



## Hydrothermal replacement of calcite by Mg-carbonates

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The transport of heat and mass through the Earth's crust is coupled to mineral reactions and the exchange of isotopes and elements between different phases. Carbonate minerals are a major constituent of the Earth's crust and play an important role in different physical, chemical and even biological processes.

In this experimental study, the element exchange reaction between calcite ( $\text{CaCO}_3$ ) and a Mg-rich fluid phase is investigated under hydrothermal conditions. Single crystals of calcite (2x2x2 mm) react with 1 ml of a 1 M  $\text{MgCl}_2$  solution at 200°C in a Teflon-lined steel autoclave for different times between one day and four weeks. The reaction leads to the formation of a porous reaction front and the pseudomorphic replacement of calcite by dolomite [ $\text{CaMg}(\text{CO}_3)_2$ ] and magnesite ( $\text{MgCO}_3$ ). Scanning electron microscopy revealed that the reaction rim consists of small Mg-carbonate rhombs closely attached to each other, suggesting that the replacement reaction takes place by a dissolution-precipitation mechanism. Typically, the observed reaction front can be divided into two different domains. The outer part of the reaction rim, i.e. from the mineral surface in contact to the fluid inwards, consists of magnesite, whereas the inner part of the rim surrounding the unreacted calcite core consists of Ca-rich dolomite. The formation of a porous microstructure that varies in different parts of the reaction rim is a direct result of the large molar volume change induced by the replacement of calcite by magnesite and dolomite. The developing porosity therefore creates fluid pathways that promote the progress of the reaction front towards the unreacted core of the single crystal.

Compositional profiles measured perpendicular to the mineral surface across the reaction rims using electron microprobe (EMPA) further revealed a compositional gradient within the reaction rim with regard to the structure-forming elements Mg and Ca. Here, the amount of Mg incorporated in both product phases increases with increasing distance from the unreacted calcite core, countered by a decrease of Ca incorporated. Both the coexistence of two different product phases and the distinct compositional gradient within the forming reaction rim are unequivocal signs of a chemical zonation of Ca and Mg in the fluid phase which mediates the element exchange between the reaction interface and the bulk solution. Atomic adsorption spectroscopy revealed that the Ca/Mg ratio in the reacted fluid increases as a function of time, reflecting the progressive exchange of Mg and Ca between the fluid and the solid phase. The time-dependence of the evolving Ca/Mg ratio can be fitted with a square root of time relation that indicates a transport controlled reaction.

We interpret the hydrothermal replacement of calcite to operate via a dissolution/re-precipitation mechanism, whereas the reaction progress is controlled by the transport of the structure forming elements through the developing reaction rim.