Outlines of Distribution of Strontium in Marine Limestones

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With 6 Figures

Abstract

The strontium content of marine limestones is governed by four factors:
Age. The aragonite-calcite transition is the reason for the strong diminution of the strontium content during diagenesis. This is efficient for 50 to 100 mill. years.
Clay mineral content. Diagenetically altered limestones show a relationship between the Sr-content and the insoluble residue. This is explained by the adsorption of Sr by clay minerals during the aragonite-calcite transition.
Salinity. Limestones of evaporitic series show a relative high Sr-content.
Environment. In alternating limestone-marl-series no relationship between the Sr-content and the insoluble residue seems to exist.

Contrary to the relationships found in recent carbonates, in fossil limestones the reef complexes have a minimal Sr-content, for they have small clay mineral content.

A. Introduction

Most investigations concerning trace elements in limestones are concerned with strontium. The several hundred analyses cited in the literature agree in average on the value of about 400 to 500 ppm Sr (Vinogradov and Ronov, 1956; Kulp, Turekian and Boyd, 1952; Fornaseri and Grandi, 1963). But single measurements yield values between 100 ppm and more than 1200 ppm. Thus it seems necessary to discuss the reasons for the differences in distribution of strontium in limestones.

Recent carbonate sediments are also well examined. Several workers have tried to use variations in the strontium content for facies analyses based on recent statements.

B. Comparison of Fossil Limestones with Recent Carbonate Sediments

Recent carbonates differ distinctly from fossil limestones in their absolute Sr-content as well as in the relative strontium contents representing each of the different facies areas. Absolute strontium contents in recent carbonates average about several 1000 ppm, and thus they are about ten times higher than those of fossil limestones (Stehli and Hower, 1961; Siegel, 1961). The relative strontium content of recent carbonates is as follows: reefs have maximum values, also in lagoonal limestones the values are high; but in the correlated basin sediments they are low. This behaviour corresponds to the distribution of aragonite and calcite in these sediments.

In fossil limestones, consisting only of calcite, the distribution is completely reversed: in reef complexes the strontium content is low, while in correlated basin sediments...
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In recent sediments it is high (see Table 1). This was found by Flügel and Flügel-Kahler (1963), Bausch (1965), Chester (1965), and Flügel and Wedepohl (1967). Contrary to the opinion of Flügel and Wedepohl (1967), this seems to be a rule of general validity; contradictory examples are not known.

Evidently, the high Sr-content of recent sediments is reduced diagenetically, and simultaneously the distribution in the facies areas is changed.

Recent carbonate sediments consist of the three phases aragonite, high-Mg-calcite and low-Mg-calcite. Only low-Mg-calcite, that is normal calcite, is stable for longer periods of time. According to Friedman (1964), no recent sediments can be found, which consist only of the stable calcite phase. Therefore, all carbonate sediments must undergo the diagenetic transition into low-Mg-calcite. In addition, there are processes of solution and pore space filling. Thus the conservation of primary strontium contents is very improbable.

Table 1. Comparison of strontium contents (in ppm) of reef- and non-reef facies in ancient limestones

<table>
<thead>
<tr>
<th>Authors</th>
<th>reef complex</th>
<th>basin limestone</th>
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</thead>
<tbody>
<tr>
<td>Flügel and Flügel-Kahler (1963)</td>
<td>300—400</td>
<td>1800 (“fore-reef”)</td>
</tr>
<tr>
<td>Bausch (1965)</td>
<td>200</td>
<td>600</td>
</tr>
<tr>
<td>Chester (1965)</td>
<td>67</td>
<td>533</td>
</tr>
<tr>
<td>Flügel and Wedepohl (1967)</td>
<td>100—200</td>
<td>500—3000</td>
</tr>
</tbody>
</table>

C. Crystal Chemistry

The modification of aragonite permits the incorporation of considerable amounts of strontium into the crystal lattice, because in the sequence of the earth-alkali carbonates the aragonite structure is realized with large cations (rKat > rCa). As is known, strontianite also crystallizes with the aragonite structure. On the other hand, the little cations prefer the calcite structure, and therefore the modification of calcite is less favorable for the incorporation of strontium.

Oxburgh et al. (1959) and Holland et al. (1963, 1964) found distribution coefficients of aragonite/solution and calcite/solution the respective values of which differ about ten times in their magnitude. Therefore, aragonite is able to pick up ten times the amount of strontium that calcite can incorporate under equal conditions.

Recent marine aragonite and calcite differ in the same manner with regard to their Sr-content (as listed by Flügel and Wedepohl, 1967). This is the reason for the different strontium contents of different facies areas: in reef- and lagoon-areas the amount of aragonite and the strontium content also are high; on the other hand, in basin sediments calcite prevails and the strontium content is low.

For calcite precipitated in sea water the Sr values should be about 950 ppm according to the distribution coefficients of Oxburgh et al. (1959) and of Holland et al. (1963, 1964) (the statement by Flügel and Wedepohl, 1967, of 2300 ppm is erroneous). — Since Sr-values found in nature are often higher, possibly other ions in sea water are of importance (not NaCl, which has no influence according to Holland et al.). Moreover, organisms are obviously able to influence the strontium content in carbonate phases, because the values for skeletal elements of aragonite-

1 Meanwhile corrected: Contr. Min. Petr. 16, 114 (1967)