_{(1-x-y)}Mg_xSr_yCO_3 \quad 3.1$$

The forward reaction which is believed to best represent the precipitation of calcium carbonates (i.e., calcite and aragonite) shows that if the composition of the reacting solution, especially the Ca^{2+}, Mg^{2+}, Sr^{2+}, and $CO_3{}^{2-}$ concentrations in solution remain unchanged while the reaction is progressing, the $CaCO_3$-seawater system is at a steady state of disequilibrium, or constant saturation state according to eqn. II.18.

Technically, the constancy of the concentrations of Ca^{2+}, Mg^{2+}, Sr^{2+}, and $CO_3{}^{2-}$ in solution is achieved by simultaneous injection of two titrants in equal amounts by a dual syringe pump to the reacting system. For each experiment, the injection rate is set in order for the mixture of the two titrants to reproduce the exact composition of the precipitating solution plus an excess in calcium, strontium, and carbonate alkalinity to compensate for the carbonate precipitation. No compensation for magnesium was attemped since the amount of magnesium incorporated in calcite (or aragonite) was insignificant compared with the amount of magnesium ions contained in the solutions. The compensation mechanism can be represented by Figure III.1.

The supply rate of excess calcium ions to the system can be determined by the following relationship based on the mechanism presented in the figure:

$$Rs(Ca^{2+}) = Ri \ ([Ca^{2+}]_{t.t.} - 2 \ [Ca^{2+}]_{s.}) \qquad III.1$$

where $Rs(Ca^{2+})$ is the supply rate (mole/hr) of excess calcium ions to the system. Ri is the injection rate (kg/hr) of the "Cation" titrant. Subscripts "t.t." and "s." represent titrant and reacting solution, respectively.

The supply rate of excess carbonate ions was calculated by the following equation:

$$Rs(CO_3{}^{2-}) = Ri \ ((A_C)_{t.t.} - 2 \ (A_C)_{s.})/2 \qquad III.2$$

Since the carbonate ionic concentration is not a directly measureable parameter, the supply rate of the excess carbonate ions is expressed as half the injection rate of excess carbonate alkalinity. Excess carbonate alkalinity can be converted into an excess of carbonate ionic concentration in consideration of the charge and mass balance of the reaction. The speciation of carbonate species in the titrant is modified as the titrant is

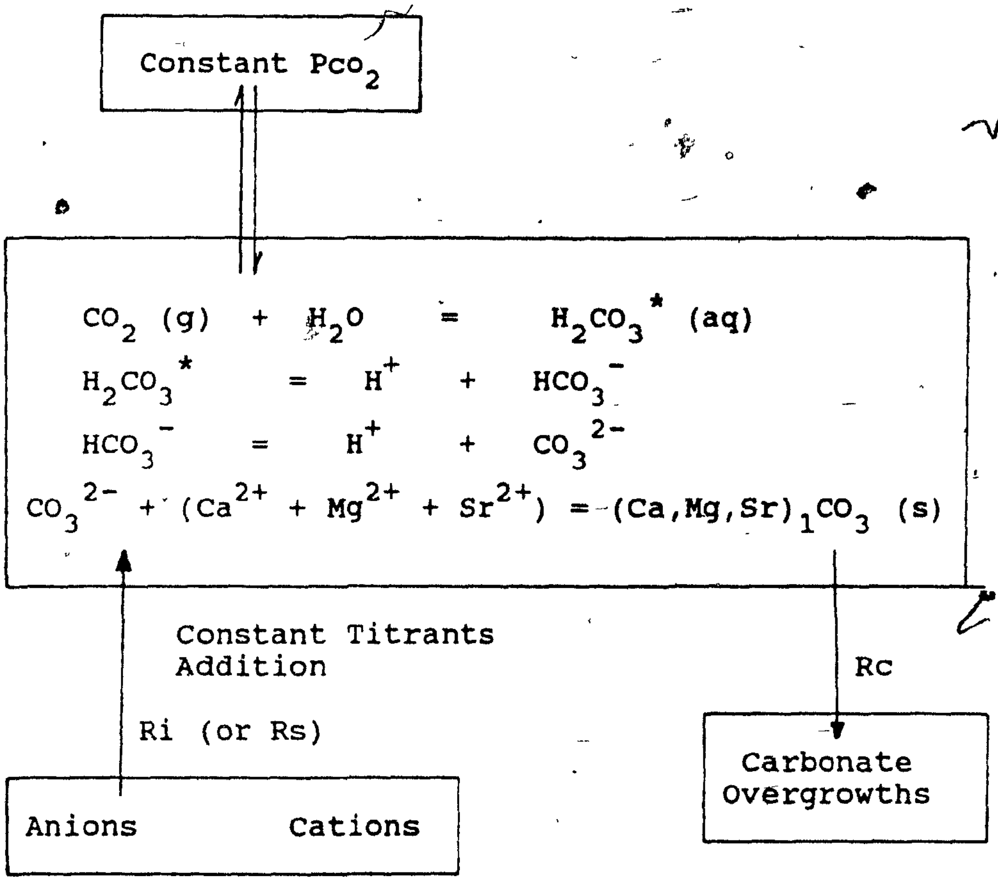


Figure III.1 Schematic Diagram of the Working Principle of the Chemo-Stat System used in this Study injected and equilibrated with the precipitating solution.

In addition, the titrant solution pair (i.e., cations vs. anions) was prepared so that the excess carbonate alkalinity content in one titrant was approximately equal to twice the excess calcium ionic concentration in the other. Thereby:

$$Rs(Ca^{2+}) \cong Rs(CO_3{}^{2-}) \qquad \text{III.3}$$

At steady state, the rate of supply of excess calcium ions and excess carbonate ions should equal the rate of their consumption, respectively. Since the only process responsible for the consumption of these ions in the system is the precipitation of calcium carbonate, the steady state precipitation rate was directly related to the injection rate of titrant. In this study, the precipitation rate was normalized to the reactive surface area of seeds in order to eliminate its influence on the precipitation rate. Variations in reactive surface area result in proportional changes in reaction rates. The correlation between normalized steady state precipitation rate and the injection rate of one of the titrant can be expressed as:

$$R\ A\ W_{s.d.} = Ri\ ([Ca^{2+}]_{t.t.} - 2\ [Ca^{2+}]_{s.}) \qquad \text{III.4}$$

and $$R\ A\ W_{s.d.} = Ri\ ((A_c)_{t.t.} - 2\ (A_c)_{s.})/2 \qquad \text{III.5}$$

where R is the normalized steady state precipitation rate (mole/hr m^2). A is the reactive surface area (m^2/g) of the seed. $W_{s.d.}$ is the weight (g) of seeds introduced into the solution.

The left side of the equation represents the consumption rate (Rc, mole/hr) of either calcium ions (eqn. III.4) or carbonate ions (eqn. III.5), while the right side is the supply rate (Rs, mole/hr) of excess calcium ions (eqn. III.4), or that of excess carbonate alkalinity (eqn. III.5).

The injection rate (Ri), which was set at the beginning of each experiment, was selected on the basis of the results of preliminary runs so that Rs was as close to Rc as possible at the time each experiment started. An advantage of this constant rate of addition system is that if there is any difference between the two rates at the initial stage of the experiment, the system will automatically adjust itself to reach a steady state after a very short period of time. For example, if Rs is higher than Rc when the experiment begins, part of the excess amount of CO_3^{2-} and Ca^{2+} will remain in the solution and the saturation state of the system will rise. The increase of saturation state, in turn, will cause an increase of the consumption rate, Rc. This process will continue until Rc equals Rs. Since Rs is set at the beginning of the experiment and there usually was a small difference between Rs and Rc, the time required for the adjustment process to complete was always shorter (< an hour) than the length of experiment (> one and half hours). Steady state was achieved when Rc equaled Rs. Similar processes of spontaneous adjustment will happen if Rs is lower than the initial Rc for an experiment.

The attainement of a steady state of disequilibrium can easily be observed by monitoring the pH in response to the quasi-instantaneous equilibrium state of the carbonic acid species in solution. A combination of eqns II.7 to II.9 results in:

$$[CO_3{}^{2-}] = K'_0\ K'_1\ K'_2\ Pco_2/\ (H^+)^2 \qquad \text{III.6}$$

Pco_2 was kept constant for all the experiments conducted in this study (see section III.2). Based on the above equation, $[CO_3{}^{2-}]$ is constant when the pH of the solution is stable. A steady state of disequilibrium is maintained, provided $[Ca^{2+}]$ remains constant.

An additional great advantage of utilizing this technique in studying carbonate reaction kinetics is that it allows factors other than the one being investigated to be kept at a desired, known, and constant state during the length of the experiment. Precise precipitation rate measurements (± 10% for calcite and aragonite, see Walter, 1986) at a known and constant saturation state are possible.

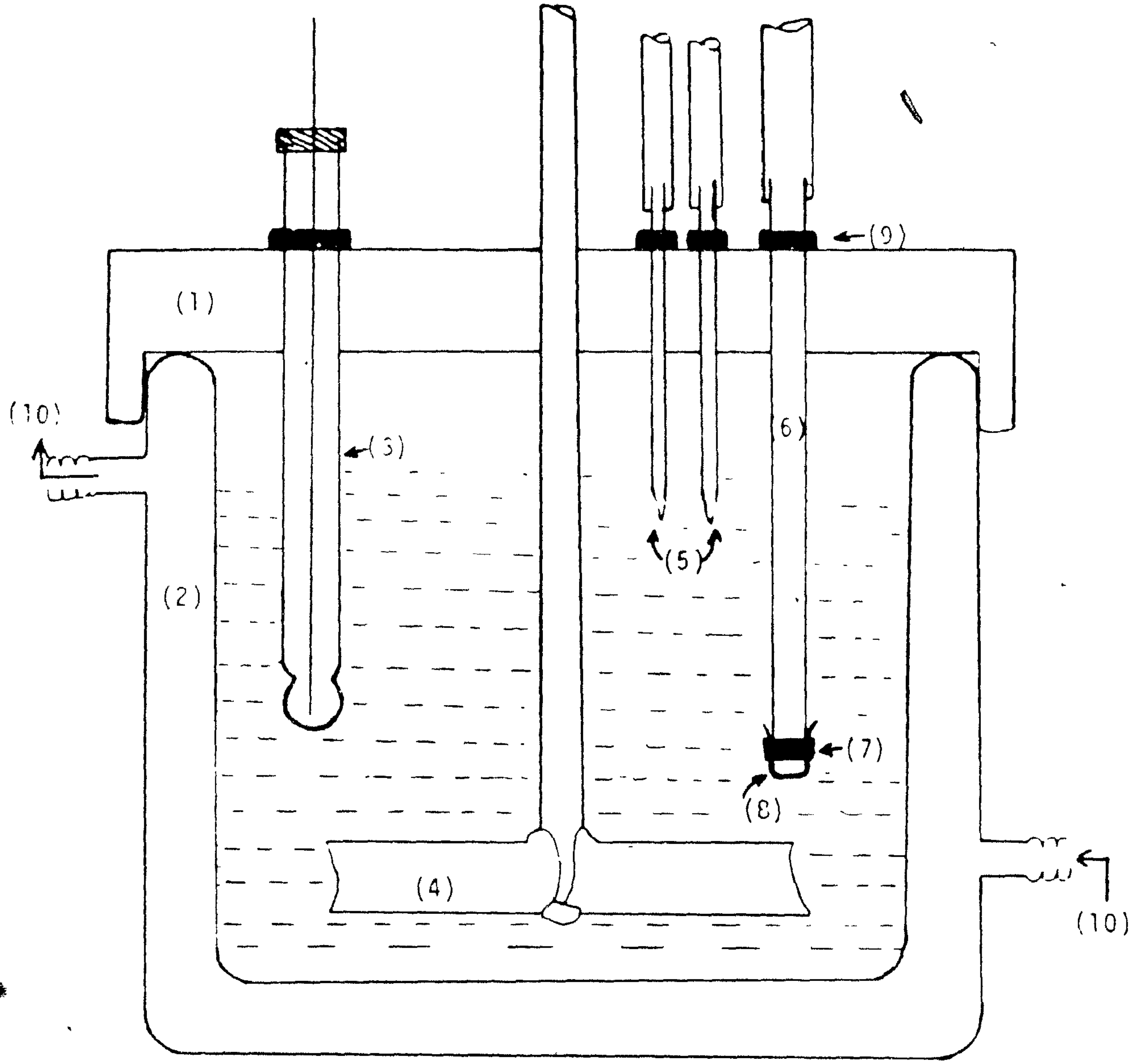
The seeded growth technique (Reddy and Nancollas, 1971) was applied in this study. It has been demonstrated that the mineralogy of carbonate precipitated from seawater is controlled by the mineralogy of the seed (e.g., Mucci, 1983; Walter, 1986; Burton and Walter, 1987). In other words, while only calcite or Mg-calcite precipitate on calcite seeds, only aragonite precipitates on aragonite seeds. This unique characteristic makes it possible for us to conduct the experiment on a certain mineral phase without worrying about the interference of other mineral phases. Furthermore, the application of the seeded growth technique in this study allowed the precipitation reaction to occur on a well-defined surface of known surface area and morphology (see section III.3), and thus yield highly reproducible results (Reddy and Nancollas, 1971; Kazmierczak et al., 1982).

As solutions are phosphate and dissolved organic carbon (DOC) free, and other parameters that may influence the normalized precipitation reaction rate (e.g., salinity, Mg/Ca, $[SO_4^{2-}]$, T, P, Pco_2) were maintained constant for a given series of experiments, the precipitation rate is believed to be strictly a function of saturation state with respect to the seed material (i.e., calcite or aragonite): $R=f(SI)$. The influence of salinity on the precipitation rate was investigated by repeating measurements in solutions of various salinities (i.e., 5, 15, 25, 35, and 44).

III.2 Experimental Devices:

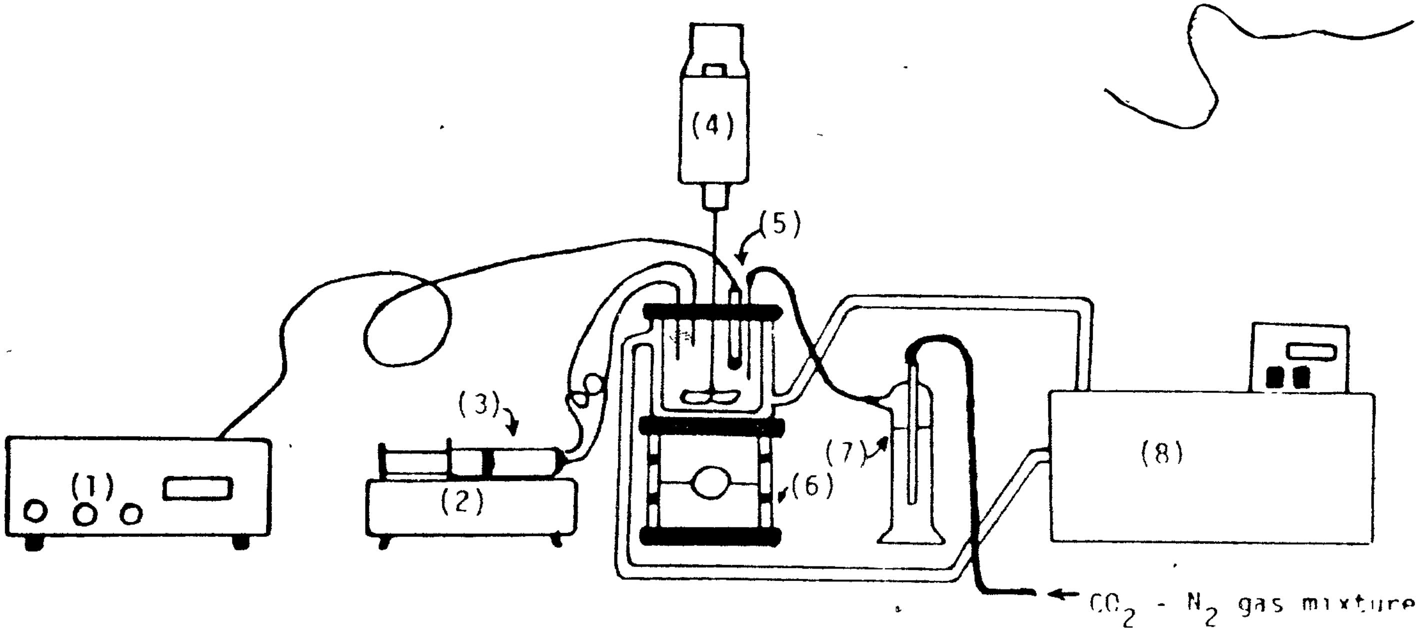
Schematic diagrams of the experimental devices are given in Figure III.2 and Figure III.3.

The reaction vessel, shown in Figure III.2, consisted of a water jacketed glass vessel with a total volume of approximately 450 ml. It was covered with a fitted PVC cap 2 cm thick. Holes bored through the cap allowed the bubbler, stirrer, electrodes and injection tips of the syringes delivering the two titrant solutions to come in contact with the reacting solution. Pieces of "Tygon" tubing were used as support collars. They permitted all the above outlined pieces, except for the stirrer, to be positioned at the desired level.



(1) PVC Cap
(2) Water Jacketed Glass Vessel
(3) Combination Glass/Reference Electrode
(4) Glass Stirrer
(5) Titrant Injection Ports
(6) Glass Bubbler
(7) & (9) Tygon Tubing Collars
(8) 0.45 micron Nuclepore Filter
(10) Circulating Constant Temperature Water

Figure III.2 Reaction Vessel



(1) pH Meter (2) Dual Syringe Pump
(3) Syringes (4) Adjustable Electric Motor
(5) Reaction Vessel (see Figure III.2 for detail)
(6) Laboratory Jack (7) Gas Scrubber
(8) Recirculating Constant Temperature Bath

Figure III.3 Precipitation Experiment Devices

The CO_2/N_2 gas mixture was supplied by high pressure 120 cu.ft. gas cylinders purchased from Liquid Carbonic Inc., Canada, with P_{CO_2} of approximately 0.3 %. Since the gas mixtures are water-free, the gas was bubbled through distilled water before being introduced into the reacting solution to prevent excessive evaporation of water. The bubbler was constructed from a glass tube fitted with a 0.45 micron Nuclepore filter held on by a small piece of "Tygon" tubing. The filter was replaced after every experiment to avoid contamination, especially by seed material and inhibitors such as PO_4^{3-}, SO_4^{2-}, Mg^{2+}, etc., through adsorption and desorption from one solution to the other.

The two titrant solutions were delivered to the reaction vessel by a Harvard Apparatus Model 975 pump. B-D brand disposable syringes with volumes of 60 ml, 20 ml, 10 ml, and 1 ml were used in order to obtain the desired injection rate for each experiment. The two syringes were connected to the reaction vessel by "Tygon" tubing fitted with glass capillary tips.

Temperature of the reacting solution was maintained constant at 25 ± 0.1°C by recirculating water from a "Brinkmann" (Model RM20) constant temperature bath through the water jacketed reaction vessel.

Stirring of the solution was provided by a two-bladed glass propeller-type stirrer, powered by an adjustable electric motor ("Caframo", Model RZR 1) mounted above the reaction vessel. This type of stirring system was utilized to prevent grinding of the calcium carbonate particles against the bottom of the reaction vessel. Stirring with a magnetic stirrer could result in an increase of the reactive surface area and in consequence cause a variation of the reaction rate. The stirring speed was chosen as the minimum value for keeping the seed material in suspension and was maintained at the same value for all the runs conducted in this study.

The system used in this study is similar to the one designed and used by Mucci and Morse (1983) with a slight modification of work procedure. A detailed description of the system was also provided by Mucci and Morse (1983) and Mucci (1986).

III.3 Materials:

A. Solutions:

Aged artificial seawater was used for all experiments carried out in this study. Artificial seawater of salinity 44 was prepared to include all major elements with the exception of HCO_3^- but including F^-, according to the method of Kester et al. (1967) modified slightly to fit the analyses of Millero (1974). Reagent grade chemicals were used for the preparation. The solution was stored for at least two months in polyethylene carboys. This procedure was used to reduce the amount of dissolved phosphate through adsorption on the walls of the container since it is a known $CaCO_3$ precipitation inhibitor. The precipitation kinetics of calcite in natural and artificial seawater have been shown to be very similar (Mucci and Morse, 1983). Seawater solutions of lower salinity were prepared by dilution with distilled water.

To a portion of the original solution (A) 14 meq/kg of $NaHCO_3$ was added in order to yield a solution (B) which would be highly supersaturated with respect to calcite (SI_c=31.2) at a Pco_2=0.003 atm. Solution B was equilibrated with pure carbon dioxide (SI_c=0.14 at Pco_2=1 atm) and kept in a refrigerator in order to prevent spontaneous nucleation. An example of the detailed compositions of solutions A and B of salinity 44 are given in Table III.1. A reacting solution of desired salinity and carbonate alkalinity was obtained by mixing weighed amounts of the two solutions, A and B, before the experiment. Solutions of identical salinity and carbonate alkalinity will have a corresponding and known saturation state at a given Pco_2 and temperature according to eqns. III.6; II.18 and II.20, provided their $[Ca^{2+}]$ is identical.

B. Titrants:

Two titrant solutions were used for maintaining the composition of the reacting solution constant during the experiment. The first titrant contained Na_2SO_4, NaF, and KBr in concentrations equal to twice those prescribed for preparing artificial seawater of the correspinding salinity. It also contained an excess of carbonate alkalinity added in the form of Na_2CO_3 and $NaHCO_3$. The second titrant solution contained $MgCl_2$, $SrCl_2$, $CaCl_2$, KCl and $B(OH)_3$ in twice the concentration of the prescribed amount for producing artificial seawater of the desired salinity. For calcite precipitation experiments, an

Table III.1 Composition of 1 kg of Artificial Seawater with Salinity = 44.00

Species	Concentration (mole/kg sw)	
	Solution A	Solution B
Na^+	0.58960	0.60360
Mg^{2+}	0.06640	0.06640
Ca^{2+}	0.01292	0.01292
K^+	0.01284	0.01284
Sr^{2+}	0.00011	0.00011
Cl^-	0.68624	0.68624
$SO_4{}^{2-}$	0.03550	0.03550
Br^-	0.001056	0.001056
T_B	0.00052	0.00052
F^-	0.00009	0.00009
$HCO_3{}^-$	0.00000	0.01400

excess of $CaCl_2$ equivalent to about half of the excess alkalinity of the first titrant solution was added to the second titrant to compensate for calcium carbonate precipitation. For aragonite precipitation runs, an excess of $CaCl_2$ and $SrCl_2$ with total concentration of half of the excess alkalinity of the first titrant solution was added. The excess $SrCl_2$ was approximately 0.00011 mole/kg. NaCl was then added to both titrant solutions so that they contained similar salt concentrations and to reestablish an ionic strength equivalent to the reacting solution after the mixing process was completed and the excess amount of Ca^{2+}, Sr^{2+} and carbonate had been precipitated. An example of the composition of the titrant solutions is given in Table III.2.

Results of preliminary experiments were used to make the required adjustments to the composition of the titrant solutions in order to maintain the composition of the reacting solution invariant during the precipitation reaction. This was a trial and error process. It was therefore possible to minimize the calcium and strontium concentration variations in the reacting solution from the initial concentrations.

As mentioned previously, no excess magnesium was mixed into the titrants since in all cases the amount of magnesium incorporated in the overgrowth was negligible compared to the reacting solution concentration. A simple mass balance calculation will demonstrate that the Mg^{2+} concentration in the solution is basically constant even if the calcium carbonate

Table III.2 Recipes of Titrant Solutions for the Precipitation Experiments of Calcite and Aragonite Conducted in Solutions with S=44.00 and SI_c=5.0 at P_{CO_2}=0.3% atm.

A. Recipes of "Cation" Titrant Solutions:

	For Calcite		For Aragonite	
	mole/kg	g/kg	mole/kg	g/kg
$MgCl_2$	0.1328	12.644	0.1328	12.644
$CaCl_2$	0.02584	2.8679	0.02584	2.8679
$SrCl_2$	0.00022	0.03488	0.00022	0.03488
KCl	0.02356	1.7565	0.02356	1.7565
$B(OH)_3$	0.001033	0.06386	0.001033	0.06386
$CaCl_2$	0.02000	2.2200	0.01989	2.2075
$SrCl_2$	0.00000	0.0000	0.00011	0.01744
NaCl	0.4557	26.6329	0.4557	26.6329

B. Recipes of "Anion" Titrant Solutions:

	For Calcite		For Aragonite	
	mole/kg	g/kg	mole/kg	g/kg
Na_2SO_4	0.07100	10.08505	0.07100	10.08505
KBr	0.002112	0.25143	0.002112	0.25143
NaF	0.000176	0.00739	0.000176	0.00739
$NaHCO_3$	0.009930	0.83420	0.009930	0.83420
Na_2CO_3	0.0200	2.1200	0.0200	2.1200
NaCl	0.5216	30.4842	0.5216	30.4842

overgrowth contains a high mole per cent of $MgCO_3$.

C. Seeds:

Baker "Instra-analyzed flux reagent" grade calcite was used as a seed material for precipitation of calcite or Mg-calcite. The seed was washed in deionized distilled water and size separated by settling using the procedure described by Mucci (1986). The seed had a surface area of 0.52 square meter per gram as determined by the Kr-BET method of de Kanel and Morse (1979). Aragonite was synthesized in the laboratory by the procedure of Wray and Daniels (1957) as modified by Katz et al. (1972) at a temperature of 70°C. X-ray diffraction (XRD) spectrometric and scanning electron microscopic (SEM) examination of this material indicated the absence of vaterite and the presence of less than 1 weight percent calcite. The aragonite seed had a surface area of 3.40 square meters per gram as determined by the Kr-BET method. Both calcite and aragonite had a well restricted size range (Calcite: 3 - 7 microns; Aragonite: 1 - 8 microns, needles) as determined by SEM examination.

III.4 Working Procedure and Conditions:

Step 1: Before each experiment, solutions of both carbonate-free (solution A) and high carbonate alkalinity content (solution B) but of equivalent salinity were mixed into the reaction vessel after being filtered through a 0.45 micron Millipore filter. The resulting solution was 350 ml in volume and would be at a known and desired saturation state after being equilibrated with Pco_2.

A N_2-CO_2 gas mixture with Pco_2 value of around 0.003 atm was bubbled through the solution and the electric stirrer was activated to accelerate the equilibration process between the solution and the gas mixture. This process can be represented by reactions 2.1, 2.2, and 2.3.

The equilibration was carried out until the pH of the solution reached a stable value as monitored by a combination glass/reference electrode (Radiometer Model GK2401C) connected to a model M84 Radiometer pH/millivolt meter. The length of time required for the system to reach an equilibrium pH value was usually less than an hour.

Step 2: Before the initiation of the precipitation reaction, a 50 ml aliquot of the reacting solution was withdrawn and transferred to a resealable plastic bottle after filtering through a 0.45 micron Millipore filter. This solution was used for later comparison of the initial and final concentrations of alkalinity, Ca^{2+}, Mg^{2+}, and Sr^{2+} in solution.

Step 3: A weighed amount (usually 0.600 g) of seed material of either calcite or aragonite was added to the Pco_2-equilibrated solution to initiate the precipitation experiment. Stirring was resumed in order to keep seeds in suspension in the solution so that the total surface area of the solids was exposed to the solution. Once the seeds were introduced, the syringe pump was activated and the exact starting time was recorded. The pH of the solution was then continually monitored by the combination glass/reference electrode. The injection rate, as discussed earlier, was set at a value which would best keep up with the precipitation rate corresponding to the solution's initial supersaturation.

For most of the experiments, the precipitation reaction was carried out until more than 0.2 millimole of carbonate was precipitated. Single precipitation experiments generally lasted more than one and half hours but less than two days. The steady state pH was precisely measured near the end of the experiment according to the method described in the next section.

Step 4: The reaction was terminated by turning off the syringe pump and stirrer. Another 50 ml aliquot of the solution was immediately withdraw using a 50 ml syringe, filtered through a 0.45 micron Millipore filter and stored in a resealable plastic bottle for later analysis and comparison with the initial solution.

The remainder of the precipitating solution was filtered through a 0.45 micron Nuclepore filter as soon as possible. The solid was rinsed with calcite-saturated distilled water to flush away the residual solution salts on the surface of the solid. The solid was then dried at room temperature and stored in a 5 ml plastic tube for later analysis of the mineralogy and composition of the overgrowth.

Step 5: The concentrations of Ca^{2+}, Sr^{2+}, Mg^{2+}, and alkalinity in both initial and final solutions were analyzed by using the methods described in the "analytical methods" section below.

III.5 Analytical methods:

The steady state pH of the reacting solution was measured by an independent combination glass/reference electrode (GK2401C) connected to a model M84 Radiometer pH/millivolt meter near the end of each experiment. The electrode was calibrated using three standard NBS buffer solutions (pH=6.838, 7.382, and 9.180). Measurements were made on the millivolt scale and converted to pH units using the Nernstian slope and E_o obtained from the least-squares fit of the calibration. The correlation of the fit was always better than 0.9999. For reactions taken in solutions of salinity 35, the "TRIS" buffer solution with salinity of 35 (Hansson, 1973) was also used to obtain pH on the Hansson scale in order to evaluate variations in liquid junction potential and compare the results of $[CO_3^{2-}]$ calculations using both sets of constants (i.e., apparent vs. stoichiometric, see discussion in later section).

Calcium concentrations were analyzed potentiometrically with EGTA using the method described by Lebel and Poisson (1976). Copenhagen IAPSO standard seawater was used to standardize the titrant solution. The precision of these measurements was ± 0.5%.

Sr^{2+} and Mg^{2+} were determined by flame AAS (atomic absorption spectrometry) following dilution in distilled water. Aqueous standards prepared in NaCl solutions of corresponding salinity were used for calibration. The precision of these measurements is estimated at ± 5 % for Sr^{2+} and ± 3 % for Mg^{2+}.

Titration alkalinities were determined by potentiometric titration with a dilute HCl solution (Edmond, 1970). A Na_2CO_3 solution was utilized for standardization of the acid. The titration was carried out until the second equivalence point corresponding to the neutralization of bicarbonate ions. Detection of the second equivalence point was computed automatically by the second derivative method using a Radiometer TTT81 digital titrator. Reproducibility of these measurements was better than 0.4%.

The reacted $CaCO_3$ was examined by X-ray diffraction spectrometry to verify that the mineralogy of the precipitates was identical to that of the seed material. Powder packs were prepared and irradiated using a Siemens Model D-500 X-ray diffractometer. The Cu-$K\alpha_1$ wavelength radiation was used as a source and the diffraction spectra were recorded using a proportional counter detector. Results confirm the results of previous studies (e.g., Mucci, 1983; Walter, 1986; Burton and Walter, 1987) which indicate that the mineralogy of the overgrowths is determined by the seed material.

CHAPTER IV

RESULTS AND DISCUSSION

IV.1 Saturation state calculations and selection of constants:

A. Saturation state calculations:

The steady state saturation state of calcium carbonate in solution was calculated from the steady state calcium and carbonate concentrations according to eqn. II.18. The steady state $[CO_3^{2-}]$ was obtained from steady state pH and titration alkalinity based on eqn. II.20. The steady state pH was precisely measured near the end of the experiment and the steady state $[Ca^{2+}]$ and A_t were obtained from the titrations of the aliquot withdrawn at the end of the experiment. Pco_2 variations of the final aliquot during its storage period due to outgassing does not affect the titration alkalinity of the aliquot unless spontaneous nucleation occurs. For practical purposes, the two equations are repeated here as eqns. IV.1 and IV.2 below:

$$SI = [Ca^{2+}]\,[CO_3^{2-}] / K^{*}sp \qquad \text{IV.1}$$

$$[CO_3^{2-}] = \frac{A_t - T_B / ((H^+)/K'_B + 1)}{(H^+)/K'_2 + 2} \qquad \text{IV.2}$$

It can be argued that equation IV.2 is only valid when both the second dissociation reaction of carbonic acid (i.e., reaction 2.3) and the first dissociation reaction of boric acid (i.e., reaction 2.5) are in equilibrium. The fulfilment of these prelimilary conditions does not constitute any particular problem in our experiments because, while the dissolution kinetics of CO_2 in water and seawater is relatively slow (Johnson, 1982), the dissociation reactions of carbonic acid and boric acid in solution are quasi-instantaneous (Lasaga, 1981). Therefore, the only disequilibrium we can expect is in the Pco_2 of the solution with respect to the gas, which does not affect the validity of equation IV.2. Calculations using measured A_t and the steady state pH indicate that the calculated Pco_2 and the composition of the gas being bubbled through the solution generally agree within ± 50 %.

B, Selection of constants:

One of the crucial part in the data analysis process is the selection of appropriate constants. Caution must be taken. This is especially true when stoichiometric and/or apparent constants are involved since these constants are a function of not only temperature and pressure, but also the composition of the solution. Only those constants which were derived under the same or similar conditions can be used.

Three constants (i.e., K'_B, K'_2, and K^*sp) have been used to calculate the saturation state. For the purpose of internal consistancy analysis, other related constants (e.g., K'_0, K'_1 etc.) were also used and therefore, will be discussed here. Fortunately, these apparent and/or stoichiometric constants have been extensively determined and investigated in seawater and seawater-like solutions. A number of data sets can be found in the literature (e.g., Lyman, 1956; Hansson, 1973; Ingle et al., 1973; Mehrbach et al., 1973; Weiss, 1974; Ingle, 1975; Berner, 1976; Mucci, 1983; etc.).

An excellent critical review and refitting of most of the important preexisting data were provided by Millero (1979). The polynomial fits of the apparent constants (K'_i) for the ionization of carbonic acid and boric acid in seawater at various salinities can best be described by the following equation:

$$\ln K_i' = \ln K^o_i + A_i S^{0.5} + B_i S \qquad \text{IV.3}$$

where K^o_i is the thermodynamic ionization constant in water; S is salinity; A_i and B_i are adjustable parameters. The temperature dependence of $\ln K^o_i$, A_i and B_i is given in the form:

$$\ln K^o_i \text{ (or } A_i, B_i) = a_o + a_1/T + a_2 \ln T \qquad \text{IV.4}$$

where a_is are constants of the polynomial fits. They can be found in Millero (1979, Table 3).

The polynomial formulas for these aparent constants at 25°C, one atmospheric total pressure, and various salinities are presented in Table IV.1.

Apparent constants based on the NBS pH scale were used in this study. The NBS scale was chosen because stoichiometric dissociation constants in seawater have only been measured for salinities greater than 20 (Hansson, 1973). Uncertainties associated with estimates of the saturation state may have been introduced by using the NBS buffer calibration system in strong electrolyte solutions (e.g., seawater), as a result of varying liquid junction potentials (Dickson, 1984). Even so, the

Table IV.1 The Salinity Dependence of Apparent and Stiochiometric Constants in Seawater at 25^{o}C (from Millero, 1979)

Constant	Data Refitting	Se	Source
K'_B	$LnK'_B=-21.2677+0.2120S^{0.5}$	0.049	(3)
	$LnK^*_B=-21.2677+0.3474S^{0.5}-0.01767S$	0.008	(1)
K'_1	$LnK'_1=-14.6248+0.1373S^{0.5}$	0.053	(3)
	$LnK'_1=-14.6248+0.1362S^{0.5}$	0.007	(4)
	$LnK^*_1=-14.6248+0.2883S^{0.5}-0.01632S$	0.021	(1)
K'_2	$LnK'_2=-23.7850+0.5909S^{0.5}-0.01530S$	0.097	(3)
	$LnK'_2=-23.7850+0.6698S^{0.5}-0.03294S$	0.033	(4)
	$LnK^*_2=-23.7850+0.8390S^{0.5}-0.05058S$	0.042	(1)
K^*sp_C	$LnK^*sp_C=-19.4178+1.2254S^{0.5}-0.06999S$	0.065	(2)

Sources:

(1) ---- Hansson (1972)
(2) ---- Ingle et al. (1973); and Ingle (1975)
(3) ---- Lyman (1957)
(4) ---- Mehrbach et al. (1973)

uncertainties are minimized since the same pH scale was used to determine both stoichiometric solubility constants and saturation states measurements (Mucci, 1983; Mucci et al., 1988). As a matter of fact, it has been demonstrated that there is no significant difference between the use of the constants given by Mehrbach et al. (1973) based on the NBS scale and those given by Hansson (1973) based on the "TRIS" buffer scale, within the standard error of these constants (Dickson and Millero, 1987), if liquid junction potential errors are accounted for. In this study, results of $[CO_3^{2-}]$ calculations using the apparent constants (i.e., Lyman, 1956; Mehrbach et al., 1973) and the stoichiometric constants (i.e., Hansson, 1973) agree within ± 5%.

The apparent dissociation constants for carbonic acid (K'_1, K'_2) determined by Mehrbach et al. (1973) on the NBS scale were selected. Values of K'_1 and K'_2 at 25°C and atmospheric pressure were obtained from the formulas of Millero (1979) for different salinities (Table IV.1). The constants which were used are listed in Table IV.2.

The first dissociation constant of boric acid (K'_B) determined by Lyman (1956) was chosen. Millero's polynomial fit and parameters were again used to obtain the constants at different salinities and at constant temperature (25°C) and pressure (one atm). The values of K'_B are found in Table IV.2.

The apparent solubility constant of carbon dioxide (K'_0) in seawater at 25°C and one atmosphere total pressure was obtained from Weiss (1974) according to the following equation:

Table IV.2, Constants Used in This Study (T=298.15K, P=1 atm, Composition of Solutions: Artificial Seawater)

Constants	S=5	S=15	S=25	S=35	S=44	Ref.
$K'_o\ 10^2$	3.319	3.150	2.991	2.839	2.709	(4)
$K'_1\ 10^7$	6.037	7.544	8.796	9.965	10.99	(2)
$K'_2\ 10^{10}$	1.775	3.822	5.849	7.772	9.341	(2)
$K'_B\ 10^9$	0.932	1.319	1.674	2.033	2.367	(1)
$K^*sp_a\ 10^7$	0.861	2.43	4.41	6.65	8.48	(3)
$K^*sp_c\ 10^7$	0.489	1.52	2.76	4.39	5.55	(3)

Note: K^*sp_a and K^*sp_c bear the unit $(mole/kg)^2$

References:

(1) ---- Lyman (1957); fitted by Millero (1979)
(2) ---- Mehrbach et al. (1973); fitted by Millero (1979)
(3) ---- Morse et al. (1980) and Mucci (1983)
(4) ---- Weiss (1974)

$$\ln K'_o = -3.379605 - 0.00520145\ S \qquad \text{IV.5}$$

The results can be found in Table IV.2.

The stoichiometric solubility constants for calcite and aragonite in seawater of various salinities were chosen from the data of Morse et al. (1980) and Mucci (1983) for many reasons. One very important reason is that unlike other stoichiometric solubility studies of $CaCO_3$ in seawater, these two investigations have put great attention on the duration of experiment to insure that the system had reached equilibrium from initial conditions of both undersaturation and supersaturation. Discrepancies with results of previous studies (especially the stoichiometric solubility of aragonite) have been ascribed to the lack of reaching equilibrium.

Furthermore, the measurements of Morse et al. (1980) and Mucci (1983) covered a wide range of salinities (5 to 44) and used similar solution compositions and seed materials as in this study.

The results of saturation state calculation and related raw data for all the runs conducted in this study are given in Appendix I. They include the steady state total alkalinity (A_t), pH (NBS), total carbonate ion concentration ($[CO_3{}^{2-}]$), total calcium concentration ($[Ca^{2+}]$), and saturation state or saturation index (SI).

As discussed in Chapter II, carbonate ion concentrations can also be obtained from other measureable parameters, such as from solution Pco_2 and carbonate alkalinity. Saturation states obtained from solution P_{CO_2} are considered less reliable since equilibrium between the gas phase and the solution is difficult to achieve at fast precipitation rates because of the relative slowness of the dissolution kinetics of CO_2 in water and seawater.

IV.2 Precipitation rate calculations:

The steady state precipitation rate of calcite and/or aragonite was calculated from the steady state injection rate of excess carbonate alkalinity. The precipitation rate was normalized to specific reactive area of the seed. For most of the runs the amount of overgrowth precipitated was less than 10 per cent of the initial weight of seeds and variations in the reactive surface area were neglected. The initial specific reactive area of seed material was therefore used in the calculations.

The normalized precipitation rate can be calculated from eqn. III.5 or eqn. IV.6 below:

$$R = Ri\ (\ (A_c)_{t.t.} - 2\ (A_c)_{s.}\ )/\ (\ 2\ A\ W_{s.d.}\ ) \qquad \text{IV.6}$$

Since Ri was constant during the experiment:

$$Ri = W_{t.t.}\ /\ t \qquad \text{IV.7}$$

where t is the duration of the experiment in hours; $W_{t.t.}$ is the weight of the "anion" titrant added to the solution in kg.

Combining eqn. IV.6 and IV.7 yields:

$$R = W_{t.t.}\ (\ (A_c)_{t.t.} - 2\ (A_c)_{s.}\ )/(\ 2\ A\ W_{s.d.}\ t\ ) \qquad \text{IV.8}$$

This equation was used to calculate the steady state precipitation rate of both calcite and aragonite under given conditions of SI and S. The measured precipitation rate and related raw data for each run are found in Appendix II.

The reaction rate can also be calculated from the steady state injection rate of excess calcium during each experiment from eqns. III.4 and IV.7. However, considering the unknown amount of substitution for calcium in the overgrowth by magnesium and strontium ions, precipitation rates derived from calcium concentrations were considered less reliable than those derived from carbonate alkalinity.

IV.3 The rate law and the rate-salinity relation:

As concluded in Section II.2, the precipitation rate can be modelled kinetically in terms of the saturation state of calcium carbonate in solution at a given salinity through the empirical rate law (i.e., eqn. II.22 or eqn. II.24). The linear correlations between Log(Rate) and Log(SI-1) for aragonite and calcite in seawater of 44, 35, 25, 15, and 5 salinity are shown individually in Figures IV.1 to IV.9. The least squares fit equations to each data set, together with the linear correlation coefficients (r) and the standard error of estimates (Se), are given in Table IV.3. Data obtained when $SI_C < 2.6$ and/or $SI_a < 1.7$ were omitted from the data sets since it appears that the $CaCO_3$ precipitation mechanism may vary when the system approaches equilibrium conditions. Results from this study seem to indicate that the boundary is somewhat near $SI_C=2.6$ for

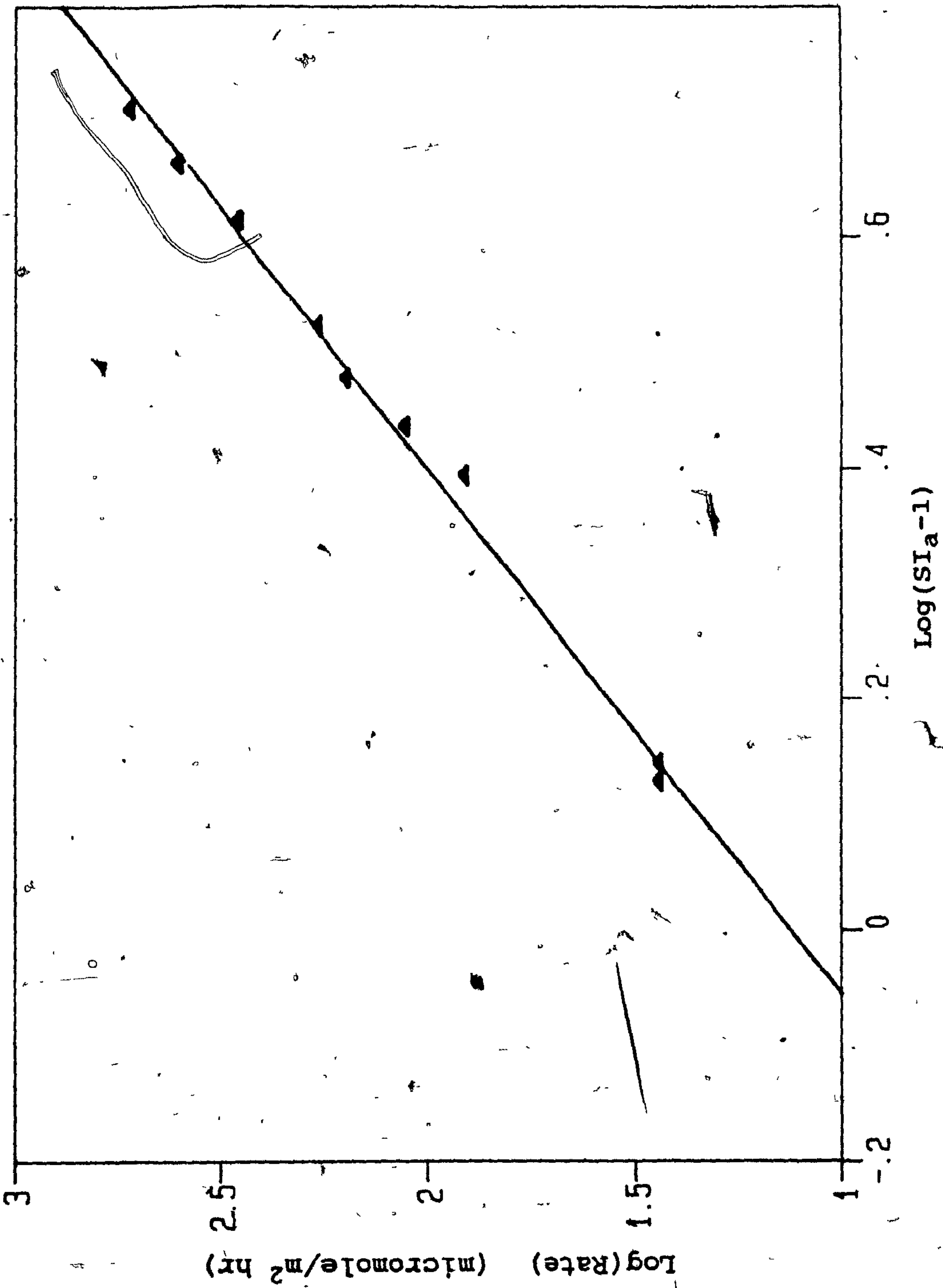


Figure IV.1. Log(Rate) vs. Log(SI_a-1) for Aragonite at S=44

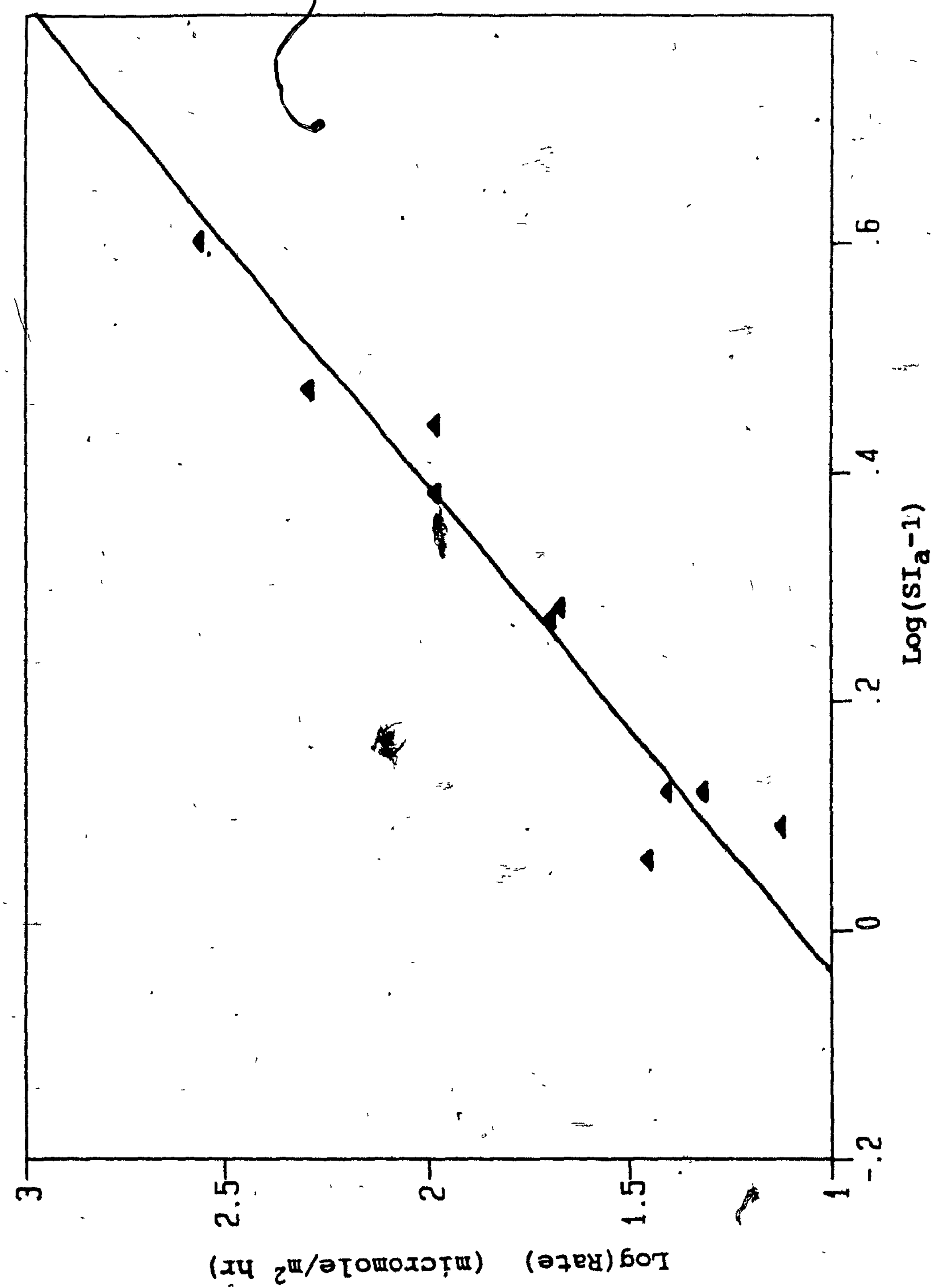


Figure IV.2. Log(Rate) vs. Log(SI_a-1) for Aragonite at S=35

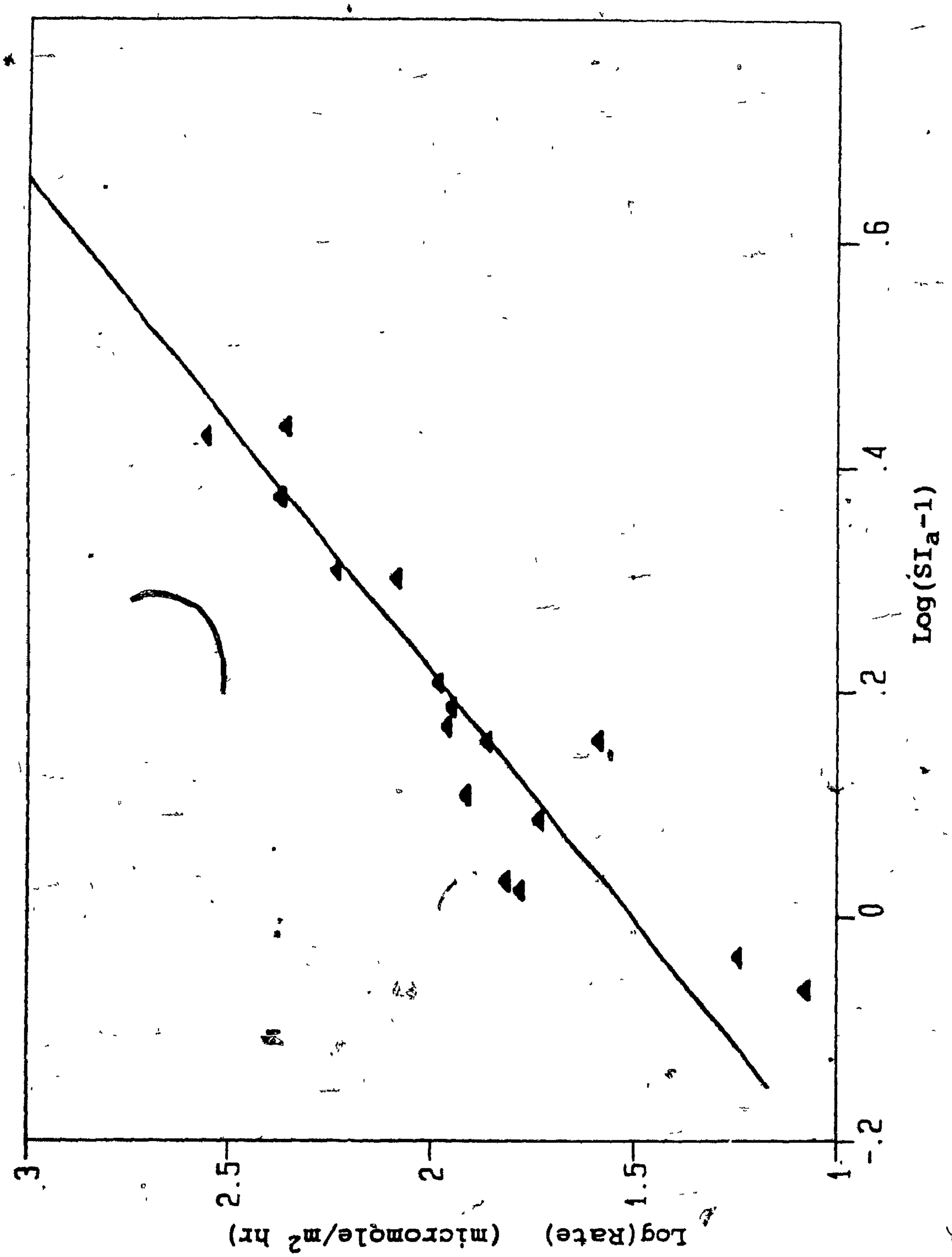


Figure IV.3. Log(Rate) vs. Log(SI_a-1) for Aragonite at S=25

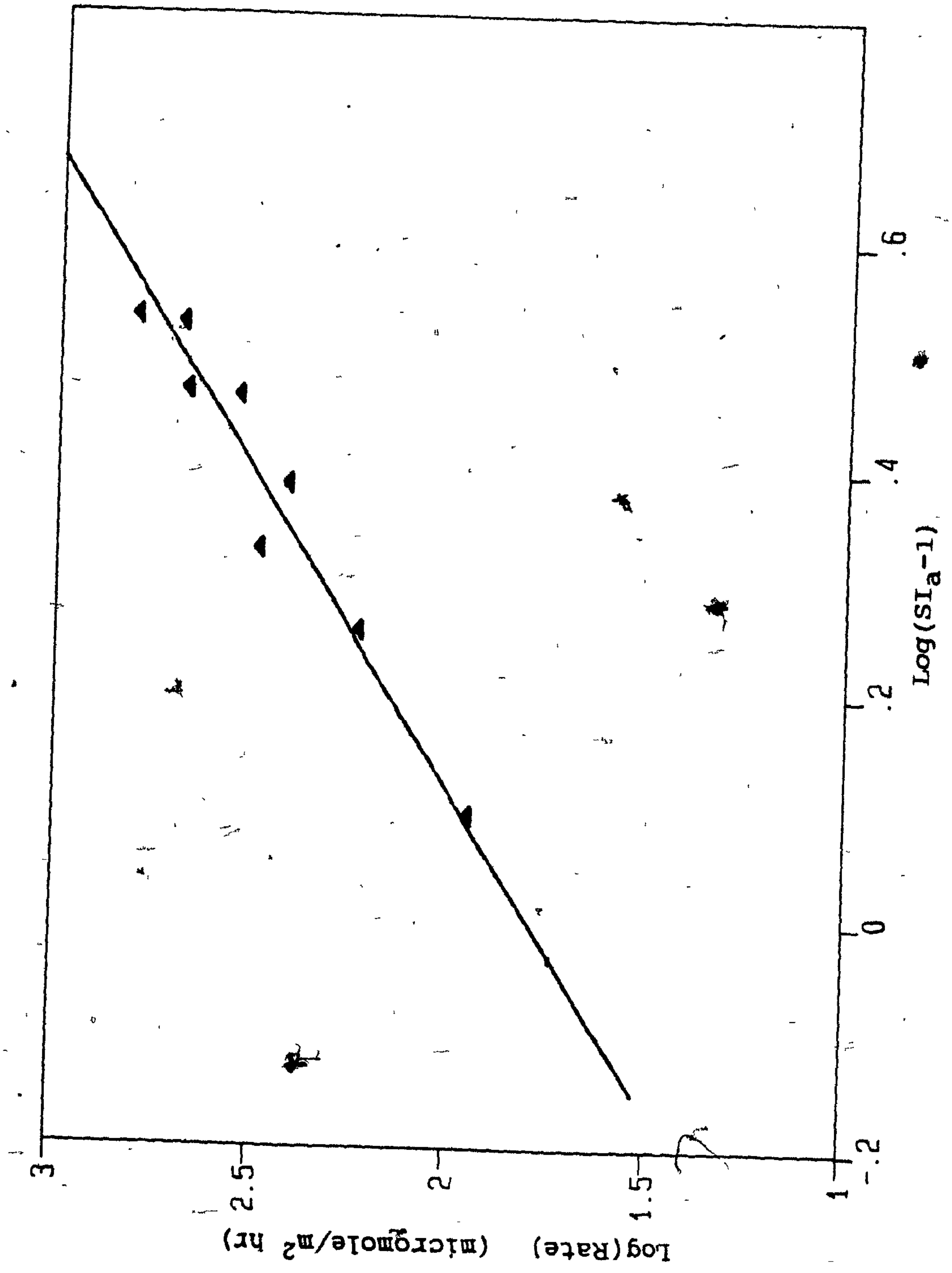


Figure IV.4. Log(Rate) vs. Log(SI_a-1) for Aragonite at S=15

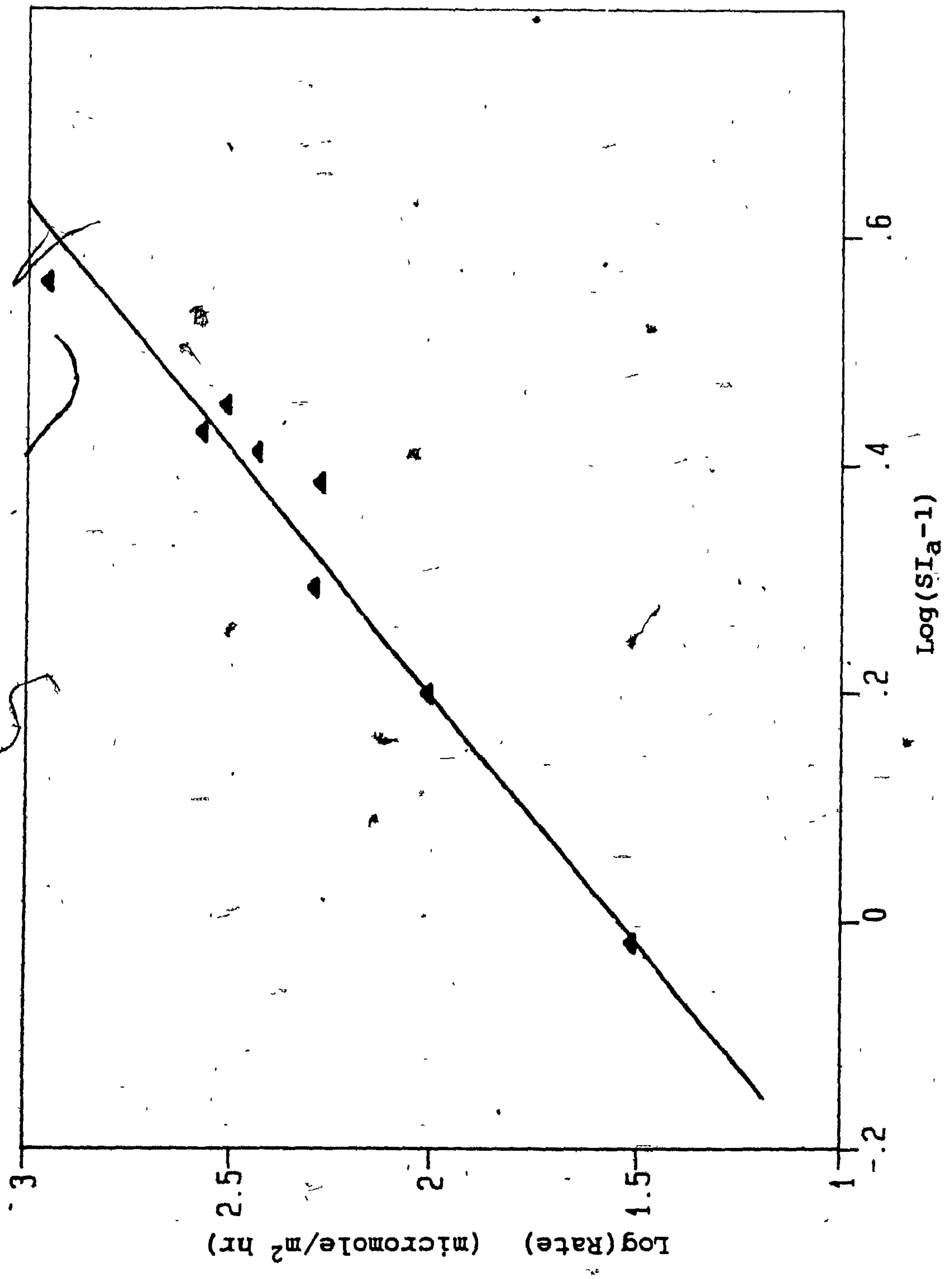


Figure IV.5. Log(Rate) vs. Log(SI_a-1) for Aragonite at S=5

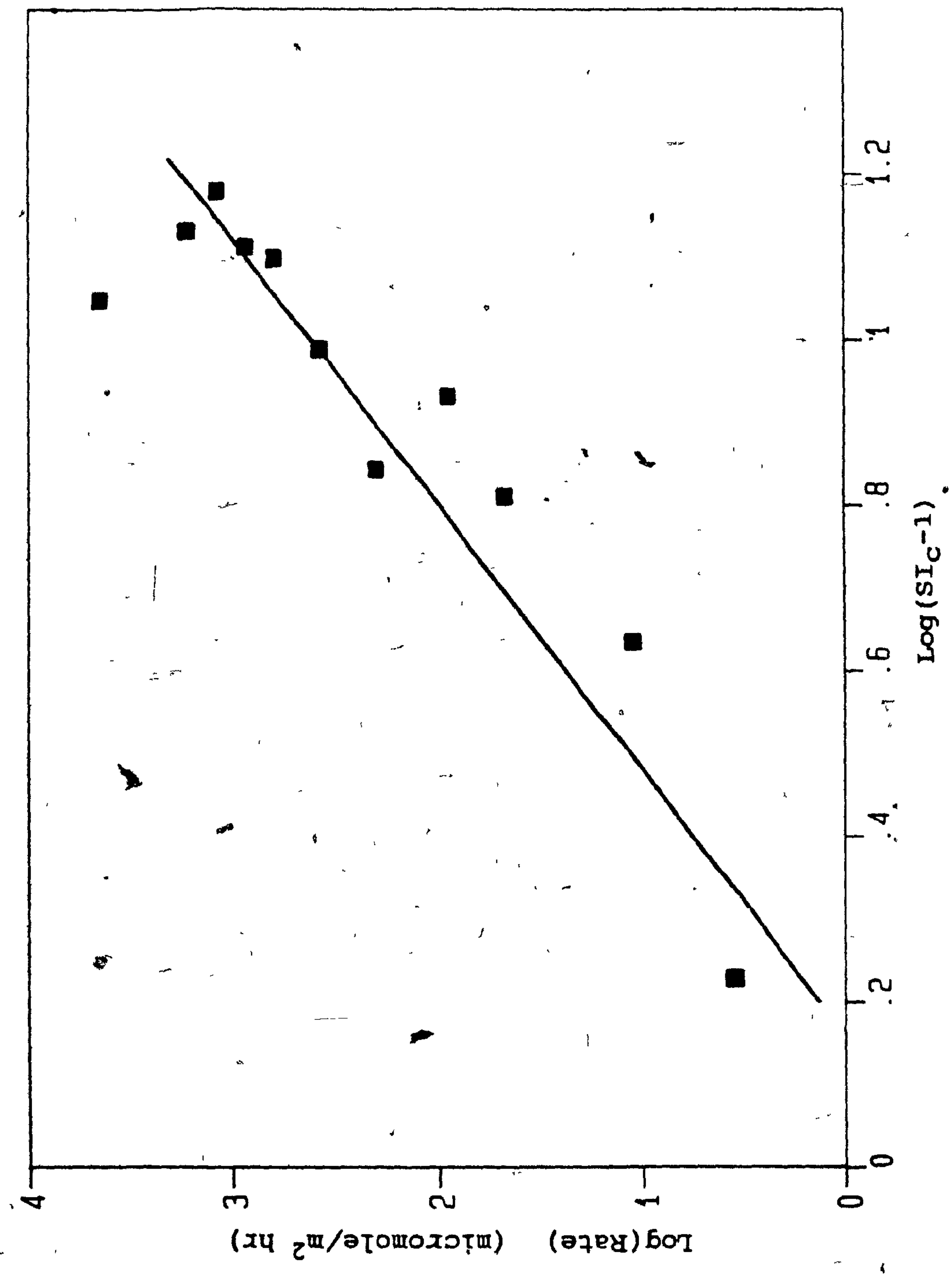


Figure IV.6. Log(Rate) vs. Log(SI$_C$-1) for Calcite at S=44

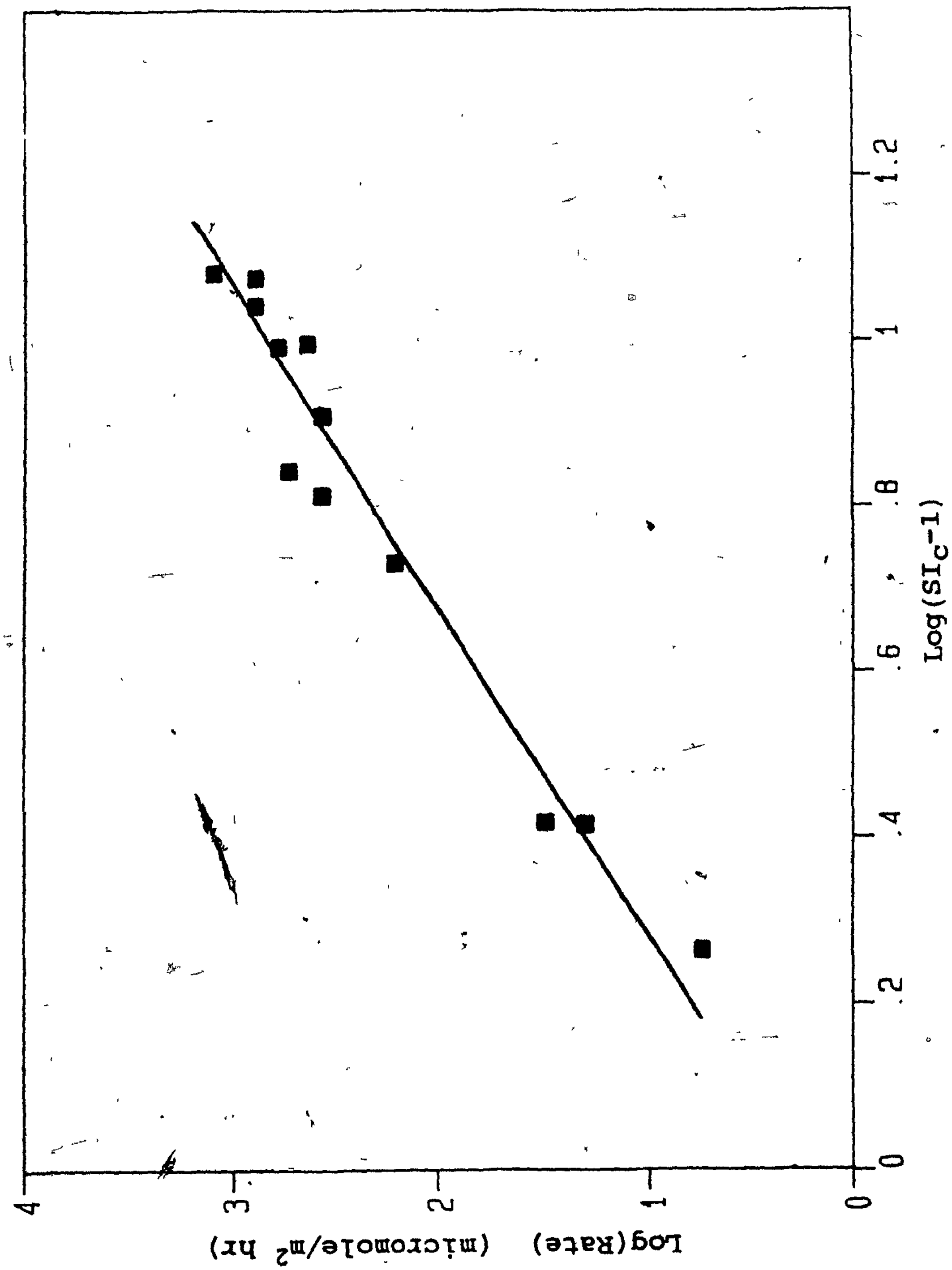


Figure IV.7. Log(Rate) vs. Log(SI_c-1) for Calcite at S=25

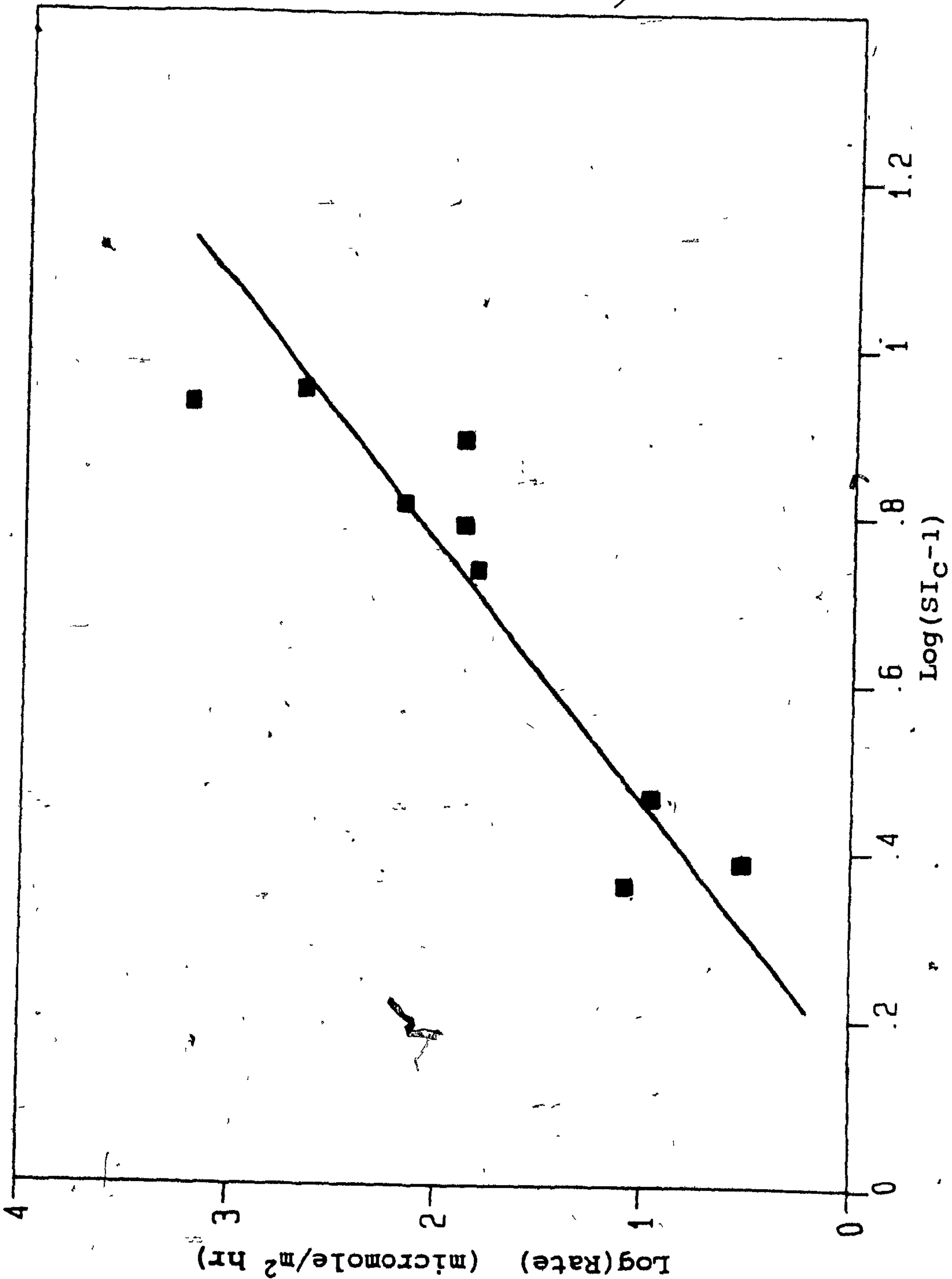


Figure IV.8. Log(Rate) vs. Log(SI_C-1) for Calcite at S=15

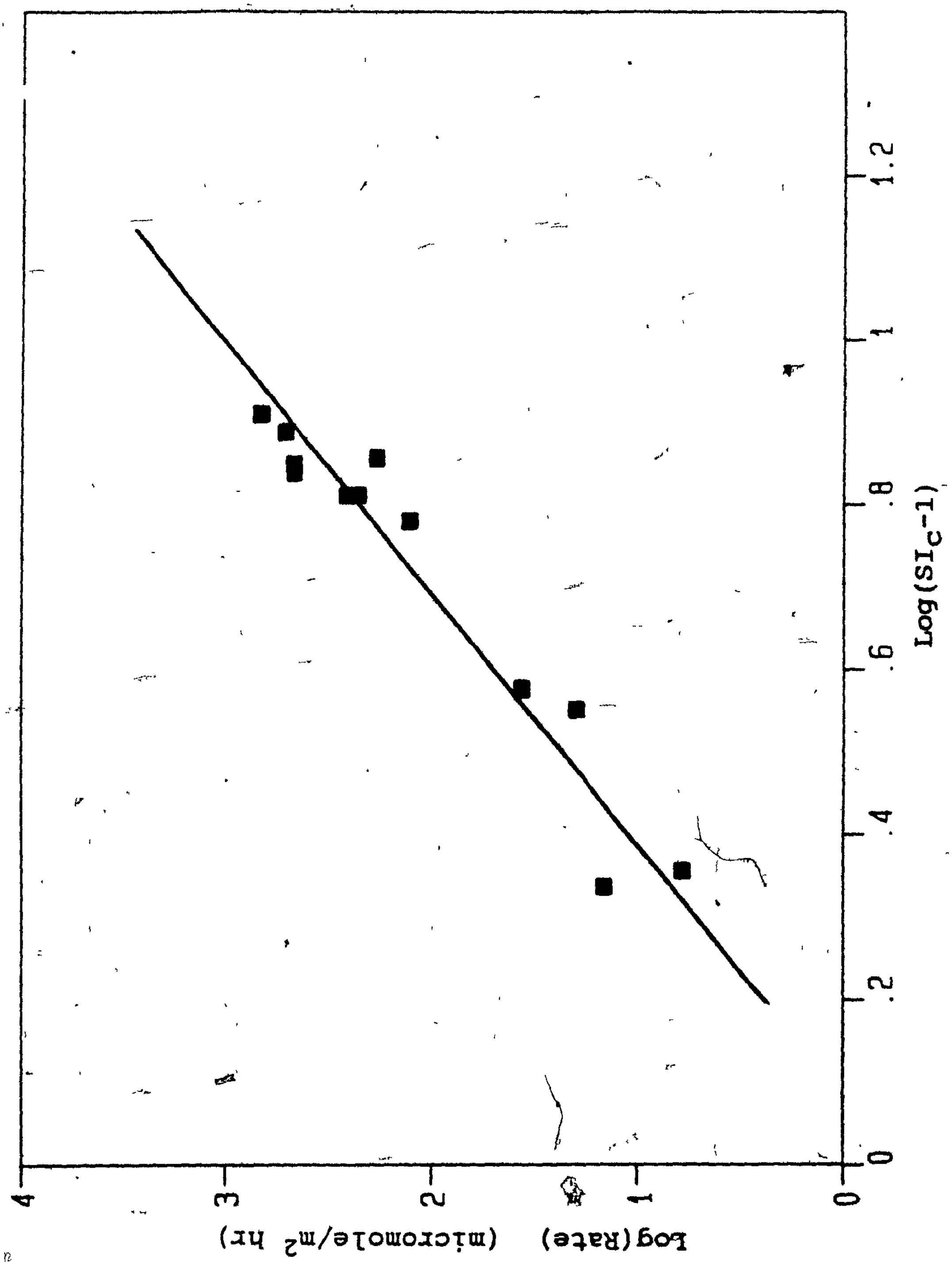


Figure IV.9. Log(Rate) vs. Log(SI_C-1) for Calcite at S=5

Table IV.3 Empirical Rate Laws for the Precipitation of Calcite and Aragonite at Various Salinities

S	Miner.	Rate vs. SI	r(%)	Se
5	cal.	LogR=3.27Log(SIc-1)-0.271	96.60	.1883
15	cal.	LogR=3.26Log(SIc-1)-0.484	91.07	.3721
25	cal.	LogR=2.53Log(SIc-1)+0.286	97.78	.1616
35	cal.	* LogR=2.80Log(SIc-1)-0.290	99.69	.0630
44	cal.	LogR=3.12Log(SIc-1)-0.505	91.38	.4074
5	ara.	LogR=2.31Log(SIa-1)+1.546	97.91	.0934
		LogR=2.89Log(SIc-1)+0.401	98.12	.0884
15	ara.	LogR=1.80Log(SIa-1)+1.800	97.15	.0714
		LogR=2.13Log(SIc-1)+1.103	97.09	.0722
25	ara.	LogR=2.28Log(SIa-1)+1.509	91.62	.1607
		LogR=2.82Log(SIc-1)+0.555	91.11	.1653
35	ara.	LogR=2.36Log(SIa-1)+1.088	96.63	.1237
		LogR=2.77Log(SIc-1)+0.274	96.81	.1205
44	ara.	LogR=2.21Log(SIa-1)+1.124	99.73	.0363
		LogR=2.52Log(SIc-1)+0.380	99.83	.0286

* from Mucci, 1986

calcite and/or SI_a=1.7 for aragonite. It is interesting to note that a SI_c=2.6 is equivalent to SI_a=1.7 since they correspond to a similar $CaCO_3$ ionic concentration product value. Unfortunately, information obtained in this study and others (e.g., Busenberg and Plummer, 1986) is not sufficient to draw a general conclusion concerning a possible change in reaction mechanism at lower saturation states. Further investigations are needed.

The changes of precipitation rates with the change in solution salinity under constant calcium carbonate saturation state are shown in Figure IV.10 and Figure IV.11 for aragonite and calcite, respectively. The square root of salinity was chosen to represent the salinity dependence of precipitation rate both for practical purposes and since in most cases, the salinity dependence of dissociation constants is expressed in this fashion (e.g., Millero, 1979).

IV.4 Discussion and Conclusions:

Results from this study confirm again that the frequently used kinetic empirical equation (i.e., eqn. II.22) can be used to precisely describe the precipitation rate of calcium carbonates in terms of their saturation state in the solution. Linear least-squares fits to the data for both aragonite and calcite at all salinity values investigated had correlation coefficients greater than 0.91. The standard error of estimates of Log(Rate) for all these regresions are generally less than 0.4 (Table IV.3).

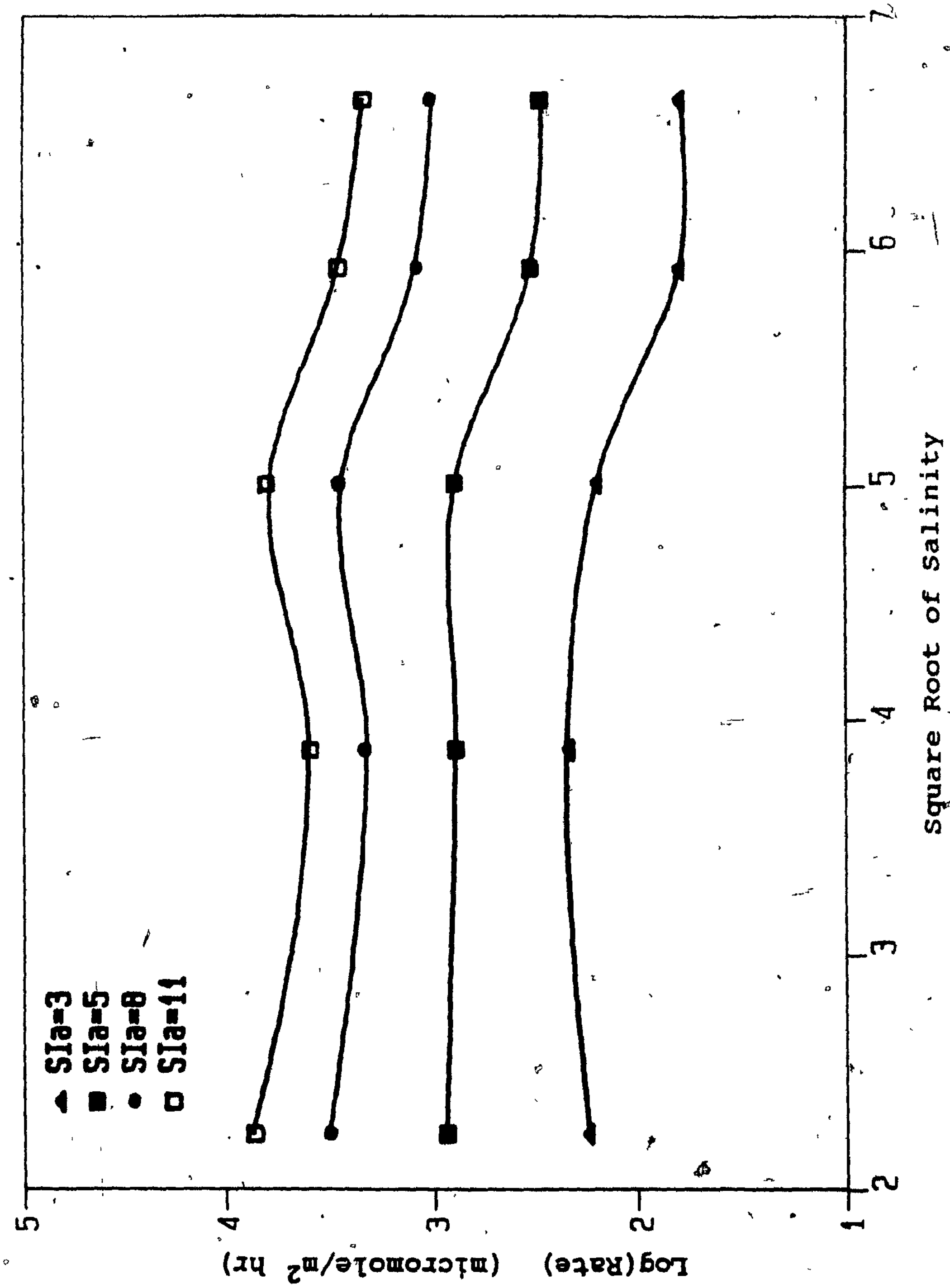


Figure IV.10. Log(Rate) of Aragonite vs. the Square Root of Salinity at various saturation states

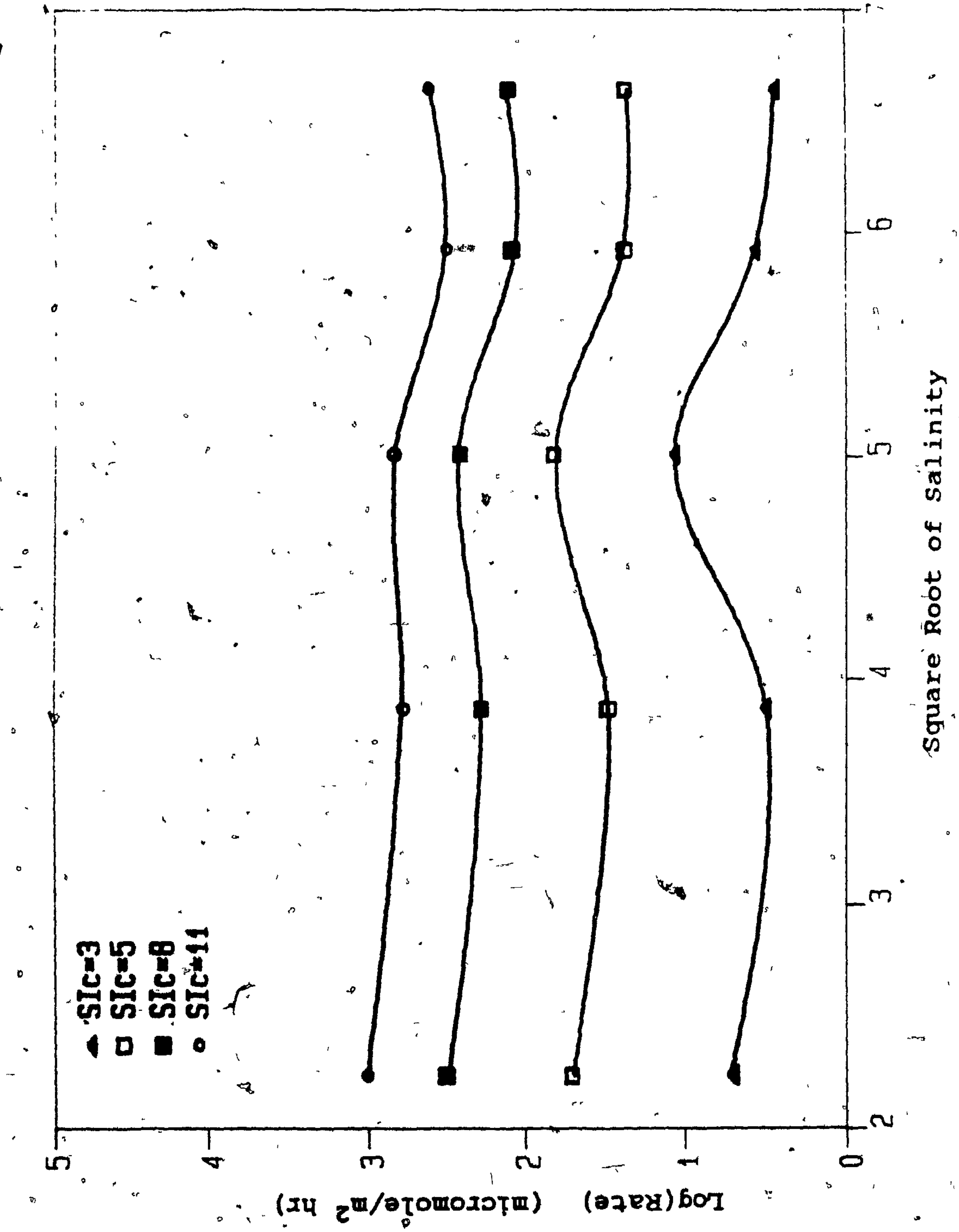


Figure IV.11. Log(Rate) of Calcite vs. the Square Root of Salinity at various saturation states

The empirical reaction order for calcite precipitation under different salinity conditions is in the range of 2.9 ± 0.4. This is in good agreement with previous studies (e.g., Mucci, 1986). The reaction order for the aragonite precipitation reaction varies from 2.4 to 1.8, or in the range of 2.1 ± 0.3 (Table IV.3) for the salinities investigated. These relatively high reaction order values further support the previous hypothesis that precipitation reactions of both aragonite and calcite under the investigated supersaturation conditions (i.e., $2.6 < SI_C < 17$) are surface reaction controlled (e.g., Morse and Berner, 1979; Mucci, 1986). Diffusion controlled reactions would have a reaction order close to one.

The thermodynamic influence of salinity on the behaviour of aragonite and calcite, or in other words, the effect of salinity on the stoichiometric solubility of aragonite and calcite, has been investigated previously (Mucci, 1983). It has been demonstrated that the stoichiometric solubility products of calcite and aragonite in seawater increases with salinity. This is due to an increase of ionic strength and ion-pairing which causes a decrease of the ion activity coefficients of calcium and carbonate ions in solution. The variation of solubility with salinity is shown in Figure IV.12. As would be expected, the parallelism of the two curves in the figure indicates that salinity changes have equivalent effects on the stoichiometric solubilities of both calcite and aragonite. Therefore, salinity has the same degree of thermodynamic influence on the behaviour

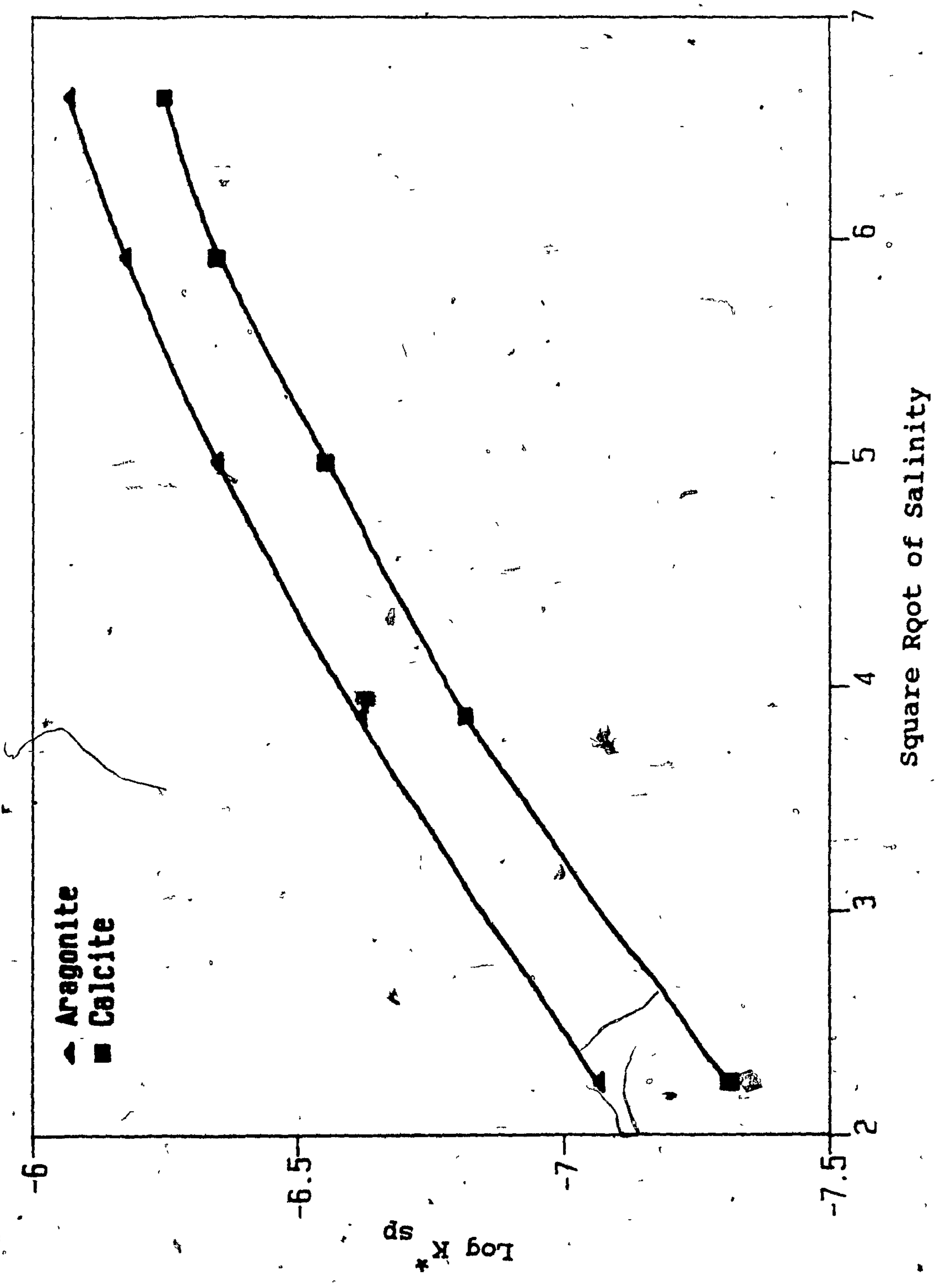


Figure IV.12. Log(K^*sp) of Aragonite and Calcite vs. the Square Root of Salinity of calcite and aragonite.

The linear correlations between Log(Rate) and Log(SI-1) at different salinities for both aragonite and calcite are gathered in Figure IV.13 and Figure IV.14, respectively, in order to visualize the kinetic influences of salinity on the precipitation rates. As can be clearly seen, within the standard error of the fit estimates, salinity changes in the range investigated (i.e., 5 to 44) have little or no kinetic effects on the precipitation reactions of calcite and some minor effects on that of aragonite. At the same saturation state, precipitation rates of aragonite decreased slightly when salinity increased from the lower range (i.e., 5 to 25) to the upper one (i.e., 35 to 44).

In order to quantitatively verify these features, data were reorganized into three groups. All calcite precipitation data were gathered as one group. For aragonite, precipitation rate data obtained under salinity values from 5 to 25 were treated as one set and the rest as another (i.e., salinities 35 and 44). Linear least-squares fits were done on these three groups of data. The results are presented in Table IV.4 and are also shown in Figure IV.15 and Figure IV.16 for aragonite and calcite, respectively. The fits were amazingly good with the correlation coefficients better than 0.92 and the standard error of the fits being less than 0.3, which are on the same order as those obtained for single salinity values. Statistically this means that within one group there is no precipitation rate change as long as the solution saturation state is kept contant.

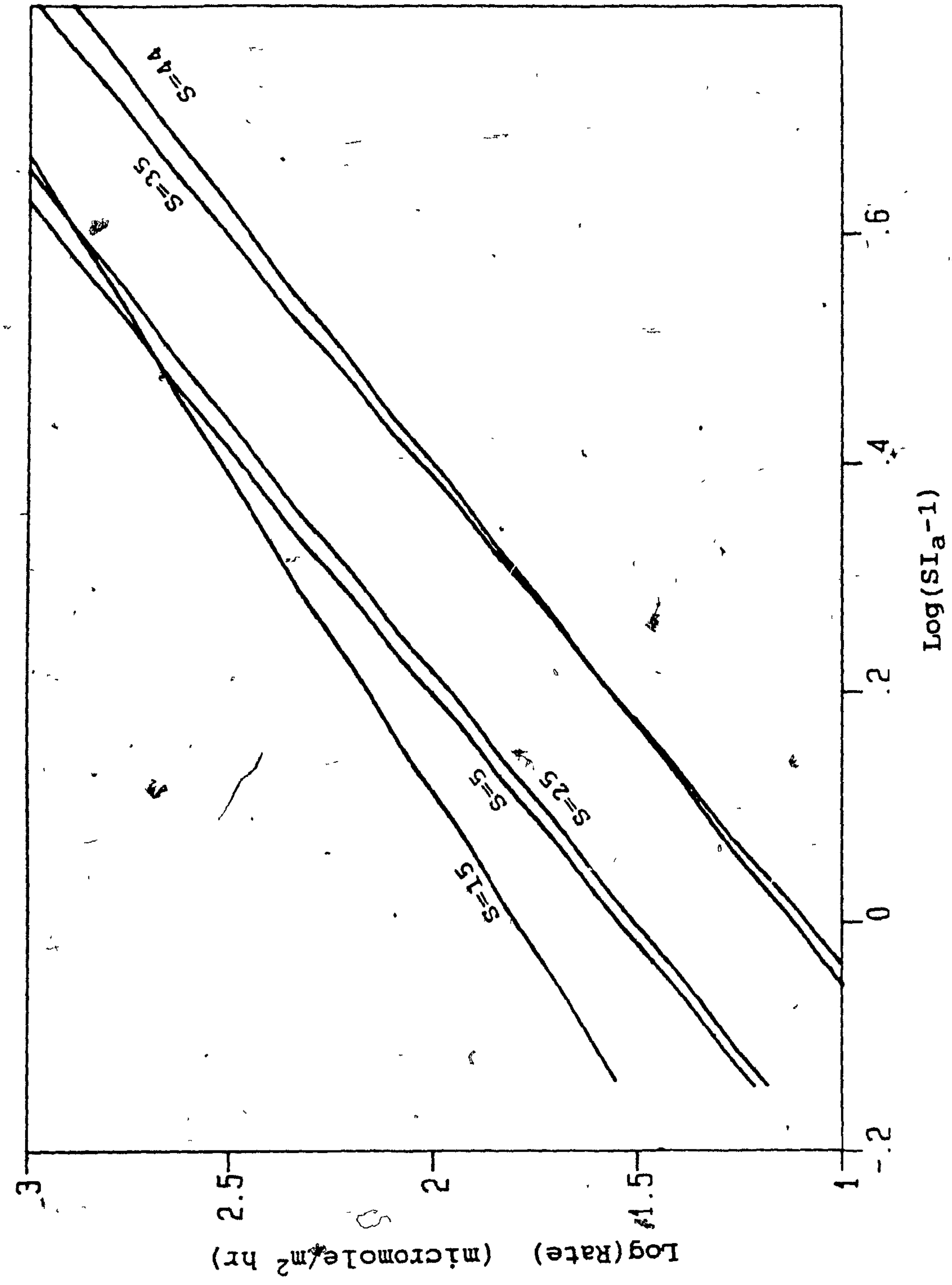


Figure IV.13. Log(Rate) vs. Log(SI_a-1) for Aragonite at Various Salinities

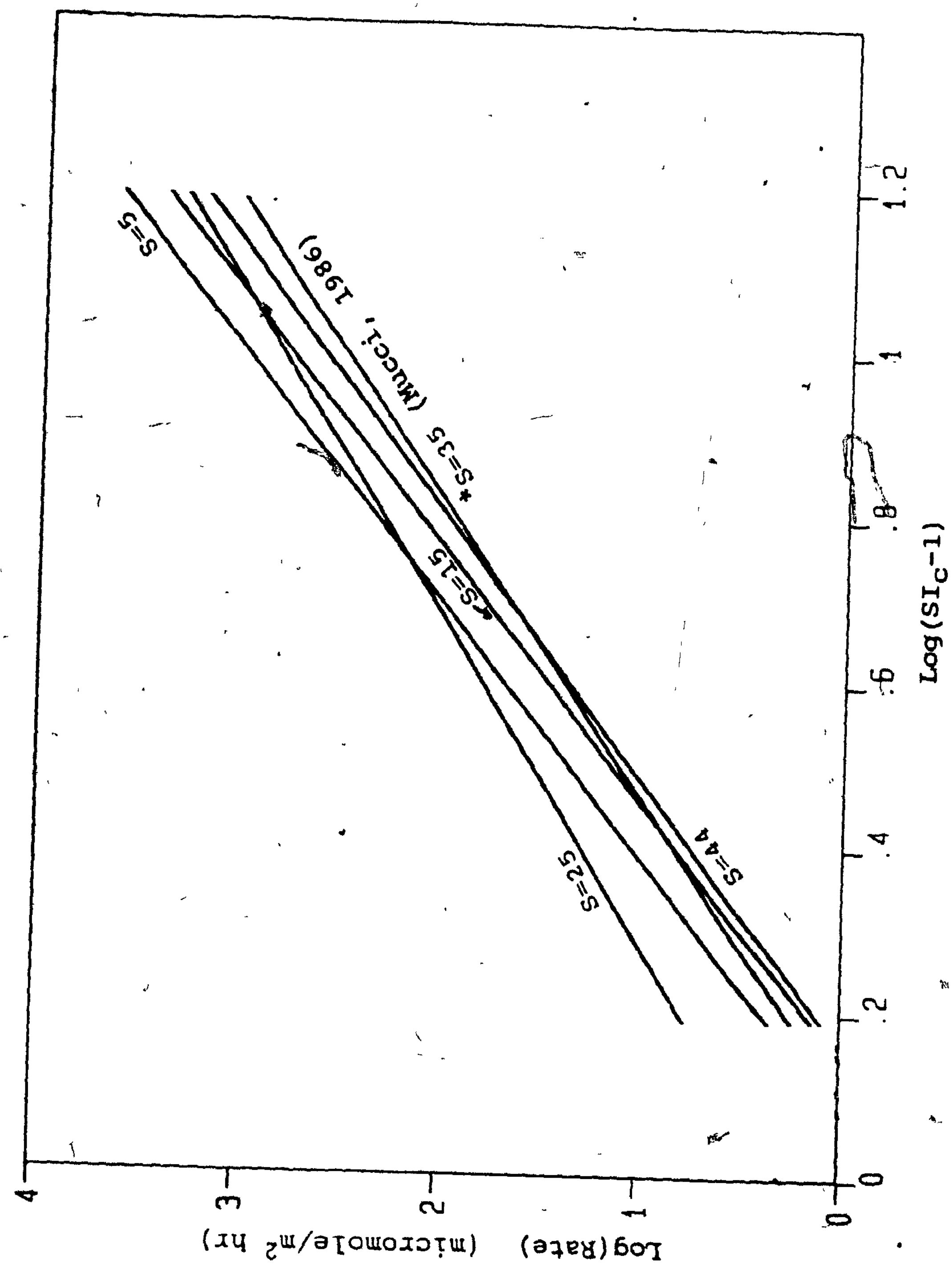


Figure IV.14. Log(Rate) vs. Log(SI_c-1) for Calcite at Various Salinities

Table IV.4 Empirical Rate Laws for the Precipitation of Calcite and Aragonite at Compatible Salinity Ranges

S	Min.	Rate vs. SI	r(%)	Se
5 to 44	Cal.	$\log R = 2.87 \log(SIc-1) - 0.106$	92.19	0.315
5 to 25	Ara.	$\log R = 2.33 \log(SIa-1) + 1.53$	95.43	0.135
		$\log R = 2.70 \log(SIc-1) + 0.622$	94.28	0.150
35 to 44	Ara.	$\log R = 2.26 \log(SIa-1) + 1.11$	98.33	0.090
		$\log R = 2.58 \log(SIc-1) + 0.358$	98.42	0.088

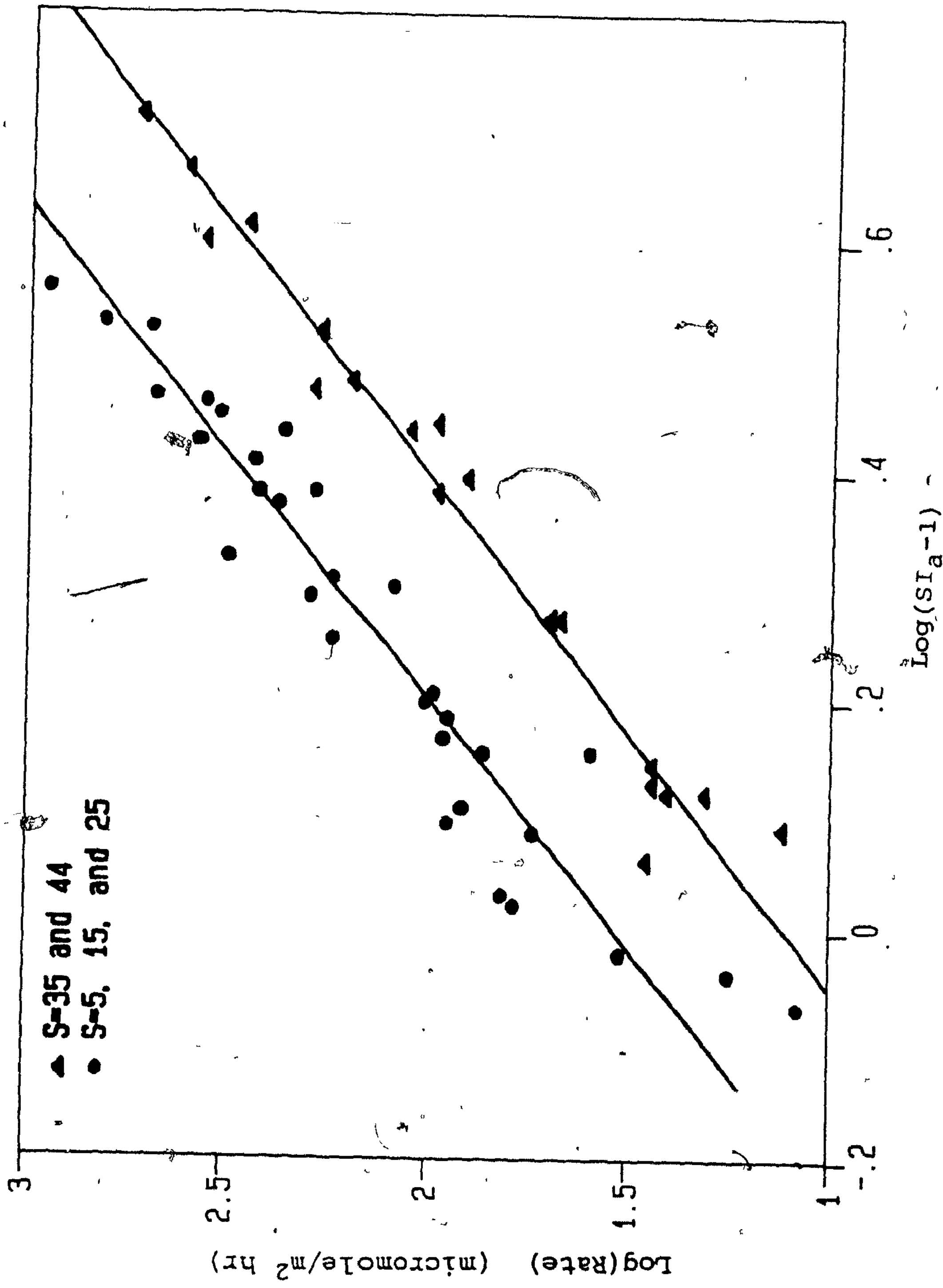


Figure IV.15. Log(Rate) vs. Log(SI$_a$-1) for Aragonite at Lower (5 to 25) and Higher Salinity (35 to 44) Ranges

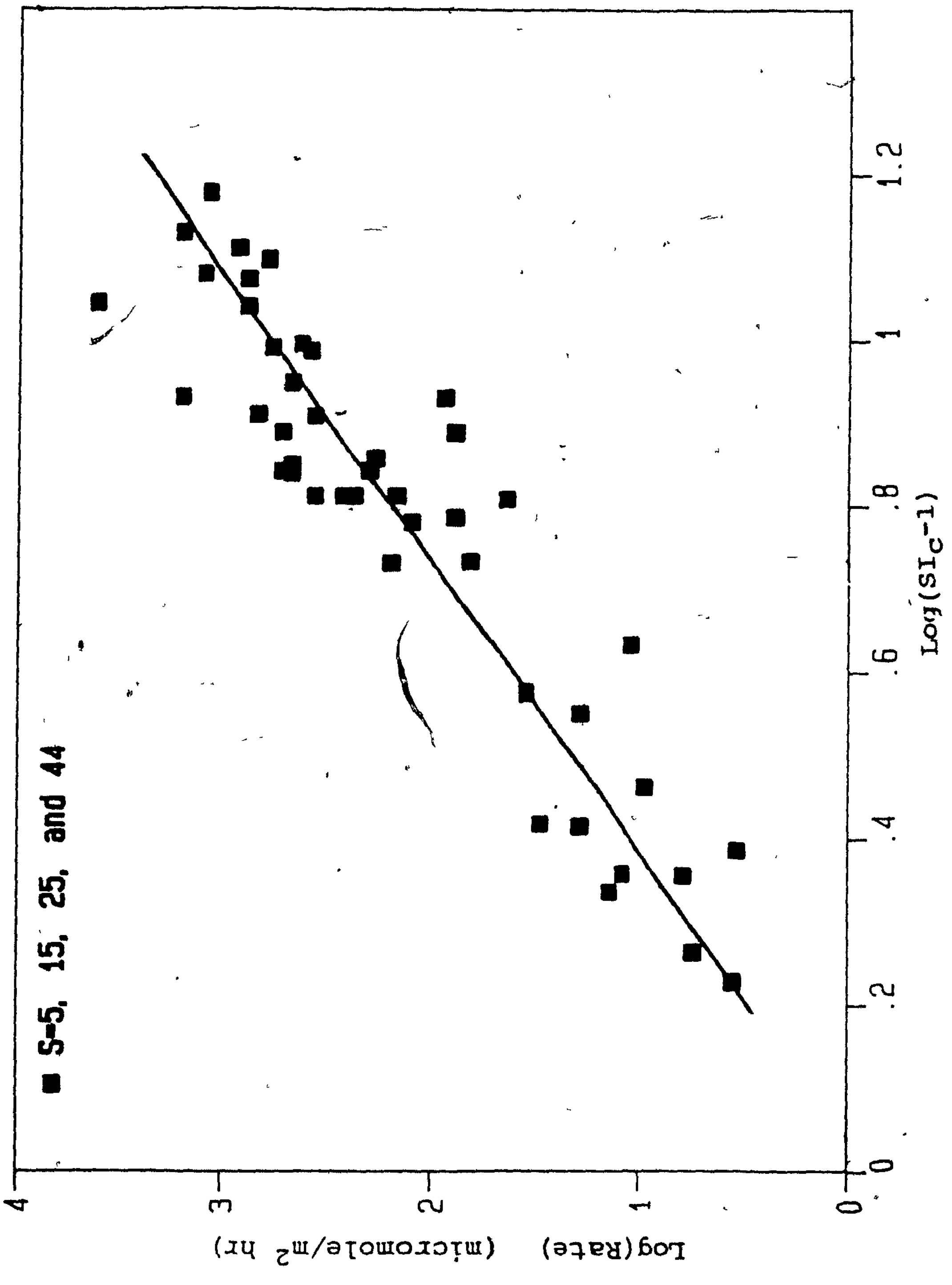


Figure IV.16. Log(Rate) vs. Log(SI_c-1) for Calcite at All Salinities Investigated

This result confirms the conclusions of previous studies (e.g., Badiozamani et al., 1977; Chen et al., 1979; Kazmlerczak et al., 1982; and Walter, 1986).

The empirical reaction order corresponding to the precipitation of calcite was close to 2.9. In the case of aragonite the empirical reaction order was around 2.3, regardless of the change of salinity within the range investigated in this study. The only difference between the rate equations for the two groups (i.e., 5 to 25 and 35 to 44) of data for aragonite is that there is a reaction rate constant difference. The difference is around 0.4, which represents a rate difference of 2.51 micromoles per square meter per hour. In other words, under the same saturation state and laboratory conditions, aragonite will precipitate 2.51 micromoles per square meter more per hour in solutions with a salinity at and/or lower than 25 than in solutions with a salinity at and/or higher than 35. An increase in salinity from 25 to 35 will slightly decrease the aragonite precipitation rate when other conditions are kept constant.

The precipitation rates of aragonite and calcite were compared after adjustment to the common $\mathrm{Log}(SI_C-1)$ scale. The results are shown in Figure IV.17. Under our experimental conditions, the precipitation reaction of aragonite is always faster than that of calcite. These results are in good agreement with those of Burton and Walter (1987) obtained at the same temperature (i.e., 25°C). However, it must be pointed out that

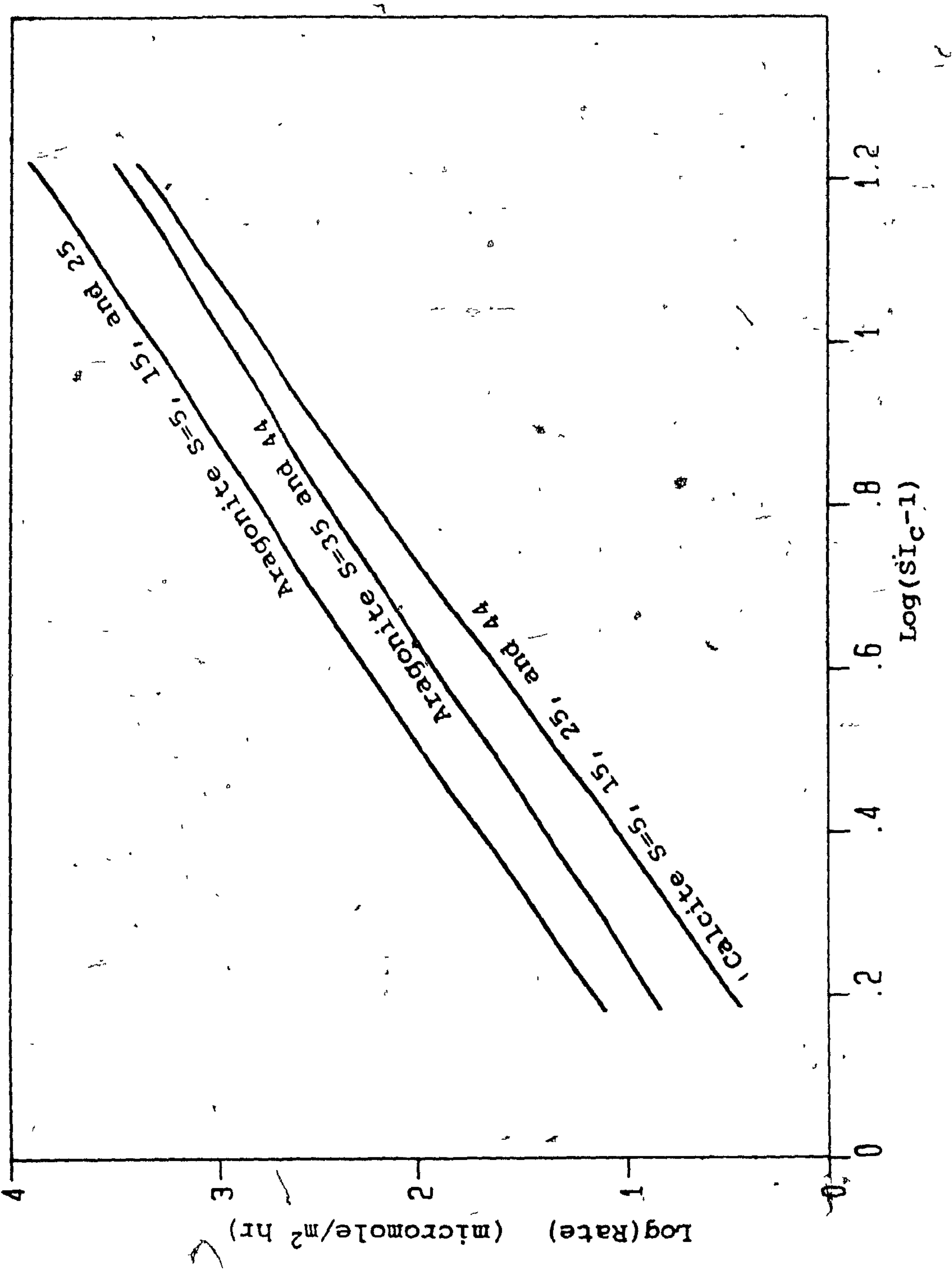


Figure IV.17. Comparison of the Precipitation Rates between Aragonite and Calcite these conclusions are only vadid within the range of supersaturation investigated. Since aragonite has a higher solubility than calcite, a seawater sample may be supersaturated with respect to calcite while being undersaturated, at or very close to equilibrium with respect to aragonite. In this case, the precipitation rate of calcite will be faster than that of aragonite no matter what the salinity or temperature is.

To summarize, the precipitation reactions of aragonite and calcite are best described by an empirical rate law (i.e., eqn. II.22). The calcite precipitation reaction has an empirical reaction order of 2.9 ± 0.4, while the empirical reaction order for the aragonite precipitation reaction is around 2.2 ± 0.4. Salinity has no significant kinetic effect on the precipitation rate of calcite and only a minor effect on the reaction rate constant of aragonite as solution salinity changed from 25 to 35 under our experimental conditions. These results concur with the conclusions of previous studies of Walter (1986) and others in solutions other than seawater. Furthermore, the precipitation of aragonite is favored to that of calcite for $SI_C > 2.6$ at all salinities investigated at 25°C, which is in agreement with the results of Burton and Walter (1987).

CHAPTER V

APPLICATIONS TO SOME GEOLOGICAL PROBLEMS

V.1 The mineralogy of cements in beachrocks:

The precipitation of calcium carbonate cements near the water-table and in the intertidal zone of tropical and sub-tropical beach sediments is a wide-spread phenomenon and a rapid process (on the order of years to tens of years) (Milliman, 1974). It is well-known that aragonite and high-Mg calcite are the two major minerals which make up the cements or matrices of beachrocks in marine environments (see numerous examples in Bricker, 1971), while low-Mg calcite dominates cements or matrices of beachrocks in fresh water environments (e.g., Friedman, 1964; Schmalz, 1971; Hanor, 1978; Binkley et al., 1980). It is also found that the phreatic cements in the back beach, where fresh ground water dominates, are predominantly low-Mg calcite, whereas the beachrock cements to the seaward are composed of high-Mg calcite and aragonite (Hanor, 1978). At first glance, these observations seem to indicate a strong link between the mineralogy of cements and the salinities of the interstitial waters.

It is generally agreed that the carbonate cements of beachrocks are inorganic precipitates. The basic mechanisms of carbonate cementation are, therefore, inherently chemical processes. The controversy is, however, as to which factor(s) caused these cements to precipitate and what controlled their mineralogy and morphology. Commonly invoked inorganic processes for the precipitation of cements include (1) precipitation generated by evaporation of seawater in beach sediments (e.g., Taylor and Illing, 1969), (2) precipitation induced by mixing of waters of diverse composition (Schmalz, 1971; Moore, 1973), and (3) deposition caused by CO_2-degassing processes (e.g., Hanor, 1978; Meyers, 1987; James and Choquette, 1983b).

Most people agree that these cements were precipitated from seawater and/or the mixture of seawater and freshwater. The salinity variation of the interstitial waters in beachrocks during the precipitation of cements is, therefore, expected and its relation to the formation, mineralogy and morphology of the cements in the beachrocks has attracted much attention. It is believed that the change of salinity is one of the major factors which initiated the precipitation processes and controlled the mineralogy and morphology of the cements in beachrocks. For example, based on a mass balance calculation, which indicated that a significant amount of calcium carbonate had been precipitated within the mixing zone, Friedman (1968) concluded that "though the chemical processes are as yet inadequately understood, cementation appears to result from direct precipitation induced by the mixing of brackish and normally saline interstitial waters". Moore (1983) also concluded that cements composed of Mg-calcite indicate a precipitation from mixed marine-fresh meteoric waters, while cements composed of aragonite indicate a precipitation from normal marine waters with no freshwater influence. Binkley et al. (1980) suggested that ionic strengths of fluids may play a significant role in determining crystal habit of beachrock cements. Folk (1974) went a step further to suggest that sodium ions inhibit the precipitation of calcite so that the calcite precipitation reactions are slow or absent in high salinity (or high ionic strength) media, such as seawater.

The solubilities of calcite (or Mg-calcite) and aragonite are functions of salinity (see Figure IV.15). Because of the non-linear correlation between salinity and solubility, the mixing of supersaturated marine and fresh waters may result in a less supersaturated or even undersaturated solution (see Runnells, 1969 and Plummer, 1975, for details). This contrasts with the hypothesis that cementation is induced simply by mixing of marine water with fresh waters. Since the change of salinity has equivalent effects on the stoichiometric solubilities of both calcite and aragonite, the mineralogy of the cements and the relative rate of their precipitation reactions are mainly a result of the kinetics of the precipitation reactions.

According to the results of this study and within the experimental conditions investigated (i.e., $5 \leqslant S \leqslant 44$, $2.6 \leqslant SI_C < 17$, $t = 25^{\circ}C$, $Pco_2 = 0.003$ atm), it is expected that changes in salinity of interstitial waters would have no or very insignificant kinetic effect on the relative precipitation rate and mineralogy of carbonate cements. Although this conclusion should not be extrapolated to those geological environments where the solution conditions deviate significantly from the experimental conditions covered in this study, there are some situations where the results of this study should apply. For example, in Boiler Bay, St. Croix, the SI_C of ground waters in the mixing zone varies from 2 (back beach) to 5 (forebeach) (based on the data of Hanor, 1978). Furthermore, there is no evidence to suggest that salinity of the solution alone has a significant kinetic effect on the precipitation kinetics of calcium carbonate at lower supersaturation states (i.e., $SI_C < 2.6$). Obviously, at $1 < SI_C < 1.5$ it is thermodynamically unreasonable to expect aragonite to precipitate from any mixed seawater solution since the solution would be undersaturated with respect to aragonite. Results from this study, as well as those from Badiozamani et al. (1977), Walter (1986), and others, therefore, indicate that the above interpretations proposed by Friedman and others are oversimplified. In addition, contrary to Folk's (1974) suggestion, results from this study indicate that the precipitation of aragonite rather than that of calcite is kinetically favoured even in dilute solutions at $SI_C > 2.6$. Thus, other factors, some of which might accompany the evaporation or mixing processes, should be called upon to explain these geological observations obtained in beachrock cements.

In fact, it has been found that factors such as the intensity of CO_2-degassing (Hanor, 1978; Meyers, 1987; James and Choquette, 1983b), temperature (Burton and Walter, 1987), cementation rate (Given and Wilkinson, 1985; Meyers, 1987), Mg/Ca concentration ratio in the solution (Folk, 1974; Berner, 1975; Folk and Land, 1975; Mucci and Morse, 1983) and others are important. However, it is beyond the scope of this paper to summarize these factors. Interested readers are referred to these references for details.

V.2 "Whitings" on the Grand Bahama Banks:

The occurrence of modern shallow water carbonate precipitation has been documented in several places, such as the Grand Bahama Banks (Smith, 1940; Cloud, 1962), the Persian Gulf (Wells and Illing, 1964), and South China Sea (Chen et al., 1979). A fascinating phenomenon called "whitings" was reported both in the Grand Bahama Banks and in the Persian Gulf. In both cases, "whitings" originated as patches of suspended fine-grained aragonite needles. The formation of the "whitings" is, however, still puzzling geologists and oceanographers. The primary area of debate has centered around whether the "whitings" represent resuspended sediments (Broecker and Takahashi, 1966) or precipitates formed from the water (Smith, 1940; Cloud, 1962).

In the Grand Bahama Banks, the geochemical and oceanographic settings are relatively simple. Surface ocean water with a salinity around 36.5 flows from the North Providence Channel and the Florida Straits towards the south through the Grand Bahama Bank. Because of the net evaporation, the salinity of the water gradually increases southward with the highest salinity value (around 44) being found half way through the Bank on the western shores of Andros Island. If one takes a north to south trip on the Banks, he will find that the waters become progressively more cloudy while the salinity of the waters increases gradually; eventually an area of common "whitings" is reached. After passing farther south into the higher salinity waters (S greater than 40), he will find that the water becomes very clear. The "whitings" form a halo on the central and northern part of the Bank around the high salinity zone (Broecker and Takahashi, 1966; Morse et al., 1984).

It has been found that the calcium carbonate removal rate is about 1.5 times faster in the low salinity waters (less than 40, where "whitings" are common) than in the high salinity waters (Broecker and Takahashi, 1966; Morse et al., 1984). This difference is, however, satisfactorily explained by the difference of supersaturation states between the two water masses (Morse et al., 1984) but cannot account for the difference in the amount of aragonite present in "whitings" and in the clear water mass. In addition, careful pH, A_t, Pco_2, and total CO_2 measurements indicate that there is no statistically significant differences in these parameters between water collected in the "whitings" and in the adjacent waters (Broecker and Takahashi, 1966; Morse et al., 1984). These lines of evidence are clearly in disagreement with the hypothesis that "whitings" are the result of a local intensification of the aragonite precipitation process.

Our experimental results indicate that within the range of 35 to 44, salinity changes have no kinetic effect on the precipitation rate of aragonite. Although our results do not provide any explanation for the cause of "whitings", they do eliminate the possibility that at a given saturation state, the inorganic precipitation reaction of aragonite is kinetically enhanced or hindered by the change of salinity.

V.3 Dolomitization in the mixing zone:

One of the most extensively studied carbonate diagenetic environment is the mixing zone, where dramatic changes, including dolomitization, are known to occur (e.g., Hanshaw et al., 1971; Badiozamani, 1973; Land, 1973; Folk and Land, 1975). Dolomite formed in this zone is mostly clear, euhedral, well-ordered rhombs (Ward and Halley, 1985). It is insignificant in quantity and is present as cement and micromatrix.

While dolomite is thermodynamically much more stable under earth surface conditions than other carbonate minerals, it is very rare in surface and shallow subsurface environments compared to its metastable counterparts (i.e., aragonite and Mg-calcite). It has been gradually realized that the principle reason for this is that in the case of dolomitization, reaction kinetics override thermodynamic constraints (Morrow, 1982; Machel and Mountjoy, 1986). That is to say, the kinetic barrier is so high that the thermodynamic potential is not great enough to overcome it in low temperature and low pressure environments, although the exact role and number of kinetic parameters is not quite clear. In the case of dolomitization in the mixing zone, salinity is often regarded as an important kinetic parameter (e.g., Hanshaw et al., 1971; Badiozamani, 1973; Folk and Land, 1975). However, as pointed out by Morrow (1982), it is not sufficient merely to state that a drop in salinity promotes dolomitization, we must know why and under what circumstances this is true if we are to make full use of this insight in our interpretation.

Two similar models have been proposed to explain the formation of dolomite in the mixing zone. They are the "Dorag" model by Hanshaw et al. (1971) and Badiozamani (1973) and the "Schizohaline" model by Folk and Land (1975).

From a chemical point of view, the "Dorag" model is based entirely on thermodynamic considerations of the consequence of the mixing process and does not include any kinetic implications. Therefore, the fundamental stand of the "Dorag" model is inconclusive or unrealistic and thus this model will not be discussed here.

The "Schizohaline" model proposed by Folk and Land (1975) is based on the relationship between crystallization and the mineralogy of the cements and micromatrices. The rationale behind this is that at high precipitation rates the metastable but simple phases (i.e., calcite and aragonite) will form, while at low precipitation rate the more stable and more complex phase (i.e., dolomite) will develop. The speed of crystallization influences the degree of order because ions that adhere to incorrect lattice positions on the surface of rapidly growing crystals are more likely to be entombed in these positions than if the crystals grow slowly. Slower growth permits a longer period of exposure to the solution of an incorrectly situated ion. Therefore, dolomite is favoured in solutions where slow precipitation occurs. Without any evidence, Folk and Land (1975) went on to conclude that the precipitation rate of dolomite decreases with the decrease of salinity. Therefore, "the lower the salinity, the easier it is for dolomite to order." (Folk and Land, 1975). This constitutes the essence of the "Schizohaline" model.

As a matter of fact, the influence of salinity on the precipitation rate is very complex and difficult to verify by both theoretical considerations and laboratory experiments. Thermodynamic and kinetic considerations indicate that dolomite can form from waters of any salinity (Machel and Mountjoy, 1986). On the other hand, it is almost impossible to conduct any experiment because of the extreme slowness of crystallization of dolomite at low temperature and low pressure conditions (Gaines, 1980; Morrow and Ricketts, 1986). Nevertheless, experimental work in this study indicates that salinity does not have the significant kinetic effects on the precipitation rates of calcite and aragonite as once was believed. Considering that dolomitization is a multi-step process, it is conceivable that some of the steps involved may be similar to those leading to the precipitation of calcite. If one of these common steps is the rate-limiting step, one could speculate that salinity variations should not play an important role in dolomitization. Otherwise, any extrapolation of the results of this study to the problem of dolomitization would be inappropriate.

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Appendix I.

Saturation States and Related Raw Data

Saturation States of Aragonite at S=44:

Exp.#	A_t	pH	$[Ca^{2+}]$	A_c	$[CO_3^{2-}]$	SI_a	$Log(SI_a-1)$
69*	3.264	7.532	12.80	3.225	0.096	1.45	-0.34
74	7.519	7.664	12.41	7.468	0.296	4.33	0.52
77	8.323	7.634	14.07	8.275	0.308	5.10	0.61
79	4.062	7.633	13.61	4.014	0.149	2.39	0.14
80	10.22	7.606	14.62	10.18	0.356	6.14	0.71
83*	2.668	7.477	13.05	2.633	0.070	1.07	-1.13
84	4.328	7.602	13.38	4.283	0.149	2.35	0.13
87	6.115	7.648	13.56	6.065	0.232	3.71	0.43
88	6.481	7.662	13.38	6.430	0.254	4.00	0.48
90	5.588	7.670	13.24	5.536	0.222	3.47	0.39
92	9.858	7.588	14.37	9.814	0.331	5.60	0.66

* Data were omitted from the linear least-squares fits;

At (meq/kg) --- steady state total alkalinity;

pH --- steady state pH (NBS scale);

$[Ca^{2+}]$ (mmole/kg) --- steady state calcium concentration;

A_c (meq/kg) --- steady state carbonate alkalinity;

$[CO_3^{2-}]$ (mmole/kg) --- steady state carbonate concentration;

SI_a --- steady state saturation state with respect to aragonite;

SI_c --- steady state saturation state with respect to calcite.

Saturation States of Aragonite at S=35:

Exp.#	A_t	pH	$[Ca^{2+}]$	A_c	$[CO_3^{2-}]$	SI_a	$Log(SI_a-1)$
1	5.276	7.897	8.83	5.219	0.285	3.78	0.44
2	4.603	7.828	8.84	4.553	0.216	2.87	0.27
3	4.525	7.736	8.84	4.484	0.175	2.33	0.12
4	4.334	7.714	9.24	4.295	0.160	2.22	0.09
5	4.732	7.851	9.67	4.680	0.232	3.38	0.38
6*	3.117	7.636	9.87	3.084	0.097	1.44	-0.35
7	4.099	7.719	10.08	4.059	0.153	2.32	0.12
8	4.791	7.785	9.21	4.746	0.205	2.84	0.27
9	3.435	7.789	9.66	3.389	0.148	2.15	0.06
10	5.279	7.873	9.62	5.225	0.272	3.93	0.47
11	6.057	7.937	9.27	5.995	0.355	4.95	0.60
12*	3.466	7.655	9.75	3.431	0.113	1.65	-0.19
13*	3.281	7.670	9.96	3.245	0.110	1.65	-0.19
14*	3.133	7.564	9.66	3.104	0.084	1.22	-0.67
15*	2.823	7.595	9.81	2.793	0.080	1.19	-0.73
16*	2.869	7.576	9.93	2.840	0.079	1.17	-0.76

Saturation States of Aragonite at S=25:

Exp.#	A_t	pH	$[Ca^{2+}]$	A_C	$[CO_3{}^{2-}]$	SI_a	$Log(SI_a-1)$
17	4.212	7.681	7.61	4.190	0.111	1.92	-0.04
18	8.930	7.648	7.45	8.910	0.220	3.72	0.43
19	7.450	7.643	7.34	7.430	0.181	3.02	0.31
20	4.522	7.641	8.35	4.502	0.109	2.07	0.03
22	5.058	7.654	8.51	5.038	0.126	2.43	0.16
23	6.114	7.667	6.94	6.093	0.157	2.47	0.17
24	7.446	7.686	6.63	7.424	0.199	2.99	0.30
25	6.811	7.610	7.22	6.792	0.154	2.53	0.18
26	4.870	7.656	8.01	4.850	0.122	2.21	0.08
27	4.857	7.606	8.30	4.839	0.109	2.05	0.02
28	5.624	7.599	8.09	5.606	0.124	2.28	0.11
32	6.407	7.592	8.25	6.389	0.139	2.61	0.21
33	3.802	7.692	7.98	3.780	0.103	1.86	-0.07
34*	2.512	7.823	6.93	2.483	0.090	1.41	-0.39
35	9.122	7.587	8.24	9.104	0.197	3.67	0.43
36	5.421	7.685	7.39	5.399	0.144	2.42	0.15
37	7.757	7.616	8.31	7.738	0.178	3.36	0.37

Saturation States of Aragonite at S=15:

Exp.#	A_t	pH	$[Ca^{2+}]$	A_c	$[CO_3^{2-}]$	SI_a	$\log(SI_a-1)$
50*	3.486	7.765	4.038	3.473	0.074	1.23	-0.64
51*	2.953	7.760	4.022	2.941	0.062	1.02	-1.61
52	8.041	7.710	4.994	8.030	0.151	3.11	0.32
53*	3.992	7.743	4.620	3.980	0.081	1.53	-0.27
63	5.547	7.782	4.442	5.534	0.122	2.24	0.09
64	6.626	7.781	4.654	6.613	0.146	2.79	0.25
65	9.362	7.736	5.058	9.350	0.187	3.89	0.46
66	10.71	7.699	5.365	10.70	0.197	4.35	0.52
67	8.253	7.758	4.796	8.241	0.173	3.41	0.38
71	10.98	7.659	5.149	10.97	0.185	3.91	0.46
72	12.38	7.636	5.378	12.37	0.198	4.38	0.53

Saturation States of Aragonite at S=5

Exp.#	A_t	pH	$[Ca^{2+}]$	A_c	$[CO_3^{2-}]$	SI_a	$Log(SI_a-1)$
106	10.36	7.945	1.87	10.36	0.157	3.41	0.38
108	11.69	7.902	2.04	11.69	0.161	3.81	0.45
109	9.102	7.946	1.84	9.098	0.138	2.95	0.29
110	8.202	8.004	1.56	8.197	0.142	2.57	0.20
111	6.661	8.026	1.39	6.656	0.121	1.95	-0.02
112	9.705	7.948	2.08	9.701	0.148	3.57	0.41
113*	6.112	7.993	1.33	6.107	0.103	1.59	-0.23
114	10.11	7.923	2.16	10.11	0.146	3.66	0.43
115*	5.886	8.005	1.12	5.881	0.102	1.33	-0.49
116	12.97	7.732	3.26	12.97	0.122	4.61	0.56

Saturation States of Calcite at S=44:

Exp.#	A_t	pH	$[Ca^{2+}]$	A_c	$[CO_3{}^{2-}]$	SI_c	$Log(SI_c-1)$
68	5.315	7.812	14.58	5.246	0.283	7.44	0.81
70	10.08	7.863	13.45	10.00	0.599	14.5	1.13
73	7.319	7.858	13.77	7.243	0.430	10.7	0.98
75	4.458	7.772	13.45	4.394	0.218	5.29	0.63
76	8.775	7.863	14.38	8.698	0.521	13.5	1.10
78	6.490	7.853	13.98	6.415	0.377	9.49	0.93
81	5.915	7.841	13.17	5.841	0.335	7.94	0.84
82*	3.169	7.576	12.93	3.126	0.103	2.39	0.14
85	12.21	7.669	13.76	12.16	0.487	12.1	1.04
89	3.462	7.589	12.93	3.418	0.115	2.69	0.23
91	10.39	7.805	14.10	10.32	0.549	14.0	1.11
94	11.44	7.849	13.48	11.36	0.662	16.1	1.18

Saturation States of Calcite at S=25:

Exp.#	A_t	pH	$[Ca^{2+}]$	A_c	$[CO_3{}^{2-}]$	SI_c	$Log(SI_c-1)$
29	6.759	7.837	8.76	6.729	0.250	7.93	0.84
30	5.611	7.911	8.48	5.576	0.242	7.44	0.81
31	9.127	7.950	7.69	9.089	0.428	11.9	1.04
38	3.230	7.888	7.53	3.197	0.132	3.61	0.42
39	4.623	7.998	7.35	4.581	0.239	6.36	0.73
40	7.804	7.984	7.58	7.764	0.393	10.8	0.99
41	2.478	7.888	7.74	2.445	0.101	2.84	0.26
42	7.697	7.964	8.09	7.658	0.372	10.9	1.00
43	9.920	7.956	7.61	9.882	0.472	13.0	1.08
44	6.028	8.033	7.50	5.984	0.335	9.09	0.91
45	2.870	7.945	7.51	2.833	0.132	3.59	0.41
46	9.197	7.985	7.62	9.157	0.464	12.8	1.07

Saturation States of Calcite at S=15:

Exp.#	A_t	pH	$[Ca^{2+}]$	A_c	$[CO_3^{2-}]$	SI_c	$Log(SI_c-1)$
47	6.707	8.008	4.71	6.686	0.241	7.48	0.81
48	6.245	8.031	4.57	6.223	0.236	7.09	0.78
49	4.533	7.837	4.42	4.518	0.113	3.27	0.36
54	10.67	7.936	4.40	10.65	0.329	9.53	0.93
56	5.903	8.163	4.49	5.875	0.294	8.68	0.89
57	3.221	8.027	4.34	3.199	0.120	3.43	0.39
58	5.704	8.056	4.27	5.681	0.227	6.38	0.73
59	9.426	8.013	4.38	9.405	0.343	9.88	0.95
60	3.955	7.997	4.28	3.935	0.139	3.90	0.46

Saturation States of Calcite at S=5:

Exp.#	A_t	pH	$[Ca^{2+}]$	A_c	$[CO_3^{2-}]$	SI_c	$\log(SI_c-1)$
95	9.800	8.091	1.91	9.794	0.205	8.03	0.85
96	6.787	8.033	1.24	6.782	0.125	3.17	0.34
100	8.900	8.182	1.51	8.893	0.228	7.03	0.78
101	11.68	8.043	2.02	11.68	0.220	9.10	0.91
102	9.625	8.161	1.55	9.618	0.235	7.47	0.81
103	9.325	8.071	2.06	9.319	0.187	7.88	0.84
104	9.006	8.158	1.67	8.999	0.219	7.46	0.81
105	10.17	8.082	2.04	10.16	0.209	8.73	0.89
117	7.038	8.092	1.51	7.032	0.148	4.55	0.55
118	8.741	8.186	1.77	8.734	0.226	8.17	0.86
119	5.971	8.096	1.26	5.965	0.126	3.27	0.36

Appendix II.

Precipitation Rates and Associated Raw Data

Precipitation Rates of Aragonite at S=44:

Exp.#	$W_{t.t.}$	$W_{s.d.}$	$(A_C)_{t.t.}$	$(A_C)_{s.}$	Time	Rate	Log(R)
69*	9.8	0.6005	34.71	3.225	5.47	12.4	1.09
74	47.4	0.6002	102.6	7.468	5.52	184	2.27
77	52.8	0.6034	66.73	9.275	2.23	289	2.46
79	51.4	0.6023	34.71	4.014	11.80	28.4	1.45
80	52.9	0.6024	102.6	10.18	2.00	531	2.72
83*	7.2	0.6030	34.71	2.633	24.03	2.14	0.33
84	52.8	0.6029	34.71	4.283	12.13	27.7	1.44
87	46.8	0.6005	66.73	6.065	5.47	114	2.06
88	50.8	0.6036	66.73	6.430	4.25	157	2.20
90	44.1	0.6019	66.73	5.536	7.23	82.9	1.92
92	49.2	0.6009	106.4	9.814	2.57	407	2.61

* Data were omitted from the linear least-squares fits;

$W_{t.t.}$ (g) --- weight of "Anion" titrant added;

$W_{s.d.}$ (g) --- weight of seed material;

$(A_C)_{t.t.}$ (meq/kg) --- carbonate alkalinity of "Anion" titrant;

$(A_C)_{s.}$ (meq/kg) --- steady state carbonate alkalinity of precipitating solution;

Time (hour) --- duration of experiment;

Rate (micromole/m^2 hr) --- precipitation rate.

Precipitation Rate of Aragonite at S=35:

Exp.#	$W_{t.t.}$	$W_{s.d.}$	$(A_C)_{t.t.}$	$(A_C)_{s.}$	Time	Rate	Log(R)
1	50.0	0.6010	57.32	5.219	5.87	97.8	1.99
2	47.9	0.6006	57.32	4.553	11.02	51.3	1.71
3	48.5	0.6040	57.32	4.484	21.92	26.0	1.42
4	49.6	0.5956	57.32	4.294	43.98	13.6	1.13
5	43.2	0.6165	57.32	4.680	5.05	97.9	1.99
6*	49.4	0.6064	46.41	3.084	43.77	11.0	1.04
7	48.4	0.6045	46.41	4.059	21.90	20.6	1.31
8	50.6	0.6331	57.32	4.746	11.70	48.0	1.68
9	10.4	0.5034	46.41	3.389	4.17	28.9	1.46
10	48.0	0.5895	57.32	5.225	2.83	198	2.30
11	52.2	0.6013	57.32	5.995	1.58	366	2.56
12*	10.8	0.6121	46.41	3.431	6.13	16.7	1.22
13*	11.0	0.6185	46.41	3.245	12.15	8.59	0.93
14*	1.00	0.5966	46.41	3.104	2.00	4.95	0.70
15*	0.93	0.6175	46.41	2.793	3.50	2.58	0.41
16*	0.97	0.6132	46.41	2.840	7.17	1.32	0.12

Precipitation Rate of Aragonite at S=25:

Exp.#	$W_{t.t.}$	$W_{s.d.}$	$(A_c)_{t.t.}$	$(A_c)_{s.}$	Time	Rate	Log(R)
17	45.9	0.6089	32.37	4.190	15.10	17.6	1.25
18	50.0	0.6016	46.84	8.910	1.55	229	2.36
19	52.0	0.6012	57.28	7.439	3.17	170	2.23
20	41.9	0.6004	32.37	4.502	3.58	66.9	1.83
22	21.6	0.6007	32.37	5.038	2.93	40.2	1.60
23	47.9	0.6024	57.28	6.093	5.67	93.0	1.97
24	45.5	0.6020	57.28	7.424	3.83	123	2.09
25	47.5	0.6008	57.28	6.792	5.62	90.4	1.96
26	43.4	0.6027	46.84	4.850	7.22	54.5	1.74
27	47.5	0.6012	39.67	4.839	5.62	62.0	1.79
28	48.0	0.6020	39.67	5.606	4.03	82.7	1.92
32	47.0	0.6020	46.84	6.389	4.00	97.8	1.99
33	46.2	0.6030	39.67	3.780	29.55	12.2	1.09
34*	10.7	0.6024	32.37	2.483	13.00	5.5	0.74
35	50.6	0.6043	64.87	9.104	1.58	363	2.56
36	47.5	0.6017	46.84	5.399	5.62	74.5	1.87
37	47.8	0.5998	57.28	7.738	2.07	237	2.37

Precipitation Rate of Aragonite at S=15:

Exp.#	$W_{t.t.}$	$W_{s.d.}$	$(A_C)_{t.t.}$	$(A_C)_{s.}$	Time	Rate	Log(R)
50*	47.0	0.5997	13.82	3.473	21.78	3.64	0.56
51*	8.8	0.6025	13.16	2.941	13.90	1.12	0.05
52	44.7	0.6007	55.63	8.030	1.40	309	2.49
53*	47.3	0.6006	15.14	3.980	4.03	20.6	1.31
63	43.5	0.5997	55.63	5.534	5.23	90.8	1.96
64	45.0	0.6004	55.63	6.613	2.75	170	2.23
65	48.4	0.6003	107.8	9.350	2.92	362	2.56
66	48.3	0.6005	107.8	10.70	2.08	490	2.69
67	49.6	0.6000	107.8	8.241	4.20	264	2.42
71	51.3	0.5999	107.8	10.97	2.22	487	2.69
72	52.6	0.6009	107.8	12.37	1.63	655	2.82

Precipitation Rate of Aragonite at S=5:

Exp.#	$W_{t.t.}$	$W_{s.d.}$	$(A_c)_{t.t.}$	$(A_c)_{s.}$	Time	Rate	Log(R)
106	46.6	0.6009	153.0	10.36	7.87	192	2.28
108	40.2	0.6018	251.9	11.69	6.77	332	2.52
109	43.2	0.6007	153.0	9.098	7.28	196	2.29
110	45.0	0.6001	153.0	8.197	14.80	102	2.01
111	47.1	0.6023	76.24	6.656	21.80	33.2	1.52
112	48.6	0.6011	153.0	9.701	5.83	272	2.44
113*	32.2	0.6004	75.24	6.107	41.08	12.3	1.09
114	48.6	0.6013	153.0	10.11	4.17	379	2.58
115*	10.7	0.6021	76.24	5.881	17.77	9.48	0.98
116	49.2	0.6029	251.9	12.97	3.00	904	2.96

Precipitation Rate of Calcite at S=44:

Exp.#	$W_{t.t.}$	$W_{s.d.}$	$(A_c)_{t.t.}$	$(A_c)_{s.}$	Time	Rate	Log(R)
68	49.5	0.6003	34.71	5.246	43.62	44.0	1.64
70	49.0	0.6004	102.6	10.00	4.08	1590	3.20
73	19.8	0.5999	66.73	7.243	4.53	366	2.56
75	2.8	0.5996	66.73	4.394	23.88	10.7	1.03
76	49.7	0.6018	102.6	8.698	11.40	593	2.77
78	30.0	0.6017	66.73	6.415	29.92	86.5	1.94
81	49.1	0.6006	66.73	5.841	22.08	196	2.29
82*	0.80	0.6018	34.71	3.126	22.32	1.63	0.21
85	49.3	0.6018	102.6	12.16	1.50	4110	3.61
89	3.6	0.6005	34.71	3.418	45.63	3.47	0.54
91	48.5	0.6002	106.4	10.32	7.92	842	2.93
94	46.6	0.6010	106.4	11.36	5.53	1130	3.05

Precipitation Rate of Calcite at S=25:

Exp.#	$W_{t.t.}$	$W_{s.d.}$	$(A_c)_{t.t.}$	$(A_c)_{s.}$	Time	Rate	Log(R)
29	48.2	0.5996	39.67	6.729	4.07	498	2.70
30	34.8	0.6018	46.84	5.576	5.77	344	2.54
31	47.3	0.6003	57.28	9.089	4.00	741	2.87
38	49.4	0.6022	10.84	3.197	11.52	30.4	1.48
39	49.6	0.6000	14.98	4.581	3.00	154	2.19
40	47.1	0.5998	57.28	7.764	5.58	565	2.75
41	20.1	0.5999	10.84	2.445	35.07	5.46	0.74
42	49.6	0.6008	57.28	7.658	8.28	402	2.60
43	48.3	0.6020	64.87	9.882	2.92	1190	3.08
44	10.8	0.6018	57.28	5.984	2.30	340	2.53
45	10.7	0.6006	10.84	2.833	4.50	19.7	1.29
46	19.6	0.6000	57.28	9.157	1.67	734	2.87

Precipitation Rate of Calcite at S=15:

Exp.#	$W_{t.t.}$	$W_{s.d.}$	$(A_c)_{t.t.}$	$(A_c)_{s.}$	Time	Rate	Log(R)
47	46.9	0.6013	55.63	6.686	21.60	147	2.17
48	17.1	0.6007	55.63	6.223	15.30	77.3	1.89
49	10.0	0.6006	15.14	4.518	8.00	12.2	1.09
54	50.9	0.6004	65.98	10.65	2.27	1610	3.21
56	40.9	0.6003	55.63	5.875	37.12	77.5	1.89
57	10.9	0.6023	13.16	3.199	35.22	3.35	0.53
58	8.8	0.6004	55.63	5.681	9.92	63.3	1.80
59	47.7	0.6018	65.98	9.405	8.00	449	2.65
60	15.8	0.6026	15.14	3.935	19.67	9.32	0.97

Precipitation Rate of Calcite at S=5:

Exp.#	$W_{t.t.}$	$W_{s.d.}$	$(A_c)_{t.t.}$	$(A_c)_{s.}$	Time	Rate	Log(R)
95	48.2	0.6016	163.4	9.794	24.00	462	2.66
96	3.5	0.5995	76.24	6.782	25.50	14.0	1.15
97	8.8	0.6254	76.24	7.625	23.20	35.6	1.55
100	27.0	0.5992	123.3	8.893	36.17	127	2.10
101	32.9	0.6014	163.4	11.68	10.88	677	2.83
102	29.8	0.6009	123.3	9.618	19.58	253	2.40
103	41.3	0.6010	153.0	9.319	19.00	467	2.67
104	21.8	0.6021	153.0	8.999	20.55	229	2.36
105	44.7	0.6014	163.4	10.16	20.58	498	2.70
117	8.3	0.6016	76.24	7.032	41.17	20.0	1.30
118	29.3	0.6018	123.3	8.734	26.63	186	2.27
119	1.36	0.6019	76.24	5.965	23.28	6.00	0.78