

Distinguishing between kinetic and equilibrium isotopic fractionations using 3 isotopes

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The mass-dependent fractionation laws that describe the partitioning of three or more isotopes are different for kinetic and equilibrium reactions [1]. The precision with which isotope ratios can be now measured is sufficient to take advantage of these differences. Taking into account masses of isotopes and achieved analytical precision, Mg is among the most sensitive elements [2]. The use of the relationship between $^{25}\text{Mg}/^{24}\text{Mg}$ and $^{26}\text{Mg}/^{24}\text{Mg}$ in terrestrial material is a clear diagnostic of kinetic fractionation and equilibrium fractionation provided the fractionation is greater than 1‰/amu and/or the number of samples is large enough for a statistical approach. Evidences for equilibrium fractionation have been found for low-Mg calcite speleothems [3], olivine-pyroxene pairs from mantle xenoliths, and marine authigenic clays. On the other hand, biologically mediated precipitates or Mg-bearing organic molecules have a clear kinetic signature.

A similar approach has been applied to Ge isotopic fractionation during adsorption and co-precipitation with Fe-oxide using the relationship between $^{74}\text{Ge}/^{70}\text{Ge}$ and $^{72}\text{Ge}/^{70}\text{Ge}$. This reveals a kinetic isotopic fractionation while the chemical and $^{74}\text{Ge}/^{70}\text{Ge}$ data could have been interpreted as closed system equilibrium and implies at least 2 different processes (precipitation and adsorption) occurring at the same time.

References

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Magnesium isotopes in bacterial dolomites: A novel approach to the dolomite problem.

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Bacterially associated dolomite has been reported from two modern hypersaline lagoons in Brazil and suspected in sediments from the Peru margin [1-2]. Cultures of bacteria isolated from the lagoon produce dolomite in the laboratory [3]. We have utilised magnesium isotopes to study these natural and laboratory dolomites.

Fractionation of magnesium isotopes is observed during dolomite formation in both the natural environment and in the laboratory. The dolomite is isotopically lighter than the medium it forms from by between $\delta^{26}\text{Mg} = -0.49\%$ and -3.07% relative to the DSM3 standard. The careful study of the behaviour of the three isotopes of magnesium reveals a kinetic isotopic fractionation process. In mono-specific laboratory cultures the isotope fractionation is seen to vary with bacterial species by up to 1.00‰. Different species of bacteria have distinct isotopic signatures. In the lagoons short cores reveal a variation in isotopic signature down-core of 1.70‰, with the most negative values coinciding with the zone of maximum dolomite formation. The value for the Peru margin dolomite of -3.99% is similar to that seen in the other environments and supports previous suggestions of a bacterially mediated origin. Taken together our results argue for a strong biological role in magnesium fixation into dolomite and suggest bacterial processes are important in resolving 'the dolomite problem'.

References

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