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Research paper

Alkaline-earth metal and rare-earth element incorporation control by ionic radius and growth rate on a stalagmite from the Chauvet Cave, Southeastern France

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ABSTRACT

A multi-element study involving major alkaline-earth cations (Mg, Ca, Sr, Ba) and trace elements like Na, U, Mn, Y and Rare Earth Elements (REE) in calcite of a stalagmite from the Chauvet Cave (SE of France) was carried out using ICP-QMS analysis. This study focused on the Chau-stm6 stalagmite which displays a record of the Last Deglaciation until the end of the Younger Dryas with ages ranging from 33 kyr to 11.5 kyr BP. In this study, profiles of the alkaline-earth elements Sr and Ba show concentrations increasing sharply at the beginning of the deglaciation while Mg and U show a decreasing trend. REY (REE + Y) concentrations decrease sharply during early deglaciation. The clear record of the onset of the Younger Dryas by stable isotopes is not well marked by these elements. The absence of a significant correlation between REY and Mn suggests that REE were here not strongly bound to particulate–colloidal phases but were mainly controlled by limestone–groundwater interaction. Shale-normalized REE patterns in stalagmite, characterized by a negative Ce anomaly and HREE enrichment compared to LREE is thought to mainly arise from the dissolution of bedrock since Chau-stm6 patterns are similar to those of the bedrock. Chau-stm6 REY patterns are even more depleted in LREE than those of the bedrock, showing that part of the LREE were removed from groundwater upstream from the stalagmite. Some particular REY pattern changes were observed for the different climatic conditions: 1) glacial samples often display a more marked negative Ce anomaly (~0.3) and a high Y/Ho ratio (~0.6); 2) Bølling–Allerød and Younger Dryas samples display a variable and less pronounced anomaly (0.5–0.8) and a lower Y/Ho ratio (0.35–0.55). Climatic changes modified the rate of the stalagmite growth which likely caused a change in the properties of element incorporation in the calcite lattice. Consequently the concentration variations of Mg, Ca, Sr, Ba, U and REY would be directly controlled by ionic radii of each element.

1. Introduction

Speleothems for reconstructing paleoclimatic and paleoenvironmental conditions have been studied for more than a decade, with most studies focusing on carbon and oxygen stable isotopes (Goede, 1994; Bar-Matthews et al., 1999; Wang et al., 2001; Genty et al., 2003). Using uranium series dating, these previous studies provide precise chronologies of climatic events such as glacial–interglacial transitions or Dansgaard–Oeschger events. They also reveal new climatic events on continents.

Because speleothem $\delta^{18}O$ and $\delta^{13}C$ values are controlled by numerous factors (McDermott, 2004), it is necessary to improve the precision and strengthen interpretations of $\delta^{18}O$ and $\delta^{13}C$, and to identify physical and chemical conditions that can be reconstructed such as temperature, redox potential, pH and pCO_2. Thus, concentrations of major and trace elements have been investigated recently, especially alkaline-earth cations, (Roberts et al., 1999; Fairchild et al., 2000), U (Ayalon et al., 1999; Hellstrom and McCulloch, 2000), S, P, Si and a few transition metals such as Fe, Mn, Zn, Cd (Borsato et al., 2007). Preliminary observations have revealed that Sr and Mg in cave waters are mainly derived from bedrock dissolution (Fairchild et al., 2006). The parameters controlling the concentration of these elements in cave waters are their concentrations in the soil and the bedrock and how both are leached, and the precipitation/dissolution during seepage (incongruent dolomite dissolution, prior calcite precipitation (PCP)). The factors controlling the incorporation of these elements are speleothem growth kinetics (Sr, Ba) (Huang and Fairchild, 2001; Treble et al., 2003), which strongly depends on rainfall changes, temperature (Mg) and the chemical composition of drip water (competition between ions for crystallographic sites). Currently, the influences of these processes are still poorly constrained. More recently, interest in yttrium and rare earth elements (REE or REY when Y is included) has emerged. A first study on several German speleothems compared Mn^{2+} concentration with total REE^{3+} (Richter et al., 2004). Annual and long-term REE and Mn-rich zones corresponding to high levels of organic carbon were identified. The authors proposed that high Mn and REE concentrations occurring during warm and humid climate were linked with increased soil weathering. Zhou et al. (2008b)

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displayed an extensive REY analysis study of Songjia Cave (central China), which confirmed this assumption. Moreover, they found a correlation between several variables (REE concentrations, La, Ce and Y anomalies, LREE/HREE ratio), which was interpreted in terms of source variations, pH and redox conditions and water residence times. These two pilot studies clearly show the potential of REY as paleoclimatic and paleohydrological proxies.

In this study, we focus on the Chau-stm6 stalagmite from the Chauvet Cave (Ardèche, Southern France), which grew during the end of the Last Glaciation and the Last Deglaciation. It has been dated by the precise U–Th method and a high-resolution stable isotope profile has been established, illustrating the well-known climatic events of the Last Deglaciation (Genty et al., 2006). Thus Chau-stm6 is very well suited for comparisons of trace element variations with the stable isotope variations during a period of considerable climate change, including the end of the last glacial period, the Bølling–Allerød (B–A) and the Younger Dryas (YD) events. A second interest of this stalagmite is the low soil contribution in its calcite, which brings to light water–limestone interactions in the karst.

Forty-seven samples along the growth axis of Chau-stm6 were drilled and in addition to these speleothem samples, three bedrock samples and four cave water samples were collected, for analysis. Using quadrupole ICP-MS (ICP-QMS), we present alkaline-earth metals, U, Mn and REY concentrations of these samples. Then stalagmite results are compared to data obtained from limestone bedrock and seepage water samples to trace the origin of the elements incorporated in the stalagmite. And second, changes in major and trace elements (including REY) are interpreted as reflecting paleoclimatic and paleohydrologic changes.

2. Geological settings

The Chauvet Cave (L = 44.23°N; l = 4.25°E; 240 m asl) is located on a hillside a hundred meters above the Ardèche valley, about 20 km west of the Rhône River bed (Fig. 1). The galleries develop through a Lower Cretaceous limestone bedrock which is fractured by microfissures. The limestone above the cave is about 50 m thick — this substantial thickness probably explains the lag of a few days between strong rainfall events and subsequent floods in the cave. It is composed of a succession of large chambers (>50 m) and its modern narrow entrance is overhanging a 10-meter high chamber. The original entrance, which was ten meters lower and much wider, collapsed between 26 kyr and 11.5 kyr BP (Delannoy et al., 2001; Genty et al., 2004). Chau-stm6 was sampled lying broken on the floor, far from the cave entrance (200 m). A map of the cave and the localisation of Chau-stm6 can be found in Genty et al. (2004).

The soil above the cave is less than 20-cm thick and the Mediterranean vegetation cover (garrigue) is composed of scattered grass, bushes and a few green oaks. The local climate is dominated by Atlantic storms, but it is also influenced by the nearby Mediterranean climate. The mean annual cave temperature is 13.0 ± 0.2 °C (Bourges et al., 2006), similar within errors to the mean annual outside temperature of 13.2 °C. Cave water was sampled in April 2009 during the high-discharge period at several dripping points.

3. Materials and methods

3.1. Sampling strategy

The Chau-stm6 stalagmite was bored with a stainless steel point microdrill (diameter: 0.7 mm). No important contamination by the drill was inferred from the low minimum concentration of the elements analyzed and by the constant values of replicate samples. Relative elemental analysis of the steel revealed that REY concentrations in calcite cannot be affected during the sampling. Between 15 and 20 mg of calcite powder was collected for 47 samples drilled close to the growth axis of the stalagmite (Fig. 1), then dissolved in HNO_3 0.5 N before dilution at Ca concentration of 100 ppm for ICP-QMS analysis. In order to avoid contaminations, no filtering or centrifugation were performed

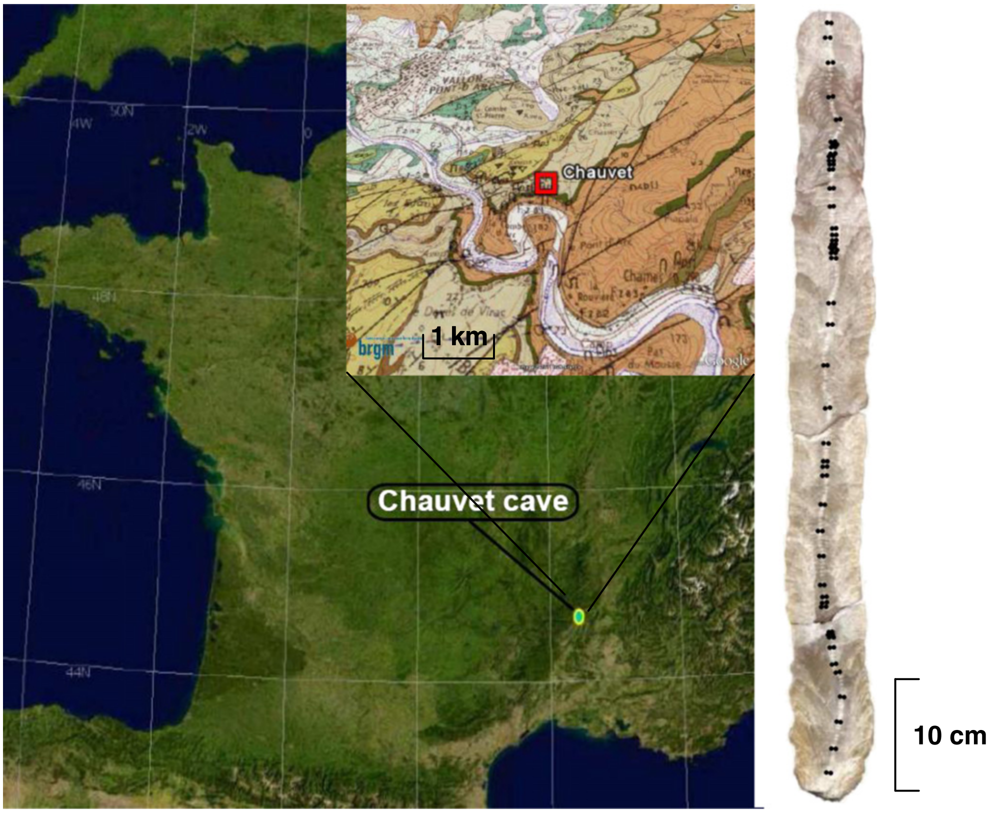

Fig. 1. Geographic and geological settings of the Chauvet Cave, France and longitudinal section of the 67.2 cm-long Chau-stm6 stalagmite.