Chemical Geology 347 (2013) 190–198

Contents lists available at SciVerse ScienceDirect

Chemical Geology

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

Prior calcite precipitation and source mixing process influence Sr/Ca, Ba/Ca and $^{87}Sr/^{86}Sr$ of a stalagmite developed in southwestern Japan during 18.0 4.5 ka

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ARTICLE INFO

Article history:
Received 20 August 2012
Received in revised form 9 March 2013
Accepted 12 March 2013
Available online 24 March 2013

Editor: U. Brand

Keywords:
Stalagmite
Sr isotopes
Prior calcite precipitation
Holocene

ABSTRACT

We measured Sr/Ca, Ba/Ca, $^{87}Sr/^{86}Sr$ ratios, $\delta^{18}O$ and $\delta^{13}C$ values in a stalagmite, which developed 18.0–4.5 thousand years ago (ka) in southwestern Japan. Dripwater and two major bedrocks (limestone and andesite) in the locality were also studied. The $^{87}Sr/^{86}Sr$ ratios of the stalagmite are relatively homogeneous (0.706852–0.706921), suggesting a steady source mixing ratio of ~40% from high-$^{87}Sr/^{86}Sr$ limestone and ~60% from low-$^{87}Sr/^{86}Sr$ andesite. The stalagmite Sr/Ca and Ba/Ca ratios were higher than the ratio expected from the dissolved fraction of limestone and andesite. The covariance among Sr/Ca, Ba/Ca, and $\delta^{13}C$ profiles suggests a significant role of prior calcite precipitation (PCP), i.e., carbonate precipitation from infiltrating water before the water drips on a stalagmite. The relationships among stalagmite Sr/Ca, Ba/Ca ratios and $\delta^{13}C$ values are consistent with the Rayleigh-type fractionation model, supporting that PCP results in successive enrichment of Sr, Ba and ^{13}C in the aqueous phase and the resulting stalagmite. The degree of PCP calculated for the stalagmite is highly variable from 0 to 85%, and generally decreased from the last glacial period to the middle Holocene. The large degree of PCP observed during 18–15 ka implies a relatively dry climate during this period, which is consistent with weak monsoon intensity inferred by the $\delta^{18}O$ values. The $^{87}Sr/^{86}Sr$ ratios of the stalagmite show a slight decrease through the entire period. The increase in the andesite-derived fraction with relatively high $^{87}Sr/^{86}Sr$ may result from accelerated silicate weathering in the epikarst with increasing temperature, humidity, and soil pCO_2.

1. Introduction

Geochemical proxies in stalagmites are important archives for understanding terrestrial paleoclimates. One of the most successful proxies is oxygen isotopes ($\delta^{18}O$). Oxygen isotope ratios have been used to reconstruct paleo-temperature and rainfall properties, such as amount, seasonality, and moisture sources (e.g., McDermott, 2004; Fairchild et al., 2006). For instance, studies of stalagmite $\delta^{18}O$ in southern China have shown that the strength of the East Asian summer monsoon responds to changes in Northern Hemisphere summer insolation (Wang et al., 2001, 2008). These studies often rely on the amount effect (Dansgaard, 1964) with regard to rainfall $\delta^{18}O$ values, although speleothem $\delta^{18}O$ values are influenced by a complex of processes in the atmosphere, epikarst and cave (e.g., Lachniet, 2009). Measuring multiple proxies should be a valuable approach for understanding the relationships among interacting processes and their influence.

Other valuable proxies in stalagmites include the trace elements. The alkaline-earth metals (Me), especially Mg and Sr, have been used as paleothermometers in marine carbonates (e.g., Nümberg et al., 1996; Shen et al., 1996). Compared with marine systems, where the Me/Ca ratio in water can be considered as a constant, cave or karst systems involve numerous processes that influence the Me/Ca ratio during mineral dissolution and precipitation (Fairchild et al., 2000; Tooth and Fairchild, 2003; Fairchild and Treble, 2009). Therefore, a constant Me/Ca ratio in dripwater is not likely throughout long time intervals.

One of the important processes controlling the Me/Ca ratio in stalagmites is prior calcite precipitation (PCP), where carbonate precipitates from infiltrating water upstream of the dripping point (Fairchild et al., 2000). In the case of alkaline-earth metals having a carbonate/water distribution coefficient much smaller than unity, PCP increases the Me/Ca ratio of both dripwater and the stalagmite. Because PCP is related to CO_2 degassing from the infiltrating water, this process is

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http://dx.doi.org/10.1016/j.chemgeo.2013.03.005

enhanced during dry periods when the water slowly descends in aerated channels in the limestone aquifer (Fairchild et al., 2000; McDermott, 2004). The stalagmite Me/Ca ratio changes with humidity, when PCP principally controls the Me/Ca ratio.

However, the Me/Ca ratios of water and stalagmites also vary with the mixing of different sources of dissolved metals. In the simplest case, there are two sources for dissolved cations: Ca-enriched limestone and an inter-karst or exotic Me-enriched source such as silicate wallrock, soil or aeolian dust. The relative proportion of the two sources controls the Me/Ca ratios in dripwater (Fairchild et al., 2006). Because the isotopic signature does not change with the degree of PCP, isotopic measurements of the relevant metal can identify sources and quantify mixing ratios of metallic cation. Strontium isotope ratios are used in this approach because the ratio ($^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$) varies predictably among different sources. Previous studies using Sr isotope ratios in stalagmites have focused on the contribution of different Sr sources (e.g., Banner et al., 1996; Goede et al., 1998; Ayalon et al., 1999; Zhou et al., 2009).

In this study, we investigated Sr sources in a stalagmite growing from the last glacial time to middle Holocene (18.0–4.5 ka) in southwestern Japan. We first identify the Sr sources and evaluate the source mixing process using the $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ ratios of bedrock in the catchment area. We evaluate the degree of PCP based on Sr/Ca and Ba/Ca ratios and δ^{13}C in the stalagmite. Finally, the age profiles of these proxies are used for interpreting trends in climate during the growth period of the stalagmite.

2. Materials and methods

2.1. Sample locality and materials

A 13-cm-long clear stalagmite, Hiro-1, was collected from the Maboroshi cave (elevation 450 m; 34°49′ N, 133°13′ E) in northeast Hiroshima Prefecture, southwestern Japan (Fig. 1a). The cave, located at the southern foot of the Chugoku Mountains, was first discovered in 1992. The cave is nearly horizontal with currently-explorable length of 740 m. The site of Hiro-1 is 150 m from the cave entrance at 350 m in altitude. The deepest part of the passage between this site and the entrance used to be blocked with muddy sediments until exploration in 1993. Therefore, the ventilation in the cave was likely limited.

The limestone plateau containing the Maboroshi cave is a part of the Akiyoshi Terrane of Carboniferous–Permian age. The limestone was deposited on a Lower Carboniferous basaltic seamount and later intruded by Cretaceous andesite (Fig. 1b), which is distributed in the catchment area and within the cave. The annual average temperature from the nearest meteorological observatory, Yuki (elevation 510 m; 34°47′ N, 133°16′ E), is 10.7 °C (1988–2007). The mean annual rainfall is 1296 mm. The catchment area is characterized by conifer-dominated forest that covers soils of one to several meters in thickness. Soil includes limestone and andesite gravel, and consists of weathered andesite, insoluble limestone residue, and possibly aeolian sediments. However, the contribution of pyroclastic material is likely minor because there is no visible ash bed in the Holocene cover in this locality. The Chugoku Mountains include only one active volcano, andesitic Mt. Sambe located ~60 km WNW from the cave. The stalagmite consists of clear calcite crystals, and the carbonate Sr/Ca and $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ were most likely inherited from the dissolved components of the dripwater.

Thirty four horizons of Hiro-1 were ^{230}Th-dated following the methods in Shen et al. (2002, 2003, 2012) with an uncertainty of 0.3–1.1% (2RSD). According to the dating results, the growth interval of the stalagmite is from 18.1 to 4.5 ka (Table 1). The record includes two hiatuses in 10.8–7.7 ka (Hiatus 1) and in 12.8–11.4 ka (Hiatus 2). Hiatus 2 would correspond to the Younger Dryas (YD, Alley et al., 1993). Paleoclimatic reconstruction has been carried out using δ^{18}O profiles from the same stalagmite for the interval 15.5–10.7 ka, which showed synchronous trends with δ^{18}O profiles from Chinese caves and Greenland ice cores (Shen et al., 2010). In this study, we present trace element and stable isotope data for the entire growth interval of the stalagmite.

Three grayish limestone specimens (A, B, and C) and three greenish andesite specimens (AN1, AN2 and AN3) were collected from the catchment area. Dripwater was collected in pre-cleaned 10-L polyethylene containers and in 15 mL glass vials at two sites (DW1 and DW2) near the stalagmite sampling point from 13 to 20 November 2009. The drip rate at the DW1 site was approximately 1 L/day, faster than at the DW2 site (~1 L/week). The dripwater samples collected in 10-L polyethylene containers were acidified with ultrapure HNO_3 to prevent mineral precipitation during storage.

2.2. δ^{18}O and δ^{13}C analysis

Powdered sub-samples (300 μg) for δ^{18}O and δ^{13}C analyses were collected at 0.2-mm spaced intervals along the stalagmite growth axis using a dental drill. The samples were converted into carbon dioxide by reaction with phosphoric acid. Oxygen and carbon isotopic ratios were measured on an isotope ratio mass spectrometer, Finnigan MAT Delta Plus, combined with an on-line preparation and introduction system, GAS BENCH, at Kyushu University. The δ^{18}O and δ^{13}C values are expressed using the conventional δ notation with respect to Vienna Pee Dee Belemnite (VPDB). Repeated measurements of a laboratory standard (powdered Jurassic limestone at Solnhofen, Germany) calibrated with NBS-19 gave analytical reproducibility better than 0.22‰ for δ^{18}O and 0.19‰ for δ^{13}C (2SD) (Hori et al., 2009).

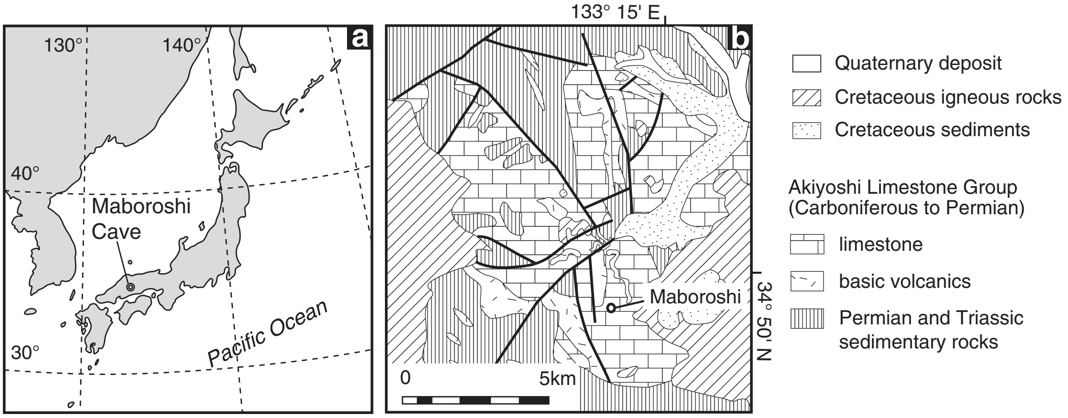

Fig. 1. (a) Location of the Maboroshi cave in southwest Japan. (b) Geological map of the study area.