The solubility of calcite in seawater solution of different magnesium concentrations at 25°C and 1 atm total pressure: A laboratory re-examination

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Abstract: The effect of magnesium ion concentration and the degree of saturation of calcium carbonate in artificial seawater solution (ASW) upon the equilibrium states of calcium carbonate solid has been studied. The apparent solubility products of pure calcite, when exposed to different magnesium-to-calcium concentration ratios in ASW increase with the increase of magnesium ion in the test solution. Their solubility values further increase by increasing the degree of supersaturation at the same magnesium concentration in ASW. The increase of surface areas, that are exposed to the same volume of the solution under the same condition tend to lower the values of the apparent solubility products. This may indicate a sort of shift from kinetic steady-state to probably a thermodynamic equilibrium. The thermodynamic solubility products that are estimated from the ion association model and the activity of calcite and magnesite in the test ASW show that the activity coefficient of magnesite is higher than that of calcite, which indicates that a nonideal solid solution is formed.

1. Introduction

The degree of saturation of seawater with respect to calcite is an important parameter for the prediction of precipitation and dissolution of calcium carbonate mineral in aquatic environment. Although, some natural waters such as marine surface seawater and pore waters are reported to be supersaturated with respect to calcite(WEYL, 1961; CLOUD, 1962; SCHMALZ and CHAVE, 1963; BERNER, 1966a; PLATH et al., 1982; MUCCI and MORSE, 1984; WALTER and MORSE, 1984) there are no inorganic precipitation of $CaCO_{3(s)}$ observed and surprisingly, the availability of fine-grained size $CaCO_{3(s)}$ does not

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change the growth of cementation fabric (BATHURST, 1964, 1974). The presence of metastable calcite phases indicates that either a lack of equilibrium (KRAUSKOPF, 1967) or a compositional thermodynamic equilibrium exists with respect to solid carbonate coating phase (WOLLAST and REINHARD-DERIE, 1977; PYTKOWICZ and COLE, 1979; KONIGSBERGER and GAMSJAGER, 1990).

The retention of supersaturation of natural water and the very slow diagenetic transformation of sediments led many investigators to study the influence of organic and inorganic additives upon the chemical and physical behavior of calicium carbonate minerals (PYTKOWICZ, 1965; JACKSON and BISCHOFF, 1971; SUESS, 1970, 1973; RUSHDI et al., 1992).

The magnesium ion in natural seawater is the third major ion in seawater and it is five times the concentration calcium ion. It is directly involved in the formation of $CaCO_{3(s)}$ solid. In marine environment natural calcite contains a range of magnesium in solid solution which is usually named magnesian calcite.

The skeletal magnesian calcite in biogenic hard parts and marine magnesian calcite in cements are the most important occurrences of these phase (SILLIMAN, 1846; CHAVE, 1952, 1954a, 1954b, 1981; LAND, 1967; SCHMALZ, 1967; PIGOTT and LAND, 1986; ANDERSON and DYRSSEN, 1987; BUSENBERG and PLUMMER, 1989). The most important contributors of skeletal magnesian calcite to shallow water marine sediments are the skeleton of calcareous red algae, benthic foraminifera, bryozoans, echiniods and barnacles (CHAVE, 1981).

Different magnesian calcite mineral have different solubility in solution and it was shown that their solubilities increases with the increase of magnesian fraction in calcite (CHAVE et al., 1962; LAND, 1967; PLUMMER and MACKENZIE, 1974; BERNER, 1975; THORSTENSON and PLUMMER, 1977; MORSE et al., 1979; SCHOONMAKER, 1981; KOCK and DISTECHE, 1984; MUCCI and MORSE, 1984; PIGOTT and LAND, 1986). The values of apparent solubility products of calcite in seawater of 34.8‰ salinity and 25℃ were reported to be between 4.24×10^{-7} to 5.94×10^{-7} $mole^2 kg^{-2}$ SW. (CLOUD, 1962b; MOLLER and PAREKH, 1975; MACINTYRE and PLATFORD, 1965; PLATH, et al., 1982; MUCCI and MORSE, 1984). It is believed that the surface area of the mineral that is exposed to the solution plays an essential role on the equilibrium conditions (WOLLAST and REINHARD-DERIE., 1977; WOLLAST and PYTKOWICZ, 1978; PYTKOWICZ and COLE, 1979; MACKENZIE et al., 1982).

The equilibrium states between calcium-magnesium carbonate mineral and aqueous solution at a given temperature and pressure are still ambiguous. It is shown that the stationary states of calcium carbonate in presence of Mg^{2+} in solution are reaction-rate and kinetically controlled(WEYL, 1967; BERNER, 1978). To explain the equilibrium state of calcite an stoichiometric saturation model is developed for non-variable solid phase(THORSTENSON and PLUMMER, 1977). They show that magnesian calcite with <5 mole % $MgCO_3$ is controlled by thermodynamic equilibrium and the occurrence of other compositions is a kinetic control. It has also been suggested (WOLLAST and REINHARD-DERIE, 1977; PYTKOWICZ, and COLE, 1979) that there is no single thermodynamic

phase that is an stable one the presence of solid solution. It is also stated that, magnesiam calcite is governed by activity products of ($^aCa^{2+}$) ($^aCO_3^{2-}$) rather than (Mg^{2+})-to-(Ca^{2+}) in aqueous phase(MACKENZIE and PIGOTT, 1982; RUSHDI, 1992).

The purpose of this work is to re-examine the effects of various magnesium concentrations, at two different degree of saturations with respect to calcite seeds having different surface areas in artificial seawater, upon the apparent solubility products of calcite. The ionic strength is to be maintained constant at a temperature of 25℃. The ion association model is used in conjunction with the mole fraction of $CaCO_{3(s)}$ in the calcite overgrowth to predict the thermodynamic solubility product of magnesian calcite in the test solution.

2. Experimental procedure
Experiment

(Mg^{2+}), (Sr^{2+}) and (H_3BO_3)-free artificial seawater, ASW, was prepared following the procedure of KESTER et al., (1967). The ASW, which had an ionic strength of 0.526M, was equilibrated with the laboratory pCO_2 for about two days by bubbling air through the solution. The bubbling was stopped when the measured pH was stable and did not change by further bubbling. The concentration of (Ca^{2+}) in this solution was 9.754 mmole kg^{-1} ASW. Various amounts of magnesium were added, from prestandardized stock solution by Mohr titration (BLADEL and MELOCHE, 1957), to prepare solutions with (Mg^{2+})-to-(Ca^{2+}) concentration ratios of 1, 2, and 5. Different amounts of pre-dried reagent grade NaCl were added to these prepared solutions to maintain the ionic strength of 0.718M. Each solution was kept in a closed bottle and its pH was measured every 24 hours, it only changed by ± 0.008pH unit. It was noticed that the pH of these solutions decreased with increasing magnesium concentrations.

A reaction cell was constructed from a glass beaker with a water jacket for the determination of the solubility products of calcite in ASW of different (Mg^{2+})-to-(Ca^{2+}) concentration ratios and constant ionic strength of 0.718 at 25℃. The cell which had a volume of 103.76

±0.03 ml was described by RUSHDI, (1993).

The calcite seeds used in this experiment were reagent grade synthetic calcite (J.T. BAKER), which were washed with double deionized distilled water (DDW) three times, filtered and dried at 110–130℃ for about four hours, then they were kept in vacuum desiccate after cooling down. The x–ray diffraction showed that they were pure calcite by $2\theta = 29.4°$. The specific surface area of calcite seeds was estimated from its density and the seed mean volume, which was determined by SEM images. It was estimated that the specific area was $0.589 \pm 0.053 \; m^3 g^{-1}$.

The combination electrode (Radiometer GK2401C) was calibrated with NBS buffers, 185f (pH=4.006 at 25℃) and 186– I –c and 186–II–c (pH=7.415 at 25℃). The slope of the electrode was determined following the instruction in PHM64 Research pH meter Operating Instruction. Usually the slope was $99.00 \pm 0.21\%$.

Before each experiment, the initial total alkalinity of each test solution was measured by Gran titration method (GRAN, 1952; DYRSSEN and SILLEN, 1967; MEHRBACH, et al., 1973) and by single–acid addition(ANDERSON and ROBENSON, 1946) which was developed by CULBERSON et al., (1970) to a pH of 4.15 ± 0.10. The standard deviation of the total alkalinity determination by both method was $\pm 5.8 \; \mu eq \; kg^{-1} ASW$. The initial pH was also measured for each test solution. The initial total carbon dioxide $\Sigma CO_{2(i)}$ was calculated from these two known parameters by using the values of first and second apparent dissociation constants of carbonic acid at different magnesium concentration described by (RUSHDI and CHEN, 1995).

The reaction cell was completely filled with the test solution and the combination electrode was allowed to equilibrate until the measured pH changed by less than 0.003 pH unit per hour at 25℃, because the drift of the electrode was measured and found to be 0.003 pH per hour. The experiments were carried out in a water bath (Aminco Constant Temperature bath ♯4–8605) at $25.00 \pm 0.05℃$. Two different degree of saturation were obtained by selecting two pH values: pH=8.1 and pH=8.6 which were achieved by adding drops of 0.1N NaOH to the test solution from a syringe with a long needle

through the hole in the stopcock while stirring. Then the piston was pushed half–way into the solution to fulsh some of the excess solution. The pH was recorded every five minutes until three successive readings were the same then the calcite seeds were added. The required weight of calcite seeds was placed in 2.5 ml Hamilton syringe with a long needle, then stirring was stopped and through the hole of the stopcock about 1.5 ml of ASW of the test solution was withdrawn into the syringe to form a slurry of calcite, which was then injected slowly into the solution without stirring. This step was done carefully to avoid any bubble trapping in the cell, and it was done at least three times to insure that all the amount of calcite was delivered into the solution and settled to the bottom of the raction cell. The piston was pushed all–the–way down to displace the excess volume of ASW through the stopcock hole. The stopcock was immediately closed to prevent CO_2 exchange and the solution was stirred. The pH was recorded with time until it reached steady–state. The steady–state value was assumed to be achieved when the change in pH was again less than 0.003 pH unit hr^{-1} assuming that our pH measurement was better than 0.008 pH unit. Although, it took between 6 to 8 hours to reach a steady–state in experiments of high solid to solution ratios, all the experiments were run for at least 48 hours. After reaching the steady–state equilibrium the solution was filtered through $0.45 \; \mu M$ Millipore filter papers. The unwashed seeds were collected, dried and stored for calcium and mangesium content determinations. Atomic adsorption analysis, AA, was used to determine the final (Ca^{2+}) concenrations. The concentration of calcium at equilibrium of each solution was determined by diluting the solution to obtain a calcium concentration of about 1.00 ppm. The original test solution was used as a standard, from which two dilutions with calcium concentration of 1.25 ppm and 0.90 ppm were prepared. Excess KCl (about 1000 ppm) was added to each solution as an ionizing suppressant to avoid the ionization of excess NaCl which may affect the $(Ca^{2+})$and (Mg^{2+}) determinations. The concentration of (Mg^{2+}) at equilibrium could be calculated by difference between the

amount to total $(Mg^{2+}+Ca^{2+})$ precipitated and the measured (Ca^{2+}) by AA analysis accordingly:

$$(Mg^{2+})_f = (Mg^{2+})_i + [(Ca^{2+})_i - (Ca^{2+})_f] \quad (1)$$

where the subscripts f and i refer to final and initital respectively. To double – check the results, it was also calculated accordingly: $(Mg^{2+})_f = (Mg^{2+})_i + [\Delta + (Ca^{2+})_f - (Ca^{2+})_i]$, where Δ is explained next in calculation.

About 10 mg of the seeds was dissolved by adding drops of 0.5M HCl and dilute to obtain about 1.00 ppm Ca^{2+} and another to obtain about 0.5 ppm Mg^{2+} to determine the calcium and magnesium content of the overgrowth by AA's method. This was done by assuming that magnesium content was compositionally homogeneous in the overgrowth coatings. The residual (Na^+) concentration on calcite was also determined by AA's analysis to calculate the residual (Mg^{2+}) and (Ca^{2+}) from the concentration ratios of these major ions to (Na^+) in the original solution.

Calculation

The total CO_2, ΣCO_2, in mole $kg^{-1}ASW$ and total alkalinity, TA, in equivalent $kg^{-1}ASW$ are defined by the equations:

$$\Sigma CO_2 = (H_2CO_3{}^*) + (HCO_3{}^-)_T + (CO_3{}^{2-})_T \quad (2)$$

and:

$$TA = (HCO_3{}^-)_T + 2(CO_3{}^{2-})_T + (OH^-)_T - (H^+)_T \quad (3)$$

because the solution is borate–free artificial seawater. $(H_2CO_3{}^*)$ is the sum of (H_2CO_3) and CO_2 in solution and the subscript T refer to Total. Carbonate alkalinity, CA, in equivalent kg^{-1} ASW is defined by eqation:

$$\begin{aligned} CA &= TA - (OH^-)_T + (H^+)_T \\ &= (HCO_3{}^-)_T + 2(CO_3{}^{2-})_T \end{aligned} \quad (4)$$

In terms of ionization fraction (BULTER, 1964, SNOEYINK and JENKINS, 1980; STUMM and MORGAN, 1982):

$$CA = \Sigma CO_2 (\alpha_1 + 2\alpha_2) \quad (5)$$

where α_i represents the ionization fraction of ith species of carbonic acid at a certain pH.

Since the precipitaion or dissolution of $CaCO_{3(s)}$ affects both the total carbon dioxide and the carbonate alkalinity, there will be a change in $\Sigma CO_2/CA$ ratio in the solution. The following equation is obtained:

$$\Delta = CA_i\{1/(\alpha_1 + 2\alpha_2)_i \\ -1/(\alpha_1 + 2\alpha_2)_f]/2[1/(\alpha_1 + 2\alpha_2)_f] - 1\} \quad (6)$$

where Δ is the number of moles of $CO_3{}^{2-}$ species that is involved in the formation or the dissolution of $CaCO_{3(s)}$ from the initial concentration i to the final concentration f (for details see INGLE, et al., 1973; PLATH and PYTKOWICZ, 1982; RUSHDI, 1993). The concentration of $CO_3{}^{2-}$ at equilibrium can be calculated by the following equation:

$$(CO_3{}^{2-})_f = (CA_i + 2\Delta) [K_2'/(x) + 2K_2']_f \quad (7)$$

The apparent solubility products is:

$$^{(Ca)}K_{sp}' = (Ca^{2+})_{T,f} (CO_3{}^{2-})_{T,f} \quad (8)$$

for calcite and:

$$^{(Mg)}K_{sp}' = (Mg^{2+})_{T,f} (CO_3{}^{2-})_{T,f} \quad (9)$$

for magnesite.

3. Result and discussion

The results of the effects of magnesium–to–calcium concentration ratios and the amount of calcite added to ASW at 25℃, upon the apparent solubility products of calcite and magnesite are shown in Table 1. The mean values of apparent solubility product in ASW for degree of supersaturations similar to natural seawater represented by pH≈8.1 versus magnesium concentration are illustrated in Figure (la) and in ASW of high degree of supersaturation represented by pH≈8.6 in Figure (1b).

Generally, the results in Table1 show that there is an increase in the values of the apparent solubility products with the increase of magnesium concentration in solution as is illustrated in Figure 1a and 1b. This trend of increase with higher magnesium concentration becomes more significant by increasing the degree of supersaturation (Figure 1b). The increase in the degree of supersaturation had no significant change on the apparent solubility products in the absence of magnesium in solution (Figure 1b). This indicates that magnesian ion in solution affects calcite solubility

Table 1. The apparent solubility products of calcite and magnesite as a function of magnesium to-calcium concentration ratios in ASW of two different degree of supersaturations and constant total ionic strength of 0.718 at 25℃.

Exp#	g calcite kg⁻¹ ASW	pH_i	pH_f	CA_i meq kg⁻¹ ASW (10^{+3})	$(Ca)_f$ mol kg⁻¹ ASW (10^{+3})	$(Mg)_f$ mol kg⁻¹ ASW (10^{+3})	$^{(Ca)}Ksp'$ mol² kg⁻² ASW (10^{+7})	$^{(Ca)}Ksp'$ mol² kg⁻² ASW (10^{+7})
				$(Mg^{2+}) : (Ca^{2+}) = 0 : 1$				
SC62	0.500	8.087	7.516	2.2935	9.6375	0.00	2.5314	⋯⋯
SC64	0.492	8.096	7.527	2.2959	9.6372	0.00	2.5968	⋯⋯
SC66	0.496	8.602	7.611	2.5062	9.4552	0.00	2.8071	⋯⋯
SC68	0.492	8.585	7.619	2.4959	9.4552	0.00	2.8806	⋯⋯
SC70	0.997	8.103	7.517	2.2979	9.6334	0.00	2.5314	⋯⋯
SC72	0.997	8.099	7.513	2.2967	9.6338	0.00	2.5083	⋯⋯
SC73	0.914	8.120	7.521	2.3024	9.6297	0.00	2.5495	⋯⋯
SC74	1.388	8.612	7.608	2.5124	9.4370	0.00	2.7760	⋯⋯
SC75	0.997	8.582	7.616	2.5031	9.4419	0.00	2.7803	⋯⋯
SC76	5.000	8.080	7.554	2.2917	9.6464	0.00	2.7803	⋯⋯
SC77	5.004	8.099	7.582	2.2967	9.6466	0.00	2.9676	⋯⋯
SC78	5.012	8.614	7.630	2.5136	9.4391	0.00	2.9253	⋯⋯
SC79	5.003	8.613	7.614	2.5130	9.4373	0.00	2.8154	⋯⋯
				$(Mg^{2+}) : (Ca^{2+}) = 2.9 : 1$				
SC80	0.499	8.096	7.531	2.2799	9.6314	28.8621	2.5314	8.1148
SC81	0.502	8.119	7.565	2.2287	9.7166	28.8621	3.1987	9.7798
SC82	0.499	8.626	7.668	2.5248	9.4970	28.8601	3.5420	10.027
SC83	0.558	8.640	7.644	2.5344	9.4834	28.8610	3.3221	9.4216
SC84	1.008	8.122	7.571	2.2876	9.6311	28.8608	3.2153	8.9040
SC85	1.001	8.157	7.573	2.2985	9.7064	28.8600	3.2390	8.9032
SC86	1.003	8.663	7.642	2.5508	9.4666	28.8620	3.2707	9.2975
SC87	1.002	8.634	7.690	2.5303	9.4094	28.8621	3.6872	10.537
SC88	5.005	8.105	7.595	2.2825	9.7263	28.8603	3.4484	9.4546
SC89	5.001	8.091	7.563	2.2785	9.7244	28.8622	3.1985	8.7702
SC90	5.000	8.628	7.614	2.5262	9.4017	28.8623	3.0790	8.8071
SC91	5.002	8.662	7.595	2.5242	9.5092	28.8622	3.0167	9.3946
				$(Mg^{2+}) : (Ca^{2+}) = 4.99 : 1$				
SC92	0.499	8.152	7.586	2.3662	9.6724	49.0910	4.7224	23.968
SC93	0.500	8.145	7.561	2.3632	9.6700	49.0908	4.4525	22.604
SC94	1.003	8.124	7.539	2.3546	9.6741	49.0914	4.2426	21.529
SC95	0.513	8.619	7.744	2.6578	9.4097	49.0923	5.7292	29.876
SC96	0.501	8.620	7.761	2.6561	9.4051	49.0781	5.8199	24.711
SC97	1.004	8.119	7.586	2.3526	9.6860	49.0923	4.7609	24.130
SC98	1.004	8.620	7.714	2.6553	9.4029	49.0901	5.3289	27.809
SC99	0.968	8.616	7.817	2.6553	9.4277	49.0720	6.8234?	35.563
SC100	1.001	8.612	7.689	2.6518	9.4050	49.0720	5.0424	26.309
SC02	5.002	8.122	7.559	2.3538	9.6854	49.0702	4.4666	22.645
SC03	5.002	8.122	7.589	2.3538	9.6854	49.0924	4.7922	24.290
SC04	4.012	8.619	7.714	2.6550	9.4030	49.0891	5.3291	27.701

products due to its' involvement in the crystal overgrowth. The increase in the surface area of calcite in solutions of lower degree of saturation shows slight effect on the values of apparent solubility products in presence of magnesium in solution. But in a solution of high degree of supersaturation, the surface area of calcite shows a noticeable influence on the apparent solubility products. Generally, the smaller surface area shows a high value of apparent solubility product at a certain magnesium concentration and this values decrease with the increase of calcite surface area in solution of the same magnesium concentration. The high values of apparent solubility products in Figure 1b could be a kinetic control
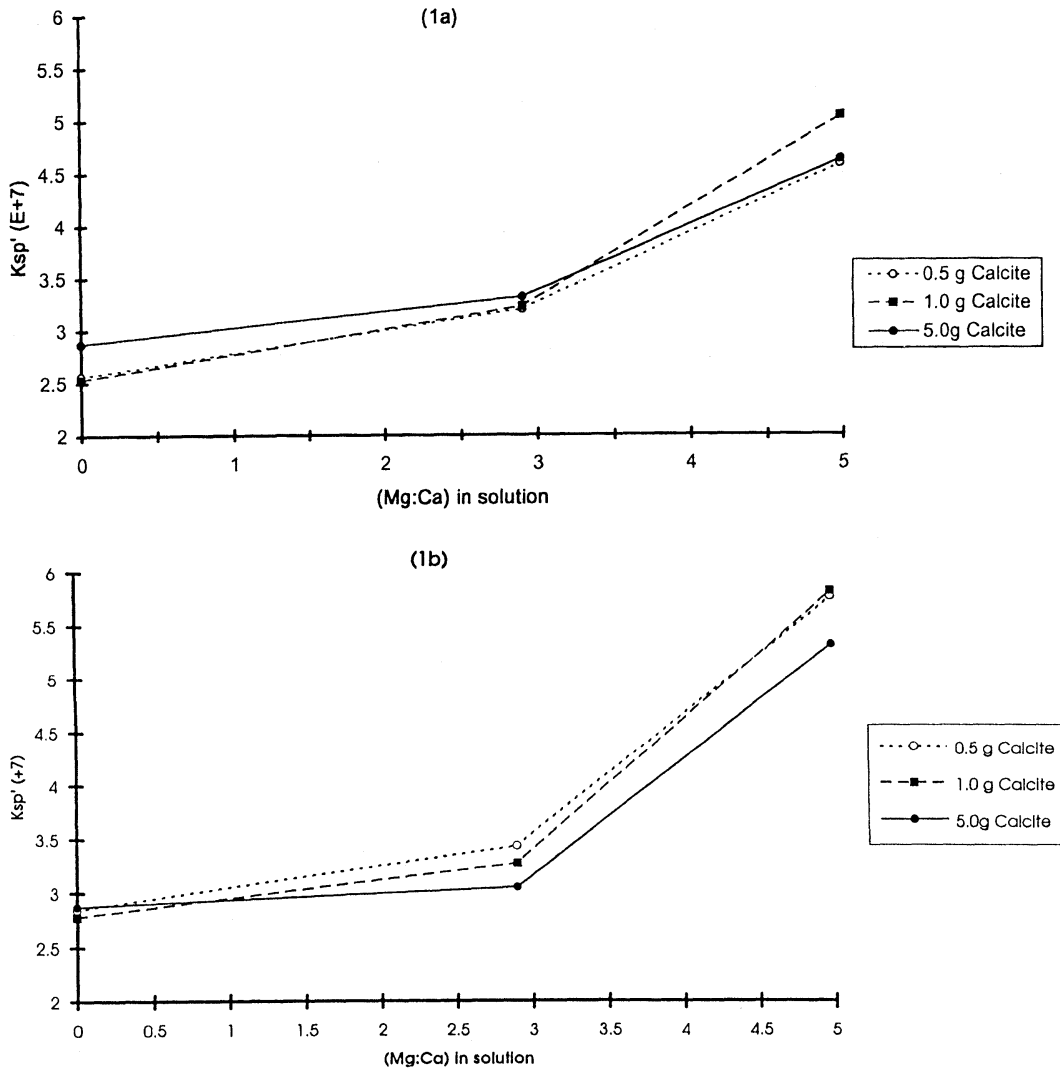
(1a)

(1b)

Fig. 1. The apparent solubility products of calcite as a function of Mg-to-Ca concentration
ratios and solid to solution ratios in artificial seawater solution at two initial pHs of
(1a) ≈ 8.1 and (1b) ≈ 8.6.

steady-state equilibrium. The increase in the value of apparent solubility product in magnesium free solutions with the increase of surface area (Figure 1a) is probably caused by the irregularity of calcite surface structure.

The increase of solubility products with magnesium concnentration in solution may be caused by the effect of magnesium ion-pairs formation and or by the increase of the mole fraction of magnesium on the surface calcite as a result of the overgrowth which enhances its' solubility (CHAVE et al., 1962; MORSE et al., 1979; SCHOONMAKER, 1981; KOCH and DISTECHE, 1984). The experiments indicate that there are two forces enhancing the involvement of magnesium in overgrowth precipitaion: the increase of magnesium concentration in solution and the increase of apparent ionic products of carbonate in solution. Therefore, the increase of magnesium fraction on calcite overgrowth surface is probably more effective upon the solubility product values of calcite than the ion

Table 2. The mole fraction $CaCO_{3(s)}$ in calcite overgrowth coatings as a function of (Mg^{2+}):(Ca^{2+}) concentration ratios in ASW, determined by AA analysis assuming that the calcite overgrowth is compositionally homogenous.

Expt #	$^xCaCO_{3(s)}$	$^xMgCO_{3(s)}$
$(Mg^{2+}) : (Ca^{2+}) : 2.92 : 1$		
SC80	0.946	0.054
SC81	0.946	0.054
SC86	0.944	0.056
SC87	0.946	0.054
SC89	0.947	0.053
SC90	0.948	0.052
SC91	0.947	0.053
$(Mg^{2+}) : (Ca^{2+}) : 4.99:1$		
SC92	0.926	0.074
SC93	0.924	0.076
SC95	0.916	0.084
SC96	0.918	0.082
SC97	0.928	0.072
SC98	0.926	0.074
SC100	0.922	0.078
SC02	0.928	0.072
SC03	0.929	0.071

pairing effect, because the activity of magnesian calcite overgrowth is not unity any more. The calcium carbonate fractions, $^xCaCO_{3(s)}$, on calcite overgrowth are shown in Table 2 as determined by AA analysis. The results show an increase of $^xMgCO_{3(s)}$ on calcite overgrowth coatings with the increase of (Mg^{2+})-to-(Ca^{2+}) concetnration ratios in ASW.

If the activity of calcite in the test solution is assumed to be a unity and do not really affect the solubility of the solid phase and by assuming that the increase of the solubility of calcite in Table 1 is mainly caused by ion-pairs formation, then the free solubility products of calcite $^{(Ca)}K_{sF}$, as well as magnesite, $^{(Mg)}K_{sF}$, in different solutions which are expressed by:

$$^{(Ca)}K_{sF} = (Ca^{2+})_{F,f} (CO_3^{2-})_{F,f} \qquad (8)$$

and:

$$^{(Mg)}K_{sF} = (Mg^{2+})_{F,f} (CO_3^{2-})_{F,f} \qquad (9)$$

may have the same values or very slight changes with the increase of (Mg^{2+}) in solution because $MgHCO_3^+$, $MgCO_3^0$, $MgCaCO_3^{2+}$ and $CaCO_3^0$ ion-pairs have been taken care of in the process of calculation. The subscripts F and f in

equations (8) and (9) are referring to free and final (equilibrium) respectively. The free and ion-pairs are calcuated for only those experiments of lower degree of supersaturation (that is, to avoid the kinetic control conditions) by using the MICROQL program (WESTALL, 1979) as shown by RUSHDI and CHEN, (1995). The values of the free solubility products are listed in Table 3. It is noticed that the value of $^{(Ca)}K_{sF}$ increase by 194%, which is the same magnitude of increment for apparent solubility product of calcite, with the increase of (Mg^{2+}) from 0 to 0.05 mole kg^{-1} ASW. This indicates that the increase of K_{sF} and Ksp' values are probably caused by the increase of magnesian calcite dissolution due to the increase in activity of the solid.

The thermodynamic solubility products of calcite, K_{so}, could be calculated from the relation:

$$^{(Ca)}K_{so} = {}^aCa^{2+a} CO_3^{2-} \qquad (12)$$

and the following equations are applied:

$$^{(Ca)}K_{so} = (\gamma_{Ca^{2+}})_{T,f}(Ca^{2+})_{T,f}(\gamma_{CO_3^{2-}})_{T,f}(CO_3^{2-})_{T,f} \qquad (13)$$

or:

$$^{(Ca)}K_{so} = (\gamma_{Ca^{2+}})_{F,f}(Ca^{2+})_{F,f}(\gamma_{CO_3^{2-}})_{F,f}(CO_3^{2-})_{F,f} \qquad (14)$$

where(γ_i) and (i) represent the activity coefficient and the concentration of the ith species respectively. The same realtions are appropriate for magnesite.

The free activity coefficient of CO_3^{2-}, $(\gamma_{CO_3^{2-}})_{F,f}$, is calculated from

$$(\gamma_{CO_3^{2-}})_{F,f} = (\gamma_{CO_3^{2-}})_T(CO_3^{2-})_T/(CO_3^{2-})_F$$

The values of $(\gamma_{CO_3^{2-}})_T$ in different(Mg^{2+})-to-(Ca^{2+}) concentration ratios in ASW are listed in Table 4 and $(CO_3^{2-})_F$ as described by RUSHDI and CHEN (1995). The free activity coefficients of magnesium and calcium cations, represented by $(M^{2+})_F$, are estimated from the equation:

$$(\gamma M^{2+})_F = (\gamma \pm MCl_2)_F^3/(\gamma \pm KCl)_F \qquad (16)$$

where $(\gamma \pm)_F$ represents the free mean activity coefficients.

The free activity coefficients of KCl, $CaCl_2$, $MgCl_2$ are calculated from the general equation

Table 3.   The free solubility products of calcite and magnesite represented by pK_{sF} as a function of $(Mg^{2+}):(Ca^{2+})$ concentration ratios in ASW.

Expt #	$-\log(Ca^{2+})_{F,f}$	$-\log(CO_3^{2+})_{F,f}$	$p^{(Ca)}K_{sF}$	$p^{(Mg)}K_{sF}$
		$(Mg^{2+}):(Ca^{2+})=0:1$		
SC62	2.380	4.600	6.980	......
SC64	2.378	4.589	6.967	......
SC66	2.397	4.550	6.947	......
SC70	2.378	4.600	6.978	......
SC72	2.371	4.604	6.975	......
SC73	2.378	4.597	6.975	......
SC74	2.380	4.555	6.959	......
SC76	2.378	4.661	6.939	......
SC77	2.371	4.534	6.905	......
SC78	2.390	4.533	6.924	......
SC79	2.387	4.549	6.936	......

Expt #	$-\log(Ca^{2+})_{F,f}$	$-\log(Mg^{2+})_{F,f}$	$-\log(CO_3^{2+})_{F,f}$	$p^{(Ca)}K_{sF}$	$p^{(Mg)}K_{sF}$
		$(Mg^{2+}):(Ca^{2+})=2.961:1$			
SC80	2.339	1.819	4.547	6.885	6.365
SC81	2.365	1.819	4.514	6.878	6.333
SC84	2.339	1.819	4.509	6.848	6.329
SC85	2.365	1.819	4.508	6.873	6.328
SC88	2.353	1.819	4.485	6.875	6.304
SC89	2.335	1.819	4.515	6.875	6.335
SC90	2.379	1.820	4.519	6.898	6.339
SC91	2.376	1.820	4.537	6.913	6.357
		$(Mg^{2+}):(Ca^{2+})=4.99:1$			
SC92	2.312	1.566	4.345	6.657	5.911
SC93	2.311	1.566	4.366	6.679	5.932
SC94	2.311	1.566	4.385	6.697	5.951
SC97	2.311	1.566	4.342	6.654	5.908
SC02	2.311	1.566	4.366	6.677	5.932
SC03	2.312	1.566	4.334	6.651	5.906

Table 4.   Total activity coefficients of bicarbonate and carbonate ions in the test solutions of various $(Mg^{2+}):(Ca^{2+})$ concentration ratios at $25\,°C$ and $I_T = 0.718$(as shown by RUSHDI and CHEN , 1995).

$(Mg^{2+}):(Ca^{2+})$	$(\gamma HCO_3^-)_T$	$(\gamma CO_3^{2-})_T$
0:0	0.574	0.117
0:1	0.553	0.065
1:1	0.539	0.060
3:1	0.529	0.054
5:1	0.505	0.033

of the activity of the electrolyte MCl_q which could be expressed in two equivalent ways:

$$^aMCl_q = (\gamma_M)_T(M)_T[(\gamma_{Cl})_T(Cl)_T]^q \quad (17)$$

and:

$$^aMCl_q = (\gamma_M)_F(M)_F[(\gamma_{Cl})_F(Cl)_F]^q \quad (18)$$

by combining equations (17) and (18) they yield:

$$(\gamma \pm MCl_q)_F = (\gamma \pm MCl_2)_T[(M)_T(Cl)_T^q/ (M)_F(Cl)_F^q]^{(1/(q+1))} \quad (19)$$

To apply equation (19), first the effective ionic strength, I_e, for each solution is calculated from:

$$I_e = 0.5[\Sigma (F)Z_{F,e}^2 + \Sigma (ip)Z_{ip}^2] \quad (20)$$

where the concentration of free ion, (F), and the ion-pair, (ip), are calculated by MICROQL program (WESTALL, 1979). Secondly, different effectivie ionic strength are used to calculate the equivalent total ionic strength of KCl, $MgCl_2$ and $CaCl_2$. This is done following the same iterative procedure which was described by JOHNSON (1979 p88) and JOHNSON and

Table 5. The constants of the equation (22) used to calculate total mean activity coefficients of electrolyte of interest (PYTKOEICA, *et al.*, 1977).

Electrolyte	A	B	C	D	E
KCl	−0.5108	1.307	0	0	0.002075
MgCl$_2$	−1.0216	1.800	−0.03365	0.1156	−0.04101
CaCl$_2$	−1.0216	1.501	0.07898	−0.01545	0

Table 6. The estimated mean total and free activity coefficients of KCl, MgCl$_2$ and CaCl$_2$, and the free activity coefficients of Mg^{2+}, Ca^{2+} and CO$_3{}^{2-}$ as a function of (Mg^{2+}) : (Ca^{2+}) concentration ratios in ASW.

(Mg^{2+}) : (Ca^{2+}) Ratio	I$_e$	KCl		MgCl$_2$		CaCl$_2$		(γMg)$_F$	(γCa)$_F$	(γCO$_3$)$_F$
		$(\gamma\pm)_T$	$(\gamma\pm)_F$	$(\gamma\pm)_T$	$(\gamma\pm)_F$	$(\gamma\pm)_T$	$(\gamma\pm)_F$			
0:1	0.610	0.619	0.803	0	0	0.4506	0.6959	0	0.4197	0.247
3:1	0.596	0.621	0.800	0.4749	0.698	0.4512	0.6922	0.4253	0.4146	0.229
5:1	0.583	0.623	0.799	0.4753	0.695	0.4520	0.6926	0.4158	0.4158	0.217

PYTKOWICZ, (1978) used to estimate the stability constants K$^*{}_{MCl}$. Then the effective ionic strengths is plotted versus total ionic strength of KCl, MgCl$_2$ and CaCl$_2$ and least square method is used to fit the data. The following equation is obtained to calculate the equivalent total ionic strength, I$_T$, of the electrolyte salts:

$$I_{T,MCl_q} = (I_{e,MCl_q} - \beta_0)/\beta_1 \quad (21)$$

where constants $\beta_0 = 0.083$; 0.107 and 0.1099 and $\beta_1 = 0.6737$, 0.5166 and 0.475 for KCl, MgCl$_2$ and CaCl$_2$ respectively. The total mean activity coefficinets of KCl, MgCl$_2$ and CaCl$_2$ are calculated from Culberson equation (PYTKOWICZ, *et al.*, 1977) after converting ionic strength to molality scale:

$$\log(\gamma\pm_{MClq}) = AI_T{}^{0.5}/(1+BI_T{}^{0.5}) + CI_T + DI_T{}^{1.5} + EI_T{}^2 \quad (22)$$

The constants of this equations are listed in Table 5.

At this point, equation (19) could be used to calculate the single free activity coefficient of the cation (M^{2+}). The values of the estimated mean activity coefficients of KCl, MgCl$_2$, CaCl$_2$ and the free single activity coefficients of Ca^{2+} and Mg^{2+} of different (Mg^{2+})-to-(Ca^{2+}) concentration ratios in ASW in molal scale are listed in Table 6.

The thermodynamic solubility products of calcite and magnesite were calculated according to equations(13) and (14), after converting the concentration of the ions into molal scale in

which the activity of the solid phase was assumed to have a value of unity. Their values are listed in Table 7, which show an increase of the thermodynamic constants values with (Mg^{2+})to-(Ca^{2+})concentration ratios in ASW. This indicates that the activity of the solid phase is more than one.

Thus, by assuming that the activity of the solid is about unity for both $^{(Ca)}$K$_{so}$ at zero (Mg^{2+}) and $^{(Mg)}$K$_{so} = 1.07 \times 10^{-8}$ moles^{2}kg^{-2}H$_2$O (GARRELS and CHRIST, 1965; ROBBIE and WALDBAUM, 1968), then the activity of the solid phase as a result of the impurities are calculated from:

$$^aCaCO_{3(s)} = {}^{(Ca)}K_{so(Mg:Ca)}/{}^{(Ca)}K_{so(Mg=0)} \quad (23)$$

$$^aMgCO_{3(s)} = {}^{(Mg)}K_{so(Mg:Ca)}/{}^{(Mg)}K_{so(Ca=0)} \quad (24)$$

where the subscripts (Mg=0), (Ca=0) and (Mg : Ca) are respectively the K$_{so}$ value when (Mg^{2+})=0, (Ca^{2+})=0 and (Mg^{2+}):(Ca^{2+}) concentration ratios in solution. The activities of the solids phases are also shown in Table 7. It is shown that the activity of magnesite is higher than calcite, which indicates a type of a nonideal solid solution is formed.

The activity coefficients of calcite, λCaCO$_{3(s)}$, and magnesite, λCaCO$_{3(s)}$, are calculated from the equations:

$$\lambda CaCO_{3(s)} = {}^aCaCO_{3(s)}/{}^xCaCO_{3(s)} \quad (25)$$

and:

$$\lambda MgCO_{3(s)} = {}^aMgCO_{3(s)}/{}^xMgCO_{3(s)} \quad (26)$$

Table 7. Estimated Kso of calcite and magnesite, assuming that the activity of the solid was unity. The values in the last two columns are the predicted values of the solid activity precipitated from different $(Mg^{2+}) : (Ca^{2+})$ concentration ratios in ASW.

Expt #	$^{(Ca)}K_{so}$ $(mole/kgH_2O)^2$ (10^{+9})	$^{(Mg)}K_{so}$ $(mole/kgH_2O)^2$ (10^{+8})	$^aCaCo_{3(s)}$	$^aMgCo_{3(s)}$
		$(Mg^{2+}) : (Ca^{2+}) = 0:1$		
SC62	3.1392	—	1	—
SC64	3.2167	—	1	—
SC70	3.1392	—	1	—
SC72	3.1600	—	1	—
SC73	3.1600	—	1	—
		$(Mg^{2+}) : (Ca^{2+}) = 2.96:1$		
SC80	3.3078	1.1225	1.0657	1.0491
SC81	3.3637	1.1083	1.0624	1.1293
SC85	3.4013	1.2200	1.0753	1.1402
SC89	3.3876	1.2936	1.0710	1.1249
SC90	3.2116	1.1906	1.0154	1.1127
SC91	3.1041	1.1428	1.9814	1.0680
		$(Mg^{2+}) : (Ca^{2+}) = 4.99:1$		
SC92	3.7221	2.0744	1.1767	1.9387
SC93	3.5390	1.9765	1.1189	1.8472
SC94	3.3971	1.8919	1.0740	1.7681
SC97	3.7521	2.0879	1.1863	1.9513
SC02	3.5529	1.9765	1.1233	1.8472
SC03	3.7721	2.0994	1.1926	1.9621
		$(Mg^{2+}) : (Ca^{2+}) = 1:0$		
1*	—	1.07	—	1

* = the value is calculated from $^{(Mg)}K_{so} = 2.82 ^{(Ca)}K_{so}$ according to ROBBIE and WALDBAUM (1968) and GARRELS and CHRIST (1965).

The calculated values of $\lambda CaCO_{3(s)}$ and $\lambda MgCO_{3(s)}$ as well as the mole fraction of magnesium in solution at equilibrium, y_f, and the mole fraction of $CaCO_{3(s)}$, in calcite overgrowth are listed in Table 8. The large increase of $\lambda MgCO_{3(s)}$ in the solid could be attributed to the effect of magnesium ion on the crystal lattice of calcite. The incorporation of smaller magnesium ion in the crystal lattice causes a distortion of the lattice which leads to a nonideal solid solution formation (RUSHDI, 1992).

The following general equilibrium reaction equation for magnesian calcite is usually used:

$$x_e Mg^{2+} + (1-x_e)Ca^{2+} + CO_3^{2-} \rightleftharpoons Mg_{x_e}Ca_{(1-x_e)}CO_3 \tag{27}$$
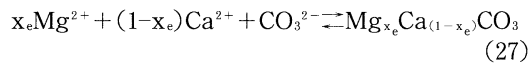
and it's thermodynamic solubility product is expressed as:

$$^{(Mg-cal)}Kso = (^aMg^{2+})^{x_e}(^aCa^{2+})^{(1-x_e)}(^aCO_3^{2-}) / (^aMgCO_3)^{x_e}(^aMgCO_3)^{(1-x)_e} \tag{28}$$

Another type of thermodynamic solubility product equation, used in literature is defined by the ion activity product (IAP) equation:

$$^{(Mg-cal)}Kso = (IAP) = (^aMg^{2+})^{x_e}(^aCa^{2+})^{(1-x_e)}(^aCO_3^{2-}) \tag{29}$$

which is similar to equation (28) except that the activity of solid magnesian calcite is assumed to be one. The two types of the above equations are used to estimate the values of thermodynamic solubility products of magnesian calcite as a function of (Mg^{2+})-to-(Ca^{2+}) concentration ratios in ASW. The results are shown in Table 9 and Figure 2. The results show slight changes in $^{(Mg-cal)}Kso$, as a function of (Mg^{2+})-to-(Ca^{2+}) concentration ratios in solution by using equation (28), whereas equation (29) shows a noticeable increase of (IAP) with respect to Mg^{2+} in solution.

Table 8. The activity coefficients of calcite and magnetite, estimated from and $^xCaCO_{3(s)}$ as a function of $(Mg^{2+}) : (Ca^{2+})$ concentration ratios in ASW.

Expt #	y_f	$^xCaCO_{3(s)}$	$^xMgCO_{3(s)}$	$\lambda\,CaCO_{3(s)}$	$\lambda\,MgCO_{3(s)}$
		$(Mg^{2+}) : (Ca^{2+}) = 2.96:1$			
SC80	0.750	0.947	0.053	1.1253	19.7943
SC81	0.750	0.946	0.054	1.1230	20.9130
SC85	0.750	0.948	0.052	1.1343	21.9927
SC89	0.750	0.949	0.051	1.1286	22.0569
SC90	0.749	0.949	0.051	1.0700	21.8176
SC91	0.749	0.951	0.049	1.0320	21.7959
		$(Mg^{2+}) : (Ca^{2+}) = 4.99:1$			
SC92	0.835	0.924	0.076	1.2735	25.5092
SC93	0.835	0.925	0.075	1.2096	24.6293
SC94	0.835	0.926	0.074	1.1598	23.8932
SC97	0.835	0.926	0.074	1.2811	26.3689
SC02	0.835	0.929	0.071	1.2091	26.0169
SC03	0.835	0.928	0.072	1.2851	27.2514

Table 9. The estimated thermodynamic solubility products of magnesian calcite as a function of $(Mg^{2+}) : (Ca^{2+})$ concentration ratios in ASW calculated by equations (28) and (29).

Expt #	$(Mg^{2+}) : (Ca^{2+})$ Ration	Equation (28) (E+9)	Equation (29) (E+9)
SC62	0:0.09	3.139	3.139
SC81	2.96:1	3.310	3.525
SC85	"	3.378	3.600
SC89	"	3.551	3.813
SC??	"	3.355	3.421
SC92	4.99:1	3.418	4.177
SC93	"	3.485	4.049
SC94	"	3.471	3.868
SC97	"	3.466	4.266
SC02	"	3.453	4.019

Finally, in ASW of magnesium-to-calcium concentration ratio of 5, the apparent solubility product, Ksp', is in agreement with Ksp' found by KOCH and DISTECHE (1984). They related that to the surface overgrowth of 2 to 3 mole% magnesian carbonate. But according to this study it may be related that to surface overgrowth of about 7.4 mole% $MgCO_3$. MUCCI et al., (1985) using Scanning Auger Microanalysis showed that the (Mg^{2+})-to-(Ca^{2+}) concentration on $CaCO_{3(s)}$ surface increases with the increase of (Mg^{2+})-to-(Ca^{2+}) concentration in solution. They strongly suggest that magnesian calcite overgrowth is in exchange equilibrium with the solution from which it precipi-

tated and that is representative of the solubility controlling phase. Our results suggest that there may be two types of controlling factors: the thermodynamic and the kinetic controls (PYTKOWICZ and COLE 1979). The thermodynamic control is effective at low degree of saturation, where by the increase of surface area showed a very slight changes and the kinetic control is effective at high degree of supersaturation where the increase of surface area plays a significant role on the steady-state condition.

4. Conclusion
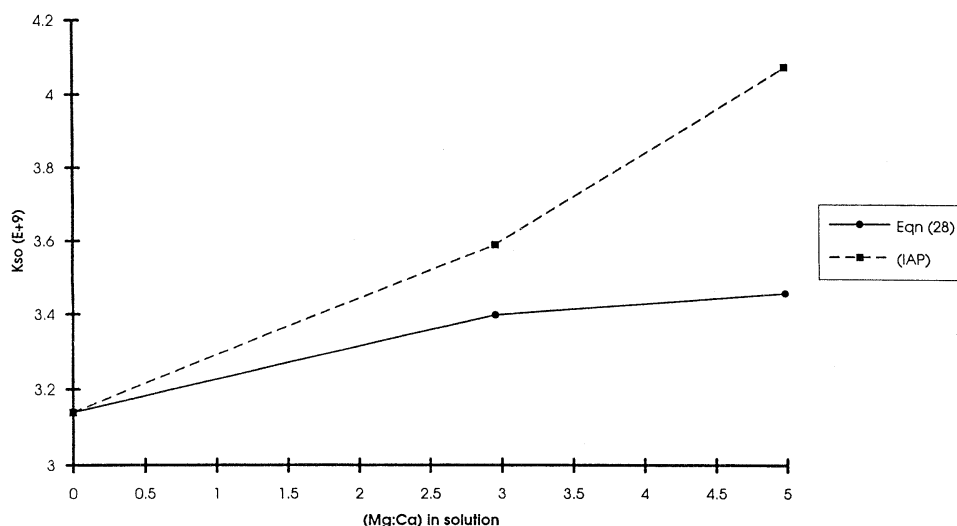
Although, the thermodynamic calculation of

Fig. 2.   Thermodynamic solubility products of magnesian calcite as a function of
Mg–to–Ca concentration ratios in artificial seawater solution represented by
equations (28) and (29).

calcite solubility in solution indicates that the activity of the solid increases due to the involvement of magnesium ion in the overgrowth process of calcite, there are other factors that may affect the solubility of calcite. Such examples are the irregularity of surface structure, shape, morphology and mineralogy of crystals. The increase of the values of thermodynamic solubility product of calcite may also indicate that there are more than one thermodynamic states, depending on the chemical and physical condition of the reaction.

One can conclude that in natural environment where the degree of supersaturation is close to saturation level, the inorganic precipitation of magnesian calcite tends to approach thermodynamic equilibrium. But when the degree of saturation is high enough to enhance the formation of high magnesian calcite overgrowth or biogenic precipitaion of high magnesian calcite, the kinetic control is favored over thermodynamic equilibrium. The kinetically controlled steady–state may approach the thermodynamic equilibrium if some process becomes effective that causes changes in the phases of the system and if enough time is given. One of these processes is the increase of solid–to–solution ratios.

Another conclusion is that the apparent solubility product values measured in laboratory experiments could be applied to environments of low degree of saturation as well as to natural system where there is a large solid–surface in contact with the solution such as in sediments or places where there are suspended particles. At high degree of saturation and in environments where there are small amount of particles, such as in open ocean surface water, the apparent solubility products measured in laboratory are still questionable.

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