2.5.P01

How does a replacement front proceed? Observations on chlorapatite-hydroxylapatite replacements

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The pseudomorphic replacement of one mineral by another is often characterised by a sharp replacement front. The movement of such a front starts from the original surface into the parent crystal. Generally, further transformation requires fluid pathways to and from the moving interface, which can be either a thin fluid film seperating parent and product and/or interconnected porosity. In fact, the generation of porosity is often associated with dissolution-reprecipitation reactions and can be explained by differences in solubility and molar volume [1].

In solid solution-aqueous solution (SS-AS) systems the pseudomorph often inherits the orientation of the parent crystal forming a topotaxial replacement. Usually, such strong crystallographic relationship has been interpreted as formed by an ion exchange mechanism.

In this study, chlorapatites have been partly transformed to hydroxylapatite using alkaline hydrothermal conditions reported in the literature [2]. The replacement reaction is topotaxial which suggests an ion exchange mechanism. However, the replaced parts also show significant porosity. This porosity cannot be explained by the differences in molar volume alone, therefore, it suggests a dissolutionreprecipitation process.

The interfacial part has been studied using scanning and transmission electron microscopy (SEM, TEM) to describe the structural and chemical relationship on (sub-)micron scale. Furthermore, the observations suggest that the development of porosity is an important factor in controlling the kinetics of the replacement reactions.

The results will be compared to those from a KBr-KCl model system for which both the theoretical formulation of the SS-AS thermodynamics and experimental data on kinetics/reaction path is available. Such comparison allows a prediction on the replacement behaviour (relative kinetics/texture) and reaction paths for various members of the apatite group such as fluorapatite.

References

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2.5.P02

Transient porosity at reaction fronts: Replacement textures from fluxgrown zircon

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Simultaneous dissolution-reprecipitation at migrating reaction fronts provides an effective reaction mechanism to attain phase transformations. The formation of porosity permits the required mass transfer in a melt or an aqueous fluid medium. Examples of preserved porosity highlight the importance of replacement processes in a wide range of geological systems [1], including natural zircon [2]. Although porosity seems indicative for the process, not all the reaction products are porous, and usually a sharp interface is developed between the parent and product domains. Thus might be caused from nanoscale interfacial fluid films or the rearrangement of micronscale pore volumes. To further explore replacement reactions, minor element enriched zircon $(Zr, Y)(Si, P)O_4$ was synthesized using the Li₂O-MoO₃ flux method. Early crystallized zircon with high (Y+P)-contents partially readjusted to changes in its physicochemical environment. The latter comprise changing melt composition due to fractionation and flux volatilization, and decreasing temperature during synthesis.

The reaction zones were detailed using scanning electron microscopy and electron microprobe analyses. The quenched textures provide an example of how space can be made and lost by means of a transient porosity along migrating reaction fronts. Within single zircon crystals, reaction zones emanate from initial tension cracks and transect primary growth features. Pervasive porous zones form sandwiched between dense zircon domains of reactant and product composition. Micronscale pores in the front develop in contact with (Y+P)enriched zircon-I, suggesting the loci of congruent zircon dissolution. Most of the dissolved material reprecipitate in the back of the porous zone, and reconstruct a dense and (Y+P)depleted zircon-II. Interconnected pores and channels provide pathways where part of the dissolved components, including most of the minor element impurities, are lost from the internal crystal volume. Three dimensional migration of the active pore volume allows to maintain topotactic relations and can result in a sharp interface between the parent and product in two dimensional sections.

References

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