

Mechanisms of metal isotope fractionation between carbonate minerals and aqueous fluids

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The chemical and isotopic composition of terrestrial and marine carbonate archives is routinely used to inform about the evolution of Earth's climatic conditions over the geological past. The isotopic toolbox available for this research has been expanded over the last two decades, due to the advances in mass spectroscopy that allowed precise measurements of non-traditional isotopes in natural carbonates. However, the reconstruction of environmental conditions during carbonate mineral formation demands detailed understanding of the physicochemical parameters affecting the incorporation and isotope fractionation of metals in mineral-fluid systems. Experimental work has shown that the isotopic composition of major and trace elements in carbonates is affected by a number of parameters including mineral growth rate, aqueous speciation and formation of metal-ligand complexes, pH and presence of foreign ions in the solid. Complementary to experiments, atomistic modelling allows to isolate the role of certain aqueous complexes or certain mechanisms of metal incorporation into minerals on isotopic fractionation, and also to predict equilibrium fractionation, which serves as a reference for the interpretation of experimental data. Here we present a critical overview of the main parameters affecting the isotopic composition of metal isotopes such as B, Ba, Ca, Li, Mg and Zn in synthetic carbonates as it has been revealed in recent experimental studies.