

Kinetic enrichments in $\Delta 47$ in high-pH surface carbonates

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The carbonate clumped isotope paleo-thermometer has been calibrated for a variety of natural and synthetic carbonates, yielding a $\Delta 47$ -temperature relationship similar to that predicted from theory. However, disequilibrium clumped isotopic signatures may arise in a number of circumstances and have been reported or predicted in some biogenic carbonates, in speleothems, and under extreme pH conditions. Here we examine kinetic enrichments in $\Delta 47$ in carbonate precipitated in hyperalkaline springs in Oman. We identify covariant enrichments in $\Delta 47$ and depletions in $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ that could facilitate the identification of carbonates precipitated at the interface between high pH fluids and the atmosphere in ancient terrestrial and extraterrestrial environments.

Peridotite-hosted travertines in Oman, formed where hyperalkaline (pH>11) Ca-OH waters react with atmospheric CO_2 , range in isotopic composition from values consistent with observed spring-water $\delta^{18}\text{O}$ and temperatures (30‰, SMOW) and atmospheric $\delta^{13}\text{C}$ (-5‰, VPDB) up to highly depleted values (14‰, SMOW $\delta^{18}\text{O}$ and -27‰, VPDB $\delta^{13}\text{C}$). Recent carbonate precipitates at these hyperalkaline springs span the entire range of this $\delta^{18}\text{O}$ - $\delta^{13}\text{C}$ trend and exhibit large enrichments in $\Delta 47$, up to 0.2‰, that covary with the depletions in $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$. These kinetic effects are thought to arise during hydroxylation of CO_2 in high-pH fluids.

These data demonstrate that the $\delta^{18}\text{O}$ - $\delta^{13}\text{C}$ trends observed in Oman travertines are primary features of the precipitates and not acquired by incorporation of carbonate sediment, filling of pore space, or later recrystallization. $\Delta 47$ mixing is non-linear, so if intermediate values along the $\delta^{18}\text{O}$ - $\delta^{13}\text{C}$ trend were produced via mixing, then $\Delta 47$ values would peak at intermediate $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ rather than forming the linear trend observed. This supports the robustness of mineral carbonation rates derived from Oman travertines.

This relationship could also help identify extinct hyperalkaline systems. E.g., hyperalkaline fluids associated with serpentinization, which could produce prebiotic conditions, may form some carbonates observed on Mars. The $\delta^{18}\text{O}$ - $\delta^{13}\text{C}$ slope in carbonates from Martian meteorites is similar to that observed in carbonates from hyperalkaline spring worldwide. Identification of a similar $\Delta 47$ - $\delta^{18}\text{O}$ trend over a broad isotopic range in Martian carbonates could suggest that hyperalkaline springs were present on the surface of Mars.