Epitaxial Growth of Dolomite on Mica

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Abstract

The epitaxial crystallization of small single crystals of calcium magnesium carbonate on mica was obtained from calcium and magnesium chloride solution with urea at 200°C. The approximate composition of carbonate is between 41–44 atom percent of magnesium, as obtained from unit cell dimensions.

In our study of the hydrothermal growth of dolomite using Medlin's method (Medlin, 1959), crystals which grew on the walls of the pressure vessel (stainless steel) had different composition and degree of order from crystals grown out of contact with this substrate. To obtain better insight into how substrates influence the magnesium concentration in the final calcium-magnesium carbonate, we performed the following experiment.

A solution containing 4.6 ml of 2.5-M $CaCl_2$ solution, 3.2 ml of 2.5-M of MgCl₂ solution, 5.8 ml of 1.7-M urea solution, with water added to 20 ml was autoclaved with freshly cleaved mica crystals in a Teflon test tube at 200°C for 24 hours. After the experiment oriented growth of rhombohedra of calcium magnesium carbonate on the mica sheet was observed.

A precession photograph of a group of 8 crystals (Fig. 1) showed that the c axis (hexagonal axis) of the carbonate is perpendicular to (001) of the mica, with an *a* axis of the carbonate parallel to the a axis of mica. The a unit cell edge of the carbonate (average of the eight crystals) was determined to be 4.851 ± 0.005 Å. A rotation photograph of one crystal isolated from this group gave $a = 4.848 \pm$ 0.007 Å, $c = 16.12 \pm 0.01$ Å. The graphs of Goldsmith et al (1958) indicate the concentration of MgCO₃ in mole percent to be 41-42 using the a dimension, and 44 using the c dimension. In control runs performed without mica, we always obtained highly ordered dolomite with composition very close to 50 mole percent MgCO₃. We believe that the lower MgCO₃ content in crystals grown epitaxially on the mica resulted from constraints imposed by the repeat period of the "hexagonal" layers of mica. This period is 5.16 Å in mica, 4.99 Å in pure calcite, and 4.81 Å in dolomite; therefore the growth of a substance with a larger unit cell is preferred, and this corresponds here to lower magnesium concentration.



FIG. 1. Group of rhombohedral crystals of calcium magnesium carbonate grown on mica. Orientation: b axis of mica vertical, a axis of mica horizontal, a axis of carbonate horizontal. Size of largest crystal in a direction is 0.015 mm.

Conversely, we assume that using a suitable substrate with smaller repeat period, the opposite effect can be expected, *i.e.*, growth of dolomite from solutions which, if crystallized without epitaxial effect, would ordinarily give magnesian calcites. This leads us to a tempting hypothesis that natural dolomitization is enhanced by certain crystalline inclusions favoring formation of the smaller dolomite cell instead of the larger calcite cell, because of interface constraints. This could explain the sharp contacts between dolomite and limestone bodies sometimes observed in nature.

Further work on epitaxial crystallization of calcium-magnesium carbonates in in progress.

References

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