DISCUSSION

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In their article on magnesium calcites, Thorstenson and Plummer (1977), assumed that they had accurate standard free energy of formation values for given Mg-calcite compositions. These standard free energy of formation values were taken from the work of Plummer and Mackenzie (1974), who obtained their values by calculations based on the assumption that rate of solution measurements made during the congruent dissolution of Mg-calcites could be used to obtain an equilibrium constant for the Mg-calcite being dissolved. Thorstenson and Plummer defended these values on the grounds that while a Mg-calcite is dissolving congruently it can be considered to be a one-component phase or a *phase of constant composition.* They claimed that although the solution composition presumed to be in equilibrium with a "one-component" Mg-calcite would not be in equilibrium with the same Mg-calcite behaving as a two-component solid solution, the activity product constant would be the same for "one-component" as for two-component Mg-calcite. Most of their article is in fact devoted to calculating the thermodynamic properties of two-component Mg-calcite solid solutions from values of free energies of formation derived from the kinetics of "one-component" Mg-calcite solution data.

We find their article to be most original and interesting, but we question the validity of the free energy of formation values on which their calculations are based. Before proceeding to a discussion of our doubts, we would like to take the liberty of trying to clarify the problem. Figure 1 is an idealized diagram to illustrate the relations between solid solutions behaving as "one-component" compounds and solid solutions behaving as "two-component" compounds. The diagram shows a theoretical ideal system, ACO_3–BCO_3–H_2O–CO_2, for which CO_2 is maintained at 1 atm pressure.

The saturation curve x-y is calculated by assuming simultaneous equilibrium between the components of the solid solutions and the aqueous solution

$$ACO_3 + CO_2 + H_2O = A^{++} + 2HCO_3^-;\ K_{ACO_3} = \frac{a_{A^{++}}\, a^2_{HCO_3^-}}{a_{ACO_3}\, P_{CO_2}} .$$

$$BCO_3 + CO_2 + H_2O = B^{++} + 2HCO_3^-;\ K_{BCO_3} = \frac{a_{B^{++}}\, a^2_{HCO_3^-}}{a_{BCO_3}\, P_{CO_2}} .$$

Point Z is the aqueous solution in equilibrium with the *solid solution* of composition $A_{0.5}B_{0.5}CO_3$. If $A_{0.5}B_{0.5}CO_3$ were a phase of *fixed composition,* its equilibrium constant could be written $K' = a^{0.5}_{A^{++}}\, a^{0.5}_{B^{++}}\, a^2_{HCO_3^-}$. Line V-O-V′, passing through Z, is the locus of points of solution composition for which K′ holds. Thus solution Z is the only aqueous solution in

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equilibrium with the *solid solution* $A_{0.5}B_{0.5}CO_3$, but solutions V-O-V′ would all be in equilibrium with a phase of the same but *fixed composition.*

The contentions of Plummer and Mackenzie (1974) and of Thorstenson and Plummer (1977) can be illustrated by attention to arrowed line H_2O-O. This line represents the path of solution composition for congruent solution of $A_{0.5}B_{0.5}CO_3$. Point O, according to these authors, is the solution composition obtained by extrapolating the experimental data for congruent solution to infinite time. According to them, point O lies on line V-Z-V′. One could say that the major contribution of the Thorstenson and Plummer paper is the translation of a series of points "O′," for various Mg-calcites, into points "Z," and thus defining the solution compositions in *two-component* equilibrium with the solids.

It is unfortunate that Thorstenson and Plummer did not dissolve their Mg-calcites into solutions already containing Ca^{++} or Mg^{++}. If they had, the reaction pathways should be like arrowed line C-S, in which the extrapolated value of the solution composition should fall at point S, on the locus of equal K′ values. If they obtained the same K′ from a vari-

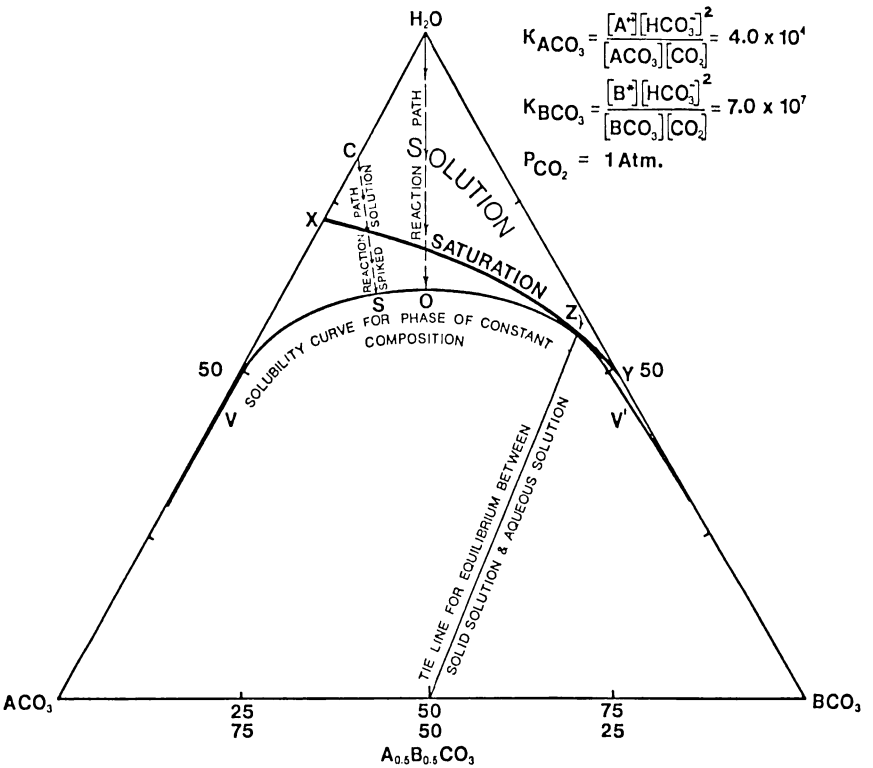

Fig. 1. Schematic relations to illustrate stabilities of solid solutions and phases of fixed composition.

ety of "spiked" solutions, it would be strong evidence in favor of the validity of their free energy of formation values.

A method of checking the free energy of formation values obtained by Thorstenson and Plummer would be to precipitate Mg-calcites from solutions of known compositions. If the phases precipitated were in equilibrium with the solutions, their free energies of formation could be calculated. Unfortunately, the results of precipitations, both in natural systems and in the laboratory, are not clear cut and are open to interpretation. We will show, however, that the information that is available from precipitations is not consistent with the results of Thorstenson and Plummer.

Figure 2 is a histogram showing the results of 35 determinations of the compositions of naturally occurring Mg-calcite inorganic marine cements from a number of different localities. The small range of compositions, no more than that attributable to temperature differences from place to place, is what would be expected if the cements had achieved equilibrium with seawater. The compositions of skeletal materials (fig. 3) show a greater range of variation than those of cements, but their mean value (about 13 mol percent Mg) is close to that of the cements (about 12 mol percent Mg). The tentative conclusion seems warranted that a 12 mol percent Mg-calcite would be close to a composition in true equilibrium with surface seawater, even though laboratory experiments yield a range of Mg contents for Mg-calcites precipitated from seawater (Berner, 1975).

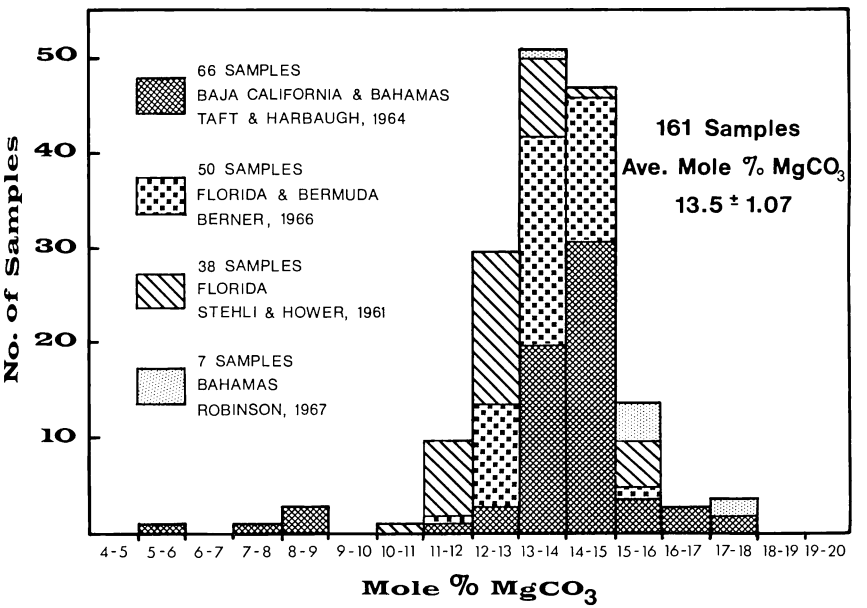

Fig. 2. $MgCO_3$ content (in mol percent) of the magnesian calcite fraction of recent marine carbonate sediments.

If 12 mol percent Mg-calcite *is* in equilibrium with seawater, its free energy of formation can be calculated from the composition of typical seawater. The result, *–266.0* kcal (for 25 degrees C), is almost exactly the value obtained by Thorstenson and Plummer (*–266.3* kcal) for the same composition.

At first sight, this result would seem to validate their work. However, if a 12 mol percent Mg-calcite is indeed in equilibrium with seawater as a two-component phase, the activities of the components, and hence their activity coefficients (λ), can be calculated from the seawater composition and the equilibria below.

$$\frac{a_{Ca^{++}}\, a_{CO_3^{=}}}{K_{calcite}} = a_{CaCO_3}$$

$$\frac{a_{Mg^{++}}\, a_{CO_3^{=}}}{K_{Magnetite}} = a_{MgCO_3}$$

$$\lambda_{CaCO_3} = a_{CaCO_3}/N_{CaCO_3}$$

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The values obtained are $a_{CaCO_3} = 2.3$; $\lambda_{CaCO_3} = 2$–3; $a_{MgCO_3} = 205$; $\lambda_{MgCO_3} = 25$. Thorstenson and Plummer calculate $\lambda_{CaCO_3} = 0.5$ and find

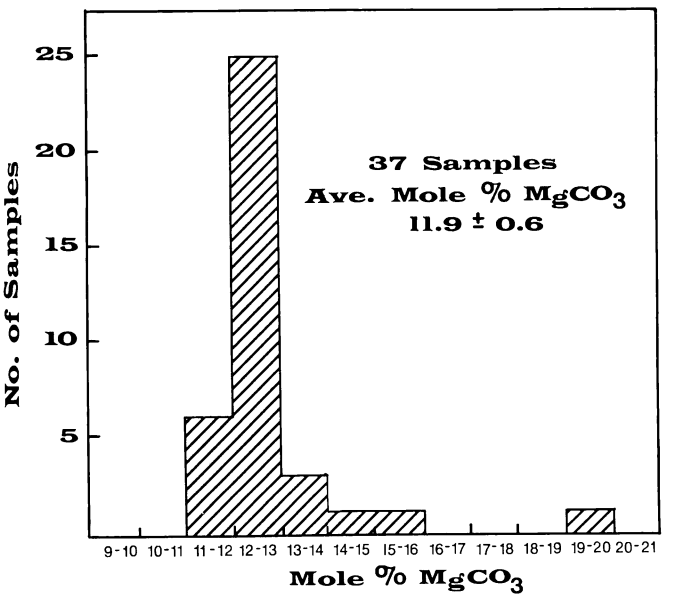

Fig. 3. $MgCO_3$ content (in mol percent) of naturally occurring magnesian calcite cements found in seawater. (37 samples: Milliman, 1971; 11 deep-sea samples; 5 samples, Atlantic sea mounts; 2 samples, West Caribbean; 3 samples, Red Sea; 2 samples, Mediterranean Sea. MacIntyre and Milliman, 1971, 24 lithified subcoastal sediment samples: 17 samples, North Carolina; 2 samples, South Carolina; 5 samples, Florida. Glover and Pray, 1971, 2 samples, cemented carbonate sands, Bahamas.)

that $\lambda_{MgCO_3} = 10^{7.9}$. Furthermore, Thorstenson and Plummer calculate that a 12 mol percent Mg-calcite is *not* in equilibrium with seawater. The Mg^{++}/Ca^{++} activity ratio in seawater is $\cong 6$; to make seawater in equilibrium with 12 mol percent Mg-calcite, Thorstenson and Plummer require an increase in Mg^{++}/Ca^{++} to 5×10^7.

We feel that the very large numbers for Mg^{++}/Ca^{++} ratios needed to stabilize many Mg-calcites as obtained by Thorstenson and Plummer are unrealistic.

As shown by Weyl (1961, 1967), nearly pure calcites and low Mg-calcites, as well as aragonites, when added to seawater, cause a lowering of pH and carbonate precipitation, when added to typical surface seawater. On the other hand, high Mg-calcites cause little if any change in pH, indicating that they are closer to equilibrium than low Mg materials. Weyl (1967) interprets the reaction of organic free seawater with excess pure calcite as the precipitation of a progressively more magnesian calcite on the original pure calcite, until equilibrium is achieved between a Mg-calcite and seawater. At our current state of knowledge, the exact composition of this "equilibrium" Mg-calcite is unknown, but the inference is strong that it is typical Mg-calcite; that is, in the 12 mol percent range. Berner (1975) found a range of 7 to 10 mol percent Mg in the carbonates he precipitated from seawater.

The reason for the marked difference between Thorstenson and Plummer's calculated activities and activity coefficients and those obtained from precipitation studies is shown indirectly in figure 4. In this figure, values of log $a_{Mg^{++}}/a_{Ca^{++}}$ from Thorstenson and Plummer plotted

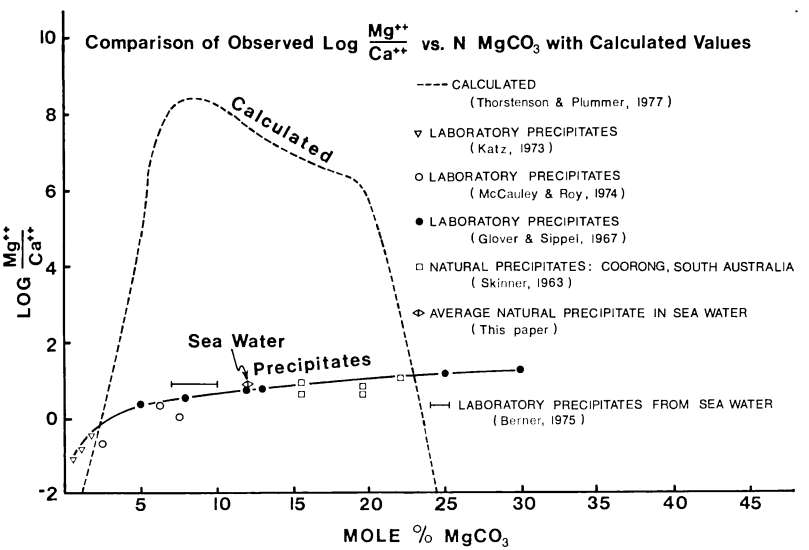

Fig. 4. Comparison of observed log Mg^{++}/Ca^{++} with calculated values.

versus mol fraction $MgCO_3$ are compared with values from a variety of precipitations, both natural and experimental. The curves differ markedly.

In summary, we consider that the activity product constants obtained by Plummer and Mackenzie (1974), which have been used by Thorstenson and Plummer to calculate thermodynamic properties of Mg-calcites, have not been demonstrated to be correct. Furthermore, evidence from precipitation studies, whereas just as puzzling, is opposed to their conclusions. We suggest that their values should not be accepted until the validity and significance of the $\Delta G°_f$ values they used for Mg-calcites have been demonstrated.

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