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Equilibrium Behaviour of Magnesian Calcite Mineral: A Theoretical Approach

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ABSTRACT. A theoretical approach is used to explain the equilibrium behaviour of magnesian calcite in aqueous solutions. This approach is based on the original work of Wollast and Reinhard-Derie, 1977, which is modified herein to consider the effects of the quantities of solid surface area to aqueous solution volume on the chemical equilibrium of magnesian calcite.

According to this theoretical approach, it is favourable that there will be more than one thermodynamic equilibrium phase for magnesian calcite. This is addressed by using the phase rule equilibrium, which shows that an additional degree of freedom is created by solid solution.

With regards to differences in the results of magnesian calcite ionic activity products obtained by different workers, they could be real thermodynamic equilibria of different states depending upon solid-to-solution ratios. One thermodynamic equilibrium may be reached, if high solid-to-solution ratio is used at certain (Mg^{2+}) : (Ca^{2+}) in the solution.

Introduction

The chemical equilibrium behaviour of calcium carbonate in aqueous solution is important for the understanding of geochemical principles, because of the effect of the CO_2-system on major metal concentrations, major minerals and biological activities. The biological activities and both chemical and physical processes make the system very complicated to predict and to apply geochemical principles in the marine environment (Bathurst, 1964; Mackenzie *et al.*, 1982).

Recent carbonate sediments are composed to a large extent of aragonite. They may contain about 50% aragonite and/or a variety of high magnesian calcite (Land, 1967; Behairy, 1980; Budd, 1988; Guo and Riding, 1992). The skeletal magnesian calcite in biogenic hard parts, and marine magnesian calcite in cements are the most important occurrences of these phases (Silliman, 1846; El-Sayed, 1984; Pigott and Land, 1986; Anderson and Dyrssen, 1987).

It is well established that the magnesium ion has a direct effect on the mineral behaviour of $CaCO_{3(s)}$ and its solubility. Laboratory studies have shown that the magnesium ion in solution plays a significant role in controlling the behaviour of carbonate solid solution (Bischoff, 1968; Bischoff and Fyfe, 1968; Folk, 1974 and 1978; Lahann, 1978a, b; Mucci and Morse, 1984b; Rushdi, 1992; Rushdi *et al.*, 1992). Magnesium ion concentration also influences the kinetics of precipitation and dissolution, the crystal morphology and mineralogy, the solubility behaviour and the diagensis of carbonate minerals (Mucci and Morse, 1984a; Mucci, *et al.*, 1985; Rushdi, 1993).

Chave *et al.* (1962) showed that the solubility of carbonate increased in the order of pure calcite, low magnesian calcite, aragonite and high magnesian calcite. The behaviour of calcite and aragonite and their solubilities at ambient temperatures are fairly well known. However, the behaviour of magnesian calcite and its solubility are not well understood and are still debated (Thorstenson and Plummer, 1977; Mackenzie *et al.*, 1982).

Magnesian Calcite in the Marine Environment

Magnesian calcite equilibrium solubility products have been studied extensively (Koch and Disteche, 1984; Walter and Morse 1984; Mucci and Morse, 1984a, b; Busenberg and Plummer, 1989). Biogenic magnesian calcite minerals were used in most of the experimental investigations of their dissolution in distilled water and seawater. The solubility of magnesian calcite is expressed as

$$^{(\text{Mg-Calcite})}IAP = [\,Ca^{2+}\,]^{(1-x)}\;[\,Mg^{2+}\,]^{x}\;[\,CO_3^{2-}\,]$$

where $^{(\text{Mg-Calcite})}IAP$ is the ionic activity product of magnesian calcite, [i] represents the activity of i and x is the mole fraction of $MgCO_3$ in the solid. The solubility measurements of magnesian calcite by various investigators are shown in Fig. 1.

The use of different approaches for aqueous carbonate system could be the main source of the discrepancies between the results of different authors. The incongruent behaviour of magnesian carbonate in solutions led to a disagreement in the theoretical interpretation of the experimental data (Chave *et al.*, 1962; Land, 1967; Plummer and Mackenzie, 1974; Thorstenson and Plummer, 1977; Pytkowicz, 1983).

In light of the above, this work will introduce the theory of low-temperature magnesian calcite solid-solution behaviour which may explain the discrepancy in the data shown in Fig. 1.

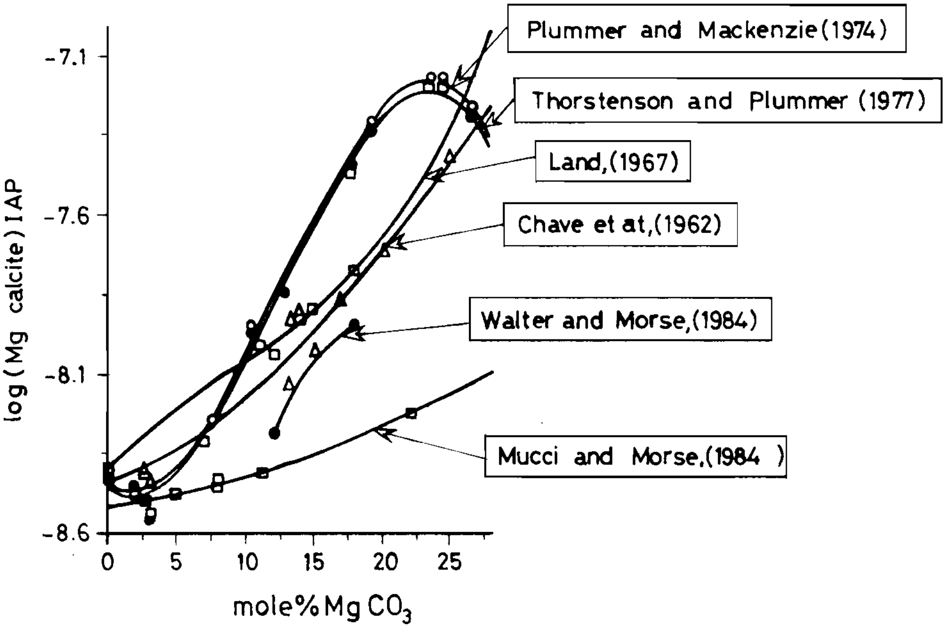

FIG. 1. The ionic activity products of magnesian calcite, as a function of mole % $MgCO_3$, obtained by different authors.

Thermodynamic Equilibrium of Magnesian Calcite

The chemical potentials in aqueous solution and in the solid phase must be the same at equilibrium. The following relationships are fulfilled in the case of magnesian calcite (Wollast and Reinhard-Derie, 1977; Pytkowicz and Cole, 1979).

$$CaCO_{3(s)} \leftarrow\rightarrow Ca^{2+} + CO_3^{2-} \; ; \; {}^{(Ca)}K_{so} = \frac{[Ca^{2+}]\,[CO_3^{2-}]}{{}^{a}CaCO_{3(s)}} \tag{1}$$

$$MgCO_{3(s)} \leftarrow\rightarrow Mg^{2+} + CO_3^{2-} \; ; \; {}^{(Mg)}K_{so} = \frac{[Mg^{2+}]\,[CO_3^{2-}]}{{}^{a}MgCO_{3(s)}} \tag{2}$$

where ${}^{(Ca)}K_{so}$ and ${}^{(Mg)}K_{so}$ are the thermodynamic dissolution equilibrium constants for pure calcite and pure magnesite and $aCaCO_{3(s)}$ and $aMgCO_{3(s)}$ are their activities respectively. The activities of calcite and magnesite can be expressed as follows:

$$a_{CaCO_{3(s)}} = \lambda_{CaCO_{3(s)}} \; x_{CaCO_{3(s)}} \tag{3}$$

$$a_{MgCO_{3(s)}} = \lambda_{MgCO_{3(s)}} \; x_{MgCO_{3(s)}} \tag{4}$$

where $\lambda CaCO_{3(s)}$ and $\lambda MgCO_{3(s)}$ are the activity coefficients of the solid and $xCaCO_{3(s)}$ and $xMgCO_{3(s)}$ are their mole fractions.

If x is the mole fraction of $MgCO_{3(s)}$ in magnesian calcite, the (1 – x) is the mole fraction of $CaCO_{3(s)}$ in the solid. Therefore, the approach of Wollast and Reinhard-Drie (1977), as developed by Pytkowicz (1983) will be followed. The conservation of mass of magnesium is expressed as

$$y = \frac{y_i\, P_i}{P} - \frac{x(P_i - P)}{P} \tag{5}$$

where y_i and y are the mole fraction of the magnesium ion in the initial and the final solution, P_i and P are respectively, the number of moles of $CaCO_3$ and $MgCO_3$ in the initial solution which are available for the formation of magnesian calcite M, and the number of moles which remains in solution after magnesian calcite precipitation. Usually $P_i > P$.

The equilibrium relationship of equation 1 and 2 may be combined as follows :

$$\left(\frac{y}{1-y}\right) = \left(\frac{x}{1-x}\right)\left(\frac{\gamma_{Ca^{2+}}}{\gamma_{Mg^{2+}}}\right)\left(\frac{\lambda_{MgCO_{3(s)}}}{\lambda_{CaCO_{3(s)}}}\right)\left(\frac{^{(Mg)}K_{so}}{^{(Ca)}K_{so}}\right) \tag{6}$$

where γ represents the activity coefficient in aqueous solution. In the case of seawater at 25°C, $\gamma Ca^{2+} = 0.228$ and $\gamma Mg^{2+} = 0.255$ (Millero and Schreiber, 1982), the ratio of $\lambda MgCO_3/\lambda CaCO_3$ increases with the increase of $(Mg^{2+}) : (Ca^{2+})$ in solution (Mucci, 1981), $^{(Mg)}K_{so} = 3.47 \times 10^{-8}$ and $^{(Ca)}K_{so} = 4.47 \times 10^{-9}$ (Smith and Martil, 1976). A graphical diagram of y versus x is shown in Fig. 2. If pure calcite seeds are used in a solution of a y_i mole fraction of magnesium, their surface magnesium content will increase because magnesian calcite coatings are formed. Therefore, the vector that corresponds to equation (6) faces downward as x increases during the process, as illustrated in Fig. 2. It should be noted that P_i decreases in solution during precipitation and the vector EC is not really a straight line, because the slope $(P_i - P)/P$ and the intercept P_i/P decrease during the processes of overgrowths (the opposite happens in a dissolution process).

When $CaCO_{3(s)}$ and $MgCO_{3(s)}$ form parts of a solution :

$$^{(Ca)}K_{so} = \frac{(\gamma_{\pm}CaCO_3)^2\ ^{(Ca)}K_{sp}}{^{\lambda}CaCO_{3(s)}\ ^{x}CaCO_{3(s)}} \tag{7}$$

$$^{(Mg)}K_{so} = \frac{(\gamma_{\pm}MgCO_3)^2\ ^{(Mg)}K_{sp}}{^{\lambda}MgCO_{3(s)}\ ^{x}MgCO_{3(s)}} \tag{8}$$

The mean activity coefficients of calcite, $(\gamma \pm CaCO_3)$, and magnesite, $(\gamma \pm MgCO_3)$, have to be estimated. The stoichiometric solubility of calcite, $^{(Ca)}K_{sp}$ and of magnesite, $^{(Mg)}K_{sp}$, can be measured. Because the composition of solid surface is not well known, x is difficult to be determined, unless it is compositionally homogenized, and only if the bulk value of x is assumed to be correct, then λ can be estimated.

The kinetic-controlled steady-state of magnesian calcite can be shifted into thermodynamic equilibrium by increasing the solid surface/solution volume ratio (Pytkowicz and Cole, 1979). This is also illustrated by the arrow in Fig. 2. Therefore, there could be more than one thermodynamic equilibrium for magnesian calcite confined to the curved BED, and one can conclude that more than one thermodynamic equilibrium state for magnesian calcite may exist depending upon the components of the solution, solid-to-solution ratios and mole fraction of the solid x at a certain temperature and pressure. This will also be explained by the phase rule equilibrium.

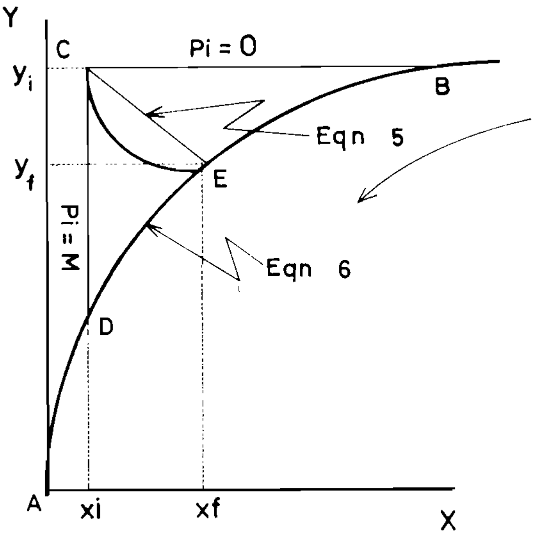

FIG. 2. Graphical representation for the final composition of solid and the solution of precipitation reaction (adapted from Wollast and Reinhard-Derie, 1977). Curve AB represents equations (6), line CB from equation (5) when $P_i = 0$, and line CD when $M = 0$; CE represents equation (5). The arrow shows the shift in thermodynamic equilibrium by increasing the solid/solution volume ratio.

Phase Rule and Degree of Freedom

The theoretical explanation for the equilibrium between a solid solution mineral and an aqueous phase can be approached by the application of the phase rule :

$$f = c - p + 2 \tag{9}$$

where f is the number of degrees of freedom of a system when the concentration units in the aqueous phase are mole fractions, c is the number of independent components, and p is the number of phases. Because the concentration units in the aqueous phase are expressed in molar (M) or molal (m), an additional quantity, which is the total number of moles, is required to convert x into M or m (Pytkowicz and Cole, 1979; Pytkowicz, 1983). Therefore, in terms of molalities :

$$f_m = f + 1 \tag{10}$$

and the number of compositional variables, C_m, that may be specified, is :

$$C_m = f_m - 2 \tag{11}$$

If $Mg_xCa_{1-x}CO_3$ is the only solid as a solid solution in the presence of vapour pressure, the system is fixed if P, T, pH and x of the solid are specified. However, in the absence of vapour pressure an additional degree of freedom must be specified such as carbonate alkalinity, CA, or total carbon dioxide, TCO_2. This shows that for each solid solution of a given composition y, there is only one equilibrium aqueous solution. This can be illustrated by xf_1, yf_1 and xf_2, yf_2 in Fig. 3.

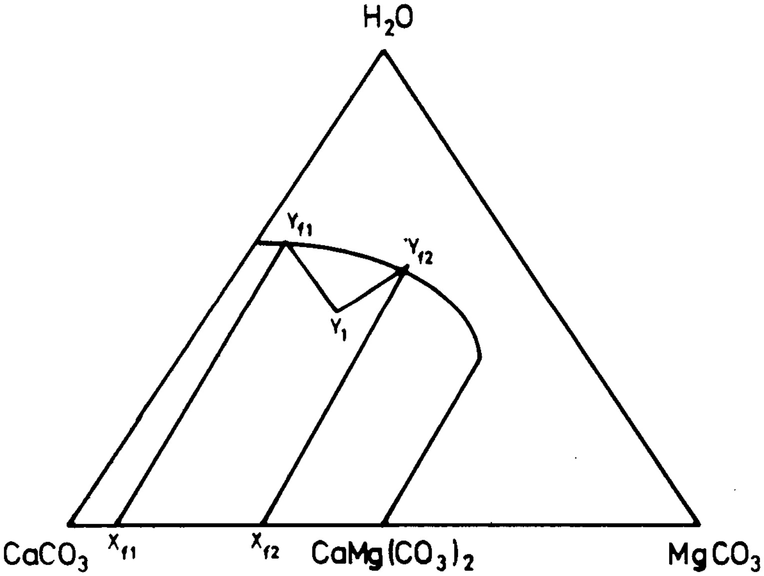

FIG. 3. Triangular diagram for precipitation. It shows more than one possible equilibrium condition, yf_1 and xf_1 or yf_2 and xf_2.

Long Hand Notations

For the previous system with three phases, vapour pressure, aqueous solution and one solid, the following equations are defined, assuming that the pH_2O and the activity coefficients are known :

$$P = pCO_2 + pH_2O \tag{12}$$

$$(CO_2)_{(l)} = sCO_2 pCO_2 \qquad (13)$$

$$(H_2O) = k_{H_2O}\, pH_2O \qquad (14)$$

$$(H_2CO_3) = K_h''\, (H_2O)\, (CO_2) \qquad (15)$$

$$(HCO_3^-) = \frac{K_1''\, (H_2CO_3)}{(H^+)} \qquad (16)$$

$$(CO_3^{2-}) = \frac{K_2''\, (HCO_3^-)}{(H^+)} \qquad (17)$$

$$(OH^-) = \frac{K_w''\, (H_2O)}{(H^+)} \qquad (18)$$

The charge balance is :

$$(H^+) + 2\,(Ca^{2+}) + 2\,(Mg^{2+}) = (HCO_3^-) + 2\,(CO_3^{2-}) + (OH^-) \qquad (19)$$

The mass balances are :

$$TH_2O + TCO_2 = (H_2O) + (H^+) + (CO_2) + (H_2CO_3) + (HCO_3^-) + (CO_3^{2-}) \qquad (20)$$

and

$$nCaCO_{3(s)} = x(nCaCO_3 + nMgCO_3) \qquad (21)$$

K represents the stoichiometric equilibrium constant. Therefore, there are 10 equations with 12 unknowns and the phase rule shows that there are two additional variables to be specified (*e.g.* pH and x). If the vapour pressure is absent, the first three equations (*e.g.* 12, 13, 14) are neglected because pCO_2 and pH_2O are lost in the system. There are then only eight equations with eleven unknowns. Therefore, 3 compositional variables beside T and P should be specified (*e.g.* pH, CA, or TCO_2 and x).

Conclusion

There is no single equilibrium phase in the case of solid solution-aqueous solution interaction. The reason for this is that an additional degree of freedom is created by solid solution. It should be noted that the single-phase thermodynamic hypothesis does not necessarily imply that there is one universal solid which is at equilibrium with all types of aqueous solutions (Fig. 2 and 3).

A partial explanation of the discrepancy among the results of the data in Fig. 1, in terms of the single-state thermodynamic hypothesis, is that the data pertain to different tie lines in Fig. 3. Therefore they could represent real thermodynamic equilibrium of different states, depending upon the Mg : Ca concentration and the solid-to-solution ratios.

One may reach the same thermodynamic equilibrium at a certain Mg-to-Ca ratio if high solid-to-solution ratio is used. This conclusion is confirmed by the result obtained by Ingle *et al.* (1973) and Plath *et al.* (1980).

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الاتزان الكيميائي لمعدن الكالسيت الماغنسيومي

معالجة نظرية

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المستخلص . ناقش الباحث الاتزان الكيميائي الحقيقي (الديناميكي الحراري) ، والنتائج المتباينة لناتج النشاط الأيوني لمعدن الكالسيت الماغنسيومي من قبل بعض الباحثين . واعتمد الباحث في معالجته لسلوك الاتزان الكيميائي الحقيقي على الدراسة التي قام بها الباحثان Wollast and Reinhand-Derie (1977) ، مع إدخال عامل التغير في كمية معدن الكالسيت الماغنسيومي الموجود في المحلول (أي التغير في نسبة كمية المعدن إلى نسبة كمية المحلول) ، كما استعان الباحث بقاعدة الصنف Phase Rule لتفسير هذا التباين .

من خلال المعالجة يتضح أن النتائج المتباينة التي حصل عليها الباحثون قد تكون في الحقيقة قيم مختلفة لاتزان كيميائي حقيقي ، وأنه ليس من الضروري أن تكون هناك قيمة واحدة معروفة لهذا الاتزان الكيميائي – كما هو معروف في سلوك معدن الكالسيت النقي في المياه النقية .