

# High-resolution and precisely dated record of weathering and hydrological dynamics recorded by manganese and rare-earth elements in a stalagmite from Central China

Houyun Zhou <sup>a,\*</sup>, Baoquan Chi <sup>a</sup>, Michael Lawrence <sup>b</sup>, Jianxin Zhao <sup>b</sup>, Jun Yan <sup>c</sup>,  
Alan Greig <sup>d</sup>, Yuexing Feng <sup>b</sup>

<sup>a</sup> Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Wushan, Guangzhou 510640, China

<sup>b</sup> Radiogenic Isotope Laboratory, Centre for Microscopy and Microanalysis, the University of Queensland, Brisbane, Queensland 4072, Australia

<sup>c</sup> School of Resources and Environmental Engineering, Hefei University of Technology, Hefei 230009, China

<sup>d</sup> School of Earth Sciences, University of Melbourne, Melbourne, 3010, Australia

Received 7 January 2007

Available online 18 April 2008

## Abstract

Manganese (Mn) and rare-earth elements (REEs) in a stalagmite (SJ3) collected from Central China were analyzed, using an ICP-MS method for the precise determination of >40 trace elements in geological samples by enriched-isotope internal standardization. Unlike speleothem Mn and REEs investigated by cathodoluminescence, which may be incorporated into crystal lattice, the Mn and REEs analyzed in SJ3 should come largely from colloidal and particle phases in groundwater and may be associated with non-carbonate inclusions. The Mn and REEs in SJ3 vary significantly during the period between 20 and 10 ka. These elements show remarkable increases since ~14.5 ka, suggesting enhanced weathering of the overlying soil layer and the host rock since the onset of the last deglaciation and the strengthening of the Asian summer monsoon. In addition, the Mn and REEs in SJ3 display significant centennial fluctuations which may reflect groundwater dynamics.

© 2008 University of Washington. All rights reserved.

**Keywords:** Mn; REEs; Speleothem; Weathering; Hydrology; East Asia; Summer monsoon

## Introduction

Calcareous speleothems are becoming increasingly important in the investigation of past climate and environment because they can grow continuously for  $10^3$ – $10^5$  yr, have a wide geographical distribution, can be dated precisely using  $U$ – $^{230}Th$  dating techniques and can be sampled at high resolution (Edwards et al., 1987; Musgrove et al., 2001; Mickler et al., 2004; McDermott 2004; Fairchild et al., 2006). Speleothem-based studies have led to significant advances in identifying and dating major shifts in the climate system (Wang et al., 2001; 2004; Yuan et al., 2004). These studies have involved many geochemical proxies, including stable oxygen and carbon

isotopes ( $\delta^{18}O$  and  $\delta^{13}C$ ) (Bar-Matthews et al., 1999; Wang et al., 2001; Yuan et al., 2004; Wang et al., 2004), uranium and strontium isotopic compositions ( $^{234}U/^{238}U$  and  $^{87}Sr/^{86}Sr$ ) (Banner et al., 1996; Goede et al., 1998; Kaufman et al., 1998; Bar-Matthews et al., 1999; Li et al., 2005; Zhou et al., 2005), and trace elements such as Sr, Mg, Ba, P, U, and Si (Roberts et al., 1998; Fairchild et al., 2001; Huang et al., 2001; Hu et al., 2005). Many speleothem proxies cannot be interpreted unequivocally. For example, speleothem  $\delta^{13}C$  record may be governed by the relative proportions of  $C_3$ - versus  $C_4$ -plants (Holmgren et al., 1995; Dorale et al., 1998), changes in ecosystem productivity in areas where  $C_4$ -type vegetation is not present (Genty et al., 2003), changes in the  $\delta^{13}C$  value of atmospheric  $CO_2$  (Baskaran and Krishnamurthy, 1993), or changes in water–rock interactions (Baker et al., 1997; McDermott, 2004). This is particularly so for more subtle shifts and shorter time periods. However,

\* Corresponding author. Fax: +86 20 85290130.

E-mail address: [hyzhou@gig.ac.cn](mailto:hyzhou@gig.ac.cn) (H. Zhou).

multiproxy studies have enormous potential in identifying process controls and fulfilling the potential of speleothems in paleoclimatical and palaeoenvironmental analysis (Fairchild et al., 2006). Therefore, identifying new proxies is one of the important fields of speleothem-based investigation of past climate and environment.

Recently, Richter et al. (2004) measured  $Mn^{2+}$  and some rare-earth elements (REEs) (such as  $Sm^{3+}$  and  $Dy^{3+}$ ) in eight stalagmites from Germany using cathodoluminescence (CL). They found that the enrichment of  $Mn^{2+}$  and  $REE^{3+}$  reflected times of more intense weathering, which usually correspond to warm and humid climatic phases. This points to some new climatic and environmental proxies in speleothem archives and suggests the possibility for investigation of a paleo-weathering process with high resolution and precisely dated chronology as well as convenience and lower cost. Although strontium isotope ratios ( $^{87}Sr/^{86}Sr$ ) are also a good proxy for weathering (Bar-Matthews et al., 1999; Frumkin and Stein, 2004; Li et al., 2005),  $^{87}Sr/^{86}Sr$  determination is costly at present. Spectral analysis of speleothem growth layer using CL is also very time-consuming, and the detection limits for  $Mn^{2+}$  and some REEs are apparently higher than obtained using other methods such as ICP-MS (Eggins et al., 1997; Richter et al., 2004). In this paper, we report the Mn and REEs records retrieved from a stalagmite (SJ3) sampled from Central China using an improved ICP-MS method, that of Eggins et al. (1997).

### Geological backgrounds and sample description

The geological setting and the  $\delta^{18}O$  and  $\delta^{13}C$  profiles from stalagmite SJ3 has been reported in a companion paper (Zhou et al., in press) and the samples have been described in detail therein. In brief, SJ3 was collected from Songjia Cave in Central China ( $107^{\circ}10'45''E$ ,  $32^{\circ}24'46''N$ ) (Fig. 1). The cave is host of the Late Permian limestone and there is no non-carbonate rock type found around the cave (Bureau of Geology and Mineral Resources of Sichuan Province, 1991). Atmospheric dust

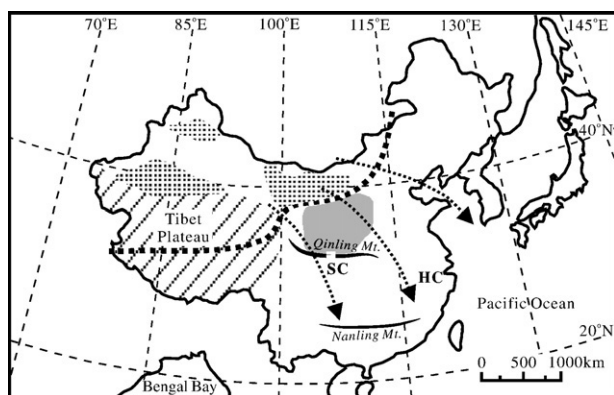


Figure 1. Locations of Songjia Cave (SC) in Central China (this work) and Hulu Cave (HC) in East China (Wang et al., 2001). Songjia Cave is on the south flank of the Qinling Mountain. The shaded area is the Loess Plateau. The dotted areas are deserts in Northwest China. The hatched area is the Qinghai–Tibet Plateau. The thick dashed line indicates the northwestern limit of the East Asian summer monsoon. The dashed arrows indicate routes of winter monsoon and dust transportation.

activity is intense in this area during the winter season and aeolian sediments are the major material sources for local soil. The overlying soil layer on the limestone capping the cave is thin (usually less than 30 cm) or absent in places, but Late Pleistocene aeolian sediments can be found sparsely in this area (Lei et al., 1998; Fang et al., 1999). This site has a typical summer monsoon climate at present with an annual mean temperature of  $15^{\circ}C$  and an annual mean precipitation of 1000 to 1200 mm. Most of the precipitation falls in the summer half year. Local vegetation consists mainly of pine, cypress and some deciduous broadleaf species.

SJ3 is 12.6 cm long. It was dated with the TIMS  $^{230}Th$  method (Zhao et al., 2001) and seven  $^{230}Th$  dates indicate that SJ3 developed between  $\sim 38$  and  $\sim 10$  ka. However, a hiatus is clear at a depth of  $\sim 84$  mm from the top of SJ3, representing a no-growth period between  $\sim 35$  and 20 ka (Fig. 2) (see also Zhou et al., in press). Mn and REEs were analyzed for the upper part of SJ3.

The upper part of SJ3 displays apparent changes in color and structure (Fig. 2). The top 6 mm of SJ3 is porous and dark grey. Dissolution of sub-samples from this section indicates a large quantity of detrital material. Microscopic examination indicates several growth hiatuses in this section. Downwards to a depth of  $\sim 40$  mm, the stalagmite looks light grey in general but with clear laminations. At the depth between 40 and 84 mm, the stalagmite looks milky and compact, in which lamination is also clearly identifiable under microscope. The thickness of the laminae is in the range of tens to hundreds of micrometers, much larger than the calculated annual growth rate of SJ3 (Zhou et al., in press), showing that these are not annual laminae. In general, for the section above the hiatus at  $\sim 84$  mm, the upper half (above the depth of  $\sim 40$  mm) is more deeply pigmented than the lower half (between the depths of  $\sim 84$  and  $\sim 40$  mm) (Fig. 2).

### Methods

The TIMS  $^{230}Th$  dating for SJ3 is described in Zhou et al. (in press). The locations of the dates are indicated in Figure 2. An age model for SJ3 was established by linear interpolation between contiguous dates according to depth from the top of SJ3. Sub-samples for trace element analysis (including Mn and REEs) were obtained in the same way as those for  $\delta^{18}O$  and  $\delta^{13}C$  analyses (Zhou et al., in press), with a spatial resolution of 0.5 mm. Each sub-sample for trace element analysis weighs between 3 and 5 mg. A total of 168 sub-samples were analyzed with an average temporal resolution of  $\sim 60$  yr per sub-sample.

The calcite sub-samples from SJ3 were analyzed at the Advanced Centre for Queensland University Isotope Research Excellence (ACQUIRE), University of Queensland using the ICP-MS method improved by Eggins et al. (1997). Sub-samples were dissolved in 2% nitric acid and diluted with dilution factors between 1000 and 1200 and then were analyzed with a Thermo X-series ICP-MS in the HEPA and charcoal filtered clean laboratories. In case detrital materials were found (in some sub-samples from the top porous 6 mm of SJ3) the sub-sample was centrifuged and the decanted solution was used for analysis. This method uses multiple enriched isotopes including  $^6Li$ ,  $^{115}In$ ,  $^{187}Re$ ,  $^{209}Bi$  and  $^{235}U$  for internal standardization. A natural rock

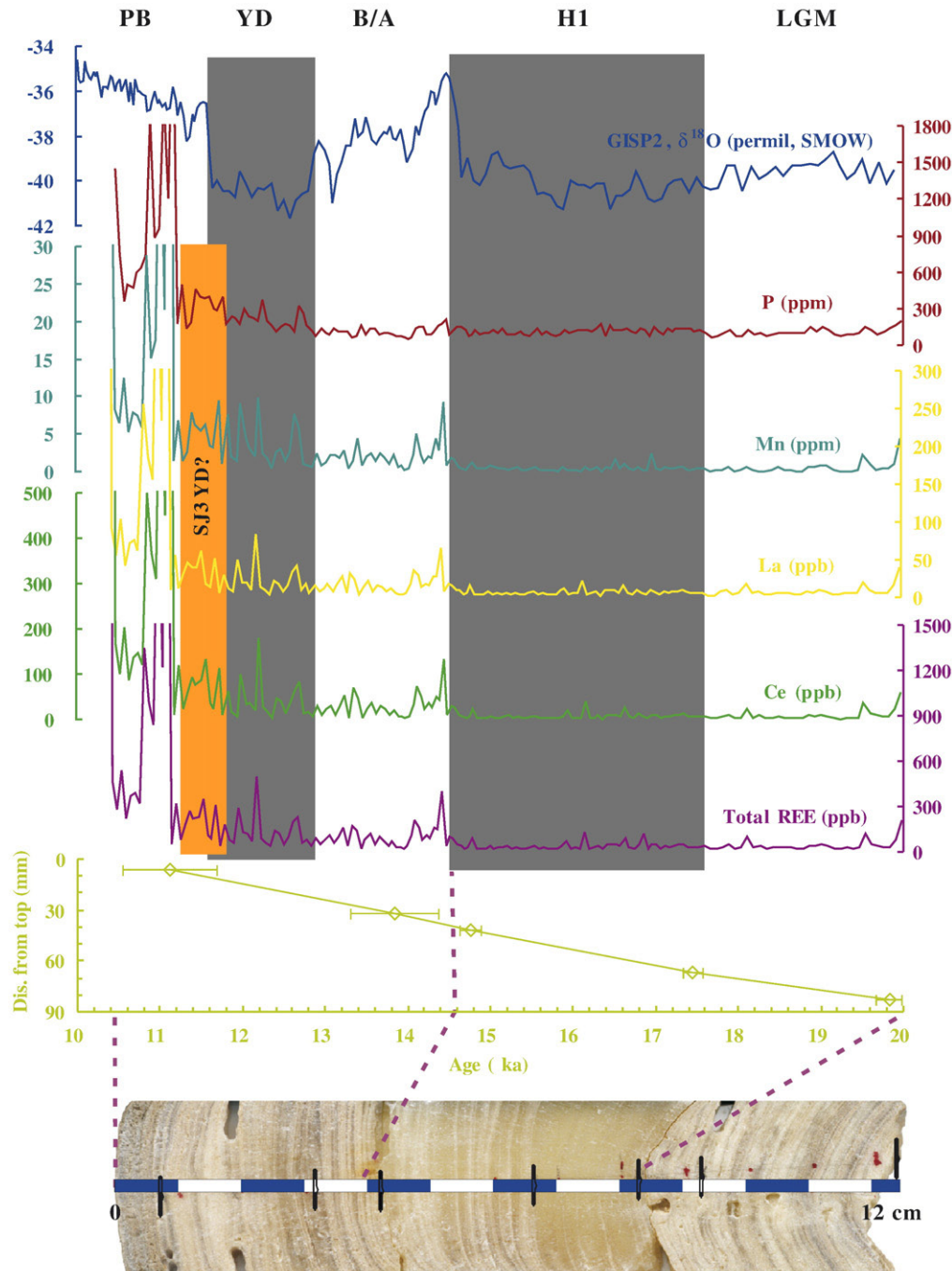


Figure 2. Stalagmite SJ3 and its Mn, P, La, Ce and total REEs records during 20–10 ka and comparison with the GISP2  $\delta^{18}\text{O}$  record from northern high latitude (Grootes et al., 1993; Stuiver et al., 1995). On the top, LGM: the last glacial maximum; H1: the cold climatic phase associated with the Heinrich event one; B/A: the Bølling–Allerød warm period; YD: the Younger Dryas cooling event; PB: the pre-Boreal period. The two grey rectangles represent the H1 cold phase and the YD cooling event recorded by the GISP2 ice core (Grootes et al., 1993; Stuiver et al., 1995). The orange rectangle marked with “SJ3 YD?” indicates the possible correlation in SJ3 with the YD event (Zhou et al., in press). On the scanning image of SJ3 show a scale bar and the locations for TIMS  $^{230}\text{Th}$  dating (vertical ellipses). It’s clear that since the onset of the last deglaciation, Mn, La, Ce and total REEs in SJ3 show remarkable increase and significant fluctuations, indicating stronger weathering and higher frequency of rainfall extremes and flushing events. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

standard, W-2 was used to replace the basalt standard BHVO-1 as used by Eggins et al. (1997) for external calibration. There are also some other minor modifications to the method used by Eggins et al. (1997) (cf. Kamber et al. (2003)). As suggested by Eggins et al. (1997), the detection limits for this method vary within a range from <1 to 10 ppt (<1–10 ppb sample

equivalent) for most higher-mass elements (with mass > 80 amu) and for lower-mass elements (with mass < 80 amu) between 10 ppt and 1 ppb (10 ppb–1 ppm sample equivalent). For REEs, Lawrence et al. (2006) suggested that the detection limits should be in the range of tens to hundreds of ppq (in solution).

River water and cave waters were collected for trace element analysis. Cave waters, including dripping water and pool water, were collected from Songjia cave and some other caves nearby. Cave water was firstly put into a big container (with a capacity of 5 l). After ~4 h of settlement, ca. 500 ml of water was transferred into a bottle (with a capacity of 500 ml) directly and acidified to pH <2 immediately with double distilled HNO<sub>3</sub>. Another 500 ml of water was filtered with 0.45 μm Millipore membrane before being transferred into a bottle and acidified to pH <2. After returning to the laboratory, about 50 ml of water from each sample was used for analyses of Ca, Mg, Sr, Ba, Al and Mn. These water samples were 10–15 times enriched on a hotplate before they were analyzed using a Varian Vista-PRO ICP-AES at the Key Laboratory of Geochemistry and Geochronology, Guangzhou Institute of Geochemistry.

## Results

The variations of Mn and rare-earth elements La and Ce in SJ3, the two having the highest concentrations among all REEs, are displayed in Figure 2. Also shown in Figure 2 are the P concentration and total REE in SJ3. For comparison the Greenland GISP2 δ<sup>18</sup>O record (Grootes et al., 1993; Stuiver et al., 1995) is also presented in Figure 2.

The Mn concentration usually ranges from hundreds to tens of thousands of ppb with an average of ~5000 ppb, while La and Ce mostly fall between several to hundreds of ppb and average ~51 and ~103 ppb, respectively. Compared with Mn and REEs, P has a much higher concentration, with the lowest value of ~50 ppm and the highest of more than 1000 ppm, averaging ~220 ppm. Total REE displays almost the same trend as La, Ce and Mn and averages ~262 ppb. It's clear that variations of Mn, La, Ce and total REE in SJ3 could be divided into two stages, which correspond with the color change of SJ3 (Fig. 2). In the pigmented portion (above 40 mm in depth), the concentrations of Mn, La, Ce and total REE are notably higher and display significant fluctuations compared with the relatively "clean" portion between 40 and 84 mm in depth. The concentrations of Mn, La, Ce and total REE for the pigmented portion average 9900 ppb, 100 ppb, 209 ppb and 507 ppb, respectively; while for the lower portion, they average 500 ppb, 7 ppb, 8 ppb and 40 ppb, respectively.

The significant shifts in concentrations and variations of Mn, La, Ce and total REE in SJ3 at the depth of ~40 mm correspond with the remarkable change in climate and environment at ~14.5 ka, the transition from the cold climatic phase associated with the Heinrich event 1 (H1) to the relatively warm and humid Bølling-Allerød (B/A) period that is indicated in the δ<sup>18</sup>O and δ<sup>13</sup>C records for SJ3 (Zhou et al., in press) and other speleothem records from East Asia (Wang et al., 2001; Yuan et al., 2004), as well as in the Greenland ice core records (Grootes et al., 1993; Stuiver et al., 1995) (Fig. 2). During the cold climatic phases before the transition (including the cold climate associated with H1 and the last glacial maximum (LGM)), Mn, La, Ce and total REE in SJ3 are relatively stable with lower concentrations. Since the onset of the last deglaciation when climate became relatively warm and humid, concentrations of Mn, La, Ce and total REE increased remarkably with significant fluctuations.

P in SJ3 displays a trend generally parallel with the Mn, La, Ce and total REE records (Fig. 2), but it also shows some differences. For example, the outstanding shift at 14.6–14.5 ka, which is evident in the Mn, La, Ce and total REE records, is not recorded by P, which P displays a notable increase much later (after ~12.8 ka) (Fig. 2).

A period of very high concentrations of Mn, P and REEs occurs between ~10.8 and ~11.1 ka (Fig. 2). The concentrations of Mn, P, La and Ce during this period are 78 ppm, 1653 ppm, 409 ppb and 737 ppb respectively, which are 7–16 times higher than their respective averages. This period corresponds to the lower part of the top 6 mm of SJ3 which is porous and rich in detrital materials. Although ages for the top 6 mm of SJ3 were linearly extrapolated and hiatuses in this part add uncertainty to this extrapolation, it seems very unlikely that these detrital materials come from human activity.

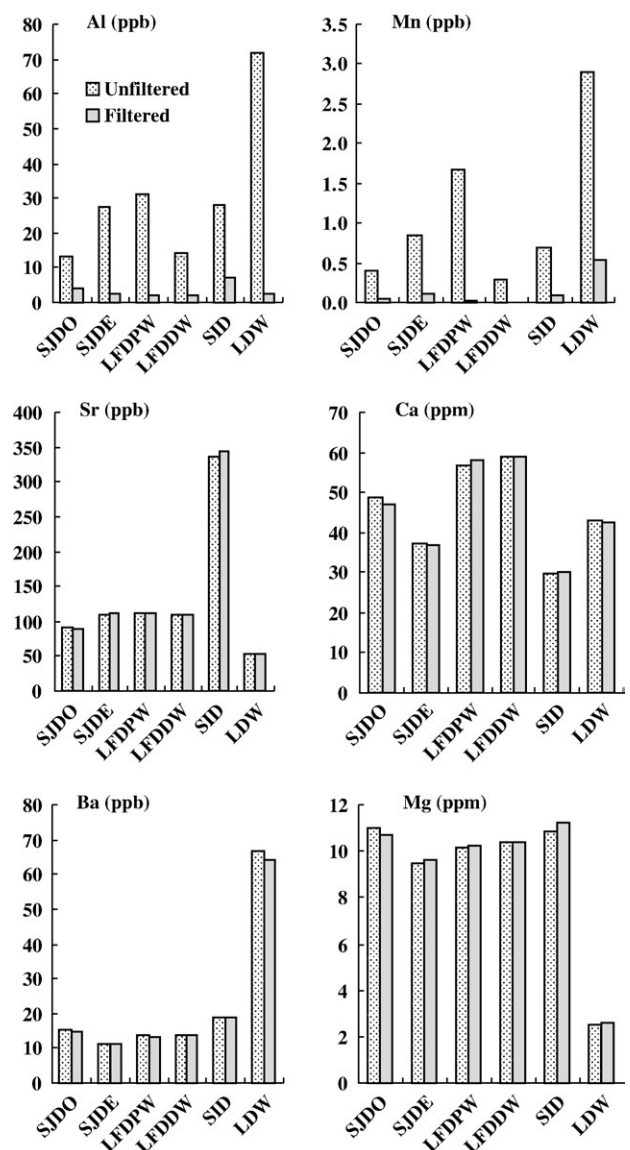


Figure 3. Concentrations of Al, Mn, Ca, Sr, Mg and Ba in cave waters and river water before and after filtering with 0.45 μm Millipore membrane.

The elemental concentrations of water samples are showed in Figure 3. For unfiltered samples, Al ranges from 13 to 77 ppb while Mn ranges from 0.3 to 2.9 ppb. Filtering removes most of the two elements with Al decreasing to (1.8–7.4) ppb and Mn to (0.01–0.53) ppb, suggesting that the two elements are mainly in colloidal and/or particle phases in cave and river waters. Contrary to Al and Mn, filtering has little effect on the concentrations of Ca, Mg, Sr and Ba (Fig. 3), suggesting that the four elements are in the dissolved phase.

## Discussion

The major sources of speleothem REEs, as suggested by Richter et al. (2004), include the siliciclastic portion of the host rocks and siliciclastic components of the soil cover. Although there is no non-carbonate host rock found around Songjia Cave, there are some siliciclastic components in the host rock of the Late Permian limestone (Zhou et al., in press). The overlying soil layer on the limestone capping the cave results from aeolian sediments and thus should be another important source of REEs to SJ3 (Gallet et al., 1996; Ding et al., 1998). The Mn in SJ3 should have similar sources, especially the overlying soil layer may be more important in providing Mn to SJ3 relative to the siliciclastic portion of the host rocks because MnO in aeolian sediments in the Loess Plateau amounts to 0.1% (Gallet et al., 1996).

Mn could be transported mainly as organic complexes (Richter et al., 2004), colloidal hydroxides and/or particle in groundwater. Although all the three mechanisms might be responsible for the Mn deposited in SJ3, the latter two, colloidal and particle phases, appear more likely, based on the following evidence. First, in the cave waters, Mn and Al concentrations decrease more than 6 times after filtering with a 0.45  $\mu\text{m}$  membrane (Fig. 3, Table 1), and the concentrations of the two elements are closely correlated with a linear positive relationship (Fig. 4), suggesting that like Al, most of the Mn in the cave waters is in colloidal/particle phases. Second, the Mn/Ca for the unfiltered cave waters averages  $\sim 25$  ppm. This value is in

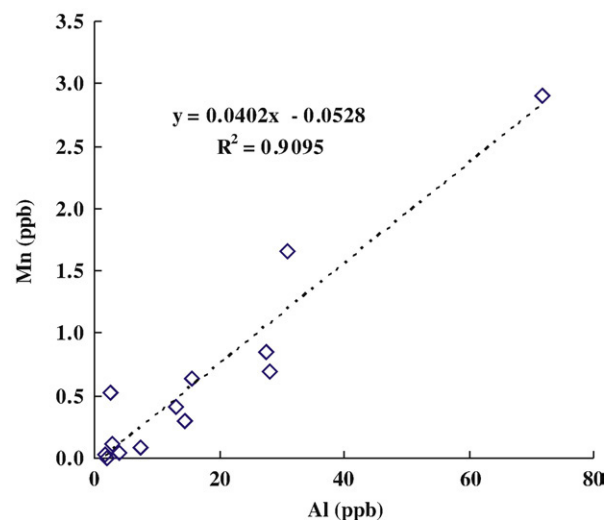


Figure 4. Linear positive correlation between the concentrations of Al and Mn in cave waters and river water.

excellent agreement with the average Mn concentration of  $\sim 9900$  ppb for the pigmented portion of SJ3, which seems to suggest that the ratio of Mn to Ca in SJ3 records directly the Mn/Ca of its parent water considering that the present-day intensity of summer monsoon may be similar to that during the last deglacial period (Yuan et al., 2004; Dykoski et al., 2005). This is not consistent with the distribution coefficient of Mn between calcite and its parent solution which is much greater than unity (Veizer, 1983 and references therein), suggesting that most of the Mn in SJ3 may not be incorporated into carbonate lattice, but is presented as non-carbonate minerals. Finally, despite the similarity between the general trends of Mn and P, there are some apparent differences between the two records, especially at the transition from the cold phase associated with H1 to the warm-humid B/A period (Fig. 2). Speleothem P was previously suggested to come from vegetation decomposition (Huang et al., 2001) and might be chelated to organic acids (Samadi and Gilkes, 1998).

REEs are mobilized during weathering processes by dissolution or alternation of host minerals in the soil cover and in the transition zone between rock and soil. Since most natural waters have extremely low REE abundances, previously it was generally assumed that substantial REE mobility is unlikely for expected fluid/rock ratios. However, many field-based studies have suggested REE mobility during weathering (McLennan, 1989; Ji et al., 2004). REEs in groundwater may exist as free ions, complexes (e.g. carbonate ( $\text{CO}_3^{2-}$ ), hydroxide ( $\text{OH}^-$ ) or organic complexes) (Brookins, 1989; McLennan, 1989) or adsorbed on mineral surface. The model for REEs mobilization proposed by Nesbitt (1979) is as follows: (1) aggressive  $\text{CO}_2$  and organic acid-charged rainwater percolates through soil horizons where some REEs are removed into solution, most likely as complexes; and (2) waters continue to migrate down and react with less altered minerals and meanwhile their pH values increase and the rare-earth elements come out of solution, either precipitated as compounds, exchanged for  $\text{H}^+$  on suitable clays or adsorbed on mineral

Table 1  
Al and Mn concentrations in cave waters and river water

Sample ID	Locus	Water type	Al/ppb		Mn/ppb	
			Unfiltered	Filtered	Unfiltered	Filtered
SJDO	Songjia Cave	Pool water	13.1	4.11	0.407	0.043
SJDE	Songjia Cave	Pool water	27.5	2.74	0.849	0.111
LFDPW	Loufang Cave	Pool water	30.9	1.82	1.665	0.025
LFDDW	Loufang Cave	Drip water	14.4	2.02	0.299	0.006
SID	Shizi Cave	Pool water	28.0	7.37	0.690	0.084
LDW	Longdongwan Cave	Pool water	71.8	2.51	2.908	0.524
RW	Nuoshui River	River water	15.6		0.634	

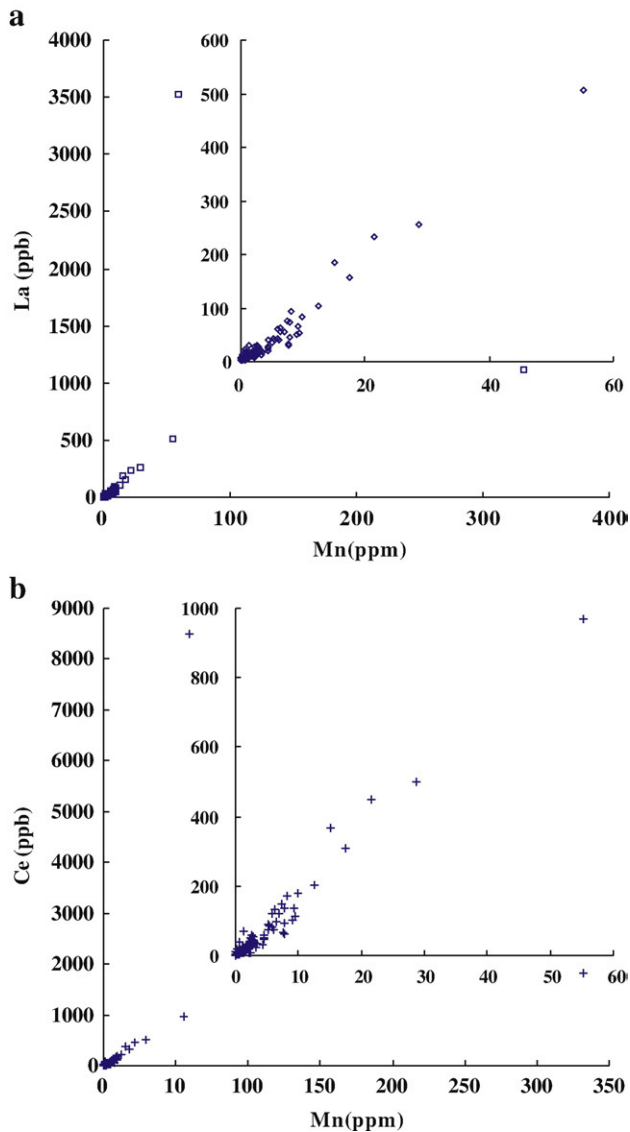


Figure 5. Correlations between Mn and La (a) and Ce (b) in SJ3. It is clear that Mn correlates positively with the REEs in SJ3. For each correlation, the inset shows an enlargement for clarity.

surface. As to the REEs in SJ3, we suggest that at least a good portion of them may be related with colloidal/particle phases of Al, Mn and Fe etc in groundwater. This is supported by: that (1) the REEs show high coherence with Mn in SJ3 (Figs. 2, 5); (2) natural Mn and REEs have been found to occur commonly jointly (Richter et al., 2004); and (3) most of the Al and Mn were removed from cave waters after filtering with a 0.45  $\mu\text{m}$  membrane (Fig. 3, Table 1), suggesting dominance of colloidal/particle phases of Al and Mn in the cave waters. Previous researches also suggested that for the most common weathering conditions, REEs are dominantly transported from weathering profile by mechanical processes (Nesbitt, 1979; Middelburg et al., 1988). Studies on REEs in seawater and foraminiferal test indicate that coatings of FeMn-rich phase on detrital particle and foraminiferal test were greatly enriched in REEs (Palmer, 1985; Sholkovitz et al., 1994). Thus we suggest that most of the REEs in SJ3 may have been transported in groundwater in

association with colloidal/particle phases of Al, Mn and Fe etc and deposited in SJ3 along with these materials. However, this needs further investigation.

When Mn and REEs transported in colloidal/particle phases in groundwater precipitate on speleothem, they might not be incorporated into the calcite lattice. Instead, they may be associated with non-carbonate minerals and presented as inclusions in speleothem. Thus the Mn and REEs we measured in SJ3 using ICP-MS (Fig. 2) are possibly different from those detected by Richter et al. (2004) using CL because only Mn and REEs incorporated into the crystal lattice of speleothem can produce luminescence emission and can be detected using CL (Gaft et al., 2005). The Mn and REEs measured by ICP-MS should include both those associated with non-carbonate mineral inclusions and those incorporated into the crystal lattice of calcite. In SJ3, however, the Mn and REEs in association with non-carbonate mineral inclusions may be dominant.

Comparison of the data presented here with those reported by Richter et al. (2004), however, indicates that the REE concentrations in SJ3 are (1–2) magnitudes lower than those obtained in the seven German stalagmites they measured. This may be explained with two causes. (1) The absolute concentrations of REEs in SJ3 may be significantly different from those in the German stalagmites, which may be related with distinct geological settings. (2) The distribution of REEs in speleothems is very inhomogeneous. While Richter et al. (2004) obtained the maximum values using the CL method, representing only part of the annual carbonate precipitation, the concentrations we measured using the ICP-MS method represents averages of at least several years (Thomas Götte, personal communication, 2007). If the average concentrations of REEs don't differ significantly between SJ3 and the German stalagmites, the 1–2 magnitudes difference between the values obtained here and reported by Richter et al. (2004) implies that calcite with high REEs as revealed by CL analysis accounts for only a very small proportion of the annual precipitation of calcite. However, this seems to be unlikely and thus we suggest that the first cause should be significant.

Although Mn and REEs in SJ3 may be distributed inhomogeneously in the annual precipitation of calcite, their long-term trends (e.g. on centennial to millennial time scale) appear to be well correlated with climate change, especially with variations in the Asian summer monsoon. For example, the significant increase in Mn and REEs in SJ3 since 14.6–14.5 ka corresponds exactly with the onset of the last deglaciation in northern high latitude (Grootes et al., 1993; Stuiver et al., 1995; Fig. 2) and the quick and sharp strengthening of the East Asian summer monsoon (Wang et al., 2001; Dykoski et al., 2005).

Fleet (1984) reported that warm and humid climate would increase REE mobilization in weathering processes. This may be due to increased  $p\text{CO}_2$  in soil air and reduced pH value in soil solution because of enhanced microbial activity and organic decomposition in soil, and increased organic matter concentration in soil and groundwater under warm and humid climate (McCarthy et al., 1998; Spötl et al., 2005). More dynamic hydrology of groundwater under warm and humid climate (Banner et al., 1996) would also contribute to REE mobilization and transportation. These mechanisms should also be applicable

for Mn. In addition, the O<sub>2</sub> content of soil air would be lowered by increased microbial activity under warm and humid climate (Richter et al., 2004), which should accelerate Mn mobilization and transportation. Therefore, we speculate that under warm and humid climate, more Mn and REEs are mobilized and removed from soil cover and host rock, transported in groundwater with most of Mn in colloidal/particle phases while most REEs may be complexed with hydroxides of Al, Mn and Fe etc, or adsorbed on colloidal/particle phases, eventually leading to higher concentrations of Mn and REEs in speleothem. This is consistent with what is observed in SJ3 (Fig. 2) because in the Asian monsoon domain, stronger summer monsoon is usually accompanied with higher temperature and more precipitation (Liu et al., 1985; An, 2000), which would enhance Mn and REE mobilization from the overlying soil layer and the host rock as well as their transportation in groundwater.

Thus the mechanisms for the Mn and REEs in SJ3 appear to be similar to that suggested by Richter et al. (2004) for these elements detected in the German stalagmites using CL. However, as mentioned above, the Mn and REEs detected by Richter et al. (2004) in the German stalagmites using CL may be incorporated into crystal lattice and come from dissolved phase of Mn and REEs in groundwater; while the majority of the Mn and REEs measured in SJ3 by ICP-MS should come from colloidal/particle phases of Mn and REEs in groundwater and may be presented in association with non-carbonate inclusions in SJ3. Both the researches presented here and reported by Richter et al. (2004) may suggest that under warm and humid climate, Mn and REEs in groundwater increase in both dissolved and colloidal/particle phases.

Other than the remarkable increases in concentration, Mn and REEs also display significant centennial fluctuations since the last deglaciation compared with the relatively stable state before 14.6–14.5 ka (Fig. 2). While interpreting the intra-annual variations of Mn and REEs in the German stalagmites, Richter et al. (2004) suggested that these elements were mobilized during the summer and autumn with more intense weathering in the soil sequences, but they were removed from soil in autumn as a result of long-lasting rainfall and a lower potential evapotranspiration. This annual two-step mechanism, however, may not be applicable for the significant centennial fluctuations of Mn and REEs in SJ3. It seems unlikely that Mn and REEs are mobilized in soil in some years and are removed from soil in the following years. On a centennial time scale, the weathering intensity should not fluctuate as significantly as illustrated by Mn and REEs in Figure 2. A possible explanation may be that these significant fluctuations of Mn and REEs reflect flushing events which are caused by rainfall extremes recharging karstic aquifers. This seems to be supported by the extremely high concentrations of Mn and REEs in the top porous 6 mm of SJ3. Other than growth hiatuses, detrital grains could be found in this part under microscope, suggesting that this part may have developed after the flow path for SJ3 was changed and when SJ3 was occasionally fed by drip water during rainfall extremes. Therefore, while the increased concentrations of Mn and REEs indicate enhanced weathering since the last deglaciation, the significant fluctuations of Mn

and REEs may reflect the hydrological dynamics of paleo-groundwater.

It might be noted that the Younger Dryas (YD) cooling event, which is evident in the GISP2 ice core record (Grootes et al., 1993; Stuiver et al., 1995) and the Hulu and Dongge speleothem records (Wang et al., 2001; Yuan et al., 2004; Dykoski et al., 2005), was not recorded by the Mn and REEs in SJ3 (Fig. 2). In another paper (Zhou et al., *in press*), it was indicated that the YD event recorded by the  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  for SJ3 was short-lived (Fig. 2) and was different from that revealed by the GISP2 ice cores in northern high latitude (Grootes et al., 1993; Stuiver et al., 1995) and the speleothem records from Hulu and Dongge caves (Wang et al., 2001; Yuan et al., 2004; Dykoski et al., 2005). This may impact the imprint of the YD event in the Mn and REEs records for SJ3. On the other hand, however, the speleothem  $\delta^{18}\text{O}$  record from the nearby Heshang Cave doesn't show the YD cooling event either (Hu et al., 2005). In the west Pacific, whether the YD event is recorded by marine sediments is also still in controversy (Zhou et al., 2007). Anyway, the reason why the YD cooling event has no effect on the Mn and REE records for SJ3 is not clear at present and more investigations should be carried out in the future.

## Conclusions

In stalagmite SJ3 collected from Songjia Cave in Central China, Mn and REEs vary significantly during the period between 20 and 10 ka, with higher concentrations occurring under relatively warm and humid climate and lower concentrations under cold-dry climate. The Mn and REEs show remarkable increases since 14.6–14.5 ka, suggesting enhanced weathering of the overlying soil cover and the host rock since the onset of the last deglaciation (Grootes et al., 1993; Stuiver et al., 1995) and the strengthening of the Asian summer monsoon (Wang et al., 2001; Yuan et al., 2004; Dykoski et al., 2005). This work suggests that the relationship between speleothem Mn and REEs records and the weathering process, first identified by Richter et al. (2004) in the German stalagmites, should be wider in extent. However, unlike the Mn and REEs detected by Richter et al. (2004) in the German stalagmites, which may be incorporated into crystal lattice, the Mn and REEs measured in SJ3 by ICP-MS should come largely from colloidal and particle phases of Mn and REEs in groundwater and may be associated with non-carbonate inclusion in SJ3. Mn and REEs in SJ3 display significant centennial fluctuations since the last deglaciation, which may reflect the hydrological dynamics of paleo-groundwater. Therefore, the Mn and REEs in SJ3 could serve as appropriate proxies for weathering intensity and hydrological dynamics of paleo-groundwater.

## Acknowledgments

We sincerely thank an anonymous reviewer for his thorough reviews and comments on this paper, and the senior editor (ES) for his comments and editing of this paper. Thanks are also due to Ms. Liu Ying and Mr. Deng Wenfeng for their help with cave water analysis, and to Mr. Huang Jie and Wu Zheng for their help in sample collection. The research is financially supported

by the project of NNSFC (40672120) and the Pilot Project of Chinese Academy of Sciences (KZCX3-SW-152).

## References

- An, Z.S., 2000. The history and variability of the East Asian paleomonsoon climate. *Quaternary Science Reviews* 19, 171–187.
- Baker, A., Ito, E., Smart, P.L., McEwan, R.F., 1997. Elevated and variable values of C-13 in speleothems in a British cave system. *Chemical Geology* 136, 263–270.
- Banner, J.L., Musgrove, M., Asmerom, Y., et al., 1996. High-resolution temporal record of Holocene ground-water chemistry: tracing links between climate and hydrology. *Geology* 24, 1049–1052.
- Bar-Matthews, M., Ayalon, A., Kaufman, A., et al., 1999. The Eastern Mediterranean paleoclimate as a reflection of regional events: Sore Qcave, Israel. *Earth and Planetary Science Letters* 166, 85–95.
- Baskaran, M., Krishnamurthy, R.V., 1993. Speleothems as proxy for the carbon isotope composition of atmospheric CO<sub>2</sub>. *Geophysical Research Letters* 20, 2905–2908.
- Bureau of Geology and Mineral Resources of Sichuan Province, 1991. Regional Geology of Sichuan Province. Geological Publishing House, Beijing.
- Brookins, D.G., 1989. Aqueous geochemistry of rare earth elements. In: Lipin, B.R., Mckay, G.A. (Eds.), *Geochemistry and Mineralogy of Rare Earth Elements*. Mineralogical Society of America, Washington D. C., pp. 200–225.
- Ding, Z.L., Sun, J.M., Liu, T.S., Zhu, R.X., Yang, S.L., Guo, B., 1998. Wind-blown origin of the Pliocene red clay formation in the central Loess Plateau, China. *Earth and Planetary Science Letters* 161, 135–143.
- Dorale, J.A., Edwards, R.L., Ito, E., González, L.A., 1998. Climate and vegetation history of the midcontinent from 75 to 25 ka: a speleothem record from Crevice Cave, Missouri, USA. *Science* 282, 1871–1874.
- Dykoski, C.A., Edwards, R.L., Cheng, H., Yuan, D., Cai, Y., Zhang, M., Lin, Y., Qin, J., An, Z., Revenauh, J., 2005. A high-resolution, absolute-dated Holocene and deglacial Asian monsoon record from Dongge Cave, China. *Earth and Planetary Science Letters* 233, 71–86.
- Edwards, R.L., Chen, J.H., Wasserburg, G.J., 1987. <sup>238</sup>U-<sup>234</sup>U-<sup>230</sup>Th-<sup>232</sup>Th systematics and the precise measurement of time over the past 500,000 years. *Earth and Planetary Science Letters* 81, 175–192.
- Eggins, S.M., Woodhead, J.D., Kinsley, L.P.J., et al., 1997. A simple method for the precise determination of >40 trace elements in geological samples by ICPMS using enriched isotope internal standardisation. *Chemical Geology* 134, 311–326.
- Fairchild, I.J., Baker, A., Borsato, A., Frisia, S., Hinton, R.W., McDermott, F., Tooth, A.F., 2001. High-resolution, multiple trace-element variation in speleothems. *Journal of the Geological Society* 158, 831–841.
- Fairchild, I.J., Smith, C.L., Baker, A., Fuller, L., Spötl, C., Matthey, D., McDermott, F., E.I.M.F., 2006. Modification and preservation of environmental signals in speleothems. *Earth-Science Reviews* 75, 105–153.
- Fang, X.M., Li, J.J., Van der Voo, R., 1999. Age and provenance of loess in West Qinling, China. *Science Bulletin* 44 (23), 2188–2192.
- Fleet, A.J., 1984. Aqueous and sedimentary geochemistry of rare earth elements. In: Henderson, J. (Ed.), *Rare Earth Element Geochemistry*. Elsevier, Amsterdam, pp. 343–373.
- Frumkin, A., Stein, M., 2004. The Sahara-East Mediterranean dust and climate connection revealed by strontium and uranium isotopes in a Jerusalem speleothem. *Earth and Planetary Science Letters* 217, 451–464.
- Gaft, M., Reisfeld, R., Panczer, G., 2005. Luminescence spectroscopy of minerals and materials. Springer 119–168, 200–209.
- Gallet, S., Jahn, B.M., Torii, M., 1996. Geochemical characterization of loess–paleosol sequence from the Luochuan section, China and its paleoclimatic implications. *Chemical Geology* 133, 67–88.
- Genty, D., Blamart, D., Ouahdi, R., Gilmour, M., Baker, A., Jouzel, J., van Exter, S., 2003. Precise dating of Dansgaard–Oeschger climate oscillations in western Europe from stalagmite data. *Nature* 421, 833–837.
- Goede, A., McCulloch, M., McDermott, F., et al., 1998. Aeolian contribution to strontium and strontium isotope variations in a Tasmanian speleothem. *Chemical Geology* 149, 37–50.
- Grootes, P.M., Stuiver, M., White, J.W.C., Johnsen, S., Jouzel, J.J., 1993. Comparison of oxygen isotope records from the GISP2 and GRIP Greenland ice cores. *Nature* 366, 552–554.
- Holmgren, K., Karlén, W., Shaw, P.A., 1995. Paleoclimatic significance of the stable isotopic composition and petrology of a late Pleistocene stalagmite from Botswana. *Quaternary Research* 43, 320–328.
- Hu, C.-Y., Huang, J.-H., Fang, N.-Q., et al., 2005. Adsorbed silica in stalagmite carbonate and its relationship to past rainfall. *Geochimica et Cosmochimica Acta* 69, 2285–2292.
- Huang, Y.M., Fairchild, I.J., Borsato, A., Frisia, S., Cassidy, N.J., McDermott, F., Hawkesworth, C.J., 2001. Seasonal variations in Sr, Mg and P in modern speleothems (Grotta di Ernesto, Italy). *Chemical Geology* 175, 429–448.
- Ji, H.B., Wang, S.J., Ouyang, Z.Y., Zhang, S., Sun, C.X., 2004. Geochemistry of red residua underlying dolomites in karst terrains of Yunnan–Guizhou Plateau II. The mobility of rare earth elements during weathering. *Chemical Geology* 203, 29–50.
- Kamber, B.S., Greig, A., Schoenberg, R., Collerson, K.D., 2003. A refined solution to Earth’s hidden niobium: implications for evolution of continental crust and mode of core formation. *Precambrian Research* 126, 289–308.
- Kaufman, A., Wasserburg, G.J., Porcelli, D., et al., 1998. U–Th isotope systematics from the Soreq cave, Israel and climatic correlations. *Earth and Planetary Science Letters* 156, 141–155.
- Lawrence, M.G., Greig, A., Collerson, K.D., Kamber, B.S., 2006. Rare earth element and yttrium variability in South East Queensland waterways. *Aquatic Geochemistry* 12, 39–72.
- Lei, X.Y., Yue, L.P., Wang, J.Q., et al., 1998. Magnetic characteristics and their paleoclimatic significance of Fengzhou loess in the Qinling Mountains of China. *Chinese Science Bulletin* 43, 1571–1575.
- Li, H.-C., Ku, T.-L., You, C.-F., et al., 2005. <sup>87</sup>Sr/<sup>86</sup>Sr and Sr/Ca in speleothems for paleoclimate reconstruction in Central China between 70 and 280 kyr ago. *Geochimica et Cosmochimica Acta* 69, 3933–3947.
- Liu, T.S., et al. (Ed.), 1985. *Loess and Environment*. China Ocean Press, Beijing, pp. 1–234.
- McCarthy, J.F., Sanford, W.E., Stafford, P.L., 1998. Lanthanide field tracers demonstrate enhanced transport of transuranic radionuclides by natural organic matter. *Environmental Science & Technology* 32, 3901–3906.
- McDermott, F., 2004. Palaeo-climate reconstruction from stable isotope variations in speleothems: a review. *Quaternary Science Reviews* 23, 901–918.
- McLennan, S.M., 1989. Rare earth elements in sedimentary rocks: influence of province and sedimentary processes. In: Lipin, B.R., Mckay, G.A. (Eds.), *Geochemistry and Mineralogy of Rare Earth Elements*. Mineralogical Society of America, Washington D.C., pp. 169–200.
- Mickler, P.J., Banner, J.L., Stern, L., Asmerom, Y., Edwards, R.L., Ito, E., 2004. Stable isotope variations in modern tropical speleothems: evaluating applications to paleoenvironmental reconstructions. *Geochimica et Cosmochimica Acta* 68, 4381–4393.
- Middelburg, J.J., van der Weijden, C.H., Woitiez, J.R.W., 1988. Chemical processes affecting the mobility of major, minor and trace elements during weathering of granitic rocks. *Chemical Geology* 68, 2253–2273.
- Musgrove, M., Banner, J.L., Mack, L.E., Combs, D.M., James, E.W., Cheng, H., Edwards, R.L., 2001. Geochronology of late Pleistocene speleothems from Central Texas: implications for regional paleoclimate. *Geological Society of America Bulletin* 113, 1532–1543.
- Nesbitt, H.W., 1979. Mobility and fractionation of rare earth elements during weathering of a granodiorite. *Nature* 279, 206–210.
- Palmer, M.R., 1985. Rare earth elements in foraminifera tests. *Earth and Planetary Science Letters* 73, 285–298.
- Richter, D.K., Götte, T., Niggemann, S., Wurth, G., 2004. REE<sup>3+</sup> and Mn<sup>2+</sup> activated cathodoluminescence in lateglacial and Holocene stalagmites of central Europe: evidence for climatic processes? *The Holocene* 14, 759–767.
- Roberts, M.S., Smart, P., Baker, A., 1998. Annual trace element variations in a Holocene speleothem. *Earth and Planetary Science Letters* 154, 237–246.
- Samadi, A., Gilkes, R.J., 1998. Forms of phosphorus in virgin and fertilised calcareous soils of Western Australia. *Australian Journal of Soil Research* 36, 585–601.
- Sholkovitz, E.R., William, M.L., Lewis, B.L., 1994. Ocean particle chemistry: the fractionation of rare earth elements between suspended particles and seawater. *Geochimica et Cosmochimica Acta* 58, 1567–1579.



- Spötl, C., Fairchild, I.J., Tooth, A.F., 2005. Cave air control on dripwater geochemistry, Obir Caves (Austria): implications for speleothem deposition in dynamically ventilated caves. *Geochimica et Cosmochimica Acta* 69, 2451–2468.
- Stuiver, M., Grootes, P.M., Braziunas, T.F., 1995. The GISP2 delta 18O climate record of the past 16,500 years and the role of the sun, ocean, and volcanoes. *Quaternary Research* 44, 341–354.
- Veizer, J., 1983. Chemical diagenesis of carbonates: theory and application of trace element technique. In: Arthur, M.A., et al. (Ed.), *Stable Isotopes in Sedimentary Geology*, SEPM Short Course, no. 10.
- Wang, Y.J., Cheng, H., Edwards, R.L., et al., 2001. A high-resolution absolute-dated Late Pleistocene monsoon record from Hulu Cave, China. *Science* 294, 2345–2348.
- Wang, X.F., Auler, A.S., Edwards, R.L., Cheng, H., 2004. Wet periods in northeastern Brazil over the past 210 kyr linked to distant climate anomalies. *Nature* 432, 740–743.
- Yuan, D.X., Cheng, H., Edwards, R.L., et al., 2004. Timing, duration, and transitions of the last interglacial Asian monsoon. *Science* 304, 575–578.
- Zhao, J.X., Hu, K., Collerson, K.D., et al., 2001. Thermal ionization mass spectrometry U-series dating of a hominid site near Nanjing, China. *Geology* 29, 27–30.
- Zhou, J.Z., Lundstrom, C.C., Fouke, B., et al., 2005. Geochemistry of speleothem records from southern Illinois: development of  $^{234}\text{U}/^{238}\text{U}$  as a proxy for paleoprecipitation. *Chemical Geology* 221, 1–20.
- Zhou H.Y., Zhao J.X., Feng Y.X., Gagan M.K., Zhou G.Q., Yan J., in press, Synchronous and distinct heinrich event one in Central and East China recorded by stable oxygen and carbon isotopic compositions in stalagmites from China. *Quat. Res.* doi:10.1016/j.yqres.2007.11.001.
- Zhou, H.Y., Li, T.G., Jia, G.D., Zhu, Z.Y., Chi, B.Q., et al., 2007. Sea surface temperature reconstruction for the Middle Okinawa Trough during the Last Glacial-Interglacial Cycle using C37 unsaturated alkenones. *Palaeogeography, Palaeoclimatology, Palaeoecology* 240, 440–453.