Noble gas concentrations in fluid inclusions as tracer for the origin of coarse-crystalline cryogenic cave carbonates

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ABSTRACT

The chemically inert behaviour of noble gases, their well-known solubility in water and the long-term constancy of atmospheric noble gas mixing ratios make them a unique tool for paleoclimate studies of groundwater. This concept has recently been extended to fluid inclusions in speleothems. Here we use noble gas concentrations of fluid inclusions contained in calcite crystals to constrain the formation history of coarse crystalline cryogenic cave calcites from Heilenbecker Cave (Germany).

Cryogenic cave carbonates form under conditions related to the freezing of cave pools and are a new archive for paleo-permafrost timing and extent. The cryogenic origin of these carbonates is typically deduced from their crystal habit and the carbon and oxygen isotope ratios, but this can be ambiguous in some cases. A geochemical method that provides clear-cut proof of the cryogenic origin of individual crystals has been lacking so far.

We examined the formation process of cryogenic cave calcites using water and noble gases extracted from inclusions in these crystals. Based on their $\delta^{13}C$ and $\delta^{18}O$ values, these calcite crystals could have also formed as 'normal', i.e. non-cryogenic, speleothems. Noble gas concentrations derived from fluid inclusions in these cryogenic calcites, however, deviate significantly from commonly observed concentrations in atmospheric air, surface water, groundwater, and stalagmites. These concentrations cannot be explained simply by a solubility component nor by the addition of various amounts of excess-air to a solubility component. The data, however, are consistent with the scenario of a slowly freezing water body lacking exchange with the cave atmosphere. The gradual freezing process leads to a partitioning of the noble gases between ice and remaining water and thereby to a pronounced over-abundance of heavy noble gases in the liquid phase recorded in the fluid inclusions of the cryogenic calcite crystals.

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1. Introduction

Cryogenic cave carbonates are a subgroup of speleothems that hold important insights into paleo-permafrost dynamics, which is of particular interest in the light of current and anticipated climatic changes in high-latitude and high-altitude regions. Vast permafrozen areas are located in the Arctic regions of Russia and Canada which are susceptible to the current warming trend (Anisimov et al., 1997; Sazonova et al., 2004; Vaks et al., 2013). A considerable temperature increase of up to several degrees in shallow permafrost was recorded throughout the Northern Hemisphere (Lachenbruch and Marshall, 1986; Nelson, 2003). The investigation of mid-latitudinal permafrost, that was present during glacial periods, may provide information about permafrost distribution and dynamics. Cryogenic cave carbonates have recently emerged as a highly useful tool to date and delineate the extent (e.g., the depth) of permafrozen areas (Richter and Riechelmann,

2008; Richter et al., 2010, 2011; Žák et al., 2012; Luetscher et al., 2013).

The occurrence of cryogenic cave carbonates is mainly linked to glacial periods (Richter et al., 2010; Žák et al., 2012) during which 'normal' speleothem growth halted (for an exception see Spötl and Mangini, 2007). Most cryogenic carbonates dated so far fall within an age range of 66 to 12 ka (Žák et al., 2012; Richter et al., 2013) and precipitated during generally cold intervals of the last glacial period. Cryogenic carbonate samples indicate that during the last glaciation the permafrost reached down to a depth of at least 65 m in Central Europe (Žák et al., 2012).

Cryogenic cave carbonates show a variety of shapes and sizes, from fine-grained powder to mm- and cm-sized single grains, and from regular rhombohedra to complex spherical forms (e.g., Žák et al., 2012). Their formation is linked to the freezing of mineralized karst water. The concentration of certain solutes (e.g., Ca^{2+} and HCO3− ions) increases in the remaining liquid due to partitioning between water and ice and the poor solubility of these solutes in ice. After reaching the saturation limit, precipitation of cryogenic minerals can occur. A large range has been observed in the oxygen and carbon isotope ratios of

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cryogenic cave carbonates, from −24 to −2‰ (δ^{18}O) and −8 to +18‰ (δ^{13}C). The range of sizes, shapes and isotopic values indicates two distinct formation pathways:

(a) Fine crystalline carbonate powder yielding positive δ^{13}C values precipitated from fast freezing of shallow cave pools or thin water films on ice (Clark and Lauriol, 1992; Lacelle, 2007; Spötl, 2008; Lacelle et al., 2009).

(b) Coarse crystalline calcites with very negative δ^{18}O values precipitated slowly from gradually freezing pool water (Žák et al., 2008, 2012; Richter et al., 2013).

Very negative δ^{18}O values (down to −24‰; Žák et al., 2012) can only be explained by precipitation from water with very negative δ^{18}O values (as high formation temperatures can be ruled out). The oxygen isotope fractionation during slow freezing of water leads to preferential partitioning of ^{18}O into the ice and to more negative δ^{18}O values in the remaining water (O'Neil, 1968; Lehmann and Siegenthaler, 1991). This way of precipitation is typical for coarse crystalline cryogenic carbonates which exhibit the most negative δ^{18}O values. A trend of decreasing δ^{18}O values from the centre to the rim of cryogenic calcite crystals has been observed (Richter and Riechelmann, 2008; Luetscher et al., 2013) confirming the model of progressive freezing of pool water concomitant with calcite crystal growth. In some cases, however, δ^{18}O values of the suspected cryogenic carbonates overlap with those of 'normal' speleothem samples. For example, in Apostelhöhle Cave, Malachitdom Cave, Na Javorce Cave, Herbstlabyrinth Cave, and Heilenbecker Cave in Central Europe cryogenic carbonates show δ^{18}O values that extend into the typical speleothem range of −5 to −10‰ (Žák et al., 2012). In these cases an unambiguous method for testing the cryogenic origin is needed.

The use of noble gases from fluid inclusions to constrain the cryogenic formation process is shown here for the first time using calcite crystal aggregates from Heilenbecker Cave. Their δ^{18}O and δ^{13}C values overlap with those of 'normal' speleothems from this cave site and therefore provide no unambiguous indication of their formation. Fluid inclusions contain aliquots of the original fluid from which the surrounding mineral precipitated. Given their chemical inert nature, noble gases are well-suited geochemical proxies to provide insights into the origin of their host minerals.

Noble gases allow to confirm the cryogenic origin of carbonate minerals in two ways. (a) Noble gas temperatures (NGTs) from fluid inclusions should either be consistent with freezing conditions or, if no NGTs can be determined, (b) the noble gas concentrations should reflect characteristic patterns that can uniquely be related to gradual pool water freezing. Under ideal conditions (low ratio of air-filled relative to water-filled inclusions, high abundance of inclusions, parent water equilibrated with air) it is possible to reconstruct the calcite precipitation temperature via noble gas analysis of fluid inclusions (Kluge et al., 2008a; Scheidegger et al., 2011; Kluge et al., 2013a).

The determination of NGTs uses the temperature-dependent solubility of gases (in particular Ne, Ar, Kr, and Xe) in water and the constant atmospheric noble gas mixing ratio in air as a reference (e.g., Kipfer et al., 2002). In speleothems formed from drip water in contact with air, the noble gas concentrations c_i (i = He,...Xe) in fluid inclusions can in general be described by a two-component model, which is known as the unfractionated excess air (UA) model (Kipfer et al., 2002). It explains the measured noble gas concentrations as a mixture of the temperature-dependent atmospheric equilibrium component $c_{i,eq}(T)$ and the addition of atmospheric air (e.g., Aeschbach-Hertig and Solomon, 2013):

$$c_i = c_{i.eq}(T) \cdot (1 + A \cdot k_i). \qquad (1)$$

The air component in Eq. (1) is written using the volume ratio A of enclosed air to water and the dimensionless Henry coefficient k_i.

Noble gas analyses are typically used to determine paleotemperatures from groundwater (Aeschbach-Hertig et al., 1999; Aeschbach-Hertig and Solomon, 2013) or from fluid inclusions in speleothems (Kluge et al., 2008a; Scheidegger et al., 2011; Kluge et al., 2013a). However, noble gas concentrations can furthermore provide valuable information about specific conditions during formation of fluid inclusions. As post-depositional changes are unlikely, noble gas concentrations in fluid inclusions directly reflect the (cryogenic) calcite formation process. We compare measured noble gas concentrations with values expected under different scenarios and focus especially on the effect of gradually freezing of cave pools.

2. Study site and samples

Loose cryogenic calcite crystals were collected on the cave floor between and on boulders at the cave chamber "Runde Halle" in Heilenbecker Cave in the Rhenish Slate Mountains, western Germany (7.34°E, 51.29° N; Fig. 1; Richter et al., 2008). The cave is located at ~200 m asl within Devonian limestone, has a mean interior temperature of ~9 ± 1 °C and shows weak ventilation only. The cave chamber "Runde Halle" is located 25 m below the surface. The coarse-crystalline cryogenic calcites collected in this chamber consist of morphologically different subsets (Richter et al., 2008) whereof spherulitic crystals with braided calcite aggregates ('Zopfsinter' in German, Fig. 2) were chosen for noble gas analysis. The braided calcite aggregates are generally smaller than 2 mm (e.g., Richter et al., 2008) and are composed of fibrous crystals with a length of ≤1000 μm and a maximum thickness of 50 μm.

Cryogenic calcites in Heilenbecker Cave yielded very negative δ^{18}O and negative δ^{13}C values (−16 to −6 and −7 to −3‰, respectively; Richter et al., 2008) consistent with a cryogenic origin (Žák et al., 2012). The investigated braided crystal aggregates showed δ^{18}O and δ^{13}C values of −6 to −12‰ and −4 to −6‰, respectively. Similar braided crystal aggregates from Malachitdom Cave showed decreasing δ^{18}O and increasing δ^{13}C values from the centre to the rim (Richter and Riechelmann, 2008). U–Th dating of the cryogenic calcites in Heilenbecker Cave resulted in an age of 31.3 ± 0.5 ka (Richter et al., 2009).

3. Methods

3.1. Noble gas extraction and measurement procedure

The extraction and measurement procedure followed the processes described in Kluge et al. (2008a). The sample consisted of ~20 crystals (to reach a bulk weight of 0.32 g) that were hand-picked to ensure a uniform crystal size and the provenance to a single cryogenic calcite sub-type (braided calcite aggregates). The calcite crystals were loaded into a stainless steel cylinder (33 cm long, 2.6 cm inner diameter, concave bottom) and evacuated overnight (>8 h). The steel cylinder was heated to 300 °C during pumping to reduce possible blank contributions to the measured noble gas amounts. The sample itself was only marginally affected by the heating as it was placed in a sample pocket (consisting of a modified hand valve) on the upper side of the cylinder and stayed below 50 °C (Marx, 2008). Two blanks of the extraction line including the stainless steel cylinder and the sample were determined before the actual sample measurement to check for leaks or high background values. The conditions during blank measurements corresponded to typical extraction conditions either during crushing or moderate heating, but included longer gas collection times (1 h gas collection during the crushing step blank at 200 °C; 70 min gas collection time during the heating step blank at 300 °C).

Noble gases and water were liberated from the cryogenic calcite crystals in a stepwise procedure. In a first step large air-filled inclusions at grain boundaries were preferentially opened, whereas in later steps the gases increasingly originated from smaller, intra-crystalline water-filled inclusions (Scheidegger et al., 2011). This procedure helps to