



Kinetics of dolomitization - new insights from carbonate replacement experiments

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Carbonate rocks are not only major constituents of the crust but also play an important role in various physical, chemical and biological processes shaping modern Earth. Reactions involving carbonates contribute significantly to the Earth's CO₂ budget and formation of low-temperature mineral deposits. Most carbonate reactions involve the replacement of one carbonate phase by another, so-called "mineral replacement". Dolomitisation, i.e. the secondary replacement of calcite by dolomite, is one of the most volumetrically-important carbonate diagenetic processes. It occurs under near surface and shallow burial conditions and can significantly modify rock properties through changes in porosity and permeability associated with the exchange of large Ca-cations by smaller Mg-cations.

Although many experimental studies have investigated carbonate reactions such as dolomitisation, most studies are conceptually limited to simple dissolution-precipitation reactions neglecting transport properties (e.g., by using powdered starting materials). This leads to questionable results when experimental rates are extrapolated to natural systems. More importantly, dolomite *in sensu stricto* could yet only be experimentally formed at temperatures far above natural conditions (> 220 °C) – an issue known as the "dolomite problem".

Analytical difficulties mean that the kinetic feedback of element transport on processes such as dolomitisation with regard to textures and microstructures have been elusive, but recent advances in analytical techniques now allow the reaction progress to be traced and quantified down to the micro-scale. Here we present results from the hydrothermal replacement of single calcite crystals which have been altered with varying fluid compositions, water-to-rock ratios, and temperatures to determine 1) the mechanism of the replacement reaction 2) the rates of mineral replacement and their controlling factors.

Experimental results reveal that the replacement process consists of a series of reactions with nucleation of a meta-stable precursor phase at the tip of the reaction front that subsequently recrystallize to form a stable carbonate phase. The mineralogy of the precursor phase (magnesite or (very) high-Mg calcite) depends on the local fluid composition at the reaction interface. It is shown that the recrystallization process changes the porosity/permeability within the reaction rim affecting the efficiency of fluid pathways connecting the reservoir fluid with the reaction front. This microstructural approach highlights the importance and dynamics of evolving fluid pathways in determining the propagation/stagnation of reaction fronts, in which reaction progress is limited by element transport. The observed series of sub-reactions are also shown to explain the thermodynamic difficulties in producing dolomite via recrystallization of high Mg-calcite in the last step of the reaction chain.

A quantitative knowledge of kinetic parameters controlling the mechanisms and rates of carbonate reactions is crucial for quantitative approaches in geoscientific fields including hydrocarbon exploration, CO₂ sequestration, marine geochemistry, paleo-oceanography, and climate modeling as well as in many non-geoscientific applications such as concrete durability, cultural heritage, nuclear waste management or scales for pipelines.