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Non-equilibrium fractionations during travertine deposition, or a new equilibrium line?

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Travertine depositing systems in the temperature range 15-70 °C were studied from stable isotope geochemical, mineralogical and sedimentological point of view. The investigated sites are located in Hungary (Egerszalók, Bükk Mts) and in Turkey (Pa-mukkale, Denizli-Basin). These two famous hot-water travertine depositing systems are similar to each other in origin and offer a good opportunity to study the stable carbon and oxygen isotope fractionations between water and calcite deposited at surficial conditions.

As a consequence of dynamically unstable environment, kinetic effects occur, thus, isotopic equilibrium is rarely obtained during the deposition of travertines. After the discharge of water to the surface, the isotopic equilibrium in the $H_2O-CO_2-HCO_3^-$ - CO_3^{2-} system is suddenly broken. In general, the deviation from the isotopic equilibrium decreases with increasing distance from the spring orifice, as the system tends to re-equilibrate under surface conditions, and the outgassing of CO_2 diminishes and precipitation rate is reduced (Gonfiantini 1968). Further from the spring orifice the water cools down and the precipitating travertine shows increasing oxygen isotope compositions, in agreement with the temperature-dependent partitioning of oxygen isotopes between travertine and water (Epstein 1953, O'Neil 1968, Pentecost 2005).

Based on our observations, morphology-related outgassing and evaporation controlled the stable isotope compositions of travertines deposited. Directly comparing the C

and O isotope compositions of the precipitating carbonates and corresponding thermal waters, a kinetic fractionation appears, which is most probably related to the rapid calcite precipitation. A further process resulting in non-equilibrium compositions is carbonate transportation along the flow path. Our data closely follow the temperature- $\Delta^{18}O_{calcite-water}$ relationship observed for other travertine localities, which is slightly shifted from the equilibrium curve and determine an empirical "travertine curve". The empirical curve match the temperature- $\Delta^{18}O_{calcite-water}$ data of Coplen (2007) determined for 33.7 °C that raises the possibility of a revised equilibrium fractionation relationship rather than true non-equilibrium curve. The results of this study can be used to reconstruct and understand fossil travertine microenvironments and accompanied stable isotope fractionation processes.

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