American Mineralogist, Volume 98, pages 1516–1525, 2013

Influence of temperature and Cl on the hydrothermal replacement of calcite by apatite and the development of porous microstructures

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ABSTRACT

Calcite ($CaCO_3$) powder was replaced by hydroxylapatite [$Ca_5(PO_4)_3OH$] in hydrothermal experiments at temperatures between 120 and 180 °C, and times between 2 and 12 h, in 1.0 M $(NH_4)_2HPO_4$ solutions. Additional experiments using concentrations of up to 2.0 M NH_4Cl as an additional component were carried out to examine the influence of Cl on the process. X-ray powder diffraction and Rietveld refinements were used to determine the proportion of parent and product phases after each experiment. The resultant data on the fraction transformed as a function of temperature and time were plotted according to the Avrami equation and an activation energy of 118 kJ/mol was determined for the replacement process without Cl in solution, whereas with 0.5–2.0 M Cl in solution, the activation energy varied from 131 to 145 kJ/mol. No simple correlation between the chlorinity of the solution and the value of the activation energy was observed. However, the data indicate that the mechanism controlling the reaction changes between 140 and 160 °C, correlating with systematic differences in abundance, size, and geometry of the porosity in the apatite formed in the replacement process. At lower temperature, the pores are small and oriented parallel to the reaction interface, whereas at higher temperature, the pores are larger and orientated perpendicular to the interface. Changes in the porosity during the replacement process make it problematic to determine a meaningful value for the activation energy for such replacement processes, since the mechanism controlling the reaction depends on factors other than the temperature, such as the availability and form of the pathways allowing the fluid to reach the unreacted core of the single crystals.

Keywords: Apatite, hydrothermal replacement, kinetic data, reaction mechanisms, activation energy