Chemical Geology 435 (2016) 79–91

Contents lists available at ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

Combining soil water balance and clumped isotopes to understand the nature and timing of pedogenic carbonate formation

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ARTICLE INFO

Article history:
Received 18 February 2016
Received in revised form 15 April 2016
Accepted 23 April 2016
Available online 26 April 2016

Keywords:
Paleosol
Seasonality
Paleoclimate
Evapotranspiration

ABSTRACT

Pedogenic carbonate is an important archive for paleoclimate, paleoecology, and paleoelevation studies. However, it can form under seasonal environmental conditions that differ significantly from the mean growing season environment or mean annual conditions, potentially complicating its use for proxy reconstructions. The observed seasonal temperature is typically, but not always, biased high relative to mean annual air temperature (MAT). To evaluate the annual timing of pedogenic carbonate formation, ten different soils were sampled across the western United States. Sites were selected to span a variety of precipitation regimes and soil orders. Precipitation regimes ranged from arid sites (mean annual precipitation (MAP) <20 cm) that receive the majority of precipitation during the winter to wetter sites (MAP >50 cm) dominated by summer precipitation. Pedogenic carbonate formation temperatures derived from clumped isotope measurements ranged between 6 and 22 °C, with most samples falling at or below MAT. Clumped isotope temperatures were compared to monthly precipitation normals and modeled monthly values of evapotranspiration and soil water content. Results show that carbonate formation temperatures agree with the annual timing of soil water depletion, suggesting soil moisture content is a primary control on the timing of pedogenic carbonate formation. Although the seasonal bias is a function of environmental factors that are difficult to reconstruct in paleo-studies, the use of other paleosol proxies can help to assess if changes in clumped isotope temperatures are a function of changes in air temperature or hydrology. These results have important implications for the production of accurate paleoclimate and paleoelevation estimates.

1. Introduction

Many soils in semi-arid to arid environments exhibit a distinct calcic horizon identifiable by an accumulation of authigenically precipitated pedogenic carbonate. Depending on the age and texture of the soil, pedogenic carbonate can precipitate as thin filaments, clast undercoatings, root casts, nodules, or continuous indurated horizons (Gile et al., 1966). Pedogenic carbonate preserved in paleosols is of particular interest in paleoclimate research. The occurrence of pedogenic carbonate provides a paleoprecipitation limit, as it tends only to form when mean annual precipitation (MAP) is less than 100 cm (Cerling and Quade, 1993; Royer, 1999; Retallack, 2005). Proxies based on the physical nature of pedogenic carbonate, such as depth in soil profile or horizon thickness, have been developed to reconstruct variables such as MAP and degree of seasonality (Retallack, 1994, 2005). Widespread interest in the geochemistry of pedogenic carbonate expanded since it was demonstrated that the oxygen and carbon isotopic composition of the carbonate was a reflection of the environment in which it formed (Cerling, 1984; Cerling and Quade, 1993). Subsequently, the oxygen isotope composition of pedogenic carbonate has been used to reconstruct paleohydrology (e.g. Amundson et al., 1996; Deutz et al., 2001; Fox and Koch, 2004), paleotemperature (e.g. Dworkin et al., 2005; Cleveland et al., 2008), and paleoelevation (e.g. Garzione et al., 2000; DeCelles et al., 2007). The carbon isotope composition of pedogenic carbonate has been used to reconstruct relative abundances of C_3 and C_4 vegetation (e.g. Quade and Cerling, 1995; Deutz et al., 2001; Fox and Koch, 2003; Levin et al., 2004) as well as atmospheric pCO_2 (e.g. Cerling, 1991; Ekart et al., 1999; Cotton and Sheldon, 2012; Montañez, 2013).

However, complications exist when using pedogenic carbonate as a paleoclimate proxy. The traditional assumption was that pedogenic carbonates form during conditions reflective of the mean growing season environment, which would typically imply soil temperature conditions between average and maximum annual soil temperature (Cerling and Quade, 1993). However, the growing season occurs at different times of the year under different climate regimes. For example, the growing season in the central plains of North America extends from spring to early autumn (Ode et al., 1980), whereas the growing season in the eastern Mojave Desert extends from late autumn to early spring (Beatley, 1974). It has also been documented in modern soils that carbonate can precipitate at times of excessive dryness when climatic conditions differ strongly from the mean growing season conditions

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http://dx.doi.org/10.1016/j.chemgeo.2016.04.023
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(Breecker et al., 2009). These findings suggest that, in some cases, a complicated seasonal bias may strongly affect the formation and isotopic composition of pedogenic carbonate.

Carbonate clumped isotope thermometry is an attractive tool to apply to the study of pedogenic carbonate, as the abundance of doubly substituted rare isotopes in carbonate is predominantly a function of temperature (Ghosh et al., 2006a; Quade et al., 2007; Passey et al., 2010; Eiler, 2011). The carbonate clumped isotope proxy has featured prominently in recent continental paleoclimate (e.g. Passey et al., 2010; Snell et al., 2013; VanDeVelde et al., 2013) and paleoelevation studies (e.g. Ghosh et al., 2006b; Quade et al., 2011; Lechler et al., 2013; Leier et al., 2013; Fan et al., 2014; Garzione et al., 2014; Huntington et al., 2015). However, relating the temperature of pedogenic carbonate formation to climatic variables such as mean annual temperature (MAT) has proven complicated when analyzing modern samples. For example, clumped isotope studies of pedogenic carbonate in East Africa, Tibet, and the Western United States revealed temperatures reflective of a warm season bias rather than MAT (Passey et al., 2010; Quade et al., 2013; Hough et al., 2014). Quade et al. (2013) highlighted many factors that could complicate the relationship between the temperature of soil carbonate formation and air temperature, including excessive ground heating, damping of temperature variation with depth, slope aspect, and vegetative shading. Despite these factors, Quade et al. (2013) were able to relate many modern carbonate-bearing soils to MAT and warmest average monthly temperature, using a depth-based ground heating model that reflected the generally observed warm-season temperature bias. However, pedogenic carbonates collected along an elevation transect in the Andes showed that clumped isotope derived temperatures can be affected by the timing of seasonal rainfall (Peters et al., 2013). Sites that received the majority of annual rainfall during the summer produced results reflective of mean annual soil temperature, whereas sites dominated by winter rainfall were biased towards warm summer temperatures (Peters et al., 2013). These results demonstrate that studies of pedogenic carbonate cannot always assume a warm-season formation bias.

This paper examines the annual timing of pedogenic carbonate formation under different climate regimes, including sites with different annual precipitation regimes and different growing seasons. This study specifically focuses on carbonate-nodule bearing soils ranging from fine to a relatively coarse texture. By comparing clumped isotope derived temperatures of carbonate formation to modeled seasonal soil temperature fluctuations, we assess the relative roles of normal climate patterns and other environmental factors. Monthly precipitation normals are considered alongside evapotranspiration in order to determine a monthly soil water balance and to assess its control on the timing of pedogenic carbonate formation. The clumped isotope temperatures will also be used to calculate a $\delta^{18}O$ value for the soil water, allowing for comparison with annual fluctuations in the $\delta^{18}O$ of precipitation.

1.1. Site distribution

Sites in this study were selected in order to span a range of soil types as well as different temperature and precipitation regimes (Fig. 1; Table 1). The soils analyzed herein represent three different soil taxonomic orders: Aridisols, Mollisols, and Alfisols. Of these three soil orders, Aridisols tend to be the least developed. They are characteristically dry soils that form in arid environments and are capable of supporting only a limited amount of plant growth. Due to a lack of moisture and productivity, chemical weathering and soil development tend to be very slow in these soils (Knight, 1991). As compared to Aridisols, Mollisols are generally more developed. They typically underlie temperate grasslands, such as the North American Great Plains and the Eurasian Steppe. The defining characteristic of a Mollisol is a thick (generally >25 cm), organic-rich A-horizon known as the mollic epipedon, which is largely a product of the extensive root system of prairie grasses (Soil Survey Staff, 2014). Of the soil orders examined in this study, Alfisols tend to be the most developed, and they are typically found under temperate deciduous forests (Buol et al., 2011). Soils analyzed as part of this study were generally of a finer-grained texture, allowing for greater water holding capacity and a slower drainage rate than coarse-grained, gravelly soils. With time, fine-grained soils will also tend to form carbonate nodules as opposed to clast undercoatings due, in part, to the lack of coarse fragments that serve to nucleate carbonate precipitation.

The sites examined in this study can be divided into four distinct precipitation regimes (Table 1). The two Southern California sites receive the least amount of rainfall, with both sites having a MAP value of less than 20 cm. The little precipitation that these two sites receive tends

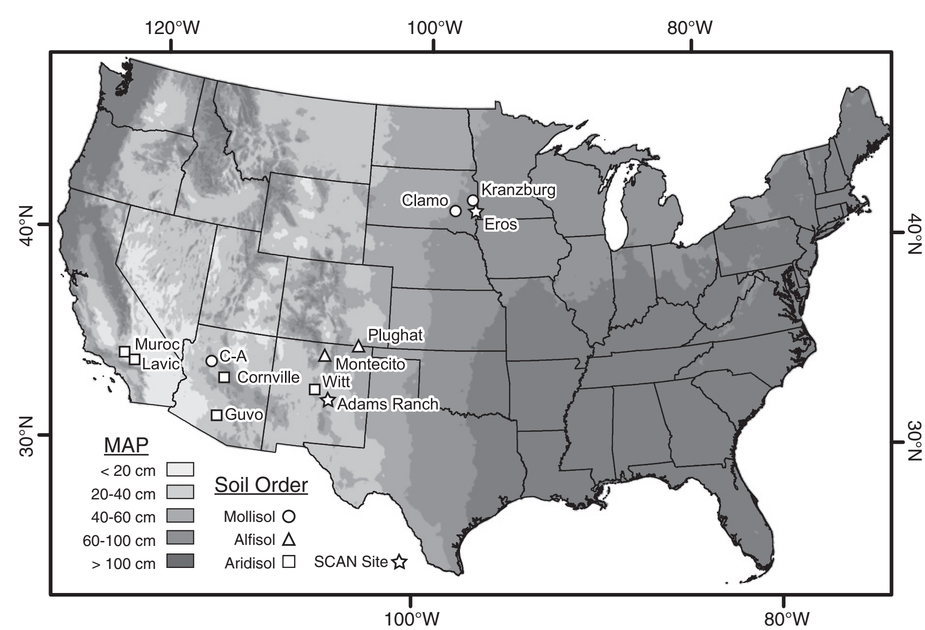

Fig. 1. Map showing sample localities for pedogenic carbonate nodules analyzed in this study along with a 4 km gridded mean annual precipitation (MAP) dataset interpolated from 1981–2010 climate normals (Prism Climate Group, 2015). Soil orders sampled include Mollisols (circles), Alfisols (triangles), and Aridisols (squares). Soil Climate Analysis Network (SCAN) sites used for data-model comparisons are shown as stars.