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Arsenic in a Speleothem from Central China: Stadial-Interstadial Variations and Implications

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ABSTRACT: In a pilot study, arsenic in a stalagmite (SJ3) collected from Central China was measured, and its association with past climate and environment was explored. Most of the SJ3 arsenic concentrations ranged from 120 to 320 ppb with the highest concentrations associated with relatively warm and humid climatic phases and lowest concentrations with cold and dry phases. The SJ3 arsenic record was very similar to the manganese record of SJ3. Variations of arsenic in SJ3 might be controlled by metal oxides of iron, manganese, and aluminum in karst groundwater at the study site, which in turn were closely related with changes in past climate and environment. A considerable proportion of arsenic was in excess over manganese in SJ3, which might be related with incorporation of arsenic into the calcite lattice during the formation of SJ3. It was speculated that more arsenic was released due to stronger weathering of the surface soils and sequestrated by metal oxides in karst groundwater under warm-humid climatic phases than under cold-dry phases. This suggested that climate shift might alter arsenic balance in sedimentary areas and aquifer systems and potentially exert significant influence on global arsenic contamination.

1. INTRODUCTION

Arsenic is a naturally occurring element in the Earth's crust, and many soils and sediments contain small amounts of arsenic.[1] It is also one of the first chemicals recognized as a cause of cancer.[2] High levels of arsenic have been leached from natural underground sources into thousands of village wells in West Bengal, India, and hundreds of thousands of people already have arsenic-induced skin lesions, and many of them also have hyperkeratoses, hardened patches of skin that may develop into cancers.[3]

The mechanisms that are responsible for arsenic contamination in groundwaters are only just starting to be understood, and attention has been largely focused on the sources of arsenic and its release into groundwater.[4,5] Much less attention has been paid to the effect of long-term climate changes, especially major climate shifts on glacial-interglacial or stadial-interstadial (Stadial or interstadial refer to a cold or warm period which is subordinate in duration and intensity to a glacial or interglacial period) time scales.[6,7] Krachler et al.[7] found that arsenic concentration in an Arctic ice core was elevated by a factor of 5 during Greek/ Phoenician, Roman, and Medieval periods and that the arsenic concentration during the Younger Dryas cold climate event is the highest during the last 16 thousand years (ka). This suggests that climate shifts may alter arsenic release and accumulation and break the balance of arsenic influx and efflux in sedimentary areas and aquifer systems. For example, in their study of the arsenic release and transport within the arsenic-contaminated Mekong

River floodplain of Cambodia, Polizzotto et al.[8] found that an annual arsenic efflux of $(2-20) \times 10^5$ kg from the aquifer through flushing and an annual influx of $(6-20) \times 10^5$ kg of arsenic to the aquifer system via sediment deposition were comparable and in equilibrium, but this equilibrium may be broken if major climate shifts lead to significant changes in arsenic release from surface soils and rocks and accumulation in sedimentary areas.

Unlike unconsolidated materials such as soils and Quaternary alluvial sediments of which the arsenic concentration may be influenced by groundwater, speleothem carbonates (Speleothems are secondary cave sediments, mostly formed in limestone or dolostone solutional caves.) are seldom altered by postdepositional processes unless redissolution takes place. Speleothems should be valuable for providing information on long-term changes in arsenic release, transport, and accumulation in response to climate shifts and thus should be of great significance for assessing arsenic balance in sediment areas and aquifer systems in response to global climate changes.

The objectives of this study were to investigate stadial-interstadial changes of arsenic in a precisely dated speleothem from
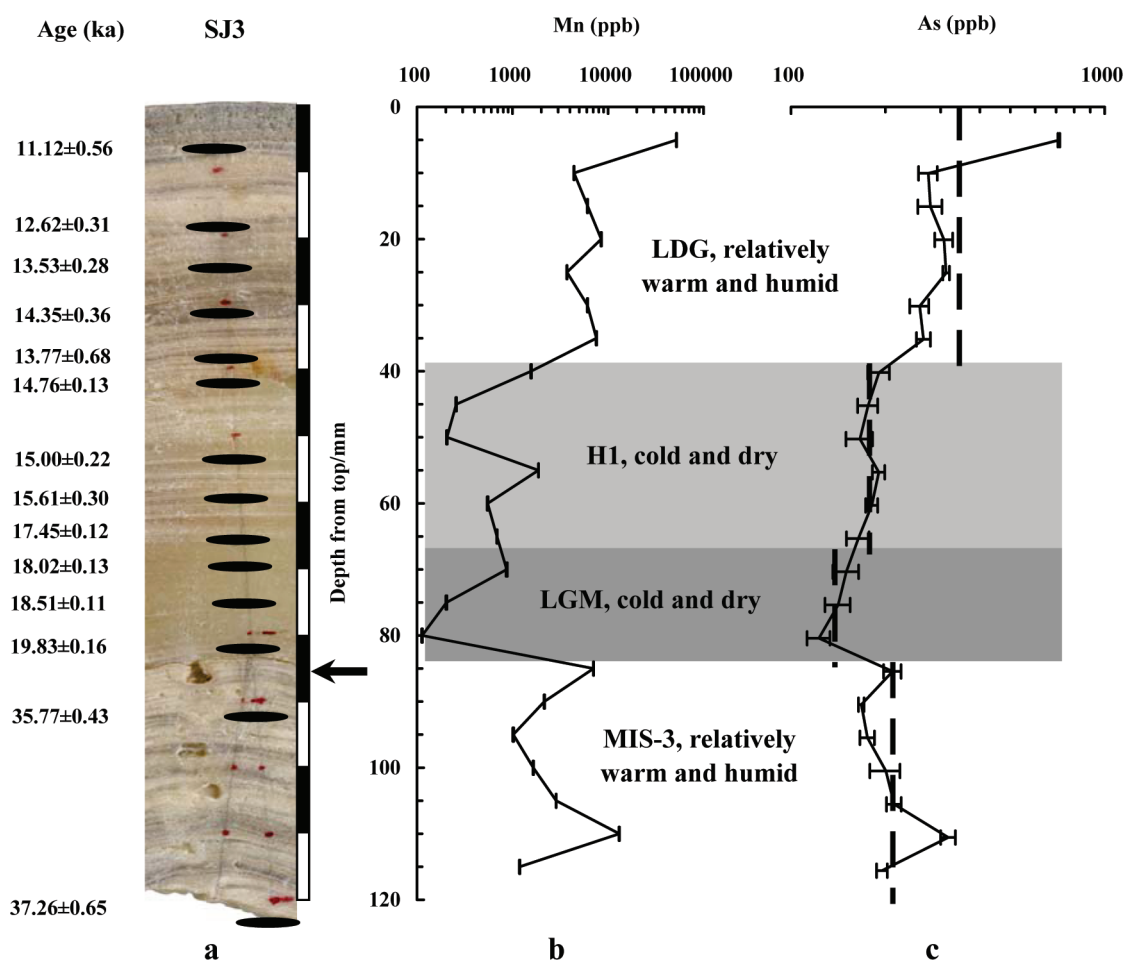
Figure 1. Image of stalagmite SJ3 (a) and its manganese (b) and arsenic (c) concentrations. Black ellipses on the image of SJ3 indicate the locations of ^{230}Th dates which are listed to the left. The black arrow indicates the hiatus corresponding to growth cessation from 35 to 20 ka. On the manganese and arsenic records the two gray rectangles highlight the cold and dry climatic phases during the LGM and H1 periods. Error bars on the manganese and arsenic records represent 1 σ analytical uncertainties. The thick dashed lines on the arsenic record represent average arsenic concentrations for each period.

Central China, their association with past climate and environment, possible controlling mechanisms and implications.

2. GEOLOGICAL BACKGROUNDS, SAMPLE DESCRIPTION, AND ANALYTICAL METHODS

The speleothem sample (stalagmite SJ3) used in this study was collected from Songjia Cave (107°10′45″E, 32°24′46″N) in Central China in the East Asian summer monsoon (EASM) regime. The initial chronology established by Zhou et al.[9] was revised by Zhou et al.[10] using additional ^{230}Th dates. The geological setting and the sample have been described in detail in Zhou et al.[9] In brief, Songjia Cave is hosted in the Late Permian limestone[11] and is located in the south flank of the Qinling Mountain. This site currently experiences a typical summer monsoon climate with an annual mean temperature of ~15 °C and an annual mean precipitation between 1000 and 1200 mm.[12] The highest temperature occurs during the summer season and most of the precipitation falls from May to October.[10] The site is also significantly influenced by the Asian winter monsoon at present and atmospheric dust activity is intensive during the winter season. Local soils derive from aeolian sediments. The overlying soil layer on the limestone capping the cave is thin

(usually less than 30 cm) or absent in places. Local vegetation consists mainly of trees including pine, cypress, and some deciduous broadleaf species.

SJ3 is 12.6-cm long and was found by the ^{230}Th dating technique to have developed between ~38 and ~10 ka before present.[10] However, a growth hiatus is apparent on the lengthwise cut surface at depth of ~84 mm from its top (Figure 1-a), corresponding to a growth cessation between ~35 and 20 ka. Therefore SJ3 formed during part of marine isotope stage (MIS) 3 (38−35 ka), the last glacial maximum (LGM) (20−17.6 ka), the period synchronous with the Heinrich Event one (H1) (17.6−14.6 ka), and the last deglacial period (LDG) (14.6−10 ka). The LGM and H1 are cold and dry climatic phases in the EASM regime compared with the LDG and MIS 3 periods which are relatively warm and humid. The top 6 mm of SJ3 is dirty and porous.

The subsamples for arsenic analysis were obtained from the cleaned cut surface of SJ3, along the growth axis, using a microdrill with a sampling interval of 5 mm. Arsenic concentrations were measured by external calibration on a Thermo X-series ICP-MS in the ACQUIRE laboratory at the University of Queensland. Arsenic in sediments is often found naturally bound by metal oxides, particularly those of iron, aluminum, and

manganese,[13] so manganese was also measured in SJ3. Iron was not measured due to iron contamination from the drill bit used and due to the lack of an appropriate standard aluminum could not be analyzed. For each subsample, four to five micrograms of calcite powder was dissolved at room temperature in a 10-cm^3 tube. A 2% double distilled HNO_3 solution spiked with a 6 ppb multi-isotope internal standard consisting of ^6Li-^{84}Sr-^{115}In-^{187}Re-^{235}U was used, and sample dilution factors were about 1200. After sample dissolution, the tubes were capped tightly before the subsamples were analyzed following methods described in Eggins et al.[14] and Lawrence et al.[15] According to the method introduced by Querol et al.,[16] the sample preparation procedures we used will not result in a loss of volatile elements such as arsenic. The minimum detection limit for arsenic is less than 15 ppt in solution, and the relative standard deviations (RSD) for arsenic measurement are usually less than 10% for lower concentrations (e.g., during the H1 and LGM phases) and less than 6% for higher concentrations (e.g., during the LDH and MIS-3 phases).

The country rock of the Late Permian limestone hosting Songjia Cave, overlying soil layer and waters in Songjia Cave were also sampled for arsenic analyses. Three rock samples were collected from the limestone capping the cave and four soil samples were obtained from a soil profile above the cave, ~40 cm in depth and each represents a 10-cm interval. Two pool waters from Songjia Cave were sampled. Water samples were put into 500 mL bottles which had been precleaned and rinsed three times and immediately acidified to pH < 2 with doubly distilled HNO_3 before the samples were transported to the laboratory for analysis. Arsenic concentrations in the limestone, soils, and waters were determined by atomic fluorescence spectrometer (AFS-230a) at the Instrumental Analysis and Research Center in Sun Yat-sen University. Pretreatment of the soil and rock samples follows the Chinese national standard protocol for soil arsenic analysis (GB/T 22105.2-2008). The minimum detection limit for arsenic is less than 2 ppb in solution, and the RSDs are less than 10%. Cave waters collected from Songjia Cave and nearby other caves were also measured for aluminum, manganese, and iron before and after filtering with 0.45 μm Millipore membranes. Aluminum and manganese were analyzed with ICP-AES at the Guangzhou Institute of Geochemistry.[17] Iron was determined at the EDSRC of National Cheng-Kung University with a SF-ICP-MS (Element 2, Thermo Fisher Scientific).

3. RESULTS AND DISCUSSION

3.1. Arsenic in SJ3 and Stadial-Interstadial Variations. Except for the subsample from the top dirty part of SJ3, arsenic concentrations ranged from 120 to 320 ppb in SJ3 (Figure 1c). A general trend was clear in the SJ3 arsenic record with higher concentrations occurring during the relatively warm and humid climate phases such as the LDG and MIS-3 and lower concentrations during the cold and dry H1 and LGM phases. The average arsenic concentration for the LDG period was 344 ppb (282 ppb if the subsample from the top dirty part of SJ3 was excluded), and for the H1, LGM, and MIS 3 periods it was 178, 138, and 211 ppb, respectively (Figure 1c).

3.2. Possible Sources of Arsenic. Most of the metals in SJ3 were likely to be derived from the host rock and overlying soil layer. Other possible sources include atmospheric deposition and sea sprays. Arsenic concentration in seawater is very low (typically around 1.5 μg L^{-1}, see Table 1 in ref 13) and the

Table 1. Arsenic Concentrations in the Limestone Host Rock, Overlying Soil Layer and Cave Waters of Songjia Cave

samples	As (μg/g)
Soil	
SJ-SI-Soil-1	14.4
SJ-SI-Soil-2	16.3
SJ-SI-Soil-3	15.2
SJ-SI-Soil-4	15.5
Limestone	
SZ-in	0.09
SI-SJ	0.07
LF-SZ	0.05
Cave Waters	
SJDE	<0.002
SJDO	<0.002

study site is more than 1000 km away from coastline,[10] so arsenic contribution from sea spray should be negligible. In general, atmospheric precipitation contributes little arsenic to surface and groundwater bodies unless significantly contaminated with industrial sources of arsenic.[13] In addition, the overlying soil layer at the study site derived mainly from aeolian sediments. Any arsenic contribution from atmospheric dust, if significant, could be regarded as a contribution from the overlying soil layer. The limestone host rock had low arsenic concentrations (Table 1) because it was precipitated from seawater which usually had a very low arsenic concentration.[13] The overlying soil layer had arsenic concentrations ranging from 14 to 16 ppm (Table 1), consistent with arsenic concentrations in the aeolian sediments deposited on the Loess Plateau.[18] The arsenic concentration in the overlying soil layer was more than 100 times higher than in the limestone. Because strontium isotopes indicated that the soil layer was a major source of the strontium deposited in SJ3,[10] despite the soil having a lower strontium concentration than the limestone (unpublished data), the arsenic in SJ3 was inferred to be dominantly derived from the overlying soil layer.

3.3. Mechanisms Controlling Speleothem Arsenic. The general trend of the SJ3 arsenic record was very similar to the variations shown by manganese (Figure 1b-c). Arsenic and manganese displayed relatively higher concentrations during the relatively warm and humid phases and lower concentrations during cold and dry phases. The correlation coefficient *r* (0.96) between the two elements was high (Figure 2). The top subsample had a much higher arsenic concentration (715 ppb) relative to other subsamples (120–320 ppb), which was similar to the distribution of manganese in SJ3 (Figure 1b-c). Even if the top subsample was excluded, a high correlation could still be observed between arsenic and manganese (r^2=0.70; Figure 2). The close correlation between arsenic and manganese in SJ3 suggested that a similar correlation might also have existed in the paleo-groundwaters from which SJ3 precipitated. This was also consistent with modern observations that the high-arsenic groundwaters of the Bengal Basin were high in iron, manganese, HCO_3^-, and phosphorus with pH values close to or greater than 7.[13]

Manganese concentrations in karst groundwater at the site showed excellent positive linear correlations with aluminum [17] and iron, elements that were transported mainly in particulate phases (probably as hydroxides and oxides, collectively referred to as oxides hereafter) (Figure 3). The importance of oxides in

controlling the concentration of arsenic in natural waters had been appreciated for a long time.[19] The major minerals binding arsenic (as both arsenate and arsenite) in sediments were the metal oxides, particularly those of iron, aluminum, and manganese, because of the strong adsorption affinity of these oxides.[20,21] In other studies selective extractions suggested that most of the arsenic in sediments was associated with iron and manganese oxides. For example, Riedel et al.[22] monitored the release of metals when a column of estuarine sediment was subjected to reducing conditions for several months and found that both arsenic and manganese were released following reduction. Frequently, the element which correlated best with arsenic in sediments was iron,[13] and indeed positive correlations existed between arsenic and iron extracted from hundreds of sediment samples from the Ganges-Brahmaputra-Meghna, Mekong, and Red River basins.[23,24] Adsorption of arsenate to hydrous iron oxides was so strong that sorbed loadings can be appreciable even at very low arsenic concentrations in solution.[25] Adsorption to hydrous aluminum and manganese oxides might also be important if these oxides were present in quantity.[26,27] Therefore, although Sthiannopkao et al.[28] found that arsenic and manganese covaried in some tube well waters from Cambodia and not in others, the similarity between the SJ3 arsenic and manganese curves (Figure 1b-c) suggested that metal oxides of manganese, and probably also aluminum and iron, played a key role in the SJ3 arsenic variations.

It might be noted that the regression line between manganese and arsenic in SJ3 intersected the arsenic-axis at ~170 ppb arsenic (146 ppb if the subsample from the top dirty part of SJ3 was excluded) (Figure 2), suggesting a relatively constant arsenic excess over manganese in SJ3 (hereafter it is notated as As_{ex}). Statistically, this meant that part of arsenic content of SJ3 correlated with factors other than manganese. A similar arsenic−manganese correlation could be observed in the Quaternary travertines of the Middle Pecora Valley, Italy.[29] The As_{ex} would be expected to vary significantly if it was caused by oxides of aluminum and iron because at the study site, aluminum and iron in karst groundwater showed a high coherence with manganese[17] which displayed remarkable stadial-interstadial changes (Figure 1b). We suggest that the As_{ex} might be related to arsenic sorbtion on the surface and incorporation into the lattice of calcite.[30−33] Alexandratos et al.[31] suggested that arsenic(V) could interact strongly with the calcite surface and uptake could occur via both adsorption and coprecipitation reactions and that calcite might be effective for partial removal of dissolved arsenate from aquatic systems. Román-Ross et al.[32] found that arsenic(III) was readily coprecipitated with calcite and that an average concentration of 30 ± 6 mM/kg of arsenic(III) could be incorporated into calcite structure in the presence of high arsenic(III) concentrations. Di Benedetto et al.[29] demonstrated that in natural systems arsenic could be incorporated into calcite lattice as arsenite. Although Le Guern et al.[34] indicated that a large proportion of arsenic was trapped by rapid precipitation of iron oxyhydroxides and a smaller proportion by calcite precipitated at hydrothermal spring outlets in the Cézallier area of the
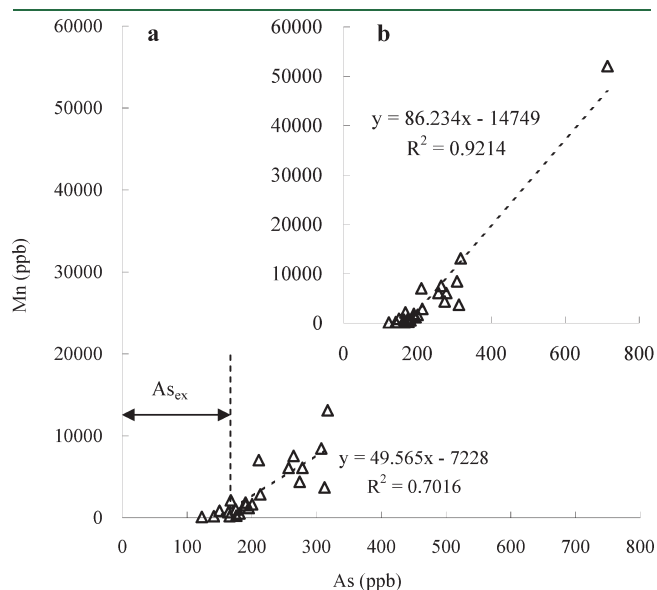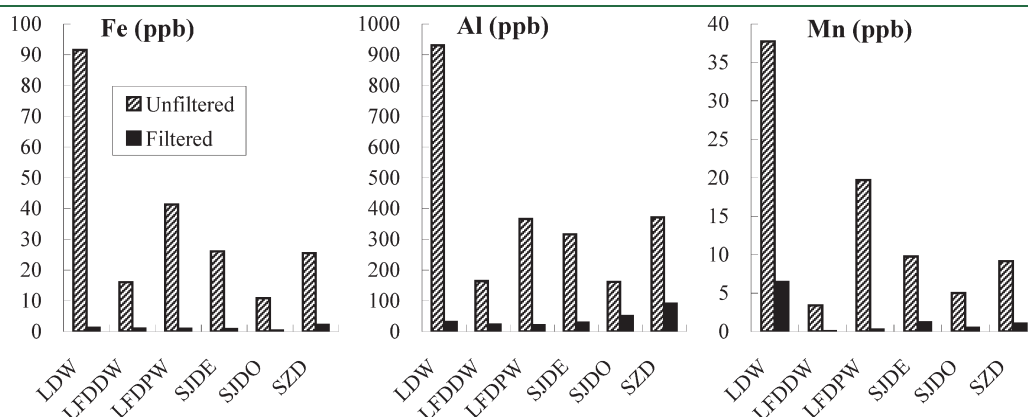

Figure 2. The linear positive correlation between arsenic and manganese in SJ3. The correlation coefficient r is very high ($r^2 = 0.92$) when the top dirty subsample was included (b). The positive correlation was still evident ($r^2 = 0.70$) if the dirty subsample was excluded (a). The arsenic−manganese correlation indicated that a considerable proportion of the arsenic in SJ3 was in excess relative to manganese (As_{ex}) which might be due to arsenic incorporation into calcite lattice during SJ3 formation.

Figure 3. Concentrations of aluminum, manganese, and iron in cave waters at the study site before and after filtering with 0.45 μm Millipore membrane. Apparently the aluminum, manganese, and iron were transported largely in particulate phases. LDW - Longdongwan Cave, pool water; LFDDW - Loufangdong Cave, drip water; LFDPW - Loufangdong Cave, pool water; SJDE - Songjia Cave, pool water near the entrance; SJDO - Songjia Cave, pool water near the outlet; SZD - Shizi Cave, pool water.

French Massif Central, iron concentrations of these springs were two to three magnitudes higher than in the karst groundwaters at the study site (Table 1 and 4 in ref34 Figure 3). In anoxic groundwaters, arsenic concentrations were found to correlate positively with concentrations of bicarbonate,[4] an anion which was far more abundant than metal oxides in karst groundwater and played a key role in speleothem formation. Thus, despite not knowing the exact species of arsenic in SJ3 and the karst groundwater at the study site, a considerable proportion of arsenic in karst groundwater might have been incorporated into SJ3 via sorption to or coprecipitation with calcite.

Because the overlying soil layer and host rock were the major sources of materials in SJ3, their weathering, both physically and chemically, would exert an important influence on the composition of SJ3. Minerals contained within the overlying soil layer were transformed to secondary phases, including oxides of iron, manganese, and aluminum under surface weathering. These were then flushed in rainfall events into groundwater and were eventually incorporated into calcareous precipitates via various processes occurring in the epikarst zone.[35] In the EASM regime, stronger summer monsoons under warm and humid climatic phases were expected to lead to more intensive weathering of the surface soil[17] and to release more arsenic as well as iron, manganese, and aluminum (probably as oxides) from the soil. However, this did not necessarily result in higher arsenic concentrations in groundwater due to the dilution effect suggested by Xiao et al.[36] The effect of climate on weathering of the host rock was complex. For example, while a warm-humid climate might lead to stronger water-rock interactions because of higher pCO_2 and lower pH groundwater, it might also result in a more dynamic hydrology and a relatively shorter residence time of karstic groundwater and hence less water-rock interaction.[37] Because iron, manganese, and aluminum were transported largely in particulate phases in karst groundwater at the study site (Figure 3), a more dynamic hydrology probably contributed to higher concentrations of iron, manganese, and aluminum in karst groundwater under warm and humid climatic phases. Arsenic was preferentially removed by metal oxides from waters, resulting in higher ratios of arsenic to metals (such as iron, manganese, and aluminum) in precipitates than in waters.[21] A combination of the two mechanisms, release from the overlying soil layer and sequestration by metal oxides in karst groundwater, might explain the higher arsenic concentrations in SJ3 under warm-humid climatic phases (Figure 1).

The nearly linear positive correlation between arsenic and manganese (Figure 2) suggested a relatively constant As$_{ex}$ under different climatic phases. The As$_{ex}$ became dominant during the cold-dry LGM and H1 phases (Figure 1). The reason why it remained stable under different climatic phases might be due to two opposite effects, i.e. a warm-humid climate led to a greater release of arsenic as well as metal oxides from the overlying soil layer, subsequently more arsenic was removed by metal oxides in karst groundwater because of the strong adsorption affinity of these oxides.

3.4. Implications. The results of the study indicated the potential for arsenic balances in sedimentary areas and aquifer systems to be broken when global climate shifts occurred because natural weathering of the surface soils and rocks provided a very important source of arsenic contamination[36,38,39] and sediments with high arsenic concentrations might serve as an important long-term arsenic source, especially under reducing conditions.[5,38,40] Therefore, global climate change, e.g. the dramatic surface temperature increase witnessed during the last one

hundred years,[41] might not only change global hydrology[42] and increase pathogen development and survival rates, disease transmission, host susceptibility, and most host-parasite systems,[43] it might also impact human health through altering the arsenic balance in sediments and groundwaters.

However, it must be noted that this study is preliminary and further research is needed. For example, the arsenic species in karst groundwater (dissolved in solution or sorbed on the surface of particulate materials; trivalent arsenite or pentavalent arsenate) and speleothem, seasonal variations in arsenic concentration and flux and their association with groundwater hydrology and meteoric precipitation at the study site, all need to be examined in the future.

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Correction to Arsenic in a Speleothem from Central China: Stadial-Interstadial Variations and Implications [*Environmental Science & Technology* **2011**, *45*, 1278–1283 DOI: 10.1021/es1032103].
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The concentration values on the *y*-axes of the Al and Mn plots of Figure 3 were accidently amplified and the corrected Figure 3 is given here. Because Figure 3 is used in the paper to indicate that (1) aluminum, manganese, and iron are transported largely in particulate phases in karst groundwater at the study site, and (2) iron concentrations in the karst groundwaters at the study site are much lower than in hydrothermal spring outlets in the Cézallier area of the French Massif Central, the corrected concentration values for Al and Mn do not impact any discussion or conclusions of the paper.
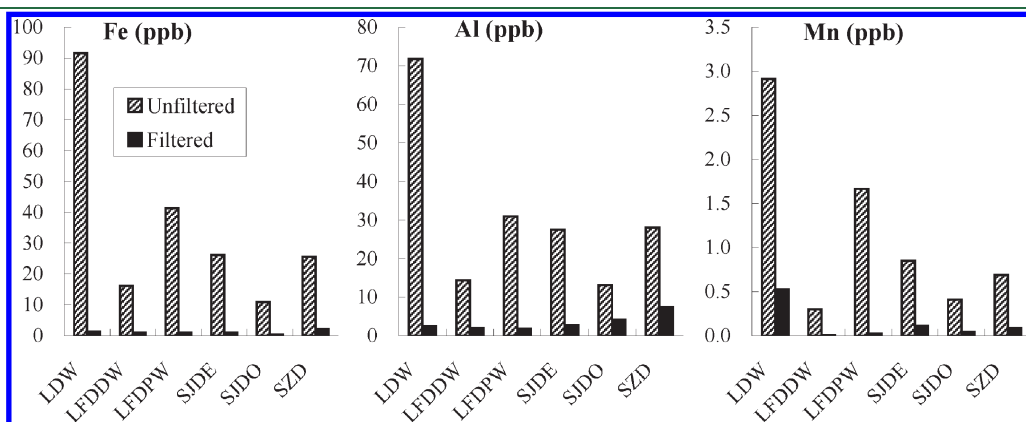

Figure 3. Concentrations of aluminum, manganese, and iron in cave waters at the study site before and after filtering with 0.45 μm Millipore membrane. Apparently the aluminum, manganese, and iron were transported largely in particulate phases. LDW - Longdongwan Cave, pool water; LFDDW - Loufangdong Cave, drip water; LFDPW - Loufangdong Cave, pool water; SJDE - Songjia Cave, pool water near the entrance; SJDO - Songjia Cave, pool water near the outlet; SZD - Shizi Cave, pool water.

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