Cryogenic cave carbonate and implications for thawing permafrost at Winter Wonderland Cave, Utah, USA

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Winter Wonderland Cave contains perennial ice associated with two types of cryogenic cave carbonate (CCC) formed during the freezing of water. CCCfine is characterized by relatively high δ13C values, whereas CCCcoarse exhibits notably low δ18O values indicating precipitation under (semi)closed-system conditions in a pool of residual water beneath an ice lid. Previous work has concluded that CCCcoarse forms during permafrost thaw, making the presence of this precipitate a valuable indicator of past cryospheric change. Available geochronologic evidence indicates that CCC formation in this cave is a Late Holocene or contemporary process, and field observations suggest that the cave thermal regime recently changed in a manner that permits the ingress of liquid water. This is the first documented occurrence of CCCcoarse in the Western Hemisphere and one of only a few locations where these minerals have been found in association with ice. Winter Wonderland Cave is a natural laboratory for studying CCC genesis.

The cryosphere is responding rapidly to climate warming, and paleoclimate records are critical for understanding the novelty of these responses1,2. A persistent challenge is that many paleoclimate archives are biased toward extremes, for instance the most extensive glacials advances3, most widespread periglacial conditions4, or sea level high- and low-stands5. Yet records of past climatic transition are crucial for placing contemporary global change into a longer-term context6. This is especially true in Arctic and high mountain environments where temperatures are warming rapidly7,8, leading to dramatic diminishment of ice extent9,10 and degradation of permafrost11–13. Thus there is an urgent need for better records of how the cryosphere changed in the past, to clarify when and how rapidly changes occurred, and in what pattern these changes unfolded across the landscape.

A unique proxy demonstrated to provide information about past episodes of permafrost thaw, a transition that is often particularly disruptive to landscapes, ecosystems and infrastructure, is cryogenic cave carbonate (CCC). These minerals form when liquid water enters a cave containing subzero temperature conditions14. As this water freezes, solutes are concentrated in the residual liquid until saturation is reached and precipitation of CCC is induced15,16. Although seasonal subzero conditions can be created inside a cave entrance by winter cold, more significant permanently subzero conditions are maintained in so-called “ice caves” by ventilation regimes that preferentially allow the ingress of winter air while excluding summer warmth17,18. For instance, caves with a single downward sloping entrance can trap cold air through density settling in winter; air that is not replaced by warmer, less dense air in the summer. Alternatively, caves with multiple entrances at different elevations are susceptible to chimney effects that support freezing conditions where large amounts of cold air are pulled into the cave in winter17,19. Either way, CCC is precipitated when water containing sufficient dissolved solutes encounters the subzero conditions.

Two types of CCC have been identified. One group, referred to as CCCfine, forms when a film of water freezes on the surface of pre-existing ice20. The large surface area of this thin layer facilitates degassing of CO2, preferentially removing 12C, and leaving the remaining water enriched in 13C through disequilibrium effects21,22. Simultaneously, the preferential incorporation of 18O in the ice is counterbalanced by evaporation of lighter 16O from the water surface, yielding a characteristically higher δ13C and relatively unaltered δ18O values20. The ice
involved in the formation of CCC$_{\text{fine}}$ does not need to be perennial, however the presence of CCC$_{\text{fine}}$ in a currently ice-free cave is nonetheless clear evidence for colder conditions in the past.

In contrast, CCC$_{\text{coarse}}$ is a more specific proxy because it forms when a migrating permafrost table driven by thaw intersects the upper part of a cave, allowing dripwater to enter and form pools on the ice surface$^{23,24}$. Because the temperature in the main part of the cave (below the permafrost table) is still subzero, these pools freeze over, creating (semi)closed-system conditions in which degassing of CO$_2$ and evaporation of water are greatly reduced$^{25}$. Slow freezing of these isolated volumes of water precipitates CCC$_{\text{coarse}}$ distinguished by notably lower values of δ$^{18}$O compared with CCC$_{\text{fine}}$$^{14,16,25}$. As is apparent throughout Arctic and high mountain environments today, elevation of ground temperature above 0 °C, thawing of permafrost, and melting of ground ice are step-changes with dramatic repercussions for landscape and environmental evolution$^{26}$. CCC$_{\text{coarse}}$, therefore, is a critical proxy because it records past episodes of permafrost thaw.

Here we report the first discovery of CCC$_{\text{coarse}}$ in North America from an unusual setting where apparently young CCC is present in association with modern perennial ice. Our work provides an important point of comparison for CCC from well-studied caves in Europe, and documents a setting in which theories for CCC genesis could be evaluated.

**Location.** The CCC studied in this project was collected from Winter Wonderland Cave (WWC) in the Uinta Mountains of northeastern Utah, USA (Fig. 1). This solution cave has developed in the Carboniferous-age Madison Limestone, a regionally extensive rock unit that in this area consists of fine to coarse-grained dolomite and limestone, with locally abundant nodules of chert$^{27}$. The entrance to WWC is at an elevation of 3140 m asl in a north-facing cliff at the edge of the karstified Blind Stream Plateau (40.53°N, 110.73°W), a sparsely forested subalpine landscape. The mean annual air temperature (1985–2020) at the Brown Duck snowpack telemetry (SNOTEL) station at a similar elevation (3223 m) 12 km to the east of WWC is 0.3 °C (https://wcc.sc.egov.usda.gov/nwcc/site?sitenum=368). Elsewhere in the Uinta Mountains, the Chepeta remote automated weather station (RAWS) at an elevation of 3694 m recorded a mean temperature of − 2.0 °C between 2000 and 2019 (https://wrcc.dri.edu/cgi-bin/rawMAIN.pl?utmCHEP). Inside WWC temperatures were consistently subzero from 2016 to 2018 (with a mean of − 0.5 °C) because of a ventilation regime that brings cold winter air in through the main entrance, which is elevated above the main part of the cave, and inhibits the entry of warm air in the summer. As a result, about half of the cave, which has a mapped length of 245 m, is floored by perennial ice up to 3 m thick. CCC is present as a lag on the ice surface, drapes rocks emerging from the sublimating ice, and occurs as discrete layers within the ice body (Fig. 2a). Additional details about the cave, its climatology, and the perennial ice are presented in Munroe (2021).

Representative CCC samples, numbered YS-1 through YS-6 (Table S1) were collected from the ice surface along with a sample (BF) from within an exposed stratigraphic section through the ice, and three samples that were submerged in small (~ 10–30 cm deep) pools (Fig. 2b) of water filling depressions in the ice (CP, YP, and TF). Additional samples of Madison Limestone bedrock and water from pools were also collected for analysis.

**Results and interpretation**

**CCC morphology.** An array of morphologies is present in the CCC samples from WWC (Figs. 2 and S1). The smallest size fractions are spherulitic, with larger aggregates reaching diameters of 50 µm, and individual spherules from 10 to 20 µm in diameter (Figs. 2c and S1a,b). This observation is corroborated by results from laser scattering, which reveal mean grain sizes from 24 to 42 µm in the <75-µm fraction. Rounded grains are typically clumped in botryoidal aggregates with smooth surfaces, and dumbbell structures are common. Occasionally more sharp-edged morphologies are present, with needle-like points that rarely exceed 5 µm in length. Larger size fractions (75–250 µm) contain rafts of aggregated grains in excess of 200 µm long. The TF samples, which were collected from the water surface, are characterized by arrow-shaped blades 10–20 µm long, grouped
into thin rafts (Figs. 2d and S1c). All of these observations match CCC morphologies reported in the literature. For instance, previous work has established that CCC often occurs as raft-like aggregates of crystals, and spherical forms23,24,28. Rafts are generally flat and composed of interlocking crystals in a manner similar to floating carbonate minerals reported from non-cryogenic cave environments29. Crystal splitting has been invoked as a mechanism for the growth of spherical forms30, which are sometimes superimposed on a branching, sheaf-life skeleton31. Finally, spherules are reported to display smooth surfaces, and often connect during growth to form dumbbell shapes23 or chains24.

On the other hand, the CCC in WWC is considerably finer than precipitates with similarly low δ18O values reported from European caves. Although there is a wide range in sizes, CCC is typically described as having crystals from < 1 to ~ 40 mm23,24,28 compared with the 10–20-µm diameter spherules common in WWC. The significance of this difference is unclear; it may simply indicate that CCC in WWC formed from smaller-volume pools, or from water with a lower total dissolved load.

Types of CCC present in WWC. Although, as their names suggest, early studies differentiated CCCfine and CCCcoarse by grain size, δ13C and δ18O values reflecting different C and O isotope fractionation mechanisms are now recognized as the only valid criteria for distinguishing between the two groups20. With this in mind, values of δ13C and δ18O indicate that both types of CCC are present in WWC (Fig. 3a), despite no consistent distinction in their grain size distributions. Samples YS-3 and YS-4 have δ13C and δ18O values averaging 6‰ and −7.3‰ respectively (Table S2), suggesting that both are CCCfine. In contrast, samples YS-1, YS-2, YS-5, YS-6, BF, CP, and YP have lower values of δ13C, averaging ~3.0‰, and notably lower δ18O values, averaging ~16.5‰. These values identify these samples as CCCcoarse (Table S2). Sample TF also plots in the CCCcoarse field (Fig. 3a), although it was collected from a pool that had just begun to freeze, which may explain why its δ18O value is less negative than the other CCCcoarse samples. For comparison, samples of the Madison Limestone collected in WWC have an average δ13C value of 2.2‰ and δ18O value of −5.9‰ (Fig. 3a). Consistency of stable isotope values within individual size fractions (<75 µm, 75–165 µm, and 165–250 µm) emphasizes that YS-5, YS-6, CP, and YP are pure CCCcoarse (Fig. 3b). In YS-1 and YS-2, CCCcoarse is concentrated in the <75-µm fraction. In contrast, YS-4 is consistently CCCfine in all size fractions.

The results of additional analyses permit further interpretation of these samples. XRD reveals that YS-3 and YS-4 (CCCfine) are a mixture of calcite and quartz (Fig. 3a), and rounded quartz grains were visible in the SEM images (Fig. S1d). The presence of quartz is confirmed in the XRF results, where sample YS-4 contains 52% SiO2 (Table S3) YS-3 and YS-4 also have much higher chondrite-normalized REE values (Table S4, Fig. S3). These observations, along with the isotope data for size fractions presented above, are evidence for a detrital component in these CCCfine samples, which were collected from bedrock shelves 50–100 cm above the current ice surface. In contrast, XRD analysis indicates that the CCCcoarse samples from the ice surface are composed solely of calcite, as are the bedrock samples (Fig. S2). Major element analysis (Table S3) reinforces the abundance of calcite in YS-6.
(70% as CaO), and Mg is considerably more abundant in YS-6 (12.2% as MgO) than in YS-4 (1.8%). Collectively these analyses support the conclusion that the CCC coarse samples are (nearly) pure precipitates, whereas the CCC fine samples are a mixture of precipitated calcite and detrital minerals.

**CCC ages.** Previous studies have successfully applied $^{230}$Th/U disequilibrium dating$^{28}$ to CCC$^{16}$. Accordingly, an attempt was made to date CCC$_{coarse}$ from WWC (Table S5). The resulting ages are imprecise due to low $^{230}$Th/$^{232}$Th ratios, a situation that has complicated other work$^{24,28}$, meaning that the correction for detrital $^{230}$Th, and the uncertainty on that correction, are large. On the other hand, one of the samples analyzed (TF) is clearly modern because it was collected in 2018 from a pool of water that was not present in 2016. The initial $^{230}$Th/$^{232}$Th for this sample was, therefore, applied to the others (with a 25% 2-$\sigma$ uncertainty) to refine the age calculations. Results indicate that the CCC in WWC likely formed during the Holocene, and nearly all of the ages have error estimates that overlap with modern (Table S5, Fig. S4). Thus these ages, imprecise as they are, are consistent with CCC formation as a recent or current process in WWC. This result is significant because the majority of published CCC ages are from the Late Pleistocene e.g.$^{23,32}$, with only a few reports of Holocene ages$^{24,25,33}$.

Two additional lines of evidence support the interpretation that the CCC in WWC is young. First, rafts of calcite from sample YS-6 yielded a radiocarbon result of $^{13}C_{Modern} \pm 0.005$, consistent with formation in the late 20th Century when calibrated with the NH1 bomb curve in OxCal 4.4$^{34}$ (Fig. S5). Second, samples of rodent fecal pellets from the ice beneath the surface lag of CCC yielded radiocarbon ages that calibrate to between AD 1560 and 1830$^{35}$ (median values) using the IntCal20 calibration curve$^{36}$. Together this evidence strongly supports the conclusion that CCC formation in WWC occurred in the late Holocene, and is still occurring today.

**Figure 3.** (a) Isotope data for samples from WWC: blue squares are bedrock; red crosses are CCC from the ice surface; CP and YP are CCC from the “clear” and the “yellow” pools, respectively; BF is from a layer of CCC within the perennial ice body. The blue and green fields delineate the typical range of isotope values for CCC$_{fine}$ and CCC$_{coarse}$ after$^{28}$. (b) Isotope values for samples YS-1, YS-4, YS-6, and YP presented by size fraction: large circle, 165–250 $\mu$m; medium circle, 75–165 $\mu$m; small circle, <75 $\mu$m.
Winter Wonderland Cave as a unique natural laboratory for the study of CCC. Because of its utility as a paleoclimate proxy, numerous studies have investigated CCC e.g.23,32,37,38. However, there are only a few reports of CCC from locations outside Eurasia21,39, and all of these are categorized isotopically as CCCfine. Winter Wonderland Cave is, therefore, the first location in the Western Hemisphere where the unique paleoclimate indicator CCCcoarse has been identified.

Furthermore, nearly all previous observations of CCC describe these minerals from locations where they are present as loose concentrations of mineral grains on an ice-free cave floor23,28. Only twice has CCCcoarse been reported in association with modern, perennial ice33,38, and a recent comprehensive review noted that “Despite increasing evidence for Holocene CCCcoarse actively forming sites have not yet been observed”44. In WWC, CCCcoarse with late Holocene to modern ages is present in association with perennial ice, making this cave an exceptional natural laboratory in which to study these precipitates and their genesis.

Furthermore, firsthand observations indicate that the situation within WWC is consistent with the model for the formation of CCCcoarse. During summer visits in 2014, 2015, and 2016, the cave was dry and the ice surface exhibited a complex pattern of elongated ridges and troughs with local relief on the order of 30 cm (Fig. 4a–c) formed as a result of sublimation40. Short-term studies in an ice cave in Alberta, Canada suggest ice sublimation rates on the order of 3 mm per year41, although rates up to 10× higher have also been reported14. Either way, extrapolation from these benchmarks suggests that the relief observed on the ice surface in 2016 reflects 104 to 105 years of sublimation without the addition of new water. In contrast, in summer 2018, and again in 2019, liquid water entered the cave, filling many of the furrows, and freezing to create a new ice surface (Fig. 4d). Deeper pools of water had lids of ice from 1 to 5 cm thick (Fig. 2b), precisely the mechanism proposed for the formation of CCCcoarse16,23,25. This water ranged from clear to a deep yellow color, and CCC was observed on the floor of each pool (Table S1). From the available data we cannot determine if this CCC precipitated from the water, or whether it was present as a lag on the ice surface before the pools formed. However, the concentration of solutes in this pool water was very high, with the highest values (K, Mg, and Ca > 200 mg/L) corresponding to the yellow color (Fig. S6), consistent with conditions necessary for mineral precipitation through freezing-induced saturation15.

The change from 2016 to 2018 suggests that the thermal state of the epikarst has shifted, at least locally, to allow liquid water to penetrate to the level of the cave (~ 100 m below the ground surface), or to produce meltwater from ice farther back in inaccessible parts of the cave system. Under extensive permafrost conditions, caves are unlikely to contain ice sourced from dripwater because the permafrost inhibits the downward movement of liquid water45. Only when permafrost is degrading is it possible for liquid water to reach a cave where...
temperatures remain consistently subzero. The available evidence supports the interpretation that WWC and its surrounding bedrock comprise a sporadic permafrost body that is currently undergoing this transition. Given the presence of several meters of layered ice and associated CCC in WWC, it seems likely that this site has had a complicated thermal history, during which lengthy (decadal scale or longer) intervals of permafrost condition in the epikarst were interrupted by thawing events that allowed water to enter the cave and create new layers of ice. The influx of water to the cave observed in the past two summers is, therefore, not entirely unprecedented. Nonetheless, numerical modeling suggests that the time window between the onset of permafrost thaw in the epikarst and ultimate loss of cave ice deposits can be relatively short 43, and studies have noted that cave ice is rapidly ablating in various locations around the world 44. Future investigations in WWC should take advantage of this singular opportunity to observe the formation of different types of CCC in (near) real time, with the goal of improving our ability to use the presence of these features in currently ice-free caves as a dateable indicator of past permafrost thaw 43.

**Conclusion**

Winter Wonderland Cave in the Uinta Mountains of Utah contains cryogenic cave carbonate (CCC) associated with perennial ice. Two types of CCC with different genesis are present and can be distinguished on the basis of O and C isotope values. CCC_{fine} is produced through open system freezing as a thin film of water flows over the ice surface. In contrast, CCC_{coarse} is produced by (semi) closed-system freezing in deeper pools of water beneath thickening lids of ice. These conditions arise during permafrost thaw, thus CCC_{coarse} records past episodes of permafrost degradation. Available age control suggests that CCC formation occurred in this cave during the late Holocene and may be a contemporary process. This cave is the first location in the world where such young CCC_{coarse} has been found, and is the first cave in the Western Hemisphere where CCC_{coarse} has been identified. Records of past cryosphere transitions are critical context for assessing contemporary changes in Arctic and Alpine environments. Winter Wonderland Cave provides a singular opportunity to test and improve theories of CCC genesis that will ultimately allow better insight into how permafrost responded to past climatic transitions.

**Methods**

**Sample preparation and analysis.** At Middlebury College, CCC samples were wet-sieved into <75, 75–250, and >250-µm size fractions. Each fraction was placed in a 50-mL centrifuge tube, and after fine sediment had settled, excess water was carefully decanted. Samples were then frozen in a ~40 °C freezer for 4 h. The uncapped centrifuge tubes were then dried overnight in a Labconco FreeZone 6 L freeze dryer. The resulting powder was lightly ground with a clean mortar and pestle and returned to each tube.

**Scanning electron microscopy.** A Tescan Vega 3 LMU scanning electron microscope (SEM) at Middlebury College was used to acquire images of the CCC in different grain size fractions. Samples were adhered to metal disks with double sided tape, coated in gold palladium, and images were captured at different magnifications in order to compare CCC morphologies. Energy dispersive X-ray spectroscopy (EDS) was applied to samples YS-3, YS-6, TS-2, CP, YP, and TF after carbon coating to determine if varying morphologies correspond to different elemental compositions. The semi-quantitative elemental results were converted to weight % oxides to differentiate between calcite, dolomite, and quartz. AZtecOne software was used to capture secondary electron and backscatter images and for elemental analysis. Weight % oxide data were transformed into structural formulae for common minerals.

**Grain size distribution.** The grain size distribution of the <75-µm fraction of each sample was determined using a Horiba LA-950. In preparation for analysis, samples were dispersed in distilled water, mixed for 30 s using a Vortex-T Genie 2, and sonified with an FS20D sonifying water bath for 1 min. A clean syringe was used to transfer an aliquot of each sample to the Horiba. Sample runs were duplicated to assess consistency. Grain size distribution data were presented as volume percentages of sand (coarse, medium, and fine), silt (coarse, medium, fine, and very fine), clay (2–1 µm), and colloid (<1 µm).

**X-ray diffraction.** Samples of the 75–250-µm fraction, as well as rock samples powdered in a shatterbox, were analyzed on a Bruker D8 Advance Model X-Ray Diffractometer at Middlebury College. The mineralogy of several samples was compared across different size fractions (<75 µm and 75–250 µm) to detect any compositional differences. As no obvious differences were detected, the fractions <75 µm and 75–250 µm were used interchangeably for future analyses depending on the volume of sample remaining. Nine samples were analyzed as bulk powders from 2° to 50° 2θ. Samples CP, YP, and TF were not large enough for a bulk powder analysis, so they were transferred to a glass slide and analyzed as oriented powders, and scanned from 2°–40° 2θ. The diffractometer operated at 40 kV and 40 mA with a solid state detector, theta-theta goniometer, and CuKα radiation. Mineral abundances were assessed using intensity ratios, and known mineral spectra peaks were identified by comparison with standard reference patterns.

**X-ray fluorescence.** Samples of the 75–250-µm size fraction were analyzed for major element composition using X-ray fluorescence (XRF) at Middlebury College. Samples were ignited at 1000 °C for 30 min in a Leco TGA-701 thermogravimetric analyzer prior to analysis to remove organics and interstitial water. Ignited samples were ground to a fine powder and combined in a 10:1 ratio of lithium borate fluxing agent to sample (6.0 g fluxing agent and 0.6 g of sample). The combined sample and fluxing agent were melted in a Claisse LeNeo fluxer at 1050 °C to form a glass disk. This process was repeated for samples YS-4, YS-6, TS-1, TS-2, and one bedrock...
sample; other samples did not contain sufficient mass in the desired particle size range for fluxing. Glass disks were analyzed using a Thermo Scientific ARL QuantX energy dispersive (ED) XRF spectrometer to measure major elements. A glass disk made from Standard Reference Material 88B (dolomitic limestone) was included in each run to assess the accuracy of measurements. The analysis quantified the abundance of oxides, which were converted to atomic abundances of major elements (Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, P).

**Inductively coupled plasma mass spectrometry.** Seven samples of the <75-µm fraction (YS-3, YS-4, YS-5, YS-6, TS-1, TS-2, and a bedrock sample), and an additional YS-4 sample of the 75–250-µm fraction, were prepared for analysis with inductively coupled plasma mass spectrometry (ICP-MS) to determine the abundance of trace and rare earth elements. Dried samples were combined in a 9:1 ratio of lithium metaborate fluxing agent to sample (1.8 g LiBO₂ and 0.2 g sample). A Cäsische Nebo fluxer was used to melt the sample and fluxing agent and dissolve the melt in 5% HNO₃. Dissolved CCC and rock samples, along with samples of water from the cave were analyzed with a Thermo Scientific iCAP Q ICP-MS at Middlebury College in conjunction with Qtegra ISDS software. Calibration curves were generated for each run, and quality control with internal standards was used to drift correct results after every five samples. Standard Reference Material 88B (dolomitic limestone) was analyzed at the beginning and end of every batch of CCC samples, and National Institute of Standards and Technology (NIST) standard 1643f. (trace elements in water) was run in conjunction with water samples.

**C and O stable isotopes.** Eleven samples (all of <75-µm size fraction except for CP and YP where the 75–250-µm fraction was used) were prepared for δ¹⁸O and δ¹³C stable isotope analysis in the Department of Geology at Union College using a Thermo GasBench II connected to a Thermo Delta Advantage mass spectrometer in continuous flow mode. Analytical uncertainties were better than 0.1 ‰ (1σ) for δ¹⁸O and 0.05‰ (1σ) for δ¹³C. All values were calibrated against international standards and reported in permil (‰) relative to Vienna Pee Dee belemnite (VPDB).

Eleven samples of bedrock, along with additional wet-sieved size fractions (<75, 75–165, and 165–250 µm) of samples YS-1 through YS-6, CP, and YP were analyzed in the Institute for Geology at the University of Innsbruck on a Thermo Scientific Delta V Plus isotope ratio mass spectrometer (IRMS) connected to a GasBench II. This system produces a typical precision (1σ) of ± 0.06‰ for δ¹³C and ± 0.08‰ for δ¹⁸O ref.46. All samples were run in duplicate.

**²³⁰Th/²³⁴U disequilibrium dating.** Five samples (YS-5, YS-6, CP, YP, and TF) were analyzed using U-Th radiometric dating techniques in the Department of Earth, Atmospheric, and Planetary Sciences at the Massachusetts Institute of Technology. Two samples were divided into three replicates (YS-5 A, B, C and YS-6 A, B, C) to assess reliability of the dating for young samples with a high potential for Th contamination. One replicate for each sample did not produce a result due to a low yield in chemistry. Approximately 0.03 g of each sample was combined with a ²²⁹Th-²³³U-²³⁶U spike, then digested and purified via iron coprecipitation and ion exchange chromatography. U and Th were analyzed on separate aliquots using a Nu Plasma II-ES multi-collector ICP-MS equipped with a CETAC Aridus II desolvating nebulizer following previously published protocols47. U-Th ages were calculated using standard decay constants for ²³⁰Th, ²³⁴U, and ²³⁸U⁴⁸–⁵⁰. Ages were recalculated by assigning sample TF an age of -61 years BP (where present is defined as AD 1950), given the observation that it formed through the cave is assumed to be ± 25% at 2-sigma.

**Data availability**
The dataset generated in this study has been deposited in the Hydroshare repository and will have the doi https://doi.org/10.4211/hs.b5f000096174af9f4e62bd2065d6 after publication.

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Author contributions:
J.M. designed the study, wrote the manuscript, and prepared the figures. K.K. participated in fieldwork, conducted the geochemical and preliminary isotope analyses, and prepared samples for U/Th dating. C.S. oversaw isotope analyses at the University of Innsbruck, D.M. and G.S.M. oversaw the U/Th dating at MIT. D.H. ensured safe passage to and from the cave, and provided the mapping upon which Fig. 1 was based. All authors reviewed the manuscript before submission.

Competing interests
The authors declare no competing interests.

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