



## Determination of aragonite trace element distribution coefficients from speleothem calcite–aragonite transitions

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### Abstract

The processes that govern the incorporation of (trace) elements into speleothems can often be linked to environmental changes. Although element incorporation into speleothem *calcite* is now reasonably well understood, current knowledge regarding trace element variability in speleothem *aragonite* is very limited. Of particular interest is whether trace element distribution coefficients are above or below one in order to assess the extent to which prior aragonite precipitation has affected speleothem aragonite trace element records.

This study uses nine calcite-to-aragonite transitions in seven speleothems from diverse environmental settings to derive the first quantitative estimates of the distribution coefficients for several elements in speleothem *aragonite*:  $D_{\text{Mg(Ar)}} = 9.7\text{E}-5 \pm 9.01\text{E}-5$ ,  $D_{\text{Ba(Ar)}} = 0.91 \pm 0.88$ ,  $D_{\text{Sr(Ar)}} = 1.38 \pm 0.53$ , and  $D_{\text{U(Ar)}} = 6.26 \pm 4.54$  (1 $\sigma$  SD). For one speleothem from western Germany, the distribution coefficients are generally higher, which is potentially related to the very low growth rates (<11  $\mu\text{m}/\text{year}$ ) of this sample. In particular,  $D_{\text{Sr(Ar)}}$  appears to show a negative correlation with growth rate when growth rate is below 20  $\mu\text{m}/\text{year}$ .

In summary, our results demonstrate that speleothem aragonite  $D_{\text{Mg(Ar)}}$  is below one,  $D_{\text{U(Ar)}}$  is considerably above one, and  $D_{\text{Sr(Ar)}}$  is above one or close to unity. For  $D_{\text{Ba(Ar)}}$ , reaching a similar conclusion is difficult due to the relatively high uncertainty. Enhanced prior aragonite precipitation will thus result in lower U and higher Mg concentrations in speleothem aragonite, although in many cases Mg in speleothem aragonite is most likely dominated by other processes. This result suggests that U concentrations in aragonitic stalagmites could serve as a very effective proxy for palaeo-rainfall.

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## 1. INTRODUCTION

Speleothems are secondary cave deposits mainly consisting of calcite or aragonite with calcite being the more common polymorph of  $\text{CaCO}_3$  (Hill and Forti, 1997). Speleothems, and in particular stalagmites and flowstones are considered as some of the most promising continental climate archives. They can serve as benchmarks, which can be reliably contrasted and compared with proxy records from complementary archives, because they can be precisely dated up to about 500 ka by the  $^{230}\text{Th}/\text{U}$ -dating technique (e.g., Scholz and Hoffmann, 2008). In addition, speleothem archives can be sampled and analyzed with up to sub-annual resolution for carbon and oxygen isotopes (McDermott, 2004; Matthey et al., 2008; Myers et al., 2015) and trace and major elemental abundances (Fairchild and Treble, 2009). Numerous studies on speleothem calcite trace element compositions have been published recently (Treble et al., 2005; Borsato et al., 2007; Fairchild and Treble, 2009; Griffiths et al., 2010; Day and Henderson, 2013; and references therein). Few studies, however, focus on trace element compositions in aragonite speleothems (Finch et al., 2001, 2003; McMillan et al., 2005; Wassenburg et al., 2012, 2013; Tan et al., 2014). The knowledge on element partitioning into speleothem aragonite is thus very limited.

Since aragonite speleothems contain much more U compared to their calcitic counterparts, they can provide excellent age models (Cosford et al., 2008; Myers et al., 2015; Ridley et al., 2015; Wassenburg et al., 2016). However, aragonite is metastable and may recrystallize to calcite under certain conditions, which results in post-depositional open system behavior of the U-series system and apparently incorrect  $^{230}\text{Th}/\text{U}$ -ages (Ortega et al., 2005; Lachniet et al., 2012). Where robust evidence that an aragonite speleothem is well preserved is available (Wassenburg et al., 2013; Myers et al., 2015), the potential to obtain exceptionally precise chronologies is high. Consequently, it is important to further investigate (i) how trace elements partition into speleothem aragonite and (ii) which controls and processes are reflected by their temporal and spatial variability.

The major crystallographic difference between calcite and aragonite lies in their different crystal structures. Aragonite is characterized by an orthorhombic crystallography, where the Ca-ion is coordinated by nine O-ions, whereas calcite has a trigonal crystallography, where the Ca-ion is coordinated by six O-ions (Swart, 2015). Due to these crystallographic differences, larger cations, such as Sr, Ba and U, are preferentially incorporated into aragonite, whereas calcite also tends to incorporate small cations, such as Mg. The corresponding trace element distribution coefficients,  $D_X$ , are defined as:

$$D_X = \frac{X/\text{Ca}_{\text{Solid}}}{X/\text{Ca}_{\text{Solution}}}, \quad (1)$$

where  $X$  represents a certain trace element. Due to the crystallographic differences, the distribution coefficients may be very different for calcite and aragonite.

Recently, Stoll et al. (2012) introduced a model that facilitates quantitative interpretations of speleothem calcite

Mg, Ba, and Sr signals in terms of prior calcite precipitation (PCP) (Fairchild et al., 2000). This process refers to the precipitation of calcite before the dripwater reaches the stalagmite (Fairchild and Treble, 2009), which occurs when the dripwater encounters empty voids within the karst with a lower partial  $\text{CO}_2$  pressure compared to the water. This forces degassing of  $\text{CO}_2$ , temporarily increasing supersaturation with respect to calcite and calcite precipitation. PCP usually refers to calcite precipitation in the aquifer above the cave, although it may also occur inside the cave (e.g., at the cave ceiling or on the surface of a stalactite). Certain environmental conditions may favor prior aragonite precipitation (PAP) instead of PCP. Fairchild and Treble (2009) first mentioned PAP, which was subsequently documented and detailed by Wassenburg et al. (2013). Both PCP and PAP are enhanced during periods of reduced aquifer recharge when more time is available for degassing and more air-filled voids exist in the aquifer. If trace element distribution coefficients are below (above) one, elevated concentrations in speleothems are typically interpreted as reflecting reduced (enhanced) infiltration and drier (wetter) climatic conditions (Johnson et al., 2006). However, cave ventilation may also control PCP (Sherwin and Baldini, 2011; Wong et al., 2011).

Quantitative and qualitative interpretations of speleothem trace element records strongly depend on well constrained  $D_X$  values. Laboratory precipitation experiments indicate that for calcite, temperature might affect  $D_{\text{Mg}(\text{Cc})}$  (Oomori et al., 1987; Day and Henderson, 2013). Other experiments suggest that precipitation rates (Lorenz, 1981; Tesoriero and Pankow, 1996; Gabitov et al., 2014) and/or solution composition (Mucci and Morse, 1983; Pingitore and Eastman, 1986) may control  $D_{\text{Mg}(\text{Cc})}$ ,  $D_{\text{Sr}(\text{Cc})}$ , and  $D_{\text{Ba}(\text{Cc})}$ . For aragonite, temperature may affect trace element distribution coefficients for Mg, Ba, and Sr (Dietzel et al., 2004; Gaetani and Cohen, 2006), whereas precipitation rates may influence aragonite distribution coefficients for U and Mg (Gabitov et al., 2008).

However, most of these experiments were designed to reflect marine environments. Within cave environments, the conditions driving  $\text{CaCO}_3$  precipitation are very different. Spelean  $\text{CaCO}_3$  precipitation is driven by rapid degassing of  $\text{CO}_2$  from thin water films (Hansen et al., 2013) with low ionic strength and the presence of (organic) colloidal phases (Fairchild and Treble, 2009; Hartland et al., 2014), whereas marine deposition occurs in high ionic strength waters and is often biologically mediated. The same arguments prompted a series of studies that aimed to determine speleothem calcite  $D_X$ . These were based on both field precipitation experiments, during which the trace element composition of calcite formed within a cave over a known time period is compared with the trace element composition of the associated dripwater (Gascoyne, 1983; Huang et al., 2001; Karmann et al., 2007; Fairchild et al., 2010; Tremaine and Froelich, 2013; Riechelmann et al., 2014), and cave analogue laboratory experiments (Huang and Fairchild, 2001; Day and Henderson, 2013). These experiments demonstrate that  $D_X$  values determined under karst analogue conditions are different from those in marine environments. Consequently,  $D_X$  values determined under

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