

Theory for isotopic fractionation during mineral precipitation from aqueous solutions

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Minerals precipitated from aqueous solution at low temperature do not generally form at isotopic equilibrium. Yet there is no general theory for how surface reaction, aqueous transport and equilibrium effects contribute to net isotopic fractionation. Better understanding of the controls on isotopic fractionation is critical for mid-mass stable isotopic systems such as Ca, Mg, Fe, Mo, and Cr, but also important for traditional elements. A theory is presented, which starts with the recognition that precipitation rates are net rates (R_{net}), the difference between a forward (precipitation; R_p) and a backward rate (dissolution; R_d). Both forward and backward rates are normally higher for light isotopic species. Isotopic equilibrium can be maintained only if $R_{\text{net}} \ll R_d$, and if there is no transport limitation in the fluid phase, a restrictive condition. Precipitation of minerals from solution can occur in four regimes: equilibrium, equilibrium-transport limited, surface kinetic, and surface kinetic-transport limited. Transitional conditions between these limiting cases are common. The regime boundaries are determined by several factors; among them the background exchange rate (R_d), the aqueous diffusivities of ions, and the hydrodynamics of the solution phase. The fractionation factor is likely to have temperature dependence, solution chemistry dependence, and mineral surface chemistry dependence in addition to rate dependence. Examples, using in particular Ca isotopes in calcite, implications, and problems with this model will be discussed.

ITCZ-monsoonal climate variability during the last 80,000 years (Cariaco Basin, Northern Arabian Sea)

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The anoxic Cariaco Basin on the northern shelf of Venezuela is a sensitive recorder of large and abrupt shifts in the hydrologic cycle of the tropical Atlantic. Sediments from the oxygen minimum zone off Pakistan in the Northern Arabian Sea represent archives of the low-latitude monsoonal climate variability.

Major element chemistry and color data have been measured on sediments from these two settings which cover the last 80,000 years with a centennial to annual resolution. Individual Dansgaard-Oeschger events can be well correlated between the two archives. An age model was set up by correlation to the $\delta^{18}\text{O}$ record of NGRIP.

These data suggest a direct connection between the position of the ITCZ over northern South America, the strength of trade winds, and the temperature gradient to the high northern latitudes, ENSO, and monsoonal climate in Asia. The mechanisms behind these decadal-scale ITCZ-monsoon swings can be further explored at major climate events such as the Younger Dryas and the Dansgaard-Oeschger events. Recently published marine, lacustrine and ice core records are interpreted in concert with our new data from the Cariaco Basin and the Arabian Sea. They indicate major reorganizations of the atmosphere/ocean system in the entire Northern Hemisphere at these warming and cooling events. The warmings seem to occur in abrupt steps of a few years, the coolings more transitional within centuries, however, decadal scale steps are superimposed.