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“Cryptic” diagenesis and its implications for speleothem geochronologies

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A B S T R A C T

Speleothems are usually considered as one of the most amenable palaeoclimate archives for U-series dating. A number of studies in recent years, however, report cases of diagenetic alteration which compromises the use of U-series systematics in speleothems, resulting in inaccurate U-Th ages. Here we present the results of a high-resolution U-Th dating study of a stalagmite (CC26) from Corchia Cave in Italy where we document a number of departures from an otherwise well-defined age-depth model, and explore potential causes for these outliers. Unlike examples illustrated in previous studies, CC26 contains no visible evidence of neomorphism, and appears, at least superficially, ideally suited to dating. Good reproducibility obtained between multi-aliquot U-Th analyses removes any possibility of analytical issues contributing to these outliers. Furthermore, replicate analyses of samples from the same stratigraphic layer yielded ages in stratigraphic sequence, implying very localized open-system behavior. Uranium loss is suggested as a causative mechanism on account of the fact that all the outliers are older than their assumed true age. A limited number of micro-voids were observed under micro-CT analyses, and it is proposed that these were pathways for U loss. Uranium-loss modelling allows us to constrain the possible timing of diagenetic alteration and indicates that the precursor for the outlier with the largest age discrepancy (309%) must have been aragonite.

This study indicates that visibly unaltered speleothems may still contain small domains that have experienced post-depositional alteration. Such “cryptic” diagenesis, as recorded in this stalagmite, has implications for the constancy of accuracy of the U-series dating technique, and suggests a need for careful examination of speleothems prior to dating, particularly in low-resolution U-Th studies.

1. Introduction

The ability to generate robust, high-precision radiometric age profiles is arguably the principal advantage of using speleothems in studies of past climate and environmental change (Fairchild et al., 2006; Hellstrom, 2003; Henderson, 2006). For accurate radiometric dating, however, the speleothem carbonate must have remained completely closed with respect to post-depositional loss or gain of uranium (U) and thorium (Th) isotopes from non-radiogenic (i.e. diagenetic) processes (Richards and Dorale, 2003). This assumption is often axiomatic in most speleothem studies because they are typically composed of a thermodynamically stable polymorph of calcium carbonate (low-Mg calcite) arranged in stacked, compact layers of columnar crystals.

In recent years, however, there has been increasing evidence for diagenetic alteration, or neomorphism, reported in speleothems (Frisia et al., 2002; Hoffmann et al., 2009; Lachniet et al., 2012; Martín-García et al., 2009; Ortega et al., 2005; Perrin et al., 2014; Railsback et al., 1994; Scholz et al., 2014; Zhang et al., 2014). Neomorphism is the process of *in-situ* transformation of a mineral into

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a polymorph (Folk, 1965). In speleothems, it includes aragonite-to-calcite transformation and calcite-to-calcite recrystallization (e.g. Frisia et al., 2002). In many cases, the chemical properties are re-set to the extent that they no longer represent the original depositional conditions (Frisia et al., 2002; Zhang et al., 2014). For speleothems, U is commonly mobilized from the site of diagenesis, leading to an increase in the $^{230}Th/^{238}U$ isotopic ratio, which results in older-than-true U-Th ages (Lachniet et al., 2012; Ortega et al., 2005). This can severely compromise the accuracy of the U-Th chronology.

Neomorphism in speleothems is diagnosed by observation of petrological details on polished cut surfaces, on thin sections of the internal microstratigraphy and/or from trace element analysis (Frisia, 1996; Frisia et al., 2002; Railsback et al., 2002; Ortega et al., 2005). Textural changes are typical of neomorphism (Frisia et al., 2002; Lachniet et al., 2012; Zhang et al., 2014), where a mosaic of equant calcite crystals shows relicts of the original aragonite needles and replaces the original fabric. However, primary features inherited from aragonite can be preserved in the secondary calcite (Lachniet et al., 2012; Zhang et al., 2014). In the case of calcite-to-calcite alteration, evidence of chemical re-setting is dependent upon micro-analytical techniques such as laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) and synchrotron radiation–based micro XRF microscopy (Scholz et al., 2014; Zhang et al., 2014). In spite of the recent interest in speleothem neomorphism, most speleothem studies assume no alteration has occurred based on a lack of visible evidence in the hand specimen.

Here, we present the results of a high-resolution geochronological study of a speleothem (CC26) from Corchia Cave (Italy) that demonstrates how an apparently pristine stalagmite can undergo localized diagenesis, not visible to the naked eye, yet significant in terms of its impact on the sequence of U-Th ages. The study was initially conceived to explore Holocene variations in the dead-carbon proportion in the speleothem and its relationship to $\delta^{13}C$ (and potentially post-glacial vegetation recovery) by combining high-resolution, multi-aliquot uranium-thorium (U-Th) analyses with high-resolution radiocarbon dating. The speleothem had been the subject of previous studies of Holocene climate variability (Zanchetta et al., 2007, 2014; Regattieri et al., 2014).

The results of the high-resolution U-Th dating campaign revealed several previously unrecognized age inversions for which we sought an explanation. Unlike the recent study of Scholz et al. (2014), the Holocene portion of CC26 contained no visible or microscopic evidence of neomorphism, with the specimen appearing ideally suited to dating. We used fabric characterization via optical microscopy, high-resolution (LA-ICP-MS) trace-element mapping and synchrotron radiation–based micro XRF microscopy to investigate the regions affected by age inversion. Additionally, we used high-resolution micro X-ray computed tomography scanning (micro-CT) to explore micro-porosity and thus possible U-loss pathways. Finally, we present a model for significant but localized U loss and the constraints on its timing.

The X-ray CT method has been used previously in studies of speleothems, beginning with the pioneering work of Mickler et al. (2004), who explored its potential in determining the growth axis in speleothems as well as its utility in the selection of material suitable for palaeoclimate research, particularly in terms of porosity. In their study Zisu et al. (2012) combined CT and magnetic resonance imaging (MRI) to distinguish between water and air-filled macro holes in a suite of 21 speleothems and explored the potential of these methods for targeting specimens for fluid-inclusion analyses. This study revealed the existence of both axial holes formed penecontemporaneously with growth in discrete layers, and post-depositional off axis holes which suggests that water escaped post-depositionally through micro fissures, crystal boundaries, connected hole systems and crystal defects. The latest study by Walczak et al. (2015) for the first time used density data based on CT scanning as a palaeoclimate proxy in a speleothem from southern Iberia. They linked changes in sample density to shifts in palaeohydrological and climate conditions above the cave. Despite its potential, the method is still underutilized. We report a new approach that extends its potential for exploring evidence for diagenesis in speleothems. Speleothems used in previous studies were characterized by significantly higher porosities than is the case for CC26. All previous speleothems were analysed at a much lower resolution (with CT slice spacing between 0.21 and 2 mm), which would not be sufficient to address the aims of our study. High-resolution micro-CT scanning, as used in our study, has the potential to provide additional support to confirm U-loss hypotheses proposed to explain the U-Th outliers.

2. Sample description and methods

2.1. Site and sample description

The CC26 stalagmite was recovered from Antro del Corchia (Corchia Cave), a large, multi-level cave system in the Alpi Apuane massif of central Italy (Piccini et al., 2008). The cave is overlain by metamorphosed Mesozoic shallow marine carbonates and siliciclastics (marbles, dolomitic marbles, dolomites, metabreccias, and calcschists) and Paleozoic basement rock (phyllites). CC26 was removed from the Galleria delle Stalattiti, a chamber located at 840 m a.s.l. The feedwaters for this chamber pass through the Upper Triassic Grezzoni dolomites, metamorphosed carbonates and calcschists (Piccini et al., 2008). The chamber's microclimate is characterized by seasonal temperature oscillations within 1 °C (mean 8.4 ± 0.3) and a high relative humidity (100 ± 0.2%) (Piccini et al., 2008). Dripwater analyses from a site within the chamber reveal minimal variability in major ion concentrations, typical of deep-seated caverns (Piccini et al., 2008): Ca^{2+} 0.82 ± 0.02 mmol/L, Mg^{2+} 0.91 ± 0.03, SO_4^{2-} 0.36 ± 0.02 mmol/L, and a Mg/Ca 1.11 ± 0.03 (mol/mol). Dripwaters are slightly supersaturated with respect to calcite and have a pH range between 8.1 and 8.4 (Baneschi et al., 2011). High Mg concentrations in CC26 (mean Mg/Ca molar ratio 0.0418; Regattieri et al., 2014), and in older speleothems from the cave (Drysdale et al., 2009), are consistent with the prevalence of dolomite above the cave chamber. The stable isotope (Zanchetta et al., 2007, 2014) and trace element profiles (Regattieri et al., 2014) of CC26 have yielded palaeoclimate information on Holocene climate variability using the original chronology of Zanchetta et al. (2007), from which an age-depth model produced from 17 U-Th determinations was derived. All ages in this chronology were in correct stratigraphic order.

CC26 shows evidence for several growth phases (Fig. 1). In the older phases (unstudied in previous work), there is clear evidence of aragonite-to-calcite neomorphism, with significant negative correlations between Mg/Ca and Sr/Ca, suggesting a partially open system (cf. Pingitore, 1982). In the present study, only the youngest growth phase (the top 157 mm of the stalagmite), which grew continuously over the last ~12 ka (Zanchetta et al., 2007), was investigated.

2.2. Sample preparation and methodology

Half of the stalagmite was sliced into a ~1 cm-thick slab and cut along its growth axis. One section was used for U-Th sampling (and for ^{14}C; not considered here) while another was used for petrographic and trace element analyses. Samples for dating (solid pieces) were extracted along the growth axis using a dental air drill fixed to a manually navigated milling machine. In total, 78 samples were extracted, 47 of which were selected for this study. The