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**Origin of Dolomite and Its Spatial and Chronological Distribution — A New Insight**

One of the oldest problems in sedimentology is the origin of dolomite. Dolomite,  $\text{CaMg}(\text{CO}_3)_2$ , is one of the most common sedimentary carbonate minerals. Its density is 2.866, and calcite's density is 2.710. The absolute abundance of dolostones, as well as the dolostone/limestone ratio, increase with geologic age. Changes in sea water magnesium concentration were invoked to explain these observations. During the last 30 years, for both scientific and economic reasons, many attempts were made to explain the scarcity of recent dolomites. Carbonate rocks composed mainly of dolomite generally have high porosities, and are important reservoir rocks for oil.

Dolomite is the thermodynamically stable carbonate phase in sea water. Its relative scarcity in recent marine carbonate sediments, therefore, cannot be explained simply by the thermodynamic properties of dolomite; dolomite formation seems to be inhibited by sea water. Most sedimentologists assumed that the formation of dolomite is mainly controlled by the dissolved magnesium/calcium ( $\text{Mg}^{2+}/\text{Ca}^{2+}$ ) ratio of sea water, the molar  $\text{Mg}^{2+}/\text{Ca}^{2+}$  ratio in sea water is 5.3. It was therefore assumed that dolomite formation requires a still higher ratio. This explanation, however, had to be abandoned, when primarily during the last 2 to 3 years, dolomite was observed as an important constituent of many modern marine organic-rich sediments; for example, in the California borderlands, Gulf of California, the Japan Trench, Cariaco basin off the coast of Venezuela, and the Solar Lake in Israel. In the Guaymas basin, for example, dolomite activity forms form pore fluids with ( $\text{Mg}^{2+}/\text{Ca}^{2+}$ ) ratios of 1 to 2. Similar dolomite formed in the Miocene Monterey Formation, either as penecontemporaneous or early diagenetic nodules or as laminated dolomite. The  $\delta^{18}\text{O}$  values of these dolomites range from  $-6$  to  $+70\text{‰}$ (PDB), and their  $\delta^{13}\text{C}$  values range from  $-30$  to  $+20\text{‰}$ .

Experiments conducted recently in our laboratory have shown that the important condition of dolomite formation is not high  $\text{Mg}^{2+}/\text{Ca}^{2+}$  ratios, but low dissolved sulfate ( $\text{SO}_4^{2-}$ ) content, which inhibits dolomite formation; sea water contains 28 mM ( $\text{SO}_4^{2-}$ ). Dolomitization of calcite is already inhibited at sulfate concentrations of approximately 5 to 7% of sea water value. Aragonite dolomitization, however, although strongly retarded at these low dissolved ( $\text{SO}_4^{2-}$ )-concentration values is inhibited at sulfate concentrations of approximately 50% of sea water's value. We have also shown that dolomitization of  $\text{CaCO}_3$  proceeds

through protodolomite, a calcium-rich disordered dolomite which would transform to dolomite if equilibrium were established. Dissolved  $\text{SO}_4^{2-}$  also retards the rates of protodolomite transformation to dolomite and dedolomitization.

Sulfate ions absorbed to the surfaces of calcite, dolomite, or aragonite may affect the kinetics of phase transformations in the carbonate system. In a sulfate-depleted environment, sulfate is rapidly desorbed; at 15° to 35°C, the process is completed in one to two days.

Thus, favorable sites for dolomite formation in the marine environment are those where dissolved  $\text{SO}_4^{2-}$  concentrations are low. The most effective processes of sulfate removal or its dilution in marine pore fluids are microbial reduction in organic-rich sediments and mixing of sea water with large amounts of fresh water. This happens, for example, in continental margin sediments with high rates of deposition, as in the Gulf of California, or in deeper water sediments associated with black shales. The presence of much dissolved  $\text{SO}_4^{2-}$  in sea water also explains the almost absence of dolomite in apparently highly favorable environments, for example, in open marine carbonates.

The relative paucity of dolomite-rich carbonate rocks (dolostones) formed during the last 100 to 120 million years, as compared with their abundance in older sediments, in particular in the Precambrian and early Paleozoic, could be explained on the basis of changes in the depositional environments and in the carbonate mineralogy of the primary calcareous sediments. These differences do not necessarily reflect changes in sea-water magnesium concentrations.