Breakdown of the Ostwald step rule: The precipitation of calcite and dolomite from seawater at 25° and 40°C

TINGTING WANG

The scarcity of modern dolomite contrasts strongly with its common abundance in Precambrian sedimentary rocks of marine origin, leading to the paradox commonly referred to as the "dolomite problem". Whereas dolomite can readily be precipitated from aqueous solutions above 100°C [1], many researchers have attempted unsuccessfully to synthesize dolomite at room temperature from natural seawater [2,3,4]. Nevertheless, by alternating between intervals of dissolution and precipitation in artificial brines, Deelman (1999) succeeded in synthesizing dolomite at low temperatures (between 313K and 333K) [5]. He concluded that multiple cycling of a solution between supersaturation and undersaturation with respect to calcite and/or aragonite would cause the metastable phases to dissolve, while preserving more stable nuclei (i.e. dolomite and/or low-magnesian calcite) in solution. In this study, natural seawater was equilibrated with CaCO₃ (mixture of calcite and aragonite) at a pCO₂ of 5%. After the solution reached equilibrium, the solid was removed by filtration and ambient air (pCO₂ ~390 ppm) was bubbled through the CO₂-charged seawater solution, leading to a highly supersaturated solution and the nucleation and precipitation of aragonite. Following the precipitation, the ambient air-equilibrated solution and the precipitate were purged with a 10% CO₂:N₂ gas mixture and all of the original precipitate was re-dissolved. Once equilibrium was reached with the gas phase, the solution should be undersaturated with respect to aragonite, in equilibrium with calcite, but remain supersaturated with respect to dolomite. The cycle was repeated 20 times and ultrapure N₂, instead of ambient air, was used in the last cycle, to maximize precipitate recovery. As the solution remains supersaturated with dolomite at all times, after each cycle, dolomite nuclei should be preserved and accumulate at the expense of aragonite and calcite. The experiments described above were carried out at 25° and 40°C. Preliminary results show that, whereas aragonite was obtained during the first few cycles, only calcite was detected in the last cycle of the experiments carried out at 25°C. Precipitates formed during the last aeration cycle at 40°C were mostly aragonite with a trace of what may appear to be dolomite. The precipitate formed at a faster rate at 40°C than at 25°C and, thus, there might not have been enough time for calcite and dolomite to precipitate. Therefore, additional air-bubbling cycles will be carried out in the weeks to come in an attempt to promote dolomite formation.

References: