Quaternary Research 81 (2014) 181–188

Contents lists available at ScienceDirect

Quaternary Research

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

Trace-element variations in an annually layered stalagmite as recorders of climatic changes and anthropogenic pollution in Central China

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ARTICLE INFO

Article history:
Received 29 September 2013
Available online 28 December 2013

Keywords:
Annually layered stalagmite
Trace elements
REE geochemistry
Climate change
Environmental pollution
Central China

ABSTRACT

We analyzed variations in the Sr/Ca, Ba/Ca, REE/Ca (REE: rare earth element), Zn/Ca, and Pb/Ca ratios preserved in an annually layered stalagmite, XL21, from central China. The stalagmite record spans the 95 year period AD 1914–2008. The Sr/Ca and Ba/Ca ratios have a significant positive correlation with the stalagmite's growth rate, suggesting that they were primarily controlled by growth-rate variations. Variations in REE/Ca ratios are consistent with local temperature changes, suggesting temperature influenced REE concentrations in the stalagmite over decadal to annual timescales. Higher temperature in this humid area can increase vegetation cover, microbial activity, and organic decomposition in the soil, resulting in enhanced pCO_2, organic matter concentration and reduced pH, and consequently increased REE mobilization from the overlying soil layer and host rock. Higher temperatures may also increase the natural Zn mobilization from the overlying soil mediated by organic matter and consequently may have led to increased Zn retention in XL21. An increasing trend is seen in the Pb/Ca ratios from XL21 since 1985, which is consistent with increased lead production in this area, and indicates an increase in mine-derived lead pollution in the local environment over the past 30 years.

Introduction

Cave speleothems are ideal for reconstructing past climatic and environmental changes because they often grow continuously, yield data at a high temporal resolution, can be accurately dated, and suffer little secondary alteration (e.g., McDermott, 2004; Fairchild et al., 2006). Studies of stable isotopes ($\delta^{18}O$, $\delta^{13}C$) preserved in speleothems from the Asian monsoon region have achieved great success in recent years (e.g., Wang et al., 2001, 2005, 2008; Fleitmann et al., 2003; Yuan et al., 2004; Cheng et al., 2009; Cai et al., 2012). However, trace-element signatures preserved in speleothems are not commonly used, and have received less attention than the stable isotope approach. Nevertheless, it has been demonstrated that trace elements incorporated into the calcium carbonate matrix (e.g., Mg, Sr, Ba, Y, P, and U) reflect past climate variability (Fairchild and Treble, 2009, and references therein). For example, Mg variations in a modern stalagmite from southwestern Australia were suggested to be an effective palaeohydrological indicator in this region on annual timescales, while Sr, Ba, and Na were suggested to depend on growth rate (Treble et al., 2003). Mg/Ca and Sr/Ca ratios in a stalagmite from southern Brazil varied in tandem with $\delta^{18}O$ during the last glacial period, and were explored as a proxy for changes in local rainfall recharge over millennial timescales (Cruz et al., 2007). Richter et al. (2004) first analyzed rare earth elements (REE) in stalagmites from Germany, and suggested that their enrichment reflected periods of more intense weathering, which usually correspond to warm and humid conditions. Another study, from central China, also showed that speleothem REE were enriched during interstadials, but became depleted during stadial periods, confirming that more intense weathering and more dynamic hydrology under warm and humid climates favor the enrichment of REE in stalagmites (Zhou et al., 2008). These latter two studies highlight the potential for using REE series preserved in speleothems to reconstruct past climate change.

With the development of the mining, smelting, and metal-treating industries, heavy metal pollution in China has become increasingly serious, and now poses a severe threat to both humans and the environment in some regions (e.g., Chen et al., 1999; Cheng, 2003). There is an increasing need to reconstruct the environmental pollution history in China to assist current environmental monitoring. Speleothems have the potential to preserve environmental pollution signals derived from the overlying soil layers (Frisia et al., 2005). In contrast to the mobility of pollutants in dendrochemical records, element mobility is not usually a problem for speleothems, except where aragonite is converted to calcite after deposition (Fairchild and Treble, 2009). Recently, Siklosy et al. (2011) provided the first successful example of using the chemical composition of a stalagmite to reconstruct the history of environmental pollution, in this case, related to U ore mining in Hungary.

In this study, we analyze variations in the Sr/Ca, Ba/Ca, REE/Ca (i.e., La/Ca, Ce/Ca, Pr/Ca, Nd/Ca, Sm/Ca, Eu/Ca, Gd/Ca, Tb/Ca, Dy/Ca, Ho/Ca, Er/Ca, Tm/Ca, Yb/Ca, and Lu/Ca), Zn/Ca, and Pb/Ca ratios over the period

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0033-5894/$ – see front matter © 2013 University of Washington. Published by Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.yqres.2013.12.001

AD 1914–2008 preserved in an annually layered stalagmite (XL21) from central China. We present direct comparisons between the trace-element records and the observed temperature and precipitation records, and discuss the main factors controlling the trace-element variations.

Cave location and sample description

Xianglong Cave (33°00′N, 106°20′E; 940 m above sea level at the entrance) is located on the southern flank of the Qinling Mountains in central China (Fig. 1). In summer, the Asian summer monsoon brings warm humid air and causes substantial monsoon rainfall at the site (>70% of the annual rainfall, Liu et al., 2003). During winter, the Siberian–Mongolian High and westerly winds maintain cold and dry conditions, and carry airborne dust from the Gobi Desert and drylands in northwestern China to the site (Wei et al., 2000). There are two lead mines 10–16 km northwest of Xianglong Cave (Fig. 1), and lead mining and smelting has taken place in the area for the past 30 years. The present-day mean annual air temperature and precipitation in this area are 13°C and 1100 mm, respectively. For data on monthly rainfall and temperature variations, see Tan et al. (2013).

The cave has a relatively thick roof (~100 m) and its known length exceeds 1.2 km; the humidity of the inner chambers is around 100%. Recharge to the karst aquifer above the cave is likely to be derived from meteoric precipitation (Tan et al., 2013). As a result of water storage in the relatively thick cave roof, infiltration is continuous even during the driest winter months. An active stalagmite (XL21), which was 4.2 cm long, was collected about 700 m from the entrance of Xianglong Cave in October 2009 (Fig. 1). The supplying dripwater entry was about 8 m above the sample site. A vertical section through the stalagmite (Fig. 2) shows regular laminae that alternate from dark, compacted layers (DCL) to white, porous layers (WPL). Here, we study the uppermost 2.9 cm of XL21, which is composed of pure aragonite, as revealed by X-ray diffraction analysis (Tan et al., 2013).

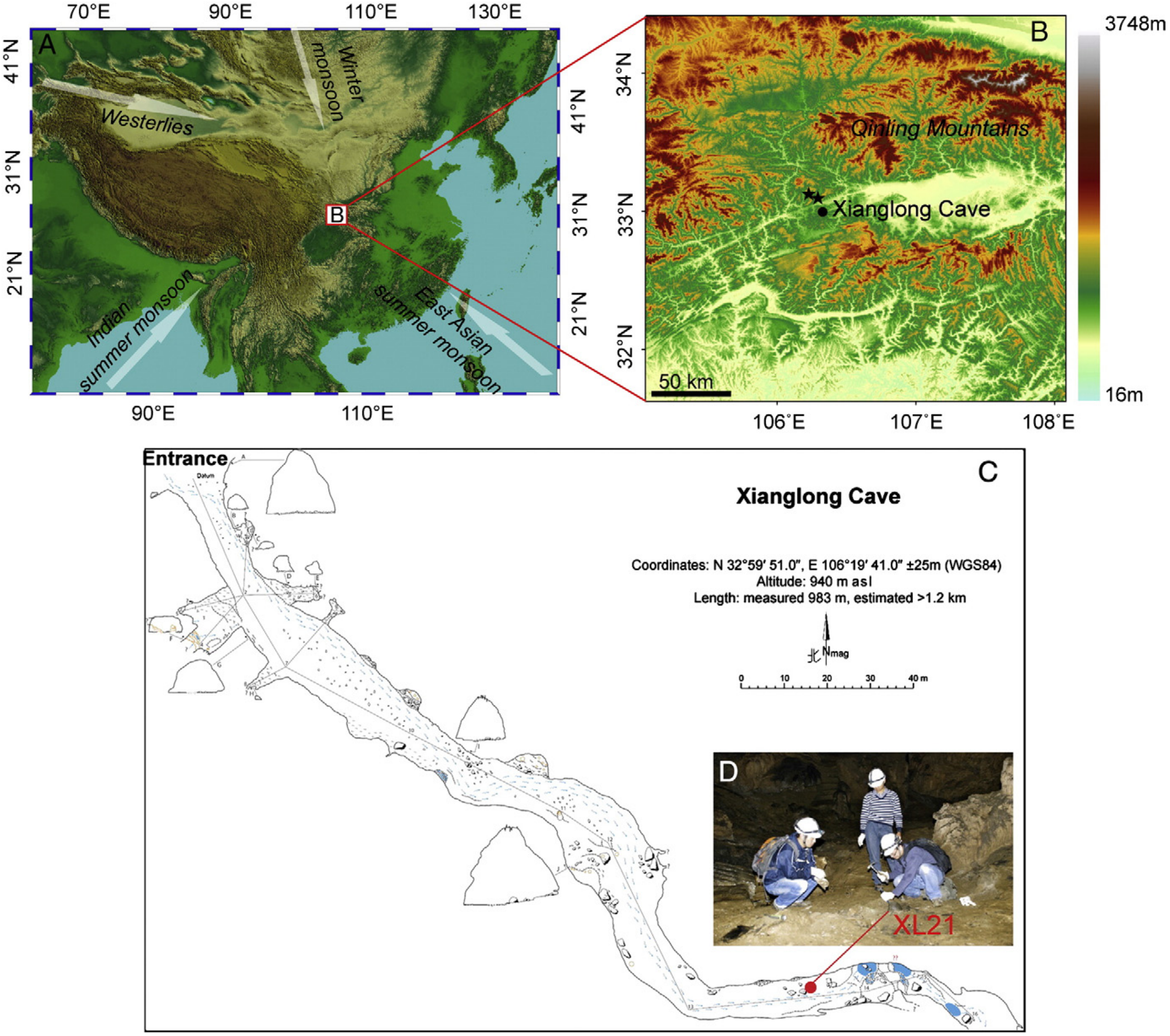

Figure 1. Location and plan view of Xianglong Cave. (A) Overview map showing the study region. Arrows indicate the directions of the East Asian summer monsoon, Indian summer monsoon, East Asian winter monsoon, and westerlies. (B) Enlarged regional topographic map showing the locations of Xianglong Cave (black dot), two lead mines (black stars), and the Qinling Mountains. Topographic GTOPO30 data are from the USGS EROS Center (Earth Resources Observation and Science Center: http://eros.usgs.gov/#/Find_Data/Products_and_Data_Available/gtopo30_info). (C) Plan view of Xianglong Cave. (D) Photograph showing the sampling site of stalagmite XL21 in the cave.