Geophysical Research Abstracts, Vol. 9, 01526, 2007
SRef-ID: 1607-7962/gra/EGU2007-A-01526

Kinetic isotope fractionation – Magic or logic?

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Kinetic stable isotope fractionation is claimed quite commonly where ‘deviating’ isotopic fractionation behavior in a system is found. In many cases, the explanation for the non-expected isotopic fractionation simply is ‘kinetic’. Thus, explaining the proper reason of the found deviation is evaded, and ‘kinetic’ is used as sort of ‘magic-term’.

In order to give a better understanding of what is kinetic isotope fractionation, an explanation of kinetic and equilibrium isotopic fractionations will be presented.

Isotopic behavior will be considered as a separate factor in a complex system comprising a number of such separate factors (i.e. isotopic and chemical ‘entities’ that are involved in the same system or process). The rate of the separate factors in relation to each other is of high importance for the resulting type of isotopic fractionation.

Equilibrium isotopic fractionation only occurs there where an equilibrium situation in the isotopic system exist, while kinetic isotope fractionation occurs in a one directional process, that may, or may not be irreversible. Common examples for kinetic isotopic fractionations are diffusional processes (one directional processes) and biological-microbial controlled processes (metabolic processes).

A wrong concept is that kinetic isotope fractionation is not repeatable. Both, kinetic and equilibrium isotopic fractionations are repeatable if the conditions of the process leading to the fractionation are repeated exactly. Any process that does not reach equilibrium, that is a steady-state condition, in principle will show a kinetic isotopic fractionation. The size of the kinetic isotopic fractionation is rate-dependent.

Some examples of different type of isotopic fractionations will be given.