THE KINETICS OF DOLOMITE PRECIPITATION WITH APPLICATION TO CHANGES IN SEAWATER SATURATION STATE OVER THE PAST 100 MA

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Abstract

The mineral dolomite and the uncertainties surrounding its origin have attracted the attention of earth scientists for over a century. The core of the dolomite "problem" is the apparent paradox posed by the paucity of dolomite in modern marine depositional environments versus its relative abundance in the sedimentary rock record. Solving this problem requires knowledge of the conditions under which the mineral forms, and the rate of precipitation under those conditions. However, direct observation of modern dolomite formation is commonly possible only in marginal or nonmarine settings that differ substantially from the marine environments represented in ancient sedimentary dolomitic rocks. Although the laboratory study of dolomite has yielded a large body of knowledge concerning its high temperature phase relations and crystal chemistry, very few data are available that quantify its precipitation rate as a function of fundamental controls such as temperature and solution composition.

As a working hypothesis, it is suggested that the precipitation rate of dolomite may be quantified and modeled in a manner similar to other carbonate minerals, through application of a rate law that represents the rate as a simple function of saturation index,

$$\mathbf{r} = k(\Omega - 1)^n.$$

This hypothesis is tested in a series of experiments by measuring the steady state rate of dolomite precipitation in a dolomite-seeded flow reactor through analysis of reacted fluid chemistry. By varying temperature from approximately 100 to 200°C and saturation index (Ω) from near saturation to ~ 100, sufficient data were collected to solve for the reaction order and Arrhenius rate constant of this rate law.

The dolomite produced in these experiments was variable in composition but typically a calcium-rich protodolomite, forming syntaxial overgrowths on the seed material. At the highest supersat-

urations obtained, formation of distinct nucleation centers was observed. These experiments do confirm a strong temperature dependence for the precipitation reaction (activation energy $\epsilon_A = 31.9$ kcal mol^{-1}) and moderate dependency on saturation index (n=2.26). These dependencies imply that long term variation in seawater temperature and saturation state, driven by pCO_2 and bulk seawater chemistry, may have brought about significant changes in the rate of dolomite formation compared to competing carbonate mineral phases. These changes would in turn be reflected in the distribution of dolomite versus calcite in the rock record, suggesting a possible resolution of the dolomite "problem" in terms of long term climatic transitions.

This hypothesis is explored by application of the model rate law to the past 100 Ma of earth history, using the BLAG model to constrain temperature and bulk seawater composition, and mass-age data for calcite and dolomite. When normalized to their present-day values over this 100 Ma interval, the ratio of precipitation rates for calcite versus dolomite correlates well with their mass-age ratios. These results suggest that a significant extent of the post-Cretaceous decrease in dolomite abundance is due to the reduction in tectonically-driven terrestrial weathering and metamorphic-volcanic CO_2 fluxes, and their attendant forcing of temperature and seawater composition.