Goldschmidt 2022 Abstract
https://doi.org/10.46427/gold2022.11942

Synthesis of REE fluorocarbonates via wall rock reactions

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The formation of REE (fluoro)carbonates in hydrothermal systems is largely governed by the chemistry of REE complexes in the hydrothermal solutions[1]. The reactions of the dissolved species with the wall rocks that are conduits for those fluids also play a role in providing precipitating ligands[2]. This interaction has been quantified both experimentally[3, 4] and from a modelling approach for specific REEs[1].

As natural hydrothermal fluids transport an assemblage of REEs, our experiments focus on the influence of both discrete and mixed REEs during reactions of hydrothermal fluids with wall rocks to produce REE bearing minerals. The influence of multiple, mixed REE is a factor that has not been extensively studied[4].

We synthesised REE (fluoro)carbonates by reacting single and mixed REE chloride solutions with a wall-rock at temperatures up to 200^{o}C. The "wall-rock" is synthetic with compositions ranging from a mixed dolomite, fluorite and apatite pellet to pellets comprised purely of the end-member compositions. La, Nd, Dy, Er and Yb were used as a representative suite of light to heavy REEs. The resulting materials were analysed by XRD, ICP-OES, SEM/EDS and SIMS to identify mineral phases and REE partitioning.

Results from mixed REE experiments and discrete La and Nd starting solutions show the formation of the economically important mineral bastnäsite (REE)CO_3F. We find this for mixtures with light and heavy REEs at equal as well as at natural hydrothermal concentrations. This is particularly noteworthy as natural bastnäsites tend to be enriched in LREE compared to HREE. Mixed REE starting solutions also resulted in the mineral monazite (REE)PO_4. However, it was synthesised with a pure apatite wall-rock; a dolomite and fluorite wall-rock containing 30% apatite did not yield monazite. In investigating REE mineralization with wall rock reactions, we find that it is crucial to consider mixtures of REEs in addition to discrete REEs to better simulate natural conditions.

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