DISCUSSION

EQUILIBRIUM, KINETICS,
AND THE PRECIPITATION
OF MAGNESIAN CALCITE FROM SEAWATER

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In an earlier paper (Berner, 1975) I suggested that the magnesium content of calcite precipitated from seawater in the laboratory and in nature reflects kinetic phenomena and does not represent exchange equilibrium of calcium and magnesium between seawater and calcite. This idea has been much more forcefully enunciated by Thorstenson and Plummer (1977) recently in this journal. They, in fact, maintain that the composition of magnesian calcites precipitated from seawater is controlled solely by their stoichiometric solubility. However, solubility control on Mg-content has been met with considerable disfavor as evidenced by the accompanying papers by Lafon (1978) and Garrels and Wollast (1978). These authors maintain that the composition of magnesian calcite cements in marine sediments suggest exchange equilibrium, so that at the Mg/Ca ratio of seawater (about 5) the equilibrium composition of calcite is about 12 mol percent MgCO₃. Furthermore, Garrels and Wollast bolster their argument by presentation of laboratory precipitation data based on the results of Glover and Sippel (1967), Katz (1978), and McCauley and Roy (1974) for magnesian calcites precipitated from solutions other than seawater.

The purpose of this note is to present data on the laboratory precipitation of magnesian calcites from seawater alone and to show that the results do not favor simple Ca–Mg exchange equilibrium between calcite and seawater.

Table 1 presents the results of several studies where magnesian calcites were precipitated from seawater in the laboratory. (Values of Ω, the degree of supersaturation, are based on measurements of pH, calculated or measured alkalinitities, and the equilibrium constants cited by Berner, 1975). Methods ranged from addition of Na₂CO₃ and NaHCO₃ to dissolution of magnesian calcite in carbonate sediments by CO₂ with subsequent degassing and precipitation, to pH stat control at a low degree of supersaturation to achieve slow precipitation. Seeds varied from reagent calcite to carbonate sediment (after removal of magnesian calcite) to laboratory glassware, atmospheric dust, et cetera. Included in table 1 are experiments by the writer, heretofore unpublished, conducted at sporadic intervals over the past 15 yrs.

It is immediately obvious from table 1 that the magnesium content of calcite precipitated in the laboratory from seawater is highly variable and does not reflect exchange equilibrium with seawater. If equilibrium were attained, a constant Mg content would be expected in all runs because the
Mg/Ca ratio of seawater is constant and equal to a value of around five. This observation is in excellent agreement with the statement by Glover and Sippel who state that the “reproducibility of the precipitations was very poor.” I have also found reproducibility to be poor. The runs presented as the second entry in table 1 were conducted at the Scripps Institution of Oceanography in 1968. They were repeated 6 months later at the University of Chicago and instead of getting 17 to 18 mol percent Mg-calcite as the predominant mineral, under the same conditions I obtained only aragonite. This irreproducibility and the fact that unstable minerals such as monohydrocalcite often formed (but only during experiments at Scripps) led me, at that time (1963) to abandon these experiments as being thermodynamically meaningless.

<table>
<thead>
<tr>
<th>Method</th>
<th>Nuclei</th>
<th>Time to precipitate</th>
<th>Ωc</th>
<th>Mol % MgCO₃</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH-stat at constant Ω (4 runs)</td>
<td>reagent calcite</td>
<td>10:50 hr</td>
<td>5-7</td>
<td>7-10</td>
<td>Berner (1975)</td>
</tr>
<tr>
<td>HCO₃⁻ + CO₃⁻ added (3 runs)</td>
<td>glass dust et cetera</td>
<td>~10 min</td>
<td>120-180</td>
<td>17-18</td>
<td>This paper</td>
</tr>
<tr>
<td>HCO₃⁻ + CO₃⁻ + water-soluble extract of marine grass added (2 runs)</td>
<td>overnight</td>
<td>170</td>
<td>16-17</td>
<td>This paper</td>
<td></td>
</tr>
<tr>
<td>SW evaporated to 70%, salinity; HCO₃⁻ + CO₃⁻ added</td>
<td>~10 min</td>
<td>~150</td>
<td>22</td>
<td>This paper</td>
<td></td>
</tr>
<tr>
<td>HCO₃⁻ + CO₃⁻ added drop by drop (0°C) (9 runs)</td>
<td>days</td>
<td>~50</td>
<td>0-1</td>
<td>Kinsman and Holland (1969)</td>
<td></td>
</tr>
<tr>
<td>HCO₃⁻ + CO₃⁻ added drop by drop (15-17°C) (8 runs)</td>
<td>days</td>
<td>~50</td>
<td>8-10</td>
<td>Kinsman and Holland (1969)</td>
<td></td>
</tr>
<tr>
<td>HCO₃⁻ + CO₃⁻ added (0°C)</td>
<td>minutes</td>
<td>&gt;200</td>
<td>14</td>
<td>Glover and Sippel (1967)</td>
<td></td>
</tr>
<tr>
<td>Florida Bay sediment + CO₂; then degas by air bubbling (2 runs)</td>
<td>low Mg calcite, aragonite, quartz, organic matter</td>
<td>~1 day</td>
<td>?</td>
<td>8</td>
<td>Winland (1969)</td>
</tr>
<tr>
<td>Florida Bay sediment + CO₂; then degas by diffusion (3 runs)</td>
<td>~3 days</td>
<td>?</td>
<td>8-10</td>
<td>This paper</td>
<td></td>
</tr>
<tr>
<td>R.G. calcite + CO₂; then degas by diffusion (2 runs)</td>
<td>reagent calcite</td>
<td>~5 days</td>
<td>?</td>
<td>9-10</td>
<td>This paper</td>
</tr>
</tbody>
</table>

"Time to precipitate”, except in pH stat runs, refers to first appearance of white precipitate and not total run length. In almost all runs Mg-calcite was accompanied by aragonite, hydrocalcite, or vaterite. Unless otherwise indicated runs were conducted at room temperature. The symbol Ωc refers to the concentration product of Ca²⁺ and CO₃⁻ divided by the same product at equilibrium with pure calcite.
Discussion

Table 1 does suggest some regularity to the results if they are viewed from a kinetic viewpoint. Those runs conducted at high degrees of supersaturation and, thus, faster rates of precipitation, tend to produce calcites higher in magnesium content. This would be expected if solubility were a major control of Mg-content. However, solubility control is not very strong because the lowest supersaturation combined with calcite seeding (Berner, 1975) did not produce the lowest magnesium content.

An additional observation is that in my (1975) calcite seeded runs, the measured rate of precipitation, at a fixed degree of supersaturation, was constant with time. This means that during precipitation the magnesium calcite overgrowth did not become continually enriched in magnesium and thus more soluble, as it grew. Otherwise the rate would have slowed with time. This observation disagrees with the continuous Mg-enrichment hypothesis of Weyl (1965).

Precipitation of Mg-calcite cement in natural sediments should be a slow process, certainly slower than the laboratory experiments presented here. Thus, exchange equilibrium may be more closely approximated as maintained by Lafon (1978) and Garrels and Wollast (1978). However, judging from the laboratory experiments, it is also quite possible that the Mg-content of marine calcite cements is kinetically controlled by the rate or rate mechanisms by which they precipitate. After all, the total range of Mg contents of marine cements (as opposed to the mode emphasized by Garrels and Wollast) is large, ranging from 6 to 21 mol percent (Milliman, 1974), and this suggests some kinetic influence. What is needed now to settle these questions is high quality thermodynamic data for magnesian calcite. I suggest that laboratory precipitations are not the way to determine this stability. Rather we need more reliable methods such as solution calorimetry of well defined, single composition synthetic Mg-calcites.

References


