# 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.

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## 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<sub>3</sub> precipitated with the trapped detrital particles. Duan et al.

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(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  $\delta^{18}{\rm O}$  and  $\delta^{13}{\rm C}$  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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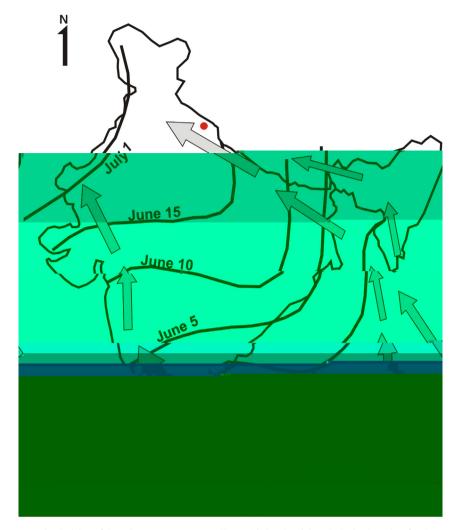


Fig. 1. Map of India showing mean annual arrival date of the Indian Summer Monsoon (lines with dates) and the principal trajectories of moisture masses associated with monsoon (arrows). The red circle indicates the location of Chulerasim cave. (For interpretation of the references to colour in this figure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

The cave is about 5 m long with a main entrance of  $\sim 3 \times 3$  m and becomes very narrow near the end ( $\sim 1 \times 1$  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  $\sim 1050-1250$  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

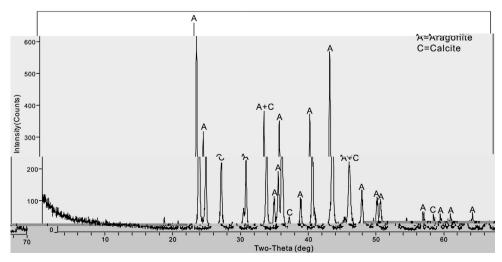


Fig. 2. X-ray diffraction (XRD) spectra of the sample, showing almost all the peaks of aragonite and only a few of calcite.

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

## 2.2. Methods

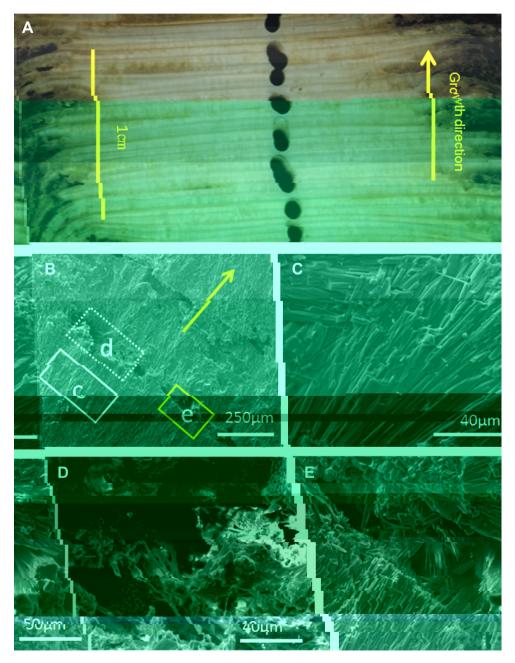
The stalagmite was cut into halves and one half was polished. The polished section of stalagmite was scanned using a precalibrated high-resolution scanner at RGB/3200 dpi conditions. The digital image was then used for laminae analysis. The X-ray diffraction (XRD) measurement was performed on about 5 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 sublayers. 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 (

- Duan, W., Cai, B., Tan, M., Liu, H., Zhang, Y., 2012. The growth mechanism of the aragonitic stalagmite laminae from Yunnan Xianren Cave, SW China revealed by cave monitoring. Boreas 41 (1), 113–123.
- Duan, W., Tan, M., Cheng, H., Zhang, Y., 2010. Intra-annual structure of aragonitic stalagmite laminae from Yunnan Xianren Cave: SEM. Quaternary Sciences in Chinese 30 (5), 1066–1067.
- Fairchild, I., Tooth, A., Huang, Y., Borsato, A., Frisia, S., McDermott, F., 1996. Spatial and temporal variations in water and stalactite chemistry in currently active caves: a precursor to interpretations of past climate. In: Bottrell, S.H. (Ed.), Proceedings of the Fourth International Symposium on the Geochemistry of the Earth's Surface. University of Leeds, Ilkley, pp. 229–233.
- Fairchild, I.J., Borsato, A., Tooth, A.F., Frisia, S., Hawkesworth, C.J., Huang, Y., McDermott, F., Spiro, B., 2000. Controls on trace element (Sr-Mg) compositions of carbonate cave waters: implications for speleothem climatic records. Chemical Geology 166 (3–4), 255–269.
- Frisia, S., Borsato, A., Fairchild, I.J., McDermott, F., 2000. Calcite fabrics, growth mechanisms, and environments of formation in Speleothems from the Italian Alps and Southwestern Ireland. Journal of Sedimentary Research 70 (5), 1183—1196
- Genty, D., Baker, A., Vokal, B., 2001. Intra- and inter-annual growth rate of modern stalagmites. Chemical Geology 176 (1–4), 191–212.

- Holmgren, K., Lauritzen, S.-E., Possnert, G., 1994. <sup>230</sup>Th<sup>234</sup>U and <sup>14</sup>C dating of a late Pleistocene stalagmite in Lobatse II Cave, Botswana. Quaternary Science Reviews 13 (2), 111—119.
- Kitano, Y., 1962. The behavior of various inorganic ions in the separation of calcium carbonate from a bicarbonate solution. Bulletin of the Chemical Society of Japan 35 (12), 1973–1980.
- Kotlia, B.S., Ahmad, S.M., Zhao, J.-X., Raza, W., Collerson, K.D., Joshi, L.M., Sanwal, J., 2012. Climatic fluctuations during the LIA and post-LIA in the Kumaun Lesser Himalaya, India: evidence from a 400 yr old stalagmite record. Quaternary International. doi:10.1016/j.quaint.2012.01.025.
- Railsback, L.B., Brook, G.A., Chen, J., Kalin, R., Fleisher, C.J., 1994. Environmental controls on the petrology of a late Holocene speleothem from Botswana with annual layers of aragonite and calcite. Journal of Sedimentary Research 64 (1a), 147–155.
- Siegel, F.R., Dort, W.J., 1966. Calcite—Aragonite speleothems from Hand-dug cave in Northeast Kansas. International Journal of Speleology 2 (1/2), 165–169.
- Spötl, C., Fairchild, I.J., Tooth, A.F., 2005. Cave air control on dripwater geochemistry, Obir Caves (Austria): implications for speleothem deposition in dynamically ventilated caves. Geochimica et Cosmochimica Acta 69 (10), 2451–2468.
- Yadava, M., Ramesh, R., Pant, G., 2004. Past monsoon rainfall variations in peninsular India recorded in a 331-year-old speleothem. The Holocene 14 (4), 517–524.