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Variations in soil carbonate formation and seasonal bias over >4 km of relief in the western Andes (30°S) revealed by clumped isotope thermometry

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ABSTRACT

Carbonate clumped isotope thermometry provides a new method for investigating long-standing questions regarding seasonal biases in soil carbonate formation and the relationship between soil carbonate formation temperatures recorded by clumped isotopes ($T(\Delta_{47})$) and surface temperatures. We address these questions by comparing C, O, and clumped isotope data from Holocene soil carbonates to meteorological and in situ soil monitoring data along a 170 km transect with >4 km of relief in Chile (30°S). This arid transect experiences a winter wet season, and a >20 °C range in mean annual air temperature. We test the hypothesis that, regardless of soil moisture conditions, soil carbonates from arid regions record warm season biases and form in isotopic equilibrium with soil water and soil CO_2. Below 3200 m, precipitation falls as rain and soil carbonate $T(\Delta_{47})$ values at depths >40 cm resemble summer soil temperatures. Above 3200 m, precipitation falls as snow and $T(\Delta_{47})$ values resemble mean annual soil temperatures. Soil carbonates from the highest site yield anomalous $\delta^{18}O$, $\delta^{13}C$, and $T(\Delta_{47})$ values indicative of kinetic isotope effects consistent with cryogenic carbonate formation. Our findings (1) demonstrate that soil carbonate $T(\Delta_{47})$ values from shallow (<40 cm) depths can be affected by short-term temperature changes following precipitation events; (2) suggest that only the largest precipitation events affect soil moisture at depths >40 cm; (3) highlight the role of the soil moisture regime in modulating the timing of soil carbonate formation, which affects the resulting carbonate $T(\Delta_{47})$ values; and (4) show that soil carbonates from high elevation or high latitude sites may form under non-equilibrium conditions. These findings underscore the importance of understanding past soil moisture conditions when attempting to reconstruct paleotemperatures using carbonate clumped isotope thermometry.

1. Introduction

The application of the carbonate clumped-isotope paleothermometer to pedogenic (formed in soil) carbonates has shed new light on a variety of paleoclimate and tectonic questions (Eagle et al., 2013; Garzione et al., 2008, 2014; Ghosh et al., 2006a; Leier et al., 2013; Passey et al., 2010; Quade et al., 2007a, 2007b, 2011; Snell et al., 2013, 2014; Suarez et al., 2011). Studies of modern soil carbonates provide context for paleoproxy interpretations by investigating the relationship between soil carbonate clumped isotope temperatures (hereafter $T(\Delta_{47})$) and the environmental conditions under which the carbonates formed (e.g., Hough et al., 2014; Passey et al., 2010; Peters et al., 2013; Quade et al., 2013). However, full utilization of soil carbonates as paleotemperature proxies has been hampered by several unresolved questions: (1) When does soil carbonate form? (2) How do soil carbonate formation temperatures relate to surface temperatures? (3) Are $T(\Delta_{47})$ values of soil carbonates from different environments (e.g., tropical versus high latitude) directly comparable? With regard to the first two questions, several studies (e.g., Breecker et al., 2009; Passey et al., 2010; Quade et al., 2013) suggest that carbonate formation is biased towards summer soil drying events, and that

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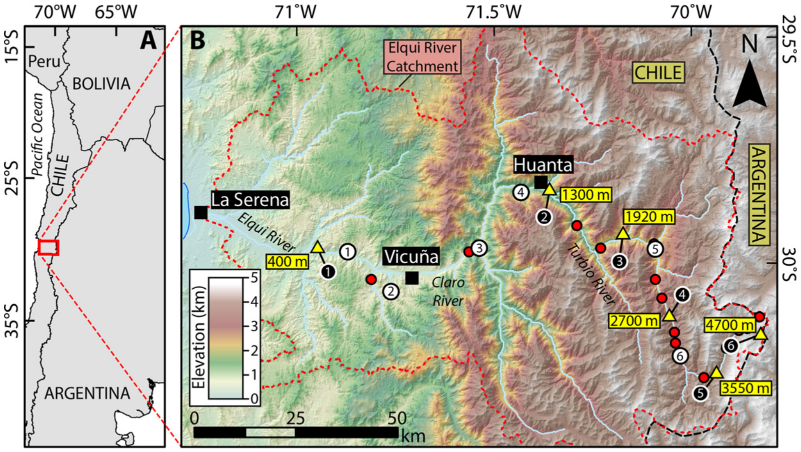

Fig. 1. (A) Shaded relief map showing the location of the 1 m soil pits (yellow triangles), single 50 cm samples (red circles), weather stations maintained by the Chilean government (numbered white circles), and the weather stations installed for this study (numbered black circles). The upper regions of the Elqui River catchment (red dashed line) lie along the Chile–Argentina border (black dashed line). (B) Map shows the location of the study area.

$T(\Delta_{47})$ values show a warm-season bias regardless of soil moisture conditions (Quade et al., 2013); however, some soil carbonates form under differing seasonal biases due to change in soil moisture (Peters et al., 2013), or under non-equilibrium conditions (e.g., Courty et al., 1994; Tabor et al., 2013), suggesting that comparing soil carbonates from different environments or determining the seasonal bias of ancient soil carbonates may not be a straightforward exercise.

We address these questions by collecting Holocene soil carbonates over >4 km of topographic relief on the western flank of the Andes, in north–central Chile (30°S). The range in environmental conditions along this transect allows us to investigate how soil carbonate $\delta^{18}O$, $\delta^{13}C$, and $T(\Delta_{47})$ values record environmental conditions under changing soil moisture and temperature regimes. At sites below the winter snow line carbonate $\delta^{18}O$, $\delta^{13}C$, and $T(\Delta_{47})$ values are consistent with a warm season bias in carbonate formation. Carbonates from above the snow line yield $T(\Delta_{47})$ values similar to mean annual soil temperature (MAST). Our findings are consistent with the hypothesis that in hot arid environments, a warm-season bias in $T(\Delta_{47})$ values predominates, but that significant changes in soil moisture conditions (e.g., effect of spring snowmelt on the timing of soil drying) can impact soil carbonate $T(\Delta_{47})$ values. Additionally, we show that in high elevation or extremely arid climates, non-equilibrium processes can lead to anomalous $\delta^{18}O$, $\delta^{13}C$, and $T(\Delta_{47})$ values that do not reflect local climate.

2. Background

2.1. Soil carbonate formation and isotopic composition

Pedogenic carbonates ($CaCO_3$) are common in arid to subhumid environments (Landi et al., 2003). Carbonate precipitation follows the reaction:

$$Ca^{2+} + 2HCO_3^- \Leftrightarrow CaCO_3 + CO_2 + H_2O \qquad (1)$$

Calcium ions are introduced into the soil water solution via deposition of dust, dissolution of minerals, and rainwater infiltration (Gile et al., 1966; Machette, 1985; Monger and Wilding, 2006). Carbon is supplied by respired (vegetation and microbes) and atmospheric CO_2, and oxygen is derived from soil waters (e.g., Cerling and Quade, 1993). Precipitation and dissolution of soil carbonates are influenced by soil conditions, including temperature, moisture and pCO_2 (e.g., Breecker et al., 2009; Drever, 1988; Stern et al., 1999). Carbonate formation occurs when the soil solution becomes supersaturated in calcite due to dewatering, CO_2 outgassing, or an increase in Ca^{2+} or HCO_3^- in the solution (Breecker et al., 2009; Retallack, 2005).

Due to the slow rate of change in soil pCO_2 and temperature, carbonates are assumed to form in isotopic equilibrium with soil CO_2 and water (Cerling and Quade, 1993). The isotopic composition of soil carbonate therefore acts as a time-integrated record of local environmental changes over hundreds to thousands of years. Soil carbonate $\delta^{18}O$ and $\delta^{13}C$ values reflect soil water isotopic compositions and soil productivity or vegetation type, respectively (Cerling and Quade, 1993; Meyer et al., 2014), whereas the clumped isotope (Δ_{47}) composition records soil temperature (Eiler, 2011; Peters et al., 2013; Quade et al., 2007a, 2007b, 2013).

Clumped-isotope thermometry provides a thermodynamics-based measurement of carbonate formation temperature (Eiler, 2007, 2011; Eiler et al., 2014; Ghosh et al., 2006b). Correlations between soil temperature data and soil carbonate $T(\Delta_{47})$ values suggest that the dewatering/outgassing events driving soil carbonate formation typically occur during the summer months, leading to a warm-season bias in $T(\Delta_{47})$ values (Hough et al., 2014; Passey et al., 2010; Peters et al., 2013; Quade et al., 2013; Suarez et al., 2011). However, it has been hypothesized that $T(\Delta_{47})$ values that do not reflect summer soil temperatures are the result of unique soil moisture balance conditions that change the seasonality of soil drying events (Peters et al., 2013).

2.2. The Elqui and Turbio valleys, Chile

The study area is situated in the Elqui River catchment of north–central Chile (Fig. 1). The Elqui River and its tributary the Turbio River have headwaters in the western flank of the Andes and outlet into the Pacific Ocean. The study area is divided into three geomorphic regions: 1) between 0 and ~750 m, the valley is a wide (500 m to 4 km) cultivated fluvial plain with alluvial fans prevalent near the valley walls; 2) between ~750 and 3200 the valley narrows (100 m to ~1 km) and is characterized by large debris fans and fluvial terraces; 3) above 3200 m, the valley widens and glacial landscapes dominate. We examine sites from 400 to 4700 m that exhibit a range of soil moisture conditions and a >20 °C range in MAST.

Precipitation is controlled by the intensity and position of the South Pacific Subtropical High (Garreaud et al., 2009; Grosjean et al., 1998) and is characterized by a winter wet season and low mean annual precipitation (MAP) at all elevations (Fig. 2, Supplemental Fig. S1). The Dirección General de Aguas (DGA; http://www.dga.cl/) maintains meteorological stations (Fig. 1 and