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Mineral composition and structure of the stalagmite laminae from Chulerasim cave, Indian Himalaya, and the significance for palaeoclimatic reconstruction

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ABSTRACT

Many noteworthy properties of climate recorded by stalagmites can result from their mineralogy and fabric as well as their mode of occurrence. In this study, X-ray diffraction (XRD) and Scanning electron microscope (SEM) investigations were carried out for a well laminated stalagmite from Chulerasim cave, north India, to identify the mineral composition and structure of the laminae. As some early reported stalagmite laminae from Thailand and Southwestern China, the laminae of this stalagmite are composed of alternating compact and porous sub-layers. The XRD results confirm that the stalagmite is composed mainly of primary aragonite, which corrects the previous interpretation. The SEM results show that the compact sub-layer is composed of elongated columnar aragonites with a general longitudinal orientation (parallel to the vertical growth axis) and the coalescence of the aragonite crystals is well developed, leaving few inter-crystalline voids. The compact sub-layer may have formed in quasi-equilibrium conditions and provides the main carrier of climate proxies. The porous sub-layer is made up of needles, drusy and fibrous aragonites intersecting each other. Accordingly, the coalescence is low, with many inter-crystalline voids, which suggests a short hiatus between two adjacent compact sub-layers. Therefore, the growth of alternation of compact/porous sub-layers may not be successive, and they may have formed in different seasons. The results suggest that, for stalagmite/palaeoclimate research, cave monitoring should be performed to reveal when and how the compact sub-layers were formed.

1. Introduction

Well laminated stalagmites are a powerful tool for the high-resolution reconstruction of past climate changes, as they encode much palaeoclimatic information in their geometry and geochemistry. The stalagmite from Chulerasim cave, Indian Himalaya, has visible laminae in hand section, showing alternation of compact and porous sub-layers. Similar couplets have been described in various aragonitic stalagmite studies. Some discussed the possible growth mechanism. Brook et al. (1999) attributed the darker layers to either dust (mainly clay) accumulation on the surface of the speleothems or to increased incorporation of humic acids. Bertaux et al. (2002) suggested that the brown layers result from the incorporation of dissolved organic matter (DOC) in the aragonite crystals. Yadava et al. (2004) considered the dark layers as $CaCO_3$ precipitated with the trapped detrital particles. Duan et al. (2010) recognized that the compact sub-layer is composed of elongated columnar aragonites with a general longitudinal orientation (parallel to the vertical growth axis), but the porous sub-layer is composed of needle aragonites forming a radiating mass. As for the Chulerasim stalagmite, although a preliminary study has shown that the time series of $\delta^{18}O$ and $\delta^{13}C$ represent rainfall amount signals (Kotlia et al., 2012), the mineral composition and the formation mechanism of the laminae are still amphibolous. This study will focus on the two aspects.

2. Materials and methods

2.1. Site description

The Chulerasim cave (29°53′08″ N: 79°21′06″ E, altitude 1254 m) is located in Chulerasim village near Chaukhutia (District Almora) in the Kumaun Lesser Himalaya, India (Fig. 1). It is developed under Precambrian limestone which extends for about 50 m above the cave. The vegetation above the cave is dominated by oak (*Quercus incana*), with *Pinus roxburghii* and small shrubs.

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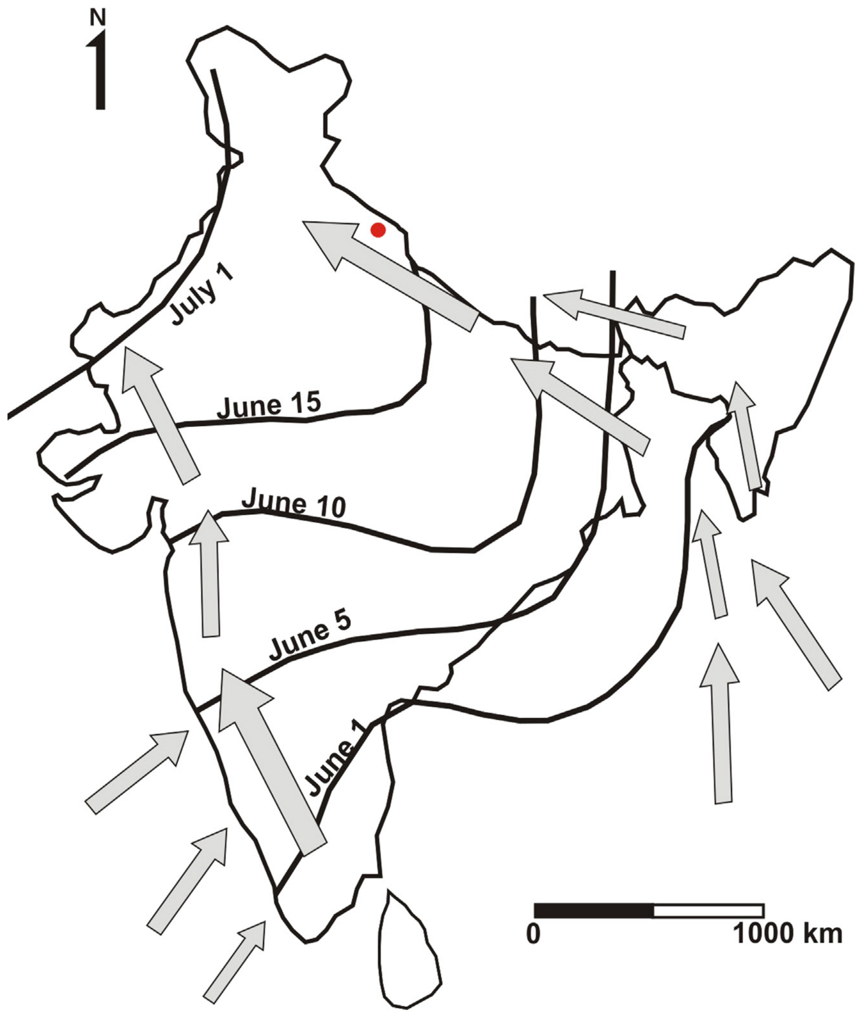

Fig. 1. Map of India showing mean annual arrival date of the Indian Summer Monsoon (lines with dates) and the principal trajectories of moisture masses associated with monsoon (arrows). The red circle indicates the location of Chulerasim cave. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The cave is about 5 m long with a main entrance of ~3 × 3 m and becomes very narrow near the end (~1 × 1 m). The stalagmite sample was collected about 4.9 m from the entrance (almost at the end) and was active when cut. The climate is sub-tropical wet/moist with warmer summers and cooler winters. The annual precipitation is ~1050–1250 mm with about 70% of the precipitation falling during the monsoon season from June to September. The humidity outside the cave ranges between 60 and 75% during

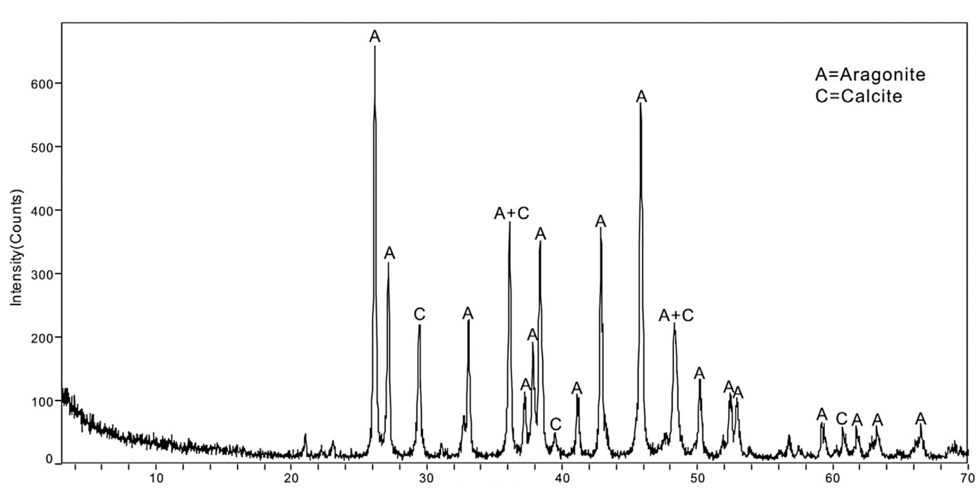

Fig. 2. X-ray diffraction (XRD) spectra of the sample, showing almost all the peaks of aragonite and only a few of calcite.

the monsoon period and 30–40% during the winter (Kotlia et al., 2012).

2.2. Methods

The stalagmite was cut into halves and one half was polished. The polished section of stalagmite was scanned using a pre-calibrated high-resolution scanner at RGB/3200 dpi conditions. The digital image was then used for laminae analysis. The X-ray diffraction (XRD) measurement was performed on about 5 mg of powder using a Rigaku D/Max-2400 powder diffractometer to identify the mineral composition. One sub-sample from the stalagmite was analyzed with a LEO1450VP scanning electron microscope (SEM). The freshly broken surface of the sub-sample was coated with carbon to provide electrical conductivity of the crystal surfaces. The XRD, SEM and laminae analyses were performed at the Institute of Geology and Geophysics, Chinese Academy of Sciences.

3. Results

3.1. Mineralogy

In the previous and preliminary study, the stalagmite was thought to be composed of calcite (Kotlia et al., 2012). However, the X-ray diffraction (XRD) spectra show that almost all the peaks are of aragonite and only a few of calcite (Fig. 2). This is because the stalagmite is composed of dominantly aragonite with only trace

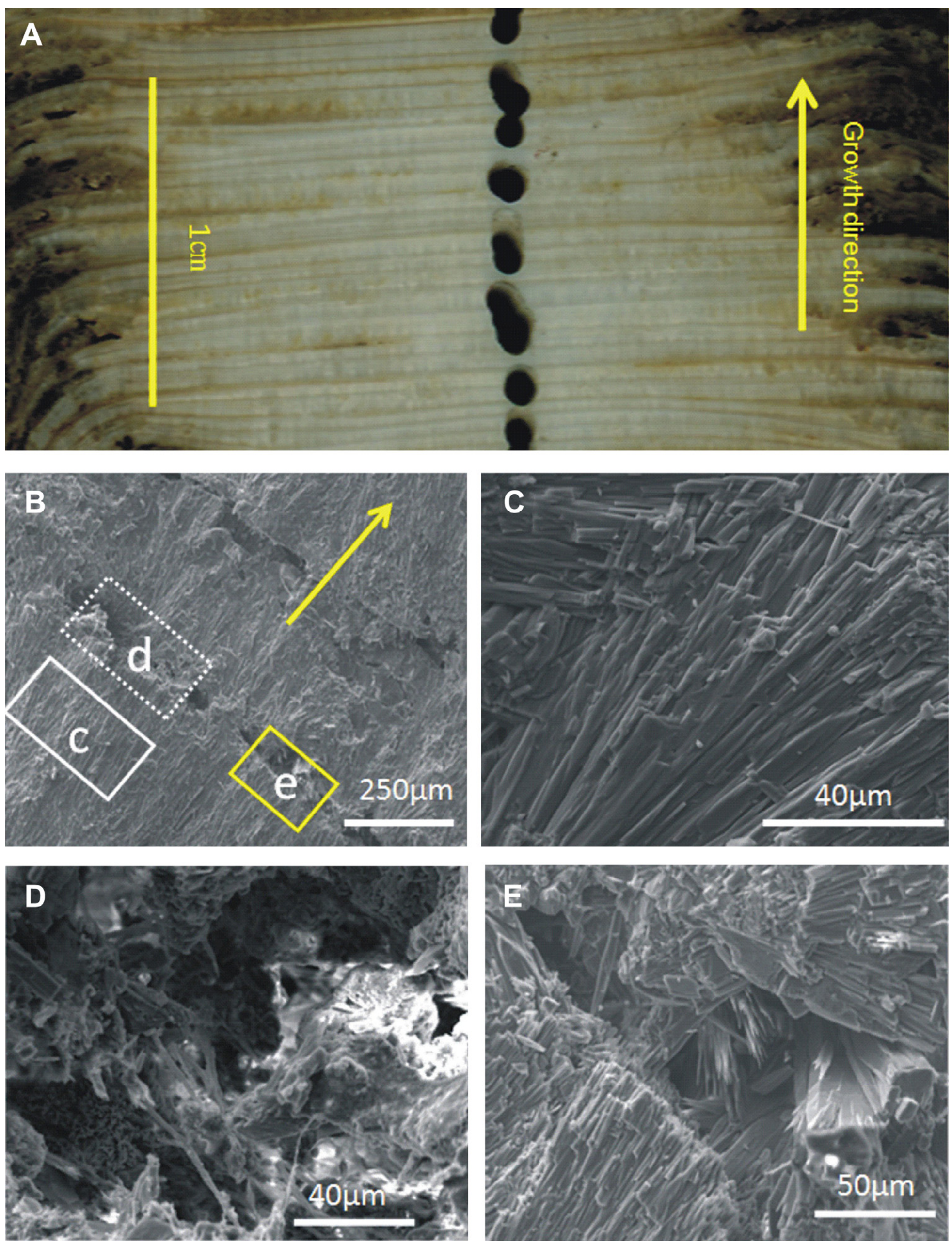

Fig. 3. Photographs of crystal structures of Chulerasim stalagmite laminae. A. Scanning image of Chulerasim stalagmite laminae showing alternating compact and porous sub-layers. B. SEM micrograph of the stalagmite laminae. The arrow points to the growth direction. C. SEM micrograph of area c identified in B, which is the compact sub-layer. D. SEM micrograph of area d identified in B, which is the porous sub-layer. E. SEM micrograph of the area e identified in B, showing the boundary of the compact/porous sub-layer.

amounts of calcite. In addition, no evidence is observed to suggest the presence of alternating aragonite/calcite laminae or that the mineralogical composition differs at discrete intervals along the growth axis, and no relict textures are observed to indicate recrystallization of calcite to aragonite. These results suggest that the aragonite was precipitated continuously and that the primary mineralogy and structure have been preserved.

3.2. Structure of the stalagmite laminae

The stalagmite has clear visible laminae in the hand section, showing alternation of thicker compact and thin porous sub-layers (Fig. 3A and B). According to the SEM micrographs, the compact sub-layer is composed of elongated columnar aragonites with a general longitudinal orientation (parallel to the vertical growth axis) (Fig. 3C). The coalescence of the aragonite crystals is well developed, leaving few inter-crystalline voids, which make the structure compact. In contrast to this, the porous sub-layer is made up of needle, drusy and fibrous aragonites intersecting each other (Fig. 3D and E). Accordingly, the coalescence is low, with many inter-crystalline voids, which leads to a low density structure.

4. Discussion

Aragonitic speleothems are usually found in caves developed in dolostone or dolomitic limestone, for example in South Africa (Holmgren et al., 1994), France (Cabrol and Coudray, 1982), USA (Siegel and Dort, 1966), Israel (Bar-Matthews et al., 1991), Brazil (Bertaux et al., 2002), Thailand (Cai et al., 2010) and China (Duan et al., 2012). That may be related to the high Mg/Ca ratio of the drip water percolating through the dolostone surrounding the cave (Bertaux et al., 2002), which could restrain the crystallization of calcite but aragonite is unaffected (Kitano, 1962; Fairchild et al., 1996; Davis et al., 2000; Duan et al., 2012). Duan et al. (2012) demonstrated that the essential factor controlling the mineral composition of stalagmites is not the climate but the surrounding lithology. The Chulerasim cave is developed in limestone (Kotlia et al., 2012); however, the stalagmite in the cave is composed mainly of primary aragonite. Furthermore, the mean annual precipitation near Chulerasim cave is $\sim$1050–1250 mm (Kotlia et al., 2012), which means the area is not arid but moist. In turn, the drip rate in the cave may not be slow enough to lead more prior calcite precipitation and can not result in an increased Mg/Ca ratio of drip water (Fairchild et al., 2000; Genty et al., 2001; Spötl et al., 2005). This observation suggests that besides the surrounding lithology and rainfall, other processes (e.g., intense evaporation rate, temperature) may also have affected the precipitation of aragonite (Bar-Matthews et al., 1991; Railsback et al., 1994).

The Chulerasim stalagmite laminae looks similar to that from Xianren cave, southwestern China. Both are not characterized by the changes of material composition but by the variation in size and morphology of the aragonite crystals of the sub-layers. In the case of the compact sub-layer, they are both constituted of elongated columnar aragonites with a general longitudinal orientation (parallel to the vertical growth axis) (Fig. 3C). Nevertheless, for the porous sub-layer, there are some differences. In Xianren cave, the porous sub-layer is composed of needle aragonites forming radiating masses (Duan et al., 2010). By contrast, in Chulerasim cave, the porous sub-layer is constituted of needle, drusy and fibrous aragonites intersecting each other (Fig. 3D and E), which suggests a short hiatus between two adjacent compact sub-layers (Fig. 3B).

The cave monitoring results of Xianren cave (Duan et al., 2012) indicate the growth mechanism and the related palaeoclimate signals of Chulerasim stalagmite laminae. The compact sub-layer composted of elongated columnar aragonites may form at near-equilibrium conditions, when the drip rate is moderate and the degassing is slow, continuous and prolonged (Frisia et al., 2000). Therefore, it could provide the main carrier of climate proxies. In contrast, the porous sub-layer consists of various highly defective aragonites, may develop in disequilibrium conditions related to very low drip rate during dry periods (Frisia et al., 2000). Furthermore, as the porous sub-layer of Chulerasim stalagmite laminae suggests a short hiatus between two adjacent compact sub-layers (Fig. 3B), the growth of alternation of compact/porous sub-layer may not be successive, and they may form in different seasons.

5. Conclusions

The Chulerasim stalagmite is constituted mainly of aragonite, though the cave is developed in limestone and the local area is moist, which suggests that besides the surrounding lithology and rainfall, other processes (e.g., intense evaporation rate, temperature, etc) also may affect the precipitation of aragonite. The stalagmite shows visible laminae, with alternation of thicker compact and thin porous sub-layers. The compact sub-layer is composed of elongated columnar aragonites with a general longitudinal orientation (parallel to the vertical growth axis) and the coalescence of the aragonite crystals is well developed, leaving few inter-crystalline voids. It may form in quasi-equilibrium conditions and preserves palaeoclimate signals. By contrast, the porous sub-layer is made up of needle, drusy and fibrous aragonites intersecting each other. Accordingly, the coalescence is low, with many inter-crystalline voids, which looks like the short hiatus between two adjacent compact sub-layers. It may develop in disequilibrium conditions related to very low drip rate during dry periods. Therefore, the growth of alternation of compact/porous sub-layer may not be successive and they may form in different seasons. The results suggest that, for stalagmite/palaeoclimate research, cave monitoring should be performed to reveal when and how the compact sub-layer forms. In addition to the isotopes, it is equally important to analyze the mineralogy and structure of laminae of the stalagmites for better elucidation of the palaeoclimatic changes.

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