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Lead concentrations and isotope ratios in speleothems as proxies for atmospheric metal pollution since the industrial revolution

Mohammed Allan [a,*], Nathalie Fagel [a], Maité Van Rampelbergh [b], James Baldini [c], Jean Riotte [d], Hai Cheng [e], R. Lawrence Edwards [e], David Gillikin [f], Yves Quinif [g], Sophie Verheyden [b,h]

[a] AGEs, Département de Géologie, Université de Liège, Allée du 6 Août, B18, Sart Tilman B-4000, Liège, Belgium
[b] Earth System Sciences Department, Vrije Universiteit Brussel (VUB), Pleinlaan 2, B-1050 Brussels, Belgium
[c] Department of Earth Sciences, Durham University, Durham DH1 3LE, UK
[d] Géosciences Environnement Toulouse (GET), UPS, IRD, CNRS, 31400 Toulouse, France
[e] Department of of Earth Sciences, University of Minnesota, 310 Pillsbury Drive, SE, Minneapolis, MN 55455, USA
[f] Department of Geology, Union College, 807 Union St, Schenectady, NY, USA
[g] Faculté Polytechnique, Université de Mons. Rue de Houdain 9, 7000 Mons, Belgium
[h] Earth and History of Life, Royal Belgian Institute of Natural Sciences, Jennerstreet 13, 1000 Brussels, Belgium

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ABSTRACT

Lead concentrations and isotope ratios from two speleothems from the Han-sur-Lesse cave in southern Belgium were measured in order to study the ability of speleothems to act as archives of atmospheric pollution. To address this aim we analyzed trace elemental Al and Pb compositions by LA-ICP-MS and ICP-MS as well as Pb isotopes by MC-ICP-MS. The results help to identify three intervals characterized by particularly high enrichment of Pb: from 1880 to 1905 AD, from 1945 to 1965 AD, and from 1975 to 1990 AD. The speleothem record shows similar changes as the known historical atmospheric pollution level in Belgium. Lead isotope ratios discriminate between Pb sources and confirm that coal and gasoline combustion, combined with regional metallurgical activities, were the predominant Pb pollution sources in the stalagmites during the last 250 years. This study opens possibilities to determine anthropogenic versus natural metal sources in well-dated speleothem archives.

1. Introduction

The increase in atmospheric metal deposition compared to prehistoric levels is particularly marked in Europe since at least 2000 years. Mining and metallurgical activities, and later coal burning and transport emissions were the principal anthropogenic sources (Nriagu, 1979; Pacyna and Pacyna, 2001; Pacyna et al., 2007). Belgium, as part of the northwestern European industrial basin, has a long industrial history. To assess the extent of atmospheric contamination, it is necessary to identify the main past and present sources of trace metal emissions. The isotopic ratios of Pb ($^{208}Pb/^{206}Pb$ and $^{206}Pb/^{207}Pb$) are used in environmental deposits to quantify anthropogenic Pb inputs compared to the natural/local background and to trace Pb emission sources (e.g., Geagea et al., 2008). Atmospheric metal pollution is directly recorded by several types of environmental archives such as lake sediments (e.g., Shirahata et al., 1980; Brännvall et al., 1999; Outridge et al., 2011), marine deposits (e.g., Gobeil et al., 1999), ice (e.g., Boutron et al., 1991, 1994; Hong et al., 1994; Rosman et al., 1997), soils (e.g., Elless and Lee, 1998) and peat (e.g., Shotyk et al., 2005; Allan et al., 2013). However, some areas with abundant past heavy metal pollution lack suitable archives due to dating uncertainties and limited spatial occurrence of some of these archives (e.g., ice). The abundance of speleothems (and stalagmites in particular) and their precise dating possibilities suggest that they might make ideal archives for the reconstruction of historical metal pollution fluxes. During the last decades, speleothem studies have enhanced our knowledge of continental climate and environment, in particular the precise chronology of past decadal to millennial climate and environmental changes up to 600 ka, limit of the U/Th dating method (Genty et al., 2003; Wang et al. 2008; Drysdale et al., 2009; Fleitmann et al., 2012). Their amenability to radiometric dating using the U-series, mainly the U/Th method (Li et al., 1989; Hellstrom et al., 1998; Kaufman et al., 1998) with a precision of better than 0.5%, combined with layer counting (e.g., McMillan et al., 2005, Genty et al., 2006; Verheyden et al., 2006) in seasonally layered speleothems offer a high resolution archive for reconstructions of past climate and environment (e.g., Fairchild and Baker, 2012). Until now, the potential of speleothems

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* Corresponding author. Tel.: +32 4 366 98 71; fax: +32 4 366 20 29.
E-mail addresses: mouhamdallan@hotmail.fr, mallan@doct.ulg.ac.be (M. Allan).

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for recording environmental pollution is largely unexplored and mainly focused on quantifying aerosol contributions in touristic caves (Chang et al., 2008; Dredge et al., 2013).

The goal of this study is to define the high Pb concentrations and Pb content variability in the upper 250 years of two northwest European speleothems. We verify the reproducibility of the Pb time-series in and between speleothems. We discuss possible drivers for the increased Pb concentration and investigate the eventual link with known anthropogenic atmospheric Pb pollution. The study therefore assesses the ability of speleothems to register past atmospheric metal fall-outs despite the transfer of the signal through the soil and the host rock. To address this aim we analyzed speleothem Pb and Al compositions by LA-ICP-MS and ICP-MS as well as Pb isotope ratios by MC-ICP-MS. The elemental and isotopic Pb signature in speleothems is compared with that of other records from the same area to establish a potential link with the historical atmospheric pollution.

1.1. State of the art

Speleothems such as stalagmites and flowstones are increasingly used for paleoclimatic research. They contain several already well-studied climate and environmental proxies (Fairchild and Baker, 2012). The oxygen isotopic composition of speleothems in tropical areas varies with changes in the monsoon intensity through changes in the contribution of summer monsoon (e.g., Wang et al., 2008; Scholte and De Geest, 2010). In northern latitudes the $\delta^{18}O$ seems influenced by temperature as well as rainfall amount (Mangini et al., 2005; Mattey et al., 2008). The spatial variability of the $\delta^{18}O$ signature of speleothems was proven to reflect the regional air circulation patterns in Europe (McDermott et al., 2011). The $\delta^{13}C$ in speleothems from regions in which most types of vegetation employ the same photosynthetic pathway, as in Europe, mainly reflects changes in the intensity of vegetation cover or soil bacterial activity (Genty and Massault, 1999). The relative contribution of isotopically light carbon from the soil compared to that of the host limestone increases in warm periods. Genty et al. (2003) demonstrated that the $\delta^{13}C$ changes recorded in the Villars speleothems from France are the equivalent of the Dansgaard–Oeschger cycles identified in polar ice cores. In addition to stable isotope ratios, speleothem trace element (e.g., Mg, Ba, Sr, U) compositions represent a large proportion of the studied speleothem proxies. These elements seem to be influenced by the vadose hydrology in the epikarst zone above the drip-water site. Therefore they may give information on the paleo-recharge amounts, i.e. balance of precipitation and evaporation, in speleothems (Baker et al., 1997; Fairchild et al., 2001). Variations in trace element concentration in stalagmites depend on: 1) chemical mobilization of elements in the soil (Blaser et al., 2000; Jo et al., 2010; 2) contributions from the surrounding limestone; 3) dry deposition of dust or tephra deposition at the surface (Dredge et al., 2013; 4) the nature of the transport from the soil zone through the host rock to the cave environment and 5) carbonate precipitation conditions (Fairchild and Treble, 2009; Fairchild et al., 2010; Jo et al., 2010; Hartland et al., 2011; Wynn et al., 2014). Little research has studied the transmission of Pb from soil to cave (e.g., Borsato et al., 2007; Baldini et al., 2012; Hartland et al., 2012). Hartland et al. (2012) showed that the Pb mobilization in forest soils overlying limestone may be strongly related to the presence of organic matter (colloidal transportation). They further suggested that the transportation by organic colloids should be indicated by covariation of elements that are strongly bound to colloids (such as Pb, Al). Borsato et al. (2007) suggested that the transport of Pb can be attributed to a combination of the effects of mobile organic matter and high flow from the soil to the speleothem. Recently, uranium (Siklosy et al., 2011), anthropogenic sulfate (Frisia et al., 2005; Wynn et al., 2008), and lead (McFarlane et al., 2013) were detected in speleothems in a specific context of pollution demonstrating their potential as archives for human impact on the environment. Wynn et al. (2010) and Frisia et al. (2005) showed that the sulfate in speleothem calcite is indicative of atmospheric pollution opening the possibility of speleothems to be archives of atmospheric pollution.

2. Material and methods

Two speleothems from the Han-sur-Lesse cave system developing in Givetian (Devonian) limestone and located in southern Belgium (Quinif and Bastin, 1986) are investigated (Fig. 1). Because the area is part of the natural reserve of Han, the area was not impacted by anthropogenic pollution, other than that derived from the atmosphere. The surface runoff over the cave system is close to zero (Bonniver, 2011) indicating that most of the natural rainfall infiltrates into the soil toward the vadose zone after some evapotranspiration, particularly during spring and summer. This percolation water feeds the speleothems in the cave.

The Proserpine stalagmite is a 2 meter long and ~1 m large stalagmite located in the Salle du Dôme in the touristic part of the Han-sur-Lesse cave system. Two cores were collected in 2011 (S1) and 2001 (S2) and used for this study. The Proserpine stalagmite is layered (two layers per year) over the last 500 years. A detailed study of the stalagmite, based on the S2 core is found in Verheyden et al. (2006). The chronology of the speleothem and thus of the cores is based on U-series dating, combined with layer counting and on ^{14}C dating of the straw incorporated in the stalagmite (Fig. 2) (Verheyden et al., 2006; Van Rampelbergh et al., 2014). Layer counting was carried out on high-resolution scans using Adobe Photoshop and by using a microscope. In 2011 the S1 core was taken at ~50 cm from the S2 core and presented a similar sedimentological pattern. The upper 13 cm from stalagmite core S1 and the upper 10 cm from core S2, are presented in this paper (Fig. 2). According to previous studies, a hiatus of at least 83 years occurred from ~1870 to 1790 AD which corresponds to a sedimentological perturbation at ~9 cm from the top of the stalagmite when core S2 was sampled in 2001 (Verheyden et al., 2006). The calcite deposition at this level is heavily disturbed with straw pieces embedded in the calcite (Verheyden et al., 2006). The straw pieces are interpreted to be relics of torches used in the cave or even from fires lit on the paleo-surface of the stalagmite to illuminate the Salle-du-Dôme chamber (Verheyden et al., 2006). The cave has been visited since 1700 AD as indicated by first perturbations in the stalagmite (Verheyden et al., 2006).

In addition to the Proserpine stalagmite cores, we present Pb concentration data from 'La Timide' stalagmite (S3), a 35.5 centimeter-long candle-shaped stalagmite. The stalagmite was sampled in 2004 in the 'Réseau Renversé', a non-touristic part of the Han-sur-Lesse cave located more than 200 m from the entrance beyond a siphon that was by-passed by a tunnel opened in 1961 AD. The stalagmite was therefore totally preserved from direct aerosol deposition until recently. The upper 3.5 cm, corresponding to the last 250 years, is presented in this paper (Fig. 2).

U-series dating was performed on an ICP-MS Finnigan ELEMENT mass spectrometer at the University of Minnesota (USA) for cores S2 (Verheyden et al., 2006) and S3 (this paper) and using a Thermo NEPTUNE MC-ICP-MS at the Laboratoire Géosciences et Environnement, Toulouse (GET) for S1 (this paper). Uranium and thorium chemical separation and purification procedures are described in Edwards et al. (1987) and Cheng et al. (2009a, 2009b). All ages are reported as years AD (Table 1).

The three stalagmites (S1, S2 and S3) were measured with different resolution and by somewhat different methods. For S1, Al and Pb concentrations were determined using a Thermo XSeries2 ICP-MS with an ESI New Wave UP-193FX Fast ExcimerArF laser of 193 nm at the Royal Museum for Central Africa (Tervuren, Belgium). Spots were made of 50 μm diameter (spaced at 500–1000 μm intervals) ($n = 205$). For S1, the upper 4 cm were duplicated by continuous ablation with a scan speed of 10–30 μm s^{-1} with 22 μm intervals between two measurements (Fig. 2). Total Al and Pb blanks were negligible and ranged from 0.0009 μg g^{-1} (for Pb) to 0.04 μg g^{-1} (for Al). Both Al and Pb blanks were below their limit of detection (0.01 μg g^{-1} for Pb and 0.2 μg g^{-1}