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Back to the basics of stable isotope fractionation. A 'complete system' approach presented.

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A presentation on kinetic and equilibrium fractionation is given, including the consequences of the different type of fractionation in interpreting isotopic values. It will be shown that change in isotopic distribution, that is a uni-directional change, is kinetic. If a system reaches a steady state situation, we reach an equilibrium situation. Both kinetic and equilibrium isotope fractionations are perfectly repeatable, as log as the same conditions are applied. Major difference between kinetic and equilibrium fractionation is that kinetic fractionation includes rate-dependence, while equilibrium fractionation does not.

Based on these views on isotopic fractionation, we have to realise that very commonly only selected parts larger, complete systems are considered. If applying just a few variables of a complete systems means the variables not included in the study must be fixed in value, or do have influence, which than is neglected. Moreover, experimentally determined isotopic fractionations as know from literature generally represent relatively simple systems with controlled values of variables, which rarely is true in more complex, natural systems. Experimental isotope fractionations are correct for the conditions as given. Empirically obtained isotopic fractionations are more complex and depend on how well the variables of the system are defined. Now, extending this to the use of isotopic proxies, it has to be realised that in almost all cases it is assumed other variables are fixed, or they just are neglected. For instance, if we consider proxies on a specific stable isotope dataset, where first temperature and secondly salinity of water is determined from the same dataset, an invalid procedure is applied. Probably both variables determined the isotopic distribution, but it is not certain which part of the isotopic distribution was induced by temperature and which by salinity. It will be shown that such interpretations are invalid and thus incorrect.