



# Incorporation of trace metals into microcodium as novel proxies for paleo-precipitation



Tao Li, Gaojun Li\*

MOE Key Laboratory of Surficial Geochemistry, Department of Earth Sciences, Nanjing University, 163 Xianlindadao, Nanjing 210046, China

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## ABSTRACT

Trace element compositions of microcodium are applied for the first time as possible paleo-proxies based on a case study on the Chinese Loess Plateau (CLP). The Mg/Ca and Sr/Ca ratios of the microcodium picked from the Holocene paleosol across the CLP show distinct positive correlation over large range of nearly one order of magnitude. Higher Mg/Ca and Sr/Ca ratios of microcodium are recorded in the sites on the northwestern CLP where less monsoonal rainfall is received. Similar large variation of the positively correlated Mg/Ca and Sr/Ca ratios has also been observed for the stream water on the CLP with the same spatial pattern. The Mg/Ca and Sr/Ca ratios of the microcodium seem to be largely controlled by the composition of soil solution as reflected by stream water rather than partition coefficient. Rayleigh distillation, and thus evolving composition of soil solution as a result of progressive precipitation of secondary calcite, is responsible for the large variation and positive correlation of the Mg/Ca and Sr/Ca ratios for both the microcodium and stream water. We propose that the bio-remains in Chinese loess may become inactive when the soil water is extracted to a degree, and then be calcified into microcodium by the infiltration of freshwater that is mixed with the highly evolved soil solutes. Thus, the Mg/Ca and Sr/Ca ratios of microcodium may record the paleo-precipitation amount by reflecting the mixing ratio between the highly evolved soil solutes with higher Mg/Ca and Sr/Ca ratios and the fresh soil water with lower Mg/Ca and Sr/Ca ratios.

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## 1. Introduction

Trace element compositions of carbonate precipitates such as speleothem (Fairchild et al., 2000), biogenic skeletons of foraminifera (Elderfield and Ganssen, 2000), coccolith (Rickaby et al., 2007), coral (Mitsuguchi et al., 1996), ostracod (Wansard et al., 1998) and gastropod (Zacherl et al., 2003) have been successfully applied to paleo-reconstruction. However, information on the incorporation of trace elements into the authigenic carbonates in soil is rare although soil carbonates may record the condition under which they are precipitated (e.g., Breecker et al., 2009; Cerling, 1984). Being preserved by continuous dust accumulation, the soil carbonates in Chinese loess provide a rare opportunity to explore the potentials of using the trace element compositions of soil carbonates as paleo-proxies.

Thick eolian deposits, which are dated back to late Oligocene (Guo et al., 2002; Heller and Liu, 1982; Qiang et al., 2011; Sun et al., 1998), mantle the Chinese Loess Plateau (CLP, Fig. 1). Chinese loess is typical calcareous soil (Liu, 1985), which contains abundant authigenic carbonates such as rhizolith, carbonate concretion, microcodium, and carbonate cement (Sheng et al., 2008). Paleo-

proxies related to the soil carbonates in Chinese loess are mainly based on stable C, O isotopes, and recently isotopologues (Chen et al., 1996; Ding and Yang, 2000; Eagle et al., 2013; Han et al., 1997; Li et al., 2007; Liu et al., 2011; Rao et al., 2006; Suarez et al., 2011; Wang and Follmer, 1998). Selective leaching of bulk samples by weak acid can extract the trace elements associated with soil carbonates in Chinese loess (Li et al., 2013). However, this method is not suitable for the elements with low partition coefficient in calcite. Dissolution of detrital carbonates and silicate minerals may dominate the contribution of these elements to the chemical extractant (Li et al., 2013).

Using the pieces of authigenic carbonates that are picked from the loess matrix may overcome the influence of detrital minerals. However, recent studies even show that the carbonate concretion and rhizolith, once regarded as purely authigenic origin, contains significantly amount of detrital minerals (Li et al., 2013; Liu et al., 2010). This work measures the Mg/Ca and Sr/Ca ratios of the microcodium picked from Chinese loess. The advantage of microcodium is that it is of purely authigenic origin due to the replacement of bio-cells by the authigenic calcite. Thus, potential wrapping of detrital grains by the matrix of authigenic calcite is minimized. Possible environmental controls on the incorporation of Mg and Sr into the microcodium are explored based on the Holocene paleosol as well as the stream chemistry on the

\* Corresponding author.

E-mail address: ligaojun@nju.edu.cn (G. Li).

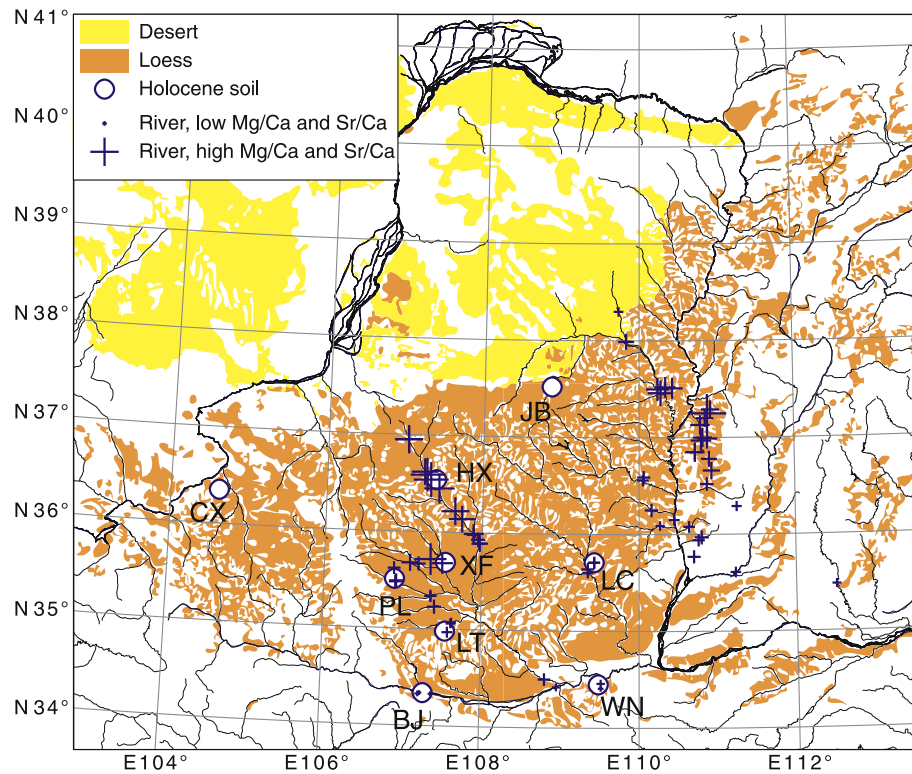


Fig. 1. Map showing the sampling sites on the Chinese Loess Plateau.

**Table 1**  
Average Mg/Ca and Sr/Ca ratios of microcodium in Holocene paleosol.

Sites	Latitude (°N)	Longitude (°E)	Precipitation (mm/yr)	Mg/Ca (mmol/mol)	Sr/Ca (mmol/mol)	n <sup>a</sup>
BJ	34.34	107.29	679	20.2	0.39	3
WN	34.45	109.49	662	12.6	0.33	5
LC	35.71	109.43	622	27.9	0.63	4
LT	34.98	107.55	606	31.7	0.62	2
XF	35.69	107.54	562	35.6	0.85	9
PL	35.51	106.90	511	60.3	1.24	4
HX	36.54	107.40	443	69.0	1.60	6
JB	37.52	108.87	395	76.9	1.98	3
CX	36.35	104.62	360	95.6	2.11	4
Average				47.8	1.08	

<sup>a</sup> Number of replicates.

CLP. The result demonstrates that the Mg/Ca and Sr/Ca ratios of the microcodium in Chinese loess may serve as proxies for paleo-precipitation.

## 2. Samples and method

Samples of Holocene paleosol were collected from nine sites across the CLP (Fig. 1). Climate on the CLP changes gradually from southeast to northwest. Northwestern CLP is much colder and drier than the southeastern CLP due to the decreasing influence of summer monsoon. The sites investigated by this work have modern precipitation amount ranging from 360 to 680 mm/yr based on local meteorological records of more than 40 yr (Table 1). To help interpretation, stream water on CLP was also collected during the September of 2012.

Microcodium were picked under binoscope. Briefly, about 200 g of sample was immersed in water. Then the dispersed sample was passed through a 200-mesh (75 μm) sieve. The >75 μm fraction is dominated by authigenic grains. Microcodium are picked from the >75 μm fraction under binoscope according to its characteristic transparent or white color and cell-like structure (Fig. 2). About

20 pieces of microcodium are picked for each sample. Observation under scanning electron microscope shows that the cell-like microcodium is cemented by very pure calcite crystals (Fig. 2). The cell-like structure of microcodium in Chinese loess is similar to those have been reported in other places (Alonso-Zarza et al., 1998; Kabanov et al., 2008; Klappa, 2009; Košir, 2004).

The picked grains of microcodium were ultrasonically cleaned in ethanol and pure water sequentially to remove the attached silicate minerals after the method applied to foraminifera (Barker et al., 2003). Cleaned samples were then dissolved in 0.075 M HNO<sub>3</sub>. Dissolved solution is separated from the residue by centrifugation.

Trace element concentrations of the dissolved products and the stream water were measured by ICP-OES. Ratio calibration method is used for the dissolved products of microcodium based on a set of mixed standards with constant Ca concentration of 80 ppm. The mixed standards are made from standard metal solution from the National Center of Analysis and Testing for Nonferrous Metals and Electronic Materials of China. A subset of the sample solution is measured for Ca concentration. Then, the rest of the sample solution is diluted to a Ca concentration of about 80 ppm for elemental ratio determination (Barker et al., 2003). Ratio calibration method

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