Reaction pathways towards the formation of dolomite

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Abstract: Little is known about the physico-chemical processes that lead to the formation of dolomite in nature. Issues requiring further investigation include: (i) the role played by amorphous carbonate precursors, (ii) the mechanisms of transformation of such precursors into proto-dolomite and dolomite, and (iii) the controlling factors of the kinetics of the reactions that eventually result in the crystallisation of highly ordered dolomite. In the article by Rodríguez-Blanco et al. in this issue entitled "A route for the direct crystallization of dolomite", the authors present experimental evidence of a three-stage process which, starting from the precipitation of an amorphous magnesium calcium carbonate, produces proto-dolomite via spherulitic growth, and subsequently ordered dolomite. This article provides new insights into reaction pathways towards the formation of dolomite.

Keywords: dolomite, amorphous precursors, dissolution-crystallisation, reaction pathways, reaction kinetics.

Ever since the geologist and mineralogist Déodat Gratet de Dolomieu described dolomite ($MgCa(CO_3)_2$) in 1791, a vast amount of research has been conducted to unravel the mechanisms of formation of this common carbonate mineral (Deelman 2011 and references therein). While dolomite crystallises easily at temperatures above 100ºC, there is still no conclusive explanation as to how it is formed at temperatures characteristic of the sedimentary cycles in the Phanerozoic. The lack of knowledge about the mechanisms leading to the formation of dolomite under ambient conditions in natural aqueous environments is usually termed as the *dolomite problem*, a scientific challenge that poses numerous physico-chemical and crystal growth questions. One of the key issues is to find out whether dolomite can be crystallised directly from aqueous solutions under certain conditions or whether the formation of crystalline and/or amorphous precursors is a prerequisite for this. If the formation of precursors is a necessary step, it is essential to identify these and to determine the reactions that eventually result in the formation of dolomite. It is also essential to investigate how these reactions are affected by factors such as cyclic changes of physico-chemical parameters (e.g. pH, temperature, supersaturation), the assistance of microorganisms that act as catalysers, and the different hydration of Mg^{2+} and Ca^{2+} ions. The problem of the formation of fully ordered dolomite in nature can only be resolved by adequately identifying and quantifying all of the reactions pathways and their controlling factors.

In their article, Rodríguez-Blanco et al. (2014) describe simple crystallisation experiments that result in the formation of dolomite following a three-stage process. In the first stage, an amorphous magnesium calcium carbonate precipitate (Mg-ACC) is instantaneously formed after mixing $MgCl_2$, $CaCl_2$ and Na_2CO_3 solutions at room temperature. Such a precipitate is characterised and identified by the authors as a precursor from which proto-dolomite and dolomite will be subsequently formed. This relevant finding supports the hypothesis that the precipitation of amorphous carbonates from aqueous solutions is a prerequisite for the formation of dolomite-like structures (e.g. Hood et al., 1974; Kelleher and Redfern, 2002; Schmidt et al., 2005; Xu et al., 2013; Pimentel and Pina, 2014). In the second stage, the Mg-ACC precursor transforms into proto-dolomite following a thermal treatment at temperatures ranging from 25 to 220 ºC. Experimental evidence indicates that this transformation occurs according to a spherulitic growth mechanism, in good agreement with the kinetic model previously derived by Gránásy

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et al. (2005) for the formation of spherulites via a growth front nucleation. In the final third stage, proto-dolomite transforms into highly stoichiometric and crystalline dolomite with clear superstructure peaks detected only at temperatures exceeding 140ºC. The observed increase in particle size and the formation of euhedral crystals suggest that an Ostwald ripening dissolution-crystallisation mechanism is a plausible pathway for transforming proto-dolomite into moderately to highly ordered dolomite (Malone et al.; 1996; Kelleher and Redfern, 2002).

The most important contribution made by Rodríguez-Blanco et al. (2014) is their detailed monitoring of the proposed three-stage process leading to the formation of dolomite from Mg-ACC precursors. By combining time-resolved synchrotron-based energy dispersive X-ray diffraction (ED-XRD) with field emission gun scanning electron microscopy (FEG-SEM), powder X-ray diffraction (PXRD) and Fourier transform infrared spectroscopy (FTIR), the authors were able not only to identify and characterise the phases formed, but also to determine the kinetics of the entire process. ED-XRD data effectively shows the progress of the transformation of initial amorphous precipitates into proto-dolomite/dolomite as a function of time. The analysis of ED-XRD data demonstrates that the transformation kinetics is similar for all experiments conducted in the temperature range from 60 to 220ºC. Only the induction times for the transformation reaction are strongly dependent on temperature. These significant conclusions suggest that the proposed reaction mechanism for dolomite formation may operate at lower temperatures, but with a much slower kinetics (Usdowski, 1994).

The complete elucidation of the *dolomite problem* undoubtedly requires further investigation. The article by Rodríguez-Blanco et al. (2014) shows that careful experimental work is fundamental for determining the potential pathways towards the crystallisation and ordering of dolomites in nature.

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