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Controls on the stable isotope compositions of travertine from hyperalkaline springs in Oman: Insights from clumped isotope measurements

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Abstract

Carbonate formation at hyperalkaline springs is typical of serpentinization in peridotite massifs worldwide. These travertines have long been known to exhibit large variations in their carbon and oxygen isotope compositions, extending from apparent equilibrium values to highly depleted values. However, the exact causes of these variations are not well constrained. We analyzed a suite of well-characterized fresh carbonate precipitates and travertines associated with hyperalkaline springs in the peridotite section of the Samail ophiolite, Sultanate of Oman, and found their clumped isotope compositions vary systematically with formation environments. Based on these findings, we identified four main processes controlling the stable isotope compositions of these carbonates. These include hydroxylation of CO_2, partial isotope equilibration of dissolved inorganic carbon, mixing between isotopically distinct carbonate end-members, and post-depositional recrystallization. Most notably, in fresh crystalline films on the surface of hyperalkaline springs and in some fresh carbonate precipitates from the bottom of hyperalkaline pools, we observed large enrichments in Δ_{47} (up to ~0.2‰ above expected equilibrium values) which accompany depletions in $\delta^{18}O$ and $\delta^{13}C$, yielding about 0.01‰ increase in Δ_{47} and 1.1‰ decrease in $\delta^{13}C$ for every 1‰ decrease in $\delta^{18}O$, relative to expected equilibrium values. This disequilibrium trend, also reflected in preserved travertines ranging in age from modern to ~40,000 years old, is interpreted to arise mainly from the isotope effects associated with the hydroxylation of CO_2 in high-pH fluids and agrees with our first-order theoretical estimation. In addition, in some fresh carbonate precipitates from the bottom of hyperalkaline pools and in subsamples of one preserved travertine terrace, we observed additional enrichments in Δ_{47} at intermediate $\delta^{13}C$ and $\delta^{18}O$, consistent with mixing between isotopically distinct carbonate end-members. Our results suggest that carbonate clumped isotope analysis can be a valuable tool for identifying and distinguishing processes not readily apparent from the carbonate bulk stable isotope compositions alone, e.g., kinetic effects or mixing of different carbonate end-members, which can significantly alter both the apparent formation temperatures and apparent radiocarbon ages. The isotope trends observed in these travertine samples could be applied more broadly to identify extinct

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hyperalkaline springs in terrestrial and extraterrestrial environments, to better constrain the formation conditions and post-depositional alteration of hyperalkaline spring carbonates, and to extract potential paleoclimate information.

Keywords: Clumped isotopes; Kinetic isotope fractionation; Alkaline springs; Travertine; Carbonate

1. INTRODUCTION

1.1. Carbonate formation in peridotite-hosted hyperalkaline springs

Springs emanating from serpentinized peridotite in the Samail ophiolite, Sultanate of Oman, are characterized by high pH (~11–12), high Ca^{2+} concentrations, and almost no dissolved inorganic carbon (DIC). These hyperalkaline springs react with atmospheric CO_2, resulting in rapid precipitation of calcium carbonate and formation of extensive travertine terraces (Neal and Stanger, 1985; Clark and Fontes, 1990; Kelemen and Matter, 2008; Matter and Kelemen, 2009; Kelemen et al., 2011; Paukert et al., 2012; Chavagnac et al., 2013a,b; Mervine et al., 2014, 2015).

The development of these Ca^{2+}-OH^- rich waters is typical of serpentinization in peridotite massifs worldwide (e.g., Barnes et al., 1967, 1978; Barnes and O'Neil, 1969; Neal and Stanger, 1985; Bruni et al., 2002; Neal and Shand, 2002; Marques et al., 2008; Szponar et al., 2013; Cardace et al., 2015). Such ultramafic systems have been the subject of diverse studies, with much interest in fate of carbon in these environments. The rapid uptake of CO_2 during natural carbonation of peridotite, estimated to currently be $\sim 10^3$ tons of CO_2 km^{-3} yr^{-1} in Oman, has been viewed as a promising analog for mineral carbon sequestration (e.g., Cipolli et al., 2004; Kelemen and Matter, 2008; Wilson et al., 2009). The development of hyperalkaline fluids during serpentinization has also been suggested as possible driver of carbonate precipitation and methane generation on Mars (e.g., Niles et al., 2005; Oze and Sharma, 2005; Ehlmann et al., 2010; Etiope et al., 2013; Niles et al., 2013), attracting attention to terrestrial hyperalkaline springs as potential Martian analogs (e.g., Szponar et al., 2013). In addition, there have been attempts to reconstruct paleoclimate in Oman (e.g. periods of aridity or humidity) based on variations in travertine morphology and the bulk stable isotope compositions of carbonates (Clark and Fontes, 1990).

Unlike typical travertines precipitated by degassing of CO_2 from calcium- and bicarbonate-rich waters of hydrothermal origin, which may record apparent equilibrium oxygen and clumped isotope compositions near spring vents (e.g., Kele et al., 2015), the isotope compositions of travertines formed at hyperalkaline springs usually deviate significantly from expected equilibrium values. Previous studies of peridotite-hosted travertines in Oman revealed positive correlations between their $\delta^{13}C$ and $\delta^{18}O$ values, with $\delta^{13}C$ vs. $\delta^{18}O$ slope of ~1.3 (Clark and Fontes, 1990; Clark et al., 1992; Kelemen et al., 2011; Mervine et al., 2014). The youngest travertines are often characterized by large depletions in ^{13}C and ^{18}O (Clark et al., 1992; Kelemen et al., 2011; Mervine et al., 2014), while preserved travertines generally exhibit relatively higher $\delta^{13}C$ and $\delta^{18}O$ values that may extend to values consistent with expected equilibrium with observed spring-water $\delta^{18}O$ and temperatures and atmospheric $\delta^{13}C$ (Neal and Stanger, 1985; Clark et al., 1992; Matter, 2005). Similar correlated depletions in $\delta^{13}C$ and $\delta^{18}O$ have been observed worldwide in other carbonates precipitated during interaction between alkaline waters and atmospheric CO_2. For example, the $\delta^{13}C$ and $\delta^{18}O$ values of fresh carbonate precipitates and travertines from hyperalkaline springs in northern California overlap significantly with values observed in Oman (O'Neil and Barnes, 1971; Kelemen et al., 2011). These depletions in $\delta^{13}C$ and $\delta^{18}O$ have typically been interpreted as a kinetic isotope effect resulting from CO_2 uptake from the atmosphere (O'Neil and Barnes, 1971; Clark et al., 1992; Wilson et al., 2010). In some cases depleted isotopic signatures in carbonates precipitated in alkaline environments may also be derived from nearby carbonate sediments, as was initially suggested for surface calcium carbonates associated with weathering of chrysotile tailings in northern British Columbia (Wilson et al., 2009).

1.2. Carbonate clumped isotope geochemistry

The carbonate clumped isotope thermometer is a relatively new paleothermometer based on the tendency of ^{13}C and ^{18}O isotopes to preferentially bond to one another (or "clump") within the CO_3^{2-} groups under thermodynamic equilibrium. This property is commonly measured as 'Δ_{47},' the excess of mass-47 isotopologue (primarily $^{13}C^{18}O^{16}O$) in the CO_2 evolved from phosphoric acid digestion of solid carbonate relative to the abundances expected for a stochastic distribution of all isotopes (Ghosh et al., 2006; Eiler, 2007, 2011; Huntington et al., 2009):

$$\Delta_{47} = \left[\left(\frac{R_{47}}{R_{47}^*} - 1\right) - \left(\frac{R_{46}}{R_{46}^*} - 1\right) - \left(\frac{R_{45}}{R_{45}^*} - 1\right)\right] \times 1000 \tag{1a}$$

where R_i is the measured ratio of the isotopologue of mass i and R_i^* is the ratio for a stochastic distribution. i.e.,

$$\Delta_{47} = \left[\frac{R_{47}}{2R_{13} \times R_{18} + 2R_{17} \times R_{18} + R_{13} \times (R_{17})^2} - \frac{R_{46}}{2R_{18} + 2R_{13} \times R_{17} + (R_{17})^2} - \frac{R_{45}}{R_{13} + 2R_{17}} + 1\right] \times 1000 \tag{1b}$$

Unlike conventional carbonate-water oxygen isotope thermometry, the extent of this clumping effect, under thermodynamic equilibrium, depends only on the equilibration temperature and not on the isotopic composition of the