



Contents lists available at ScienceDirect

Quaternary International

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

Stable isotope geochemistry of pedogenic carbonates in loess-derived soils of northeastern Iran: Paleoenvironmental implications and correlation across Eurasia

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ARTICLE INFO

Article history:

Available online xxx

Keywords:

Paleosols
Paleoclimate
Stable isotopes
Eurasian loess belt

ABSTRACT

Despite the occurrence of pedogenic carbonates in loess/paleosol sequences of northern and northeastern Iran, there is no information about stable isotope geochemistry of pedogenic carbonates in these regions. This paper presents the first stable isotope data on pedogenic carbonates in loess derived soils of northeastern Iran, southern Eurasian loess belt. Carbon and oxygen stable isotope values of pedogenic carbonates in different landforms were measured using mass spectrometry. Based on climatic data, there is no possibility for soil leaching and pedogenic carbonate formation under the present arid conditions. Stable oxygen and carbon isotopic data suggest two separate periods of carbonate formation. These periods are characterized by either lower or higher temperatures during post glacial than today and paleoecological conditions dominated by C₃ and C₄ plants, respectively. Hemispheric correlation of loess deposits based on isotopic data of pedogenic carbonates shows a strong positive correlation for the post glacial carbonates nodules of northeastern Iran and European Russia. This suggests a similar mechanism of carbonate formation and also the impact of Westerlies in these regions. We present the first quantitative isotopic data for paleoenvironment of northeastern Iran. However, more quantitative investigations about the Holocene and the last interglacial paleoenvironments of northeastern Iran are needed.

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1. Introduction

Paleosols formed in direct contact with climatic and environmental conditions that prevailed at the time of their formation, and represent one of the most powerful tools for reconstructing past environments (Sheldon and Tabor, 2009). Paleosols in loess/paleosol sequences are generally regarded as the result of interglacial or interstadial climates in different regions of the world (Bradley, 1999; Rutter et al., 2003; Khormali and Kehl, 2011; Muhs, 2013; Lauer et al., 2015) and are correlated with global and astronomical timescale climatic changes (Billard, 1993; Kehl et al., 2005). There is evidence that climate during previous interglacials was warmer and more humid than during the present one leading to enhanced chemical weathering in soils (Muhs, 2013). Therefore, the

study of interglacial soils can provide insights about global warming phenomenon.

Pedogenic calcite forms in well-drained soils by the complex interaction of climate, parent material and vegetation, and usually by transfer of bicarbonate ions and supersaturation of soil solution with respect to calcite (Cerling, 1984; Łącka et al., 2009; Sheldon and Tabor, 2009). Rapid evaporation and soil freezing can accelerate the formation of secondary carbonates (Cerling, 1984). Therefore, seasonality favors the formation of pedogenic carbonate formation (Yang et al., 2012). Pedogenic carbonates are isotopically formed in equilibrium with the ambient environment, and are good indicators of past climatic and environmental conditions (Cerling and Quade, 1993; Kovda et al., 2014). Hence, isotopic signals in pedogenic carbonates can provide information about climatic and ecological changes in landscapes (Cerling and Quade, 1993; Kovda et al., 2014). Due to its sensitivity to environmental changes, stable isotopic composition of pedogenic carbonates are widely used for the study of Quaternary paleoenvironment of loess/paleosol sequences (e.g., Łącka et al., 2009; Barta, 2011; Yang et al., 2012;

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Kovda et al., 2014). Łacka et al. (2009) studied the stable isotopic composition of different forms of pedogenic carbonates in Eastern Europe. Yang et al. (2012) used the stable isotopic composition of pedogenic nodules to reconstruct environmental change over Chinese Loess Plateau (CLP) and pointed out that a southward-increasing shift of C₄ plants occurred during the Holocene.

The Eurasian loess belt could be regarded as one of the most important Quaternary terrestrial record of climatic and environmental change on global scale (Billard, 1993; Bradley, 1999). The loessic sequences of Eurasia vary greatly in thickness, source and age and represent records of long-term variation of Quaternary environmental changes (Billard, 1993). The last phase of loess deposition have occurred during MIS2 in the Russian plains (Rutter et al., 2003), Chinese Loess Plateau (Yang et al., 2012), northern Iran (Kehl et al., 2005) and northeastern Iran (Okhravi and Amini, 2001).

Loess/paleosol sequences in northern and northeastern Iran, which are located on the southern edge of the Eurasian loess belt, can present insights about the late and middle Quaternary climatic conditions in southern Eurasia (Kehl et al., 2005; Frechen et al., 2009; Karimi et al., 2011). Silt particles in loess sequences in northeastern Iran were transported in aeolian suspension mode, and deposited during glacial periods under a windy, dry and cold climate (Okhravi and Amini, 2001). The chronostratigraphy of loess/paleosol sequences in northern (Kehl et al., 2005; Frechen et al., 2009) and northeastern Iran (Karimi et al., 2011), grain-size properties of loess deposits in northeastern Iran (Okhravi and Amini, 2001; Karimi et al., 2009) and magnetic susceptibility of a loess/paleosol sequence in northeastern Iran (Karimi et al., 2013) have been investigated in recent years. Despite the occurrence of pedogenic carbonates in loess/paleosol sequences of northern Iran (Khorrami and Kehl, 2011) and northeastern Iran (Karimi et al., 2011), however, there is no information about stable isotope geochemistry of pedogenic carbonates in loess/paleosol sequences of northern and northeastern Iran.

The objectives of this study were i) to reconstruct quantitative environmental condition of the northeastern Iran using stable isotope geochemistry of soil carbonates and ii) to correlate the Holocene paleoenvironmental conditions of the selected sites across Eurasia loess belt using stable isotopic composition of pedogenic carbonates.

2. Methods and materials

2.1. Study area

The study area is located in southern Mashhad, northeastern Iran, at the southern edge of Eurasian loess belt (Fig. 1). The area is situated between 59° 30' to 60° 00'E and 36° 00' to 36° 15'N with an elevation of 950–1150 m above the mean sea level. Climatological data of Mashhad synoptic station (1951–2005) was used to assess the present climatic conditions. In general, southern Mashhad is characterized by an arid to semi-arid climate with mean annual precipitation and temperature of about 250 mm and 14.2 °C, respectively. The annual potential evapotranspiration is about 1509 mm based on the Blaney-Criddle method. Soil temperature and moisture regimes of the study area are thermic and aridic boarder on xeric, respectively.

The study area is located at the foothill of Binaloud Mountain in southern Mashhad. There are three main landscapes in the area including granitic hilly land (GHL), piedmont of granitic hilly lands (PGHL) and piedmont plain (PP). The isolated loess covers occurred on nearly flat crests of GHL. The PGHL has been covered by nearly continuous loess deposits. The PP is mainly composed of sediments transported from GHL and PGHL.

Loess derived soils in GHL and PGHL are mainly under rainfed wheat and barley cultivation and those in PP mostly under irrigated wheat, barley and alfalfa. The C₃ plants are the main natural vegetation in GHL where *Carex* spp. is the dominant species followed by *Agropyron* sp. and *Astragalus* sp.

2.2. Sections and laboratory analyses

Six sections on GHL, PGHL and PP were selected for isotopic study of pedogenic carbonates (Fig. 1). The sections were described according to Keys to Soil Taxonomy (Soil Survey Staff, 2014b) and genetic horizons were sampled. Air-dried soil samples were passed through a 2-mm sieve, and used for physicochemical analyses. Calcium carbonate equivalent (CCE) was measured by acid neutralization. Particle size distribution was determined after the removal of organic carbon with 30% H₂O₂ and sand, silt and clay fractions were measured using the pipette method after addition of dispersants and shaking (Soil Survey Staff, 2014a).

Undisturbed soil samples were air-dried and impregnated by resin. Thin sections were studied under plane and crossed polarized lights. The micromorphological descriptions follow the terminology of Stoops (2003).

2.3. Isotope analyses

Pedogenic carbonates in Bk and Btk horizons were mainly composed of soft nodules. For isotopic analysis, ten nodules of pedogenic carbonates were collected from each horizon. The samples were collected from below the depth of 25 cm to reduce the effects of CO₂ diffusion and evaporation on isotopic enrichment (Cerling, 1984; Cerling and Quade, 1993). The pedogenic carbonates of each horizon were crushed and mixed. Then, about 800 µg of each sample was reacted with 100% phosphoric acid to release CO₂ gas. The CO₂ was purified and analyzed using mass spectrometry.

Isotopic data presented here are the mean of triple measurements for each sample and are reported in the standard δ notation relative to Pee Dee Belemnite (PDB) standard (Hoefs, 2009). The values are calculated by the equation below:

$$\delta(\text{‰}) = \left[\left(\frac{R_{\text{Sample}}}{R_{\text{Standard}}} \right) - 1 \right] \times 1000 \quad (1)$$

where R is the ratio of ¹³C/¹²C or ¹⁸O/¹⁶O in sample and standard.

The isotopic composition of past meteoric water was determined using the model presented by Cerling (1984).

$$\delta^{18}\text{O}_{\text{H}_2\text{O}} = -1.361 + 0.955 \delta^{18}\text{O}_{\text{C}} \quad (2)$$

where δ¹⁸O_{H₂O} and δ¹⁸O_C are stable oxygen isotopic values for meteoric water (vs. SMOW) and pedogenic carbonate (vs. PDB), respectively.

A third-order polynomial model (spatial simulation model) (Eq. (3)) and a linear regression model (Eq. (4)) suggested by Dworkin et al. (2005) were used to estimate temperature of calcite crystallization by using oxygen isotopic composition of pedogenic carbonate. This method uses combined equations of the fractionation of oxygen isotopes during the process of condensation and process of calcite crystallization and the analytical error of the method is about ±0.5 °C (Dworkin et al., 2005; Sheldon and Tabor, 2009).

$$-0.50T^3 + (\delta^{18}\text{O} + 152.04)T^2 - 2.78 \times 10^6 = 0 \quad (3)$$

$$\delta^{18}\text{O} = 0.49T - 12.65 \quad (4)$$

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