ARTIFICIAL MIXED CARBONATES IN THE CaCO₃ - MgCO₃ SERIES

B. G. Erenburg

Western Siberian Geological Administration
Original article submitted September 22, 1960

A series of rhombohedral mixed calcium-magnesium carbonates, containing from 17 to 50 molar %MgCO₃, which do not change during prolonged keeping or when heated to 300°, was prepared by precipitation from solutions at temperatures below 100° under atmospheric pressure. The dimensions of the unit cells of the artificial mixed carbonates vary smoothly with the composition.

The x-ray patterns of the mixed carbonates do not offer any grounds for assigning them to the interlayer type of structure. Their crystal lattices must conform to the type of substitutional solid solutions. The ratio of the unit cell constants c/a for dolomite is less than the corresponding value for a disordered mixed carbonate of the same composition as dolomite.

Because of the considerable difference between the radii of the calcium and magnesium ions (1.04 and 0.74Å) it is to be expected that the possibilities for formation of isomorphous mixtures of their compounds, including carbonates, are limited [1, 2]. In fact, until recently neither any native nor any artificial carbonates of calcium and magnesium with considerable mutual isomorphous substitution were reliably known.

More recently, extensive use of x-ray diffraction methods made it possible to establish the existence of natural biogenic limestones containing at least up to 20 molar %MgCO₃ in the form of substitutional solid solutions [3, 4]. It was claimed that such isomorphous mixtures cannot be made by chemical precipitation and that they are unstable under the conditions of the earth's surface [3]. This is confirmed by experimental investigations [5, 6] in which it was shown that at 900° and high CO₂ pressure (sufficient to prevent dissociation of carbonates) calcite containing about 25%MgCO₃ is in equilibrium with dolomite, whereas the corresponding equilibrium value at 500° is only 5%MgCO₃ in calcite. In other experiments certain rhombohedral mixed carbonates, named "protodolomite" by the authors, were artificially prepared from various mixtures of native and artificial calcium-magnesium carbonates; their composition was more or less close to that of dolomite, but always with an excess of CaCO₃ over the ideal content [7]. In most cases their MgCO₃ content varied from 40 to 50 molar %, and in only two cases did it fall to 36 and 33 molar %. The authors [7] oppose the assignment of these substances to the CaCO₃ - MgCO₃ isomorphous series, and regard them as analogs of dolomite, imperfect with regard to structural order.

However, the literature does not contain any references to the possible preparation of isomorphous mixtures of calcium and magnesium carbonates by direct chemical precipitation. The assertion by some authors (see above) that this is impossible in principle is unjustified. On the contrary, our data on the formation of artificial

*The crystal structure of dolomite is characterized by the presence of Ca²⁺ and Mg²⁺ ions in separate and regularly alternating plane networks. Therefore the composition of dolomite is always close to CaCO₃·MgCO₃. In isomorphous mixtures all the cation positions are equivalent, since the cations replace each other statistically. According to Goldsmith [7], there is some degree of order in the mutual arrangement of the cations in "protodolomite," in contrast to isomorphous mixtures. In one of the possible structure models this order consists of partial enrichment of individual cation layers with calcium or magnesium; these planes do not alternate in a simple Ca-Mg-Ca-Mg sequence.
mixed carbonates in the series CaCO₃–MnCO₃ [8], CaCO₃–FeCO₃, and MgCO₃–MnCO₃ [9] suggested that under certain conditions, it is possible to prepare mixed calcium–magnesium carbonates, at least in a certain range of concentrations.

We precipitated the mixed carbonates by slow addition of a mixture of calcium and magnesium chloride solutions to a mixture of sodium carbonate and bicarbonate solutions with continuous stirring. In the same way as was found in the preparation of mixed magnesium and manganese carbonates [9], the phase composition of the magnesium-containing precipitates is fairly complex and depends on the composition of the original mixture, the temperature, and the dilution of the solutions. At high magnesium concentrations basic magnesium carbonate and at low magnesium concentrations aragonite is precipitated together with the mixed rhombohedral carbonate; rise of temperature favors aragonite formation. At high concentrations of the original solutions and definite proportions of the components two carbonate phases of the same crystal structure (calcite type) but with different (and variable) Ca: Mg ratio are precipitated instead of the one mixed carbonate.

Our task did not include a detailed investigation of the influence of the precipitation conditions on the phase composition of the precipitates, but it was necessary to find in which single-phase mixed carbonates should be precipitated as far as possible. These conditions were found empirically. In most of the experiments the original mixtures of molar CaCl₂ and MgCl₂ solutions (in the required proportions) were used in six-fold dilution, and mixtures (1:1) of molar Na₂CO₃ and NaHCO₃ solutions were used in two-fold dilution; the temperature of the mixture during precipitation was 50 ± 3° (some samples were prepared under somewhat different conditions). Absence of extraneous lines in the x-ray patterns of the mixed patterns was the criterion of a one-phase character. This is obviously a rough criterion, but because of the high degree of dispersion of the precipitates another and more reliable criterion was difficult to find. It is therefore possible that our mixed carbonates contained up to several percent of other phases as impurities.

The precipitates prepared as described were washed with distilled water and alcohol, filtered off with the aid of a water-jet pump, heated gently (250°) and investigated by chemical and x-ray methods. The results of chemical analysis showed that they always contained somewhat less magnesium than the original mixtures, because of the considerable solubility of magnesium carbonate.

The x-ray patterns were obtained with iron radiation in cameras 143.15 mm in diameter, with NaCl as the internal standard. All the x-ray patterns correspond to the calcite type of structure. The lines on the x-ray