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EQUILIBRIUM CRITERIA FOR TWO-COMPONENT SOLIDS REACTING WITH FIXED COMPOSITION IN AN AQUEOUS PHASE—EXAMPLE: THE MAGNESIAN CALCITES

DONALD C. THORSTENSON* and L. NIEL PLUMMER**

ABSTRACT. If a mineral reacts with fixed composition in an aqueous phase — even if the mineral is a member of a solid solution series — the chemical potentials cannot be equated between phases. Using the Gibbs-Duhem relation, equations are derived that permit calculation of chemical potentials in a two-component solid from data obtained in a series of stoichiometric dissolution experiments.

Using the data of Plummer and Mackenzie (1974), chemical potentials are calculated for the $CaCO_3$ and $MgCO_3$ components in magnesian calcites. The results show that even metastable thermodynamic equilibrium can never be achieved between high Mg-calcites and natural waters, and that the Mg content of magnesian calcites should be governed primarily by the activity product of $Ca^{2+}{}_{(aq)}$ and $CO_3^{2-}{}_{(aq)}$, rather than the $Mg^{2+}{}_{(aq)}/Ca^{2+}{}_{(aq)}$ ratio in the aqueous phase.

INTRODUCTION

Carbonate minerals seldom occur in nature as pure phases, and research in carbonate geochemistry in recent years shows a steadily increasing interest in the chemistry of the "foreign" ions present in the common carbonate minerals. Much of the impetus for this work lies in the hope that the presence of these ions in the carbonate minerals can provide diagnostic information as to the sedimentary and diagenetic environments in which they formed. This, in turn, is simply part of the more general problem of predicting thermodynamic stabilities and reaction rates of minerals in natural environments. The recent emphasis on kinetic studies tends to obscure the fact that a knowledge of thermodynamic stabilities is still of fundamental importance. This is not only a function of the need to predict reaction paths and end products of diagenesis but also arises from the dependence of theoretical dissolution models on mineral solubilities, which in turn depend on their thermodynamic properties.

The need for thermodynamic data for non-ideal minerals is apparent. However, the calculation (or estimation) of these data at low temperatures is made extremely difficult, and interesting, by the abundant kinetic problems. These kinetic effects lead to persistent occurrence of metastable minerals, even on a geologic time scale, and pose many problems in laboratory studies — inhibition of nucleation and reaction, failure to achieve equilibrium, et cetera. The kinetic problems also introduce complexities in attempting to apply equilibrium criteria to laboratory and/or field observations. Within limits, equilibrium thermodynamics can be applied in many cases; however, attempts to do so have frequently been poorly defined and in some instances erroneous.

Studies of the incorporation of foreign ions in carbonates have been primarily focused on Mg, Sr, Fe, Mn, and Na; the magnesian calcites, in particular, have been the subject of a great deal of recent work. (See

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* Dept. of Geological Sciences, Southern Methodist University, Dallas, Texas 75275
** U.S. Geological Survey, Reston, Virginia 22092

references in Bathurst, 1971; Bricker, 1971; Lippman, 1973; Milliman, 1974; more recent work includes Barnes and O'Neil, 1971; Bencini and Turi, 1974; Benson, Achauer, and Matthews, 1972; Benson, 1974; Berner, 1975; Folk, 1974; Folk and Land, 1975; Katz and others, 1972; Katz, 1973; Meyers, 1974; Möller and Parekh, 1975; Nash and Pittman, 1975; Plummer and Mackenzie, 1974; Veizer and Demorvic, 1974; Weber, 1973; and White, ms.) The experimental studies generally have one thing in common — the minerals may be treated as two-component phases. We present here an examination of the thermodynamic relations and criteria for equilibrium between two-component solid phases (of fixed and variable composition) in contact with aqueous solutions of fixed and variable composition. A method is derived for obtaining equilibrium relations from non-equilibrium experimental data at low temperatures. The derived relations are used to evaluate the thermodynamic properties of magnesian calcite solid solutions and to predict the conditions of stable and metastable occurrence of magnesian calcites in aqueous solutions.

The key to understanding the thermodynamic relations lies in making the distinction as to whether the solid-solution mineral behaves as a phase of fixed or variable composition in the environment (natural or laboratory) under consideration. This, in turn, is a function of the kinetics of the mineral reactions and the time scale of the process involved. Thus in a laboratory experiment or a short-term diagenetic process, a two-component mineral may react with invariant composition, while its occurrence and distribution through geologic time may be governed by its behavior as a phase of variable composition.

This distinction between fixed and variable composition in multicomponent solid phases is not new. It is implicit in the discussions of equilibrium found in most thermodynamics texts (although not generally elaborated on); the thermodynamic implications were discussed in some detail by Gibbs (1876, 1878). We have used the thermodynamic relations derived by Gibbs, via the Gibbs-Duhem equation, to derive equations that allow equilibrium relations for two-component minerals to be obtained from congruent dissolution solubility data *without* making the assumption that thermodynamic equilibrium is achieved in the experiments.

THERMODYNAMIC RELATIONS

For a system at equilibrium,

$$dG = -SdT + VdP + \sum_i \mu_i dn_i = 0, \tag{1}$$

where:

G = Gibbs free energy of the system
S = entropy of the system
V = volume of the system
T = temperature
P = pressure

n_i = number of moles of component i in the system

μ_i = chemical potential of component i in the system, defined by

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j \neq i}} .$$

At constant T and P

$$dG = \sum_i \mu_i dn_i = 0. \tag{2}$$

This relation provides the criteria for equilibrium among phases and for equilibrium in reacting systems. For the transfer of any component i between two arbitrary phases, α and β, eq (2) becomes

$$\mu_{i,\alpha} dn_{i,\alpha} + \mu_{i,\beta} dn_{i,\beta} = 0, \tag{3}$$

and since

$$dn_{i,\beta} = -dn_{i,\alpha},$$

we obtain

$$(\mu_{i,\alpha} - \mu_{i,\beta}) dn_{i,\alpha} = 0. \tag{4}$$

For an arbitrary transfer of component i between phases α and β, at equilibrium, $dn_{i,\alpha} \neq 0$, and eq (4) requires that $\mu_{i,\alpha} = \mu_{i,\beta}$. Therefore, at equilibrium

$$\mu_{i,\alpha} = \mu_{i,\beta} \tag{5}$$

for all i, α, and β.

Eq (2) also provides the equilibrium criteria for any chemical reaction that may take place in the system. Eq (2) may be written

$$dG = \sum_i \mu_i dn_i = \sum_i \nu_i \mu_i d\xi,$$

or

$$dG/d\xi = \sum_i \nu_i \mu_i \tag{6}$$

where

ν_i = stoichiometric coefficient of component (or species) i in a balanced chemical reaction (+ for products, − for reactants)

ξ = reaction progress variable defined by

$$d\xi = \frac{dn_i}{\nu_i} .$$

Introducing the definition of activity by the relation

$$\mu_i = \mu_i^\circ + RT \ln a_i \tag{7}$$

where

R = gas constant

a_i = thermodynamic activity of species i

μ_i° = chemical potential of species i in its standard state,

and substituting into eq (6), we have, at equilibrium

$$\Delta\mu_r^\circ = \sum_i \nu_i \mu_i^\circ = -\sum_i RT \ln (a_i^{\nu_i}) \tag{8}$$

where

$\Delta\mu_r^\circ$ = the standard free energy of reaction,

and we may then define the equilibrium constant K_{eq} by

$$\Delta\mu_r^\circ = -RT \ln K_{eq} = -\sum_i RT \ln (a_i^{\nu_i}) \; . \tag{9}$$

We now examine more closely the application of equilibrium criteria from eqs (2), (6), and (9) to low temperature geochemical systems. Three cases which we refer to as stable thermodynamic equilibrium, metastable thermodynamic equilibrium, and stoichiometric saturation must be distinguished.

We will use the magnesian calcites as examples in discussing the principles involved, and for purposes of this discussion we make the following *assumptions* (to be demonstrated later in this paper):

1. A low-magnesian calcite (exact composition unknown), denoted by $Ca_{1-x}Mg_x\,CO_3$, can be thermodynamically stable in an aqueous phase containing Ca^{2+}, Mg^{2+}, and CO_3^{2-}.
2. High-magnesian calcites, denoted by $Ca_{1-y}Mg_y\,CO_3$, are thermodynamically unstable relative to low Mg–calcite and dolomite.

STABLE THERMODYNAMIC EQUILIBRIUM

The criteria for stable thermodynamic equilibrium are:

A. $dG/d\xi = 0$ for all reactions among chemical species present in the system.

B. $dG/d\xi \geqq 0$ for any possible reaction involving the components of the system.

and, as a consequence of (A) and (B),

C. $\mu_{i,\alpha} = \mu_{i,\beta}$, for the ith component (or species) in phases α and β.

For example, if a low Mg–calcite is at stable thermodynamic equilibrium ($T = 25°$, $P = 1$ atm) with an aqueous phase, from (A) $dG/d\xi = 0$ for the reactions

$$Ca_{(1-x)}Mg_xCO_3 = (1-x)Ca^{2+}{}_{(aq)} + xMg^{2+}{}_{(aq)} + CO_3{}^{2-}{}_{(aq)}, \tag{10A}$$

$$Ca_{(1-x)}Mg_xCO_3 + H^+{}_{(aq)} = (1-x)Ca^{2+}{}_{(aq)} + xMg^{2+}{}_{(aq)} + HCO_3{}^-{}_{(aq)}, \tag{10B}$$

$$Ca_{(1-x)}Mg_xCO_3 + H_2CO_{3(aq)} = (1-x)Ca^{2+}{}_{(aq)} + xMg^{2+}{}_{(aq)} + 2HCO_3{}^-{}_{(aq)}, \tag{10C}$$

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et cetera.

From (B), $dG/d\xi > 0$ for reactions such as

$$\mathrm{Ca_{(1-x)}Mg_xCO_3 = (1-x)CaCO_{3(calcite)} + xMg^{2+}{}_{(aq)} + xCO_3{}^{2-}{}_{(aq)}}, \tag{11A}$$

$$\mathrm{Ca_{(1-x)}Mg_xCO_3 = (1-x)CaCO_{3(calcite)} + xMgCO_{3(magnesite)}} \tag{11B}$$

$$\vdots$$

et cetera.

It is conceivable that the aqueous phase composition might be exactly that required for equilibrium with another mineral phase, even though that phase is not present. For example, if the aqueous phase were exactly saturated with dolomite, (B) also implies that $dG/d\xi = 0$ for reactions such as

$$\begin{aligned}&\mathrm{2Ca_{(1-x)}Mg_xCO_{3(Mg\text{-}calcite)} + (1-2x)Mg^{2+}{}_{(aq)}}\\ &\quad \mathrm{= CaMg(CO_3)_{2(dolomite)} + (1-2x)\ Ca^{2+}{}_{(aq)}},\end{aligned} \tag{12A}$$

$$\begin{aligned}&\mathrm{Ca_{(1-x)}Mg_xCO_{3(Mg\text{-}calcite)} + (1-2x)Mg^{2+}{}_{(aq)} + (1-2x)CO_3{}^{2-}{}_{(aq)}}\\ &\quad \mathrm{= (1-x)CaMg(CO_3)_{2(dolomite)}},\end{aligned} \tag{12B}$$

$$\vdots$$

et cetera.

Finally, condition (C) requires that

$$\mu_{\mathrm{CaCO_3}{}_{(\mathrm{Mg\text{-}calcite})}} = \mu_{\mathrm{CaCO_3}{}_{(\mathrm{aq})}}, \tag{13A}$$

and

$$\mu_{\mathrm{MgCO_3}{}_{(\mathrm{Mg\text{-}calcite})}} = \mu_{\mathrm{MgCO_3}{}_{(\mathrm{aq})}}, \tag{13B}$$

which implies the following relations, based on the choice of calcite and magnesite at 25°C and 1 atm total P as standard states for the components $\mathrm{CaCO_3}$ and $\mathrm{MgCO_3}$, respectively;

$$(a_{\mathrm{CaCO_3}{}_{(\mathrm{Mg\text{-}calcite})}})(K_{\mathrm{calcite}}) = a_{\mathrm{Ca}^{2+}{}_{(\mathrm{aq})}}\, a_{\mathrm{CO_3}^{2-}{}_{(\mathrm{aq})}}, \tag{14A}$$

and

$$(a_{\mathrm{MgCO_3}{}_{(\mathrm{Mg\text{-}calcite})}})(K_{\mathrm{magnesite}}) = a_{\mathrm{Mg}^{2+}{}_{(\mathrm{aq})}}\, a_{\mathrm{CO_3}^{2-}{}_{(\mathrm{aq})}}. \tag{14B}$$

METASTABLE THERMODYNAMIC EQUILIBRIUM

The criteria for metastable thermodynamic equilibrium are:

A. $dG/d\xi = 0$ for all kinetically feasible reactions among species present in the system.

B. $\mu_{i,\alpha} = \mu_{i,\beta}$ for the ith component (or species) in phases α and β.

C. $dG/d\xi < 0$ for at least one reaction. This reaction may involve species or phases not present and kinetically prevented from forming or a kinetically prohibited reaction among phases or species present in the system.

For a high Mg–calcite, in metastable equilibrium with an aqueous phase, (A) requires that $dG/d\xi = 0$ for reactions analogous to 10A, 10B, . . . ; that is,

$$Ca_{(1-y)}Mg_yCO_{3(Mg\text{-}calcite)} = (1-y)Ca^{2+}{}_{(aq)} + yMg^{2+}{}_{(aq)} + CO_3{}^{2-}{}_{(aq)}, \qquad (15)$$

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et cetera.

From (B),

$$(a_{CaCO_3}{}_{(Mg\text{-}calcite)})(K_{calcite}) = a_{Ca^{2+}}{}_{(aq)}\, a_{CO_3{}^{2-}}{}_{(aq)}, \qquad (14A)$$

$$(a_{MgCO_3}{}_{(Mg\text{-}calcite)})(K_{magnesite}) = a_{Mg^{2+}}{}_{(aq)}\, a_{CO_3{}^{2-}}{}_{(aq)}, \qquad (14B)$$

Finally, (C) requires that $dG/d\xi < 0$ for at least one reaction such as,

$$Ca_{(1-y)}Mg_yCO_{3(Mg\text{-}calcite)} = (1-2y)CaCO_{3(calcite)} + y\,CaMg(CO_3)_{2(dolomite)}, \qquad (16A)$$

$$Ca_{(1-y)}Mg_yCO_{3(Mg\text{-}calcite)} = (1-y)CaCO_{3(calcite)} + y\,Mg^{2+}{}_{(aq)} + y\,CO_3{}^{2-}{}_{(aq)}, \qquad (16B)$$

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et cetera.

We have defined the criteria for stable and metastable thermodynamic equilibrium in detail in order to show clearly the distinction between these thermodynamic states and the condition we term stoichiometric saturation.

STOICHIOMETRIC SATURATION

We use the term stoichiometric saturation to refer to equilibrium between an aqueous phase and a multi-component solid in situations where, owing to kinetic restrictions, the composition of the solid remains invariant, *even though the solid phase may be part of a continuous compositional series.* Consider the congruent dissolution of a magnesian calcite in an aqueous phase. If the process takes place in a sufficiently short time that the solid does not change composition; that is, it dissolves stoichiometrically, the reaction can be written

$$\begin{aligned} Ca_{(1-x)}Mg_xCO_{3(Mg\text{-}calcite)} &\rightarrow (1-x)Ca^{2+}{}_{(aq)} \\ &+ xMg^{2+}{}_{(aq)} + CO_3{}^{2-}{}_{(aq)}. \end{aligned} \tag{17}$$

As originally noted by Gibbs, when a solid reacts with fixed composition, even though it is of potentially variable composition (a member of a solid solution series), equating the chemical potentials of *individual* components in different phases is no longer valid. In our example, this means that eqs (13A) and (13B) are no longer applicable as equilibrium criteria. There are several ways of explaining this, the most concise being that (Gibbs, 1961, p. 79-82) if the solid reacts with fixed composition, it is thermodynamically a 1-component phase, and therefore from eq (2), the only equilibrium constraint that can be derived is (T, P = const)

$$dG = 0 = \sum_i \mu_i dn_i = \sum_i (\nu_i\mu_i)\, d\xi,$$

or

$$dG/d\xi = 0 = \nu_{solid}\mu_{solid} + \sum_i \nu_i\mu_{i\,(aq)}. \tag{18}$$

Applying (18) to reaction (17), as written,

$$\begin{aligned} dG/d\xi = 0 &= (1-x)\mu_{Ca^{2+}(aq)} + x\mu_{Mg^{2+}(aq)} \\ &+ \mu_{CO_3{}^{2-}(aq)} - \mu_{Ca_{(1-x)}Mg_xCO_{3(s)}}, \end{aligned}$$

from which

$$\begin{aligned} \Delta\mu^\circ{}_{reaction} &= (1-x)\mu^\circ{}_{Ca^{2+}(aq)} + x\mu^\circ{}_{Mg^{2+}(aq)} \\ &+ \mu^\circ{}_{CO_3{}^{2-}(aq)} - \mu^\circ{}_{Ca_{(1-x)}Mg_xCO_{3(s)}}, \end{aligned}$$

and

$$\Delta\mu^\circ{}_r = -RT \ln K_{eq}(x) = -RT \ln \frac{a^{(1-x)}{}_{Ca^{2+}(aq)}\, a^x{}_{Mg^{2+}(aq)}\, a_{CO_3{}^{2-}(aq)}}{1}. \tag{19}$$

Thus in a reaction with a solid of fixed composition the *only* equilibrium constraint is expressed by

$$IAP = K_{eq}(x), \tag{20}$$

where, for reaction (17),

$$IAP = a^{(1-x)}{}_{Ca^{2+}(aq)}\, a^x{}_{Mg^{2+}(aq)}\, a_{CO_3{}^{2-}(aq)} = K_{eq}(x). \tag{21}$$

Berner (1975) recognized the need for distinguishing between metastable equilibrium and stoichiometric saturation when dealing with the thermodynamics of the magnesian calcites. Plummer and Mackenzie (1974), in calculating the activities of $CaCO_3$ and $MgCO_3$ in magnesian calcites, failed to make this distinction and incorrectly assumed that the aqueous solubility of magnesian calcites represents a metastable thermodynamic equilibrium.

There are several points that should be emphasized here concerning stoichiometric saturation as expressed by eq (21).

A. The numerical value of $K_{eq}(x)$ in (21) is a function of the composition of the solid phase; this dependence arises both through variation in the molar free energy of the solid phase and in the dependence of $\Delta\mu^\circ_r$ on x in eq (19). The condition IAP $= K_{eq}(x)$ will always be valid for stoichiometric saturation, but the numerical values of both terms will vary with x.

B. The constraint IAP $= K_{eq}(x)$ for saturation is valid regardless of whether the phases involved are stable or metastable. The only restriction involved in the derivation of eqs (19) through (21) is that the composition of the solid phase remains fixed.

C. Finally, if the constraint of fixed solid composition is removed, that is, if sufficient time is allowed for the solid phase to adjust its composition via solid-state diffusion and/or recrystallization, the criteria for chemical equilibrium revert back to the "standard" relations for multiphase equilibrium, namely

$$\mu_{i,\alpha} = \mu_{i,\beta} \text{ for all i, } \alpha\text{, and } \beta.$$

D. Stoichiometric saturation, defined by IAP $= K_{eq}(x)$, is a necessary condition for thermodynamic equilibrium as well. Obviously if IAP $= K_{eq}(x)$ holds for any solid of fixed composition, it must hold for the particular solid phase that happens also to be in thermodynamic equilibrium with a given aqueous phase. If, for example, a magnesian calcite has achieved stoichiometric saturation in a dissolution experiment and the system is then allowed to react for a sufficiently long time, the pathway to thermodynamic equilibrium (metastable or stable) may be viewed as a continuum of stoichiometric saturation states in which both the magnesian calcite and the solution adjust their compositions until $\mu_{CaCO_{3\,(s)}} = \mu_{CaCO_{3\,(aq)}}$ and $\mu_{MgCO_{3\,(s)}} = \mu_{MgCO_{3\,(aq)}}$.

An understanding of the concept of stoichiometric saturation is necessary for the understanding of any process — laboratory or natural — in which the solids react with fixed composition. In laboratory studies the basic problem in determining the thermodynamic characteristics of multicomponent minerals at low temperatures is one of kinetics. Many reaction rates are so slow that laboratory experiments can be expected to achieve only stoichiometric saturation at best, and experimental data must be interpreted with this in mind. The use of compositional data from naturally coexisting minerals and solutions to compute thermodynamic properties does not provide unequivocal results, because this approach *assumes* equilibrium has been obtained in order to derive the thermodynamic properties of the minerals in question. The persistence of unstable minerals for geologically significant time spans (classic examples being aragonite and high Mg–calcites) demonstrates the unreliability of this assumption.

We propose that the most fundamentally sound method for determining the thermodynamic properties of multicomponent minerals at low temperatures lies in the use of carefully controlled laboratory experiments in which stoichiometric saturation can be demonstrated. The experimental determination of stoichiometric saturation, although feasible, is not a simple task, as shown by the study of Plummer and Mackenzie (1974). In the case of 2-component minerals, the data from a series of stoichiometric saturation experiments involving a range of solid phase compositions can be used to derive the desired thermodynamic equilibrium relations as a function of composition. We derive the necessary relations for magnesian-calcites in the following section. Generalization to any other mineral that may be considered as a 2-component phase should be obvious.

DERIVATION OF EQUATIONS

Again consider the dissolution reactions of a magnesian calcite

$$Ca_{(1-x)}Mg_xCO_{3(s)} = (1-x)Ca^{2+}{}_{(aq)} + xMg^{2+}{}_{(aq)} + CO_3{}^{2-}{}_{(aq)}, \tag{17}$$

where the solid is considered as a 2-component phase with end-members $CaCO_{3(calcite)}$ and $MgCO_{3(magnesite)}$[1]. Eqs (21), (14A), and (14B) show that at thermodynamic equilibrium the following conditions must hold:

$$K_{eq}(x) = a^{(1-x)}{}_{Ca^{2+}(aq)}\, a^{x}{}_{Mg^{2+}(aq)}\, a_{CO_3{}^{2-}(aq)}, \tag{21}$$

$$a_{Ca^{2+}(aq)}\, a_{CO_3{}^{2-}(aq)} = (K_{calcite})\, (a_{CaCO_3(Mg\text{-}calcite)}), \tag{14A}$$

and

$$a_{Mg^{2+}(aq)}\, a_{CO_3{}^{2-}(aq)} = (K_{magnesite})\, (a_{MgCO_3(Mg\text{-}calcite)}). \tag{14B}$$

$K_{eq}(x)$ can be determined experimentally, and the activities of the aqueous species can be obtained from a knowledge of composition and solution theory. In order to determine the thermodynamic properties of magnesian calcites, we need to find a relationship between the solid phase activities of $CaCO_3$ and $MgCO_3$ and the experimentally measurable parameters at stoichiometric saturation.

Substituting (14A) and (14B) in (21) and taking the logarithm;

$$\log K_{eq}(x) = (1-x)\log a_{CaCO_{3(s)}} + x \log a_{MgCO_{3(s)}}$$
$$+ (1-x)\log K_{calcite} + x \log K_{magnesite}. \tag{22}$$

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[1] The end-members could also have been chosen as calcite and dolomite.

To evaluate the rate of change of $K_{eq}(x)$ as a function of x, partial differentiation gives

$$\frac{\partial}{\partial x}\left(\log K_{eq}(x)\right) = (1-x)\frac{\partial}{\partial x}(\log a_{CaCO_{3(s)}}) - \log a_{CaCO_{3(s)}} - \log K_{calcite} + x\frac{\partial}{\partial x}(\log a_{MgCO_{3(s)}}) + \log a_{MgCO_{3(s)}} + \log K_{magnesite}. \quad (23)$$

The Gibbs-Duhem equation,

$$\sum_i n_i d\mu_i = 0 \quad (24)$$

provides a means of expressing the functional relationship between the activity of one component in a given phase and the activities of the remaining components in that phase. Application of the Gibbs-Duhem equation to the binary solid phase shows that

$$(1-x)\frac{\partial}{\partial x}(\log a_{CaCO_{3(s)}}) + x\frac{\partial}{\partial x}(\log a_{MgCO_{3(s)}}) = 0. \quad (25)$$

This is a general property of binary solutions (compare, Denbigh, 1968, p. 216). Eq (23) can therefore be written

$$\log a_{CaCO_{3(s)}} = -\frac{\partial}{\partial x}\left(\log K_{eq}(x)\right) + \log a_{MgCO_{3(s)}} - \log K_{calcite} + \log K_{magnesite}. \quad (26)$$

Eqs (22) and (26) can be solved for $a_{CaCO_{3(s)}}$ and $a_{MgCO_{3(s)}}$ if data for $K_{eq}(x)$ as a function of x are known experimentally. Solving (22) for $\log a_{MgCO_{3(s)}}$, substituting in (26), and rearranging gives

$$\log a_{CaCO_{3(s)}} = -x\frac{\partial}{\partial x}\left(\log K_{eq}(x)\right) + \log K_{eq}(x) - \log K_{calcite}. \quad (27)$$

An analogous derivation for $a_{MgCO_{3(s)}}$ yields

$$\log a_{MgCO_{3(s)}} = (1-x)\frac{\partial}{\partial x}\left(\log K_{eq}(x)\right) + \log K_{eq}(x) - \log K_{magnesite}. \quad (28)$$

Finally, combining (14A), (14B), (27), and (28) yields the interesting result

$$\log\left(\frac{a_{Mg^{2+}(aq)}}{a_{Ca^{2+}(aq)}}\right) = \frac{\partial}{\partial x}\left(\log K_{eq}(x)\right), \quad (29)$$

which defines the Mg^{2+}/Ca^{2+} ratio in a solution at thermodynamic equilibrium with a given magnesian calcite.

Eqs (27), (28), and (29) provide a means of evaluating the thermodynamic equilibrium characteristics of the magnesian calcites (or any other binary solid solution minerals) from a knowledge of the equilibrium constants $K_{eq}(x)$, which may be obtained from congruent dissolution experiments. The fact that, for a given Mg–calcite, IAP = $K_{eq}(x)$ is a necessary constraint for both stoichiometric saturation and thermodynamic equilibrium thus allows the determination of thermodynamic parameters from experiments that never need to achieve thermodynamic equilibrium.

Another commonly used approach to describe the incorporation of minor elements in carbonate minerals involves the use of distribution coefficients, defined by eq (30) for magnesian calcite:

$$D = \frac{\left(\dfrac{x}{1-x}\right)}{\left(\dfrac{m_{Mg^{2+}(aq)}}{m_{Ca^{2+}(aq)}}\right)} \tag{30}$$

where m denotes molality.
The distribution coefficient is a measure of the Mg/Ca ratio in the solid phase relative to that in the aqueous phase. The distribution coefficient can be related to the equilibrium constant as follows. From eq (30)

$$\frac{x}{1-x} = D\left(\frac{a_{Mg^{2+}(aq)}\,\gamma_{Ca^{2+}(aq)}}{a_{Ca^{2+}(aq)}\,\gamma_{Mg^{2+}(aq)}}\right). \tag{31}$$

Taking logarithms and introducing eq (29), we obtain

$$\log D = \log\left(\frac{x}{1-x}\right) - \log\left(\frac{\gamma_{Ca^{2+}(aq)}}{\gamma_{Mg^{2+}(aq)}}\right) - \frac{\partial}{\partial x}\left(\log K_{eq}(x)\right). \tag{32}$$

Caution must be exercised in the use of eq (32). The variation of D as a function of composition, x, predicted by (32) is based on the assumption that the solid phase is at thermodynamic equilibrium (stable or metastable) with the aqueous phase. The distribution coefficients are generally measured via precipitation experiments, and it is difficult to determine whether these experiments tend to approach thermodynamic equilibrium, as opposed to stoichiometric saturation.

In a system for which $K_{eq}(x)$ data are available, a comparison of D's calculated from eq (32) with measured D's should provide some indication of the degree to which thermodynamic equilibrium is approached in such experiments.

THERMODYNAMIC EQUILIBRIUM RELATIONS FOR THE MG–CALCITES

In the preceding sections, we have simply used the magnesian calcites as an example to illustrate the thermodynamic derivations. We now apply these results to estimation of the thermodynamic properties of the Mg–calcites at 25°C and 1 atm total pressure. The basis for the following calculations are the experimental data for the dissolution of Mg–calcites obtained by Plummer and Mackenzie (1974).

These authors obtained estimates of $K_{eq}(x)$ from dissolution experiments at constant P_{CO_2}. The equilibrium pH was estimated from inverse time plots of data from the congruent portion of the dissolution experiments. The saturation state of the aqueous phase and the implied $K_{eq}(x)$ were then calculated from this pH and the Mg/Ca ratio of the dissolving phase. There is no evidence to indicate that equilibrium — or stoichiometric saturation — was ever achieved experimentally. In one experiment with *Amphiroa Rigida,* dissolution of a 23 mol percent $MgCO_3$ phase was still occurring after 1800 hrs when the experiment was ended. The aqueous phase at that time had a Mg^{2+}/Ca^{2+} ratio of 1.4 and was supersaturated with respect to calcite by a factor of 2.

Figure 4 shows that this solution would be saturated with a 9 mol percent Mg–calcite, but that either (or both) the Mg^{2+}/Ca^{2+} ratio in solution and $IAP_{calcite}$ must be greatly increased before saturation can be achieved with a 23 mol percent Mg–calcite. This illustrates a fundamental difficulty in experimental work with the magnesian calcites. In order to achieve stoichiometric saturation with a high magnesian calcite, either $IAP_{calcite}$ must be so high that a low Mg–calcite is likely to precipitate, or the Mg^{2+}/Ca^{2+} ratio in solution must be so high that dissolution/precipitation kinetics will be strongly inhibited by the aqueous Mg^{2+} ion.

In the following discussion we assume that the values of $K_{eq}(x)$ obtained by Plummer and Mackenzie (1974) represent stoichiometric saturation. The equilibrium constants as a function of composition are presented in table 1 (the values have been slightly revised to be consistent with the thermodynamic data and aqueous model given as a footnote to table 1). An estimated best fit curve of log $K_{eq}(x)$ versus composition is given in figure 1. The values of $\partial(\log K_{eq}(x))/\partial x$ are tabulated in table 2 and illustrated in the figures that follow. Each figure is discussed in detail below.

Figure 2 shows the $a_{Mg^{2+}(aq)}/a_{Ca^{2+}(aq)}$ ratios, calculated from eq (29), in an aqueous phase at thermodynamic equilibrium with the magnesian calcites. Within the limits of uncertainty in the original data and the curve fitting estimates, the following conclusions can be drawn from figure 2:

1. Only magnesian calcites containing 1 to 5 mol percent $MgCO_3$ and those containing 20 to 25 mol percent $MgCO_3$ can exist at thermodynamic equilibrium in natural waters. Pure, or nearly pure, calcites ($MgCO_3 < 1$ percent) require solutions with extremely low $a_{Mg^{2+}}/a_{Ca^{2+}}$ ratios in the aqueous phase to maintain thermodynamic equilibrium.
2. Of the two groups of calcites that can exist at thermodynamic equilibrium, only the low Mg–calcites can attain stable equilibrium. The 20 to 25 mol percent Mg–calcites achieve only metastable equilibrium, as they require solutions that are super-

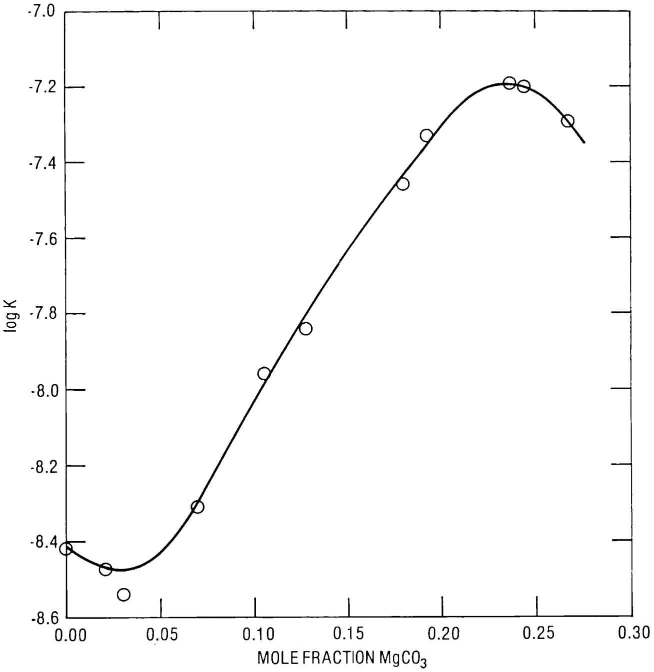

Fig. 1. Plot of log $K_{eq}(x)$ against mole fraction $MgCO_3$, (x), in magnesian calcites. $K_{eq}(x) = a^{(1-x)}_{Ca^{2+}(aq)} a^{x}_{Mg^{2+}(aq)} a_{CO^{2-}_3(aq)}$ at stoichiometric saturation. Data for log $K_{eq}(x)$ are revised slightly from Plummer and Mackenzie (1974); see footnote to table 1.

saturated with respect to calcite (or the low Mg–calcites) to satisfy the IAP = $K_{eq}(x)$ relation.

3. The shape of the curve in figure 2 (and in figs. 3 and 4) is affected somewhat by the shape of the particular curve chosen to fit the log $K_{eq}(x)$ data in figure 1. The slope of the curve in figure 2 is given by

$$\frac{\partial \log\left(\dfrac{a_{Mg^{2+}(aq)}}{a_{Ca^{2+}(aq)}}\right)}{\partial x} = \frac{\partial^2 \log K_{eq}(x)}{\partial x^2} . \qquad (33)$$

From figure 1, in the range $0 < x < 8$ percent, $\partial^2 (\log K_{eq}(x))/\partial x^2$ is large and positive. In the 8 percent $< x <$ 20 percent range, as we have drawn the curve, $\partial^2(\log K_{eq}(x))/\partial x^2$ is small and negative; thus the corresponding line in figure 2 has a slight negative slope. If the data in figure 1 were fit with a straight line from 8 percent $< x <$ 20 percent, the line in figure 2 would be horizontal between these compositions. Finally, in the 20 percent $< x <$ 28 percent range, $\partial^2 (\log K_{eq}(x))/\partial x^2$ is large and negative, and the $a_{Mg^{2+}(aq)}/a_{Ca^{2+}(aq)}$ show the corresponding pronounced decrease. We have not attempted any detailed interpretation of the shape

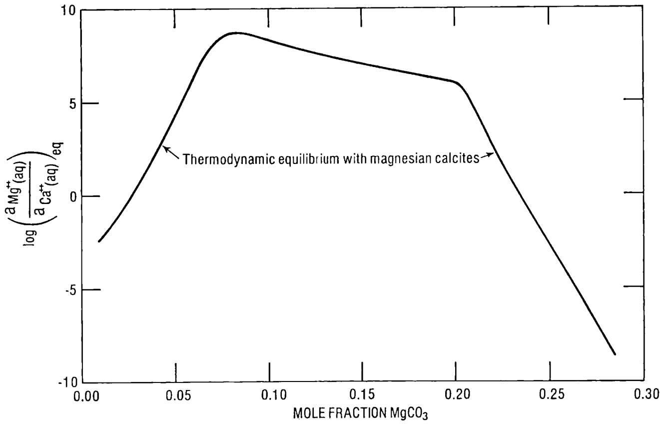

Fig. 2. Equilibrium ratios of $a_{Mg^{2+}(aq)}/a_{Ca^{2+}(aq)}$ as a function of $MgCO_3$ content in magnesian calcites. Log $(a_{Mg^{2+}(aq)}/a_{Ca^{2+}(aq)})$ values are calculated from eq (29); see table 2. The $a_{Mg^{2+}(aq)}/a_{Ca^{2+}(aq)}$ values are those necessary to maintain thermodynamic equilibrium (defined by $\mu_{MgCO_3(s)} = \mu_{MgCO_3(aq)}$ and $\mu_{CaCO_3(s)} = \mu_{CaCO_3(aq)}$) between an aqueous phase and magnesian calcites.

TABLE 1

Estimated stability of Mg–calcites at 25°C and 1 atm total pressure

Composition	pH*	log K_{eq}**	$\Delta G°_f$***
$CaCO_3$ (calcite)	6.02	−8.426	−269.96
$Ca_{(0.980)}Mg_{(0.020)}CO_3$	6.02	−8.47	−269.55
$Ca_{(0.970)}Mg_{(0.030)}CO_3$	6.00	−8.54	−269.41
$Ca_{(0.931)}Mg_{(0.069)}CO_3$	6.10	−8.31	−268.18
$Ca_{(0.896)}Mg_{(0.104)}CO_3$	6.24	−7.96	−266.87
$Ca_{(0.873)}Mg_{(0.127)}CO_3$	6.29	−7.84	−266.17
$Ca_{(0.821)}Mg_{(0.179)}CO_3$	6.44	−7.46	−264.42
$Ca_{(0.808)}Mg_{(0.192)}CO_3$	6.49	−7.33	−263.94
$Ca_{(0.764)}Mg_{(0.236)}CO_3$	6.55	−7.19	−262.71
$Ca_{(0.756)}Mg_{(0.244)}CO_3$	6.55	−7.20	−262.53
$Ca_{(0.733)}Mg_{(0.267)}CO_3$	6.52	−7.29	−262.11

* Estimated pH of solution at stoichiometric saturation with the given composition at 0.97 atm CO_2 from (Plummer and Mackenzie, 1974).

** Taken to be log IAP, that is, $(1-x)\log a_{Ca^{2+}(aq)} + x \log a_{Mg^{2+}(aq)} + \log a_{CO_3^{2-}(aq)}$ for the phase $Ca_{(1-x)}Mg_xCO_3$ in solution at stoichiometric saturation. The composition of the solution at stoichiometric saturation was calculated from pH and P_{CO_2} using a simple iterative computer program. Activity coefficients of charged species in aqueous solution were calculated using extended Debye-Hückel expressions and those for neutral species were calculated from the relation $\log \gamma_i° = 0.1I$ where $\gamma_i°$ is the activity coefficient of the *ith* neutral species, and I is ionic strength. The following species were assumed present in aqueous solution: Ca^{2+}, Mg^{2+}, $MgHCO_3^+$, $CaCO_3°$, $MgCO_3°$, H_2CO_3*, HCO_3^-, CO_3^{2-}, H^+, and OH^-. The $CaHCO_3^+$ pair was ignored because of the uncertainties in the aqueous model (Jacobson and Langmuir, 1974; Plummer and Mackenzie, 1974). Sources of the equilibrium constants used are as follows: $MgHCO_3^+$ and $MgCO_3°$, Siebert (ms); $CaCO_3°$, Reardon and Langmuir (1974); H_2CO_3* (that is, $CO_{2(aq)} + H_2CO_3°$) and Henry's law constant for H_2CO_3*, Harned and Davis (1943); HCO_3^-, Harned and Scholes (1941); H_2O, Helgeson (1969).

*** Calculated from log $K_{eq}(x)$ using $\Delta G°_f(Ca^{2+}_{(aq)}) = -132.30$ kcal/mol, $\Delta G°_f(Mg^{2+}_{(aq)}) = -108.70$ kcal/mol (Parker, Wagman, and Evans, 1971), and $\Delta G°_f(CO_3^{2-}_{(aq)}) = -126.17$ kcal/mol (Wagman and others, 1968).

TABLE 2

Interpolated log $K_{eq}(x)$ values, slope estimates, and solid phase activity coefficients for magnesian calcites at thermodynamic equilibrium with an aqueous phase

Mole fraction $MgCO_3$ (x)	* $-\log K_{eq}(x)$	** $\frac{\partial \log K_{eq}(x)}{\partial x}$	*** $\log \lambda_{CaCO_{3(s)}}$	† $\log \lambda_{MgCO_{3(s)}}$	†† $\log\left(\frac{a_{Mg^{2+}(aq)}}{a_{Ca^{2+}(aq)}}\right)_{eq}$
0.00	8.426	—	0.000	—	—
0.01	8.45	−2.5	+0.005	−0.84	−2.5
0.02	8.47	−1.2	−0.01	+0.14	−1.2
0.03	8.48	+0.7	−0.06	+1.81	+0.7
0.04	8.46	+2.3	−0.11	+3.24	+2.3
0.05	8.43	+4.1	−0.19	+4.86	+4.1
0.06	8.37	+6.2	−0.29	+6.77	+6.2
0.07	8.31	+8.1	−0.42	+8.47	+8.1
0.08	8.21	+8.8	−0.45	+9.07	+8.8
0.10	8.03	+8.2	−0.38	+8.44	+8.2
0.12	7.87	+7.7	−0.31	+7.92	+7.7
0.14	7.71	+7.5	−0.27	+7.68	+7.5
0.16	7.57	+6.9	−0.17	+7.11	+6.9
0.18	7.43	+6.4	−0.07	+6.65	+6.4
0.20	7.31	+6.1	−0.01	+6.36	+6.1
0.21	7.25	+4.9	+0.25	+5.39	+4.9
0.22	7.22	+2.7	+0.72	+3.63	+2.7
0.23	7.20	+1.0	+1.11	+2.30	+1.0
0.24	7.20	−0.7	+1.51	+0.98	−0.7
0.25	7.21	−2.7	+2.02	−0.54	−2.7
0.26	7.25	−4.5	+2.48	−1.91	−4.5
0.27	7.31	−6.0	+2.87	−3.03	−6.0

* Log $K_{eq}(x)$ values are from the curve in figure 1.

** Average of visual estimates by Thorstenson and Plummer.

*** Calculated from eq (27) and the definition $\lambda_{CaCO_{3(s)}} = a_{CaCO_{3(s)}}/(1-x)$.

† Calculated from eq (28) and the definition $\lambda_{MgCO_{3(s)}} = a_{MgCO_{3(s)}}/x$. Log $K_{magnesite} = -8.09 = \log (a_{Mg^{2+}(aq)} a_{CO_3^{2-}(aq)})$ at equilibrium; from Christ and Hostetler (1970).

†† Calculated from eq (29).

of these curves because of the latitude available in fitting the original data. However, any reasonable fit of the data in figure 1 must produce results similar to those shown in our figure 2; that is, $a_{Mg^{2+}(aq)}/a_{Ca^{2+}(aq)}$ must achieve values in the range 10^8 to 10^9 for $x \cong 10$ percent and remain very high until $x \cong 20$ percent, then decrease drastically.

Our interpretation of these data is that in the composition range 8 to 20 percent $MgCO_3$, which encompasses the majority of the magnesian calcites (biogenic or inorganic) present at the Earth's surface, *the chemistry of the Mg–calcites will be determined entirely by stoichiometric saturation relations in the aqueous phase.* The attainment of thermodynamic equilibrium requires impossibly high Mg^{2+}/Ca^{2+} ratios in the aqueous phase, and even if attained, it appears that there should be little or no dependence of the composition of the solid phase on the Mg^{2+}/Ca^{2+} ratio in the aqueous phase.

Figure 3 depicts the solid phase activities and activity coefficients for $CaCO_3$ and $MgCO_3$ as a function of Mg–content of the calcite, as predicted by eqs (27) and (28). In the 0 to 8 mol percent $MgCO_3$ range, the activity coefficient for $CaCO_3$, λ_{CaCO_3}, can be approximated by regular solution behavior (compare Garrels and Christ, p. 44-46), although λ_{MgCO_3} shows extreme variation. In the 8 to 20 mol percent $MgCO_3$ range, there is little or no dependence of the activity coefficients on the $MgCO_3$ content of the solid phases. From 20 to 28 mol percent $MgCO_3$, reciprocal changes of about 10 orders of magnitude in both λ_{CaCO_3} and λ_{MgCO_3} are

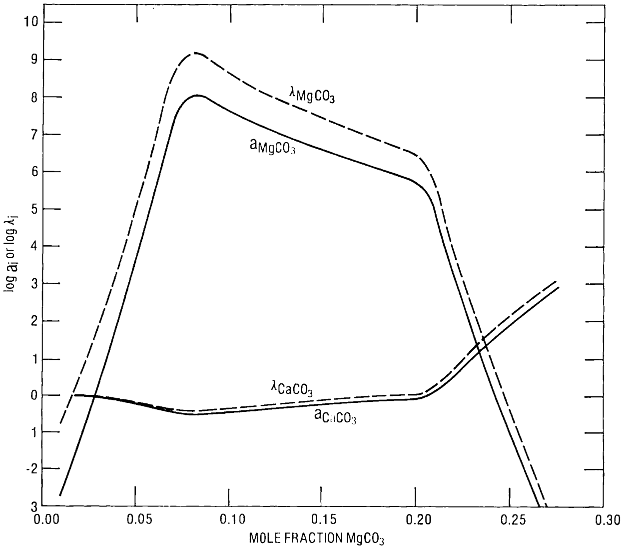

Fig. 3. Activities and activity coefficients of the components $CaCO_3$ and $MgCO_3$ in the magnesian calcites. Activities of $CaCO_3$ and $MgCO_3$ are calculated from eqs (27) and (28), respectively, using the data in table 1. Activity coefficients are obtained from the relation $\lambda_i = a_i/x_i$, where x_i = mol fraction of component i in the solid phase.

required, if thermodynamic equilibrium is to be maintained. We believe that these data support the conclusions drawn from figure 2, namely that only the low Mg–calcites can be expected to achieve thermodynamic equilibrium with natural waters, whereas the high Mg–calcites are controlled by stoichiometric saturation. The lack of changes in λ's in the 8 to 20 mol percent $MgCO_3$ range and the required order-of-magnitude changes in λ's for 20 to 28 mol percent $MgCO_3$ support the earlier conclusion that thermodynamic equilibrium is physically unrealistic.

We believe that the combined data of figures 2 and 3 support the following conclusions:

1. The chemistry of Mg–calcites with 0 to 3 or 4 mol percent $MgCO_3$ can be governed by thermodynamic equilibrium, and this, in fact, will be stable equilibrium. The actual composition of the low Mg–calcite at stable thermodynamic equilibrium depends on $K_{eq}(x)$ and the composition of the aqueous phase as given by eqs (14A), (14B), (21), (27), and (28).
2. In natural waters, the behavior of Mg–calcites with $MgCO_3 > 3$ to 4 mol percent will be governed only by stoichiometric saturation considerations.
   A. In the range 4 to 8 percent, although (stable) thermodynamic equilibrium is theoretically possible, it seems unrealistic, simply on the basis of mass requirements, to expect significant formation of a mineral with > 90 percent $CaCO_3$ from solutions with $Mg^{2+}{}_{(aq)}/Ca^{2+}{}_{(aq)} > 100{:}1$.
   B. In the 8 to 28 mol percent $MgCO_3$ range, the physical conditions required for maintenance of thermodynamic equilibrium seem unrealistic, as discussed earlier.

STOICHIOMETRIC SATURATION AND MAGNESIAN CALCITES

If we accept the foregoing conclusions, we need to investigate the implications of stoichiometric saturation for the behavior of the Mg–calcites, and we need a convenient scheme for evaluating the $MgCO_3$ content of a magnesian calcite at stoichiometric saturation with any given solution. These relations can best be obtained by expressing the equilibrium constants as functions of the ion activity product for $Ca^{2+}{}_{(aq)}$ and $CO_3{}^{2-}{}_{(aq)}$, and the $Mg^{2+}{}_{(aq)}/Ca^{2+}{}_{(aq)}$ ratio in the aqueous phase:

$$K_{eq}(x) = a^{(1-x)}{}_{Ca^{2+}(aq)}\, a^{x}{}_{Mg^{2+}(aq)}\, a_{CO_3{}^{2-}(aq)} \qquad (21)$$

or

$$K_{eq}(x) = (a_{Ca^{2+}(aq)}\, a_{CO_3{}^{2-}(aq)}) \left(\frac{a_{Mg^{2+}(aq)}}{a_{Ca^{2+}(aq)}} \right)^{x} \qquad (34)$$

or

$$\log\left(\frac{a_{Mg^{2+}(aq)}}{a_{Ca^{2+}(aq)}} \right) = -\frac{1}{x}(\log IAP_{calcite}) + \frac{\log K_{eq}(x)}{x}. \qquad (35)$$

Eq (35) is interpreted as follows: For any given value of x, that is, for a particular Mg–calcite, the condition of stoichiometric saturation can be satisfied by many combinations of $a_{Ca^{2+}(aq)}$, $a_{CO_3^{2-}(aq)}$, and $a_{Mg^{2+}(aq)}$, the only constraint being that eq (21) must be satisfied.

Eq (35) shows that solutions satisfying this constraint will plot as a line with slope of $-1/x$ on a graph of log $a_{Mg^{2+}(aq)}/a_{Ca^{2+}(aq)}$ versus $IAP_{calcite}$.

A series of such lines for various values of x (for various Mg–calcites) is plotted in figure 4. The composition of Mg–calcite at stoichiometric saturation with a given solution may be estimated from figure 4 by simply locating the point on the diagram representing the solution composition; the composition of the corresponding Mg–calcite will be given by the line passing through that point.

For any given Mg–calcite (any line in fig. 4), there will be one particular solution that is at thermodynamic equilibrium, as well as stoichiometric saturation. This point can be found by using the solid phase activities (from fig. 3) and the relations

$$a_{Ca^{2+}(aq)}\, a_{CO_3^{2-}(aq)} = (K_{calcite})\,(a_{CaCO_{3}(s)}), \tag{14A}$$

and

$$a_{Mg^{2+}(aq)}\, a_{CO_3^{2-}(aq)} = (K_{magnesite})\,(a_{MgCO_{3(s)}}). \tag{14B}$$

The major conclusion to be drawn from figure 4 is that even allowing for a variation of 10^4 in the $Mg^{2+}{}_{(aq)}/Ca^{2+}{}_{(aq)}$ ratio of natural waters (from 0.01 to 100), the primary factor governing the Mg–content of the magnesian calcites with $x > 0.05$ is the activity product of $Ca^{2+}{}_{(aq)}$ and $CO_3{}^{2-}{}_{(aq)}$. If stoichiometric saturation controls the chemistry of magnesian calcites in seawater, with its constant ratio of $Mg^{2+}{}_{(aq)}/Ca^{2+}{}_{(aq)}$, the Mg content of the calcites at 25°C should be determined solely by the degree of supersaturation of the water with respect to calcite.

A large literature that deals in some way with the stability of magnesian calcites (Chave and others, 1962; Jansen and Kitano, 1963; Berner, 1967 and 1975; Lerman, 1965; Weyl, 1965; Land, 1967; Winland, 1969; Barnes and O'Neil, 1971; Katz, 1973; Plummer and Mackenzie, 1974; Möller and Parekh, 1975) has accumulated over the past 15 yrs. Many of these studies have focused on the relative stability differences among calcite, aragonite, and magnesian calcites. Few have attempted to determine the thermodynamic properties of the magnesian calcite solid solution. Lerman (1965), using a free energy mixing model, extrapolated high temperature (400°C) magnesian calcite stability data to 25°C and found large departures from stable solid solutions at low temperatures. Plummer and Mackenzie (1974) assumed their stoichiometric saturation data represented thermodynamic equilibrium and obtained results less stable than Lerman's. The solid phase activities and activity coefficients of $CaCO_3$ and $MgCO_3$ calculated using the thermodynamic theory of this paper and the stoichiometric saturation data of Plummer and Mackenzie (1974) indicate that most magnesian calcites at 25°C are far more nonideal than has been previously recognized. Although the computed values of λ_{MgCO_3} and λ_{CaCO_3} in the solid are very large, they find some support in

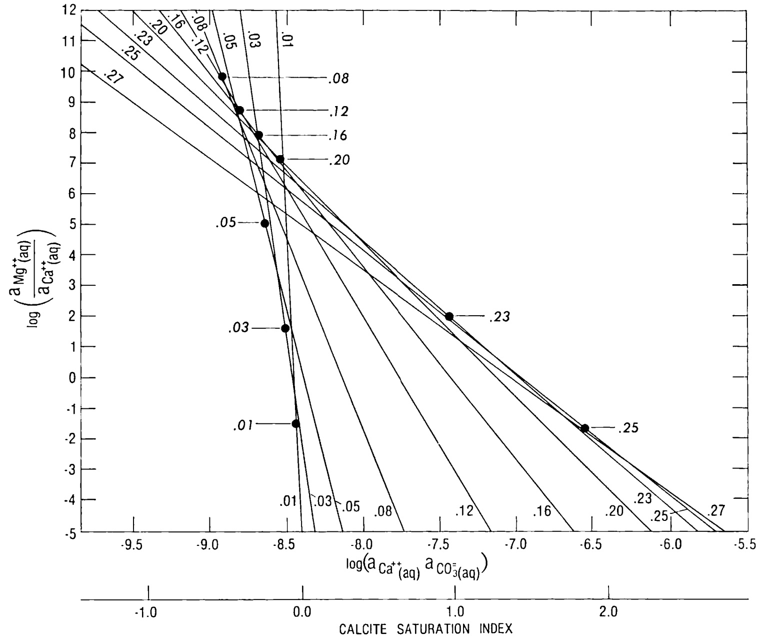

Fig. 4. Log ($a_{Mg^{2+}(aq)}/a_{Ca^{2+}(aq)}$) versus log ($a_{Ca^{2+}(aq)}a_{CO_3^{2-}(aq)}$) for solutions at stoichiometric saturation with magnesian calcites of various compositions. Each line on the diagram represents the range of $Ca^{2+}_{(aq)}$, $Mg^{2+}_{(aq)}$, and $CO_3^{2-}{}_{(aq)}$ activities that satisfy the equation $K_{eq}(x) = a^{(1-x)}_{Ca^{2+}(aq)}a^{x}_{Mg^{2+}(aq)}a_{CO_3^{2-}(aq)}$ for the indicated value of x. Lines were computed from eq (35). The point on each line at which the solution is at thermodynamic equilibrium with the Mg–calcite is shown; these points were obtained from the data of table 2. Numbers used in labeling lines and points represent the mol fraction $MgCO_3$ in the magnesian calcites.

the coprecipitation data on Sr^{2+} in calcite obtained by Kinsman and Holland (1969). Kinsman and Holland assumed the coprecipitation represented thermodynamic equilibrium and obtained a λ_{SrCO_3} of 70. The composition of the calcite to which this value of λ_{SrCO_3} corresponds is unclear but is presumably less than 1 mol percent $SrCO_3$. Our data indicate a comparable value for magnesium in calcite, that is, $\lambda_{MgCO_3} \cong 100$, at about 4 mol percent $MgCO_3$.

SUMMARY AND CONCLUSIONS

1. The thermodynamic relations at 25°C and 1 atm total pressure for binary solid solution compounds at equilibrium with an aqueous phase have been presented. If, as is generally the case at 25°C, changes in composition of the solid phase are very slow, the assumption of thermodynamic equilibrium in experimental work is almost certainly invalid, and it is questionable in many natural environments. Under these conditions, the behavior of the solid phases must be interpreted on the basis of stoichiometric saturation.

2. A method has been derived for determining the thermodynamic characteristics of binary solids, if stoichiometric saturation data are available as a function of solid phase composition.

3. Using this method, the solid phase activities of the components $CaCO_3$ and $MgCO_3$ in magnesian calcites have been determined.

4. We have demonstrated that in natural waters, thermodynamic equilibrium can control the Mg–calcites with < 5 mol percent $MgCO_3$. The occurrence of other compositions is governed by stoichiometric saturation, which is a kinetic state.

5. In nearly all natural waters, the most important factor governing the chemistry of the magnesian calcites is the activity product $(a_{Ca^{2+}(aq)})(a_{CO_3^{2-}(aq)})$ rather than the $Mg^{2+}{}_{(aq)}/Ca^{2+}{}_{(aq)}$ ratio in the aqueous phase.

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