The potential of the hen eggshell as rare earth element sorbent and segregator

Rateau R*[1], Drost K[1], Maddin M[1], Szucs A[1], Terribili L[1], Rodriguez-Blanco JD[1]
*lead presenter: rrateau@tcd.ie
[1] iCRAG. Department of Geology, School of Natural Sciences, Trinity College Dublin, the University of Dublin, Ireland.

The green energy transition, critical to keep global warming as low as possible, depends heavily on sourcing rare earth elements (REE, defined here as the lanthanides, Ln) [1]. One avenue of research, still in its infancy, is the production of REE from secondary waste sources, such as e-waste recycling, bauxite red muds, or acid mine drainage (AMD), which can contain up to a few 10s of ppm of REE in solution [2]. REEs have affinity for carbonates (*e.g.*, bastnäsite, a rare earth carbonate, is one of the main REE ore worldwide), due to similar ion radii of Ca^{2+} and most Ln^{3+}. Previous studies have demonstrated the typical recrystallisation pathways from Ca-Mg carbonate to rare earth carbonates at different temperatures [3]. Carbonate might be the ideal material to be used to neutralize AMD acidity and concentrate the REE in solids for easier extraction. When compared to the behavior of non-biogenic carbonates [3], biocarbonates often present a more complex structure, porosity, and chemistry, which might affect the sorption of REE and recrystallisation pathways in unique ways and help identifying characteristics that favor or hinder the sorption and/or partitioning of REE (*e.g.*, light *vs* heavy).

In this study, we investigated hen eggshells as a potential sorbent for REE at various experimental conditions (10-7,000 ppm La-Nd-Dy, 30-205 °C, up to 3 months). We mapped out the diffusion patterns of REE in the calcite shell using laser-ablation inductively-coupled mass spectrometry. REE preferentially diffuse along the calcite crystal boundaries and fractures as well as along the pore network. The pattern is visible both at low and high REE concentrations. Recrystallisation pathways were defined using powder XRD. Recrystallisation occurs only at high REE starting concentration, follow the general, temperature-dependent, calcite → lanthanite → kozoite → hydroxylbastnäsite pathway, and given sufficient time replaces 100% of the calcite. Crystal morphologies were identified using SEM secondary electron imaging. Two recrystallisation fronts of large prismatic kozoite occur at high temperatures, while spherulitic growth occur at lower temperature. REE partitioning was characterized using energy dispersive X-ray spectroscopy. Nd is preferentially taken from the liquid and homogeneously distributed in the rare earth carbonates, while La and Dy are partially spatially partitioned within the crystals. The results points towards hen eggshells as effective REE sorbents and rough segregators of light *vs* heavy REE.

References

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