by Gerald M. Friedman

Temperature and salinity effects on $^{18}$O fractionation for rapidly precipitated carbonates: Laboratory experiments with alkaline lake water—Perspective

An important factor involved in determining the isotopic composition of precipitating lake minerals is their mineralogy. In the Dead Sea (Israel) the aragonite-calcite ratio of lake carbonate sediments can be correlated with $\delta^{13}$C and $\delta^{18}$O fractionation. Increasing aragonite concentration conforms to an increase in the heavier carbon and oxygen isotopes. The enrichment of the heavier isotopes is explained by strong evaporation during the formation of aragonite, when the lighter isotopes are preferentially removed as part of CO$_2$. Calcite was formed as a result of degradation of gypsum through the activity of bacteria which preferentially use lighter isotopes from their carbon source. In a hypersaline lake at Salt Flat, Texas (US), layers of isotopically-heavy and isotopically-light carbonate sediments alternate in beds similar to those of the Dead Sea. As in the Dead Sea, the light layers are composed for the most part of calcite which has resulted from the bacterial decomposition of gypsum. At Salt Flat the isotopically heavy carbonate is dolomite, and not aragonite as in the Dead Sea.

Li et al. (1997) discuss the precipitation of lacustrine carbonates under rapidly changing conditions of salinity, alkalinity, and temperature. One of the factors that may be involved in determining the isotopic composition of lake carbonates is the mineralogy of the precipitating carbonates, especially aragonite and low-magnesian calcite.

In the study of carbonates of the Dead Sea in the rift valley of the Levant and a continental playa in West Texas oxygen and carbon isotopes showed a near-linear relationship. Li et al. (1997) only measured the oxygen isotopic composition, but I shall note that of carbon as well.

Figures 1 and 2 illustrate the relationship between the aragonite content of nearshore sediments of the Dead Sea and their $\delta^{13}$C/$^{12}$C and $\delta^{18}$O/$^{16}$O ratios. These figures show a linear relationship between the aragonite content and isotope composition of the carbonates (aragonite and calcite) present in the sediments. The correlation lines in Figures 1 and 2 have been computed by the method of least squares. Aragonite has been taken as the independent variable and the isotope ratios as the dependent variable. The coefficient of isotope ratio is explained by the variation in the aragonite content. The coefficient of correlation ($r$) for the relationship between aragonite content and oxygen isotope ratios is 0.90. This correlation is significant; statistically, $82\% (r^2)$ of the variation in the oxygen isotope ratio is explained by the variation in the aragonite content. An increasing aragonite content of the sediment is accompanied by enrichment of the heavier carbon and oxygen isotopes. The sediment with the highest aragonite content shows the greatest enrichment in heavier isotopes. Figure 3 shows the relationship between the aragonite content and the $\delta^{18}$O/$^{16}$O ratio for offshore sediments of the Dead Sea. The relationship is approximately linear, with increasing aragonite content being accompanied by enrichment in the heavier oxygen isotope. The coefficient of correlation ($r$) is 0.78. Figure 4 is a plot of $\delta^{13}$C/$^{12}$C against oxygen $\delta^{18}$O/$^{16}$O for both nearshore and offshore sediments. This plot, which displays a linear relationship with a correlation coefficient ($r$) of 0.89, indicates that with increasing enrichment in the heavier oxygen isotopes there is a corresponding increase in the heavier carbon isotopes.

Table 1 shows the mineralogical and geochemical compositions of pairs of black and white layers (varves) of the sediments studied. This table shows that white layers: 1. contain abundant aragonite, 2. are enriched in the heavier isotopes, whereas black layers are enriched in the lighter isotopes, and 3. have a much higher strontium content than the black layers (Friedman, 1965).

The ratio $\delta^{13}$C/$^{12}$C in limestones is related to the environment of deposition and to post-depositional diagenetic changes. The recent carbonate sediments of the Dead Sea have not undergone dia-

Figure 1. Relationship between aragonite content and isotope ratios.

Figure 2. Relationship between aragonite content and isotope ratios.
Table 1. Composition of sediment pairs (white and black layers)*, Dead Sea.

<table>
<thead>
<tr>
<th>Color of layer</th>
<th>Aragonite (%)</th>
<th>Strontium (p.p.m)</th>
<th>δ13C</th>
<th>δ18O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pair 1 White</td>
<td>63</td>
<td>4,000</td>
<td>+3.61</td>
<td>+2.81</td>
</tr>
<tr>
<td>Black</td>
<td>N.D.**</td>
<td>890</td>
<td>-3.13</td>
<td>-2.05</td>
</tr>
<tr>
<td>Pair 2 White</td>
<td>40</td>
<td>4,000</td>
<td>+0.81</td>
<td>+2.54</td>
</tr>
<tr>
<td>Black</td>
<td>N.D.**</td>
<td>1,000</td>
<td>-1.08</td>
<td>-1.82</td>
</tr>
</tbody>
</table>

*These samples contain gypsum.

**N.D. = none determined. The carbonate mineral in these samples is calcite; other samples of black layers analyzed were found to contain both calcite and aragonite (Neev, 1964).

genetic changes by post-depositional contacts with fresh water. Therefore, the carbon isotope ratios must reflect the environmental conditions under which the carbonate sediments were deposited.

Carbonate precipitated in a non-marine environment tends to be enriched in the lighter carbon isotope (12C) as compared to marine limestone. In non-marine carbonates, 13C can be concentrated by strong evaporative processes in which the lighter carbon isotope is preferentially removed as part of CO2. Figure 1 shows that with increasing aragonite content a more or less progressive enrichment in 13C takes place in Dead Sea carbonate (r=0.92). In fact, enrichment in 13C has taken place to the extent that carbonate samples have typical "marine" values.

Marine water has a greater 18O content than fresh water and, as with carbon isotopes, fresh-water carbonates are deficient in the heavier (18O) isotope as compared to marine carbonates. However, enrichment in 18O in non-marine carbonates can result from strong evaporation. Figure 2 indicates that for nearshore sediments of the Dead Sea, as the aragonite content increases, the carbonate shows a tendency to be enriched in the heavier oxygen isotope (r=0.90). This essentially confirms the inference already made from the distribution of the carbon isotopes that the aragonite is formed under the conditions of intense evaporation. In Figure 3, aragonite content and oxygen isotope composition have been plotted for sediments from deeper water. This figure indicates that also in offshore sediments of the Dead Sea aragonite enrichment is for the most part accompanied by concentration of the heavier oxygen isotope (r=0.78). A statistically significant correlation was obtained between the aragonite content and the isotopic composition of the carbonates in samples, despite the presence of a notable gypsum content, and it is estimated that the correlation would hold even better if only the carbonate isotopes in the samples had been used.

These data and interpretations support the conclusions by Neev (1963, 1964) who suggested that high temperatures were the mechanism that triggers the mass precipitation of aragonite in the Dead Sea.

In the hypersaline lake of Salt Flat, West Texas, United States of America, layers of isotopically-heavy and isotopically-light carbonate sediments occur in alternating beds similar to those of the Dead Sea (Friedman, 1996). The light layers, as in the Dead Sea, are composed for the most part of calcite which has resulted from the bacterial decomposition of gypsum in which the lighter isotopes are drawn from the carbon source (Feeley and Kulp, 1957, p.1844). Neev (1963, 1964) has suggested a similar bacterial origin for the Dead Sea calcite. Lighter calcite occurrences, both for the Dead Sea and Salt Flat, Texas, may reflect bacterial fractionation. At Salt Flat the isotopically heavy carbonate is dolomite and not aragonite as in the Dead Sea.

My study is essentially deductive. The approach has been to relate the isotopic composition to the aragonite and calcite contents in the studied samples and to explain the observed correlations. To confirm these explanations it is necessary to measure the isotopic composition of Dead Sea waters, of aragonite and calcite actually precipitating, and formed diagenetically, and of detrital limestones which may have served as a source for the Dead Sea carbonates. Such a study would be ambitious, but would lead to important information on sedimentary processes in carbonates. Li et al. (1997) study falls in this category and is a beginning in our understanding of oxygen isotopic fractionation for rapidly precipitated carbonates in lacustrine settings.

References


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