

Transient epitaxial overgrowths in the CaCO_3 - REECO_3OH system formed during mineral replacement reactions

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Rare earth elements (REEs) are essential components of many green energy technologies and electronic devices, thus, to cover the future REEs need, it is critical to understand the interaction of REE elements with common carbonate minerals in natural deposits.

This study explores the surface precipitation of oriented REE carbonates during the interaction of individual and multiple REE bearing (La, Ce, Pr, Nd, Dy) aqueous solutions with calcite and aragonite (CaCO_3) at low hydrothermal conditions (25-220 °C) [1,2]. This mineral-fluid interaction was translated into a temperature-dependent solvent-mediated surface precipitation and subsequent pseudomorphic mineral replacement of the CaCO_3 seeds by newly formed REE carbonates. The complex replacement sequence included the crystallisation of metastable kozoite (orthorhombic REECO_3OH), which took place via the formation of individual spindle-shaped crystals following a transient non-random orientation on the surface of the host grains, gradually covering their full surfaces.

Our experiments show that the likelihood of formation of the oriented overgrowth and its stability are controlled by structural constraints which in turn depend on four factors: temperature, ionic radii and ionic potential of the REE in the system, and dissolution rate of the host CaCO_3 minerals. Pure La- to Nd-bearing kozoites always display some orientation on the surface of the host grains. However, pure Dy-kozoite does not tend to grow epitactically on the CaCO_3 polymorphs and instead it forms spherulitic morphologies, resulting in aggregates with orientational defects. Dy-bearing kozoite only forms oriented overgrowths when its structure contains multiple REE.

An explanation of the epitaxial overgrowth's configuration and the atomic arrangement of the structures of the CaCO_3 polymorphs and REE-kozoite will be discussed. These replacement processes are relevant for the understanding of mineralization reactions occurring in REE-bearing carbonatite deposits and demonstrate that these elements can be rapidly immobilized as REE hydroxycarbonates, even at low hydrothermal conditions.

References

- [1] Szucs AM et al. Reaction Pathways toward the Formation of Bastnäsité: Replacement of Calcite by Rare Earth Carbonates. *Crystal Growth & Design*, 2021;21(1):512–527.
- [2] Szucs AM et al. Targeted Crystallization of Rare Earth Carbonate Polymorphs at Hydrothermal Conditions via Mineral Replacement Reactions. *Global Challenges*. 2022;2200085.