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U-Pb dating of speleogenetic dolomite: A new sulfuric acid speleogenesis chronometer

Victor J. Polyak^{1*}, Paula P. Provencio², and Yemane Asmerom¹

¹Earth & Planetary Sciences, University of New Mexico, Albuquerque, New Mexico 87131 USA

²Institute of Meteoritics, University of New Mexico, Albuquerque, New Mexico 87131 USA

Abstract: The 1100-meter Big Room elevation level of Carlsbad Cavern, New Mexico USA, formed 4 Ma by hypogenic sulfuric acid speleogenesis (SAS). The age of the Big Room level of 4.0 ± 0.2 Ma was previously determined by dating alunite, a byproduct of speleogenesis, using the $^{40}\text{Ar}/^{39}\text{Ar}$ method. Duplication of these results is possible by radiometric dating of other byproducts interpreted to be speleogenetic (a byproduct of speleogenesis) such as calcite and dolomite in certain settings. XRD and TEM analyses of sample 94044, a piece of crust collected within the Big Room level of SAS just below Left Hand Tunnel indicate that this dolomite sample we interpret to be speleogenetic is as well-ordered crystallographically as the Permian bedrock dolomite, possibly reflecting its SAS origin. Three U-Pb analyses were performed on subsamples A1, A2, and A3 of sample 94044, and two, A1 & A2, produced out-of-secular equilibrium results due to the presence of authigenic quartz and/or later re-distribution of uranium in the dolomite crust, which prevented the calculation of an isochron age. Because subsample 94044-A3 exhibited $\delta^{234}\text{U}$ and $^{230}\text{Th}/^{238}\text{U}$ values consistent with secular equilibrium, we were able to generate a $^{238}\text{U}/^{204}\text{Pb}$ - $^{206}\text{Pb}/^{204}\text{Pb}$ model age of 4.1 ± 1.3 Ma on the dolomite crust (94044) that we interpret to be reliable. The 4.1 Ma age of the speleogenetic dolomite crust agrees with the 4 Ma $^{40}\text{Ar}/^{39}\text{Ar}$ age for the timing of speleogenesis of the Big Room level. While $^{40}\text{Ar}/^{39}\text{Ar}$ -dating of speleogenetic alunite- and jarosite-group minerals remains the primary way to determine absolute timing of hypogenic SAS, here we demonstrate that U-Pb dating of speleogenetic dolomite can be used to complement or independently measure the timing of SAS. This method of dating SAS could be applicable in caves where the more soluble SAS-indicator minerals such as gypsum, alunite, and jarosite have been removed.

Keywords: U-Pb dating, sulfuric acid speleogenesis, dolomite, XRD, TEM

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INTRODUCTION

Carlsbad Cavern, New Mexico USA, is a classic example of 'fossil' hypogene sulfuric acid speleogenesis (SAS). Carlsbad Cavern, along with other caves in the Guadalupe Mountains such as Lechuguilla Cave, is well-studied with respect to hypogenic SAS (Fig. 1; Hill, 1987; Polyak et al., 1998; Palmer & Palmer, 2000; Jagnow et al., 2000; Klimchouk, 2007; Kirkland, 2014). This type of speleogenesis leaves behind mineral byproducts such as alunite, jarosite, gypsum, quartz, and dolomite (Polyak & Provencio, 2001). The advantage of this is obvious: these byproducts preserve direct evidence of speleogenesis. One of the byproducts, gypsum, was used to advance the concept of SAS (Hill, 1987). Another byproduct, alunite, was

used to constrain the absolute timing of speleogenesis (Polyak et al., 1998), and define four major episodes of SAS in the Guadalupe Mountains area at 11, 6, 5, and 4 Ma. The 4 Ma episode of speleogenesis formed passages in Carlsbad Cavern at the Big Room level (Fig. 1). The $^{40}\text{Ar}/^{39}\text{Ar}$ method is ideal for dating alunite and jarosite, however, other dating methods may also be suitable for some of these byproducts. Here we test the U-Pb dating of dolomite crust that we interpret to be speleogenetic (a byproduct of speleogenesis) that formed at the 4 Ma Big Room level (~1100 meters elevation above sea level today).

Dolomite forms in caves as a secondary deposit in speleothems (Thraillkill, 1968; Fischbeck, R. & Müller, 1971; Barr-Matthews et al., 1991; Hill & Forti, 1997; Martín-Pérez et al., 2012 and citations within).

*polyak@unm.edu

Fig. 1. Line map profile of Carlsbad Cavern and photographs of crinkle crust typical of dolomite crusts interpreted to be speleogenetic in origin. These two photographed occurrences are in Left Hand Tunnel of Carlsbad Cavern near the area where sample 94044 was collected in 1994. The green circle is the area of collection. Two major levels of SAS are added to the profile. The Glacier Bay level is defined by results at this level from Glacier Bay in Lechuguilla Cave. Elevation in masl = meters above present sea level. Cave map was provided by Stan Allison and Carlsbad Caverns National Park.

Dolomite has also been reported as a speleogenetic byproduct in Guadalupe Mountains caves (Polyak & Provencio, 2001; Palmer & Palmer, 2012). Speleogenetic dolomite seems to most commonly occur as crusts (Figs. 1 & 2; indurated pastes, crinkle crusts, crusts with desiccation cracks). A piece of crust interpreted to be a byproduct of speleogenesis

was collected from an area below Left Hand Tunnel at approximately the 4-Ma Big Room level of Carlsbad Cavern. The dolomite crust (sample 94044) was collected in 1994 for the purpose of studying cave dolomite occurrences and identifying a yellow mineral on its surface. The yellow mineral was identified as the hydrated uranium vanadate known as tyuyamunite.

Fig. 2. Thin section of dolomite crust from Lechuguilla Cave (sample 94040). The base of this crust is interpreted to be primary speleogenetic dolomite and has a thickness of ~8 mm, equivalent to the micritized rims described by Palmer & Palmer (2012). The fibrous and botryoidal dolomite deposited on the primary crust is likely a later stage deposit similar to the evaporative phases described by Palmer & Palmer (2012). The arrows point to desiccation cracks. The entire crust is dolomite.

The crust also contains authigenic quartz. Both, tyuyamunite and quartz make up the outer layers of the crust and probably precipitated after the dolomite formed. However, the quartz may have formed very soon after speleogenesis. An initial uranium (U)-thorium (Th) analyses of a piece of sample 94044 showed that this crust contained sufficient uranium for U-Pb dating and was in near-secular equilibrium of the radioactive decay of the ^{238}U system. Given that the dolomite crust formed during SAS, if dateable by the U-Pb method, it should produce an age equivalent to the Big Room level of speleogenesis, which is 4 Ma. Richards et al. (1998) and Woodhead et al. (2006; 2012) demonstrated that speleothem calcite and aragonite are dateable using the U-Pb dating method. Numerous studies since have corroborated their findings. Our results add further characterization of these dolomite crusts that are presumed to be speleogenetic using scanning electron microscopy (SEM), transmission electron microscopy (TEM), and, U, Th, and Pb isotopic analyses. We propose that this new isotopic evidence provides another way in which the absolute timing of hypogenic SAS can be determined.

METHODS

SEM and optical petrography were used to examine the dolomite crust fragment. High-resolution TEM and XRD were used to examine the degree of crystallinity of the cave dolomite. Minerals were identified using XRD. For our isotopic study, sample 94044 was cleaned and broken in numerous pieces weighing 15 to 50 mg in the University of New Mexico Radiogenic Isotope clean laboratory, three of which were selected for U-Pb dating. They were dissolved in 15N nitric acid and spiked with a ^{232}Th - ^{233}U - ^{236}U - ^{205}Pb solution. Eichrom 1x8, 200-400 mesh chloride form anion resin chemistry was used to clean and separate U, Th, and Pb. The separates were analyzed on a Thermo Neptune multicollector inductively coupled plasma mass spectrometer. Standards used for fractionation control and gain values were NBL-112 for U runs, NBS-981 for Pb runs, and an in-house $^{230}\text{Th}/^{229}\text{Th}$ solution for Th runs. PBDAT (Ludwig, 1991) was used to reduce the data. Our three subsample analyses did not form a U-Pb isochron age, which is the more traditional and robust way of reporting U-Pb ages (Richards et al. 1998; Woodhead et al. 2006; 2012). However, because of the high concentration of U relative to Pb, a more simple 'model age' method was used based on $t = (1/\lambda) \ln(((^{206}\text{Pb}/^{204}\text{Pb})_{\text{measured}} - ^{206}\text{Pb}/^{204}\text{Pb}_{\text{initial}}) / ((^{238}\text{U}/^{204}\text{Pb})_{\text{measured}}) + 1)$, where t = age in years and λ is the decay constant for ^{238}U (Faure, 1986). The $\delta^{234}\text{U}$ value = $[(^{234}\text{U}/^{238}\text{U})_{\text{measured}} / (^{234}\text{U}/^{238}\text{U})_{\text{eq}} - 1] \times 1000$ ‰, where ratios are atomic ratios, eq = secular equilibrium, and ‰ = permil. An initial $\delta^{234}\text{U} = 1500 \pm 500$ ‰ and an initial $^{206}\text{Pb}/^{204}\text{Pb} = 21 \pm 2$ were used in the $^{238}\text{U}/^{204}\text{Pb} - ^{206}\text{Pb}/^{204}\text{Pb}$ model age calculation and cover the expected range of values that come from measurements of speleothems in the Guadalupe Mountains (Polyak et al., 2001; 2004; Asmerom et al., 2013; Decker et al., 2015; initial $^{206}\text{Pb}/^{204}\text{Pb} = 20.8 \pm 1.9$

measured for Arthur and Margaret Palmer's dolomite sample CB907, an indurated speleothemic dolomite paste from Lake of the Clouds, Carlsbad Cavern, unpublished). The $^{206}\text{Pb}/^{204}\text{Pb}$ was corrected for the initial $\delta^{234}\text{U}$ value after Denniston et al. (2008). Errors reported for the model age are absolute 2σ analytical errors based on those reported for the measured ratios of $^{238}\text{U}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$, initial $\delta^{234}\text{U}$, initial $^{206}\text{Pb}/^{204}\text{Pb}$, and errors related to ^{238}U and ^{235}U decay constants published by Schoene et al. (2006). Decay constants for ^{234}U and ^{230}Th are from Cheng et al. (2013).

RESULTS

XRD, SEM, and mineral assemblage results for dolomite crust

XRD of sample 94044 indicates the presence of dolomite, quartz, and traces of calcite. A trace of tyuyamunite was indicated by analyzing a few of the yellow crystals using a Gandolfi XRD camera, a single crystal device that can simulate powder diffraction results. Petrographic examination of sample 94044 shows micro-quartz near the crust surface (Fig. 3), and densely crystalline dolomite near the base of the crust. The occurrence of quartz near the surface of the crust is similar to quartz described in replacement dolomite by Palmer and Palmer (2012; their Fig. 21). Figure 4 shows SEM images of tyuyamunite, dolomite

Fig. 3. Photomicrographs taken with crossed polarized light showing authigenic quartz and porous dolomite at the top and more densely crystallized dolomite at the bottom of sample 94044.

and quartz. The dolomite crust is porous in the middle and at the top near the contact with the quartz, and may be evidence that a soluble phase existed, such as gypsum, that has been since removed. Sample 94044 dolomite crust is likely a H_2SO_4 -micritized rind described by Palmer & Palmer (2012) that formed between the bedrock and speleogenetic gypsum rind during speleogenesis. Our XRD results show that the speleogenetic dolomite is as well-ordered crystallographically as the Permian bedrock dolomite (Fig. 5), which is an unexpected finding for low temperature-formed non-marine dolomite, and may reflect its SAS-related origin.

Microstructural observations

The superstructure of the dolomite lattice is based on comparison to the non-superstructure calcite lattice and is clearly exemplified by XRD powder patterns of northesite $[\text{BaMg}(\text{CO}_3)_2]$ (Lippmann, 1973). Alternating Ca and Mg cation layers along the c-direction produces the superstructure of dolomite. Dislocations, defects, excess Ca, changes in the alternating sequence of the cation layers, or non-perfect orientations of the CO_3 ions in the dolomite structure can produce microstructural disorder, which in turn produces contrast in intensity of high resolution TEM images (Gunderson & Wenk, 1981; Wenk et al., 1983, 1991; Van Tendeloo et al., 1985). These are referred to as modulated microstructure in crystals. The microstructural disorder, when periodic, produces modulations of contrast in the TEM images. Modulated microstructures can be highly

Fig. 4. SEM images of authigenic quartz and dolomite (top) and authigenic quartz and tyuyamunite plates (bottom) near the top of 94044 dolomite crust.

Fig. 5. A) An XRD expression of the crystallinity of the dolomite can be determined by measuring the order ratio, the intensity of the [015] divided by the intensity of the [110]. The crust dolomite we consider speleogenetic and bedrock dolomite order ratios are similar. A sample of dolomite we interpret to be speleothemic rather than speleogenetic has significantly lower values than speleogenetic dolomite; B) Unit-cell dimensions measured for the speleogenetic dolomite are slightly calcian (50.3 to 52.0 mole% CaCO_3), and are the same as the bedrock dolomite.

ordered and produce Moiré fringes (parallel dark/light contrast), or they can form less-defined two- or three-dimensional patterns of light/dark contrast. HRTEM imaging shows these periodic changes in the lattice fringe pattern at a nanoscale.

Moiré fringes and other intensity modulations were observed in samples 94036 (interpreted to be a speleogenetic dolomite crust from Lechuguilla Cave) and 94044 (Fig. 6). Continuous nanoscale modulations were observed in the high resolution TEM lattice fringe images of sample 94036 indicating probable periodic disorder in three dimensions. In contrast, sample 92006, speleothemic dolomite from Spider Cave, Carlsbad Caverns National Park, showed fewer modulations, and we interpret this as indicating scarcely isolated nanoscale regions of coherent superlattice. Therefore, the dolomite structure of sample 92006 has more disorder with respect to Mg and Ca cation layers. This is supported by the XRD data, which show very weak superstructure in sample 92006 dolomite, and moderately well-developed dolomite superstructure in the dolomite of samples 94036 and 94044. Samples 94036 and 94044 seem to show modulated microstructures that are typical for moderately well-ordered calcian dolomites. TEM results hint that crusts 94036 and 94044 are not typical of speleothemic dolomite, and like the XRD results, show microstructure similar to the bedrock dolomite. These observations are subtle, but show that the crusts that we are interpreting as speleogenetic have a well-ordered microstructure similar to the Permian bedrock

Fig. 6. High-resolution TEM micrographs of three cave dolomite samples. A) Modulations of intensity related to modulated microstructure in the dolomite of sample 94036, a speleogenetic dolomite; B) Fast fourier transform of (A) may provide a different look at the modulated microstructure by removing interference intensities. Note the apparent dislocation in the circled region; C) Micrograph of sample 94044 showing modulated microstructure, an indicator of moderately well-ordered calcian dolomite; D) Micrograph of sample 92006 showing slightly fewer intensity modulations consistent with its lower XRD-derived order ratio (Fig. 5) and its less well-ordered structure.

dolomite, which likely reflects on the SAS-related origin of the crust.

U-Th-Pb isotope results

Our first U-series analysis showed that sample 94044 contains 64 $\mu\text{g/g}$ U, and that the dolomite is in secular equilibrium ($\delta^{234}\text{U} = -5 \pm 7 \text{‰}$; $^{230}\text{Th}/^{238}\text{U} = 0.99 \pm 0.02$) and too old for U-series dating. Table 1 shows the results of the three subsample U-Pb analyses. The three sets of results did not form an U-Pb isochron age, and two analyses, subsamples 94044-A1 and -A2, show distinct $\delta^{234}\text{U}$ evidence for some type of alteration/diagenesis. All three subsample analyses provided $^{230}\text{Th}/^{238}\text{U}$ ratios equal to 1.0 (secular equilibrium) and show that the crust has probably been unaltered for at least the last 600 ka, or that alteration/diagenesis were subtle. One analysis, 94044-A3, shows secular equilibrium for both $\delta^{234}\text{U}$ ($-0.8 \pm 1.0 \text{‰}$) and $^{230}\text{Th}/^{238}\text{U}$ (1.001 ± 0.005). A $^{238}\text{U}/^{204}\text{Pb}$ - $^{206}\text{Pb}/^{204}\text{Pb}$ model age was calculated for each subsample. The model ages decreased with more negative $\delta^{234}\text{U}$ values and varied from 4.1 to 0.7 Ma, with A1 & A2 yielding model ages of 0.7 ± 0.4 Ma and 1.7 ± 0.7 Ma, respectively. The most reliable model age, based on secular equilibrium of $\delta^{234}\text{U}$ and $^{230}\text{Th}/^{238}\text{U}$, is 4.1 ± 1.3 Ma (2 σ).

Table 1. U, Th, and Pb data for sample 94044 A1, A2, and A3.

Sub-Sample	^{238}U ($\mu\text{g/g}$)	^{232}Th (ng/g)	Pb ($\mu\text{g/g}$)	$\delta^{234}\text{U}_{\text{meas}}$
A1	65.06 ± 0.12	3.48 ± 0.14	0.150 ± 0.027	-7.56 ± 0.99
A2	70.68 ± 0.09	305.47 ± 13.04	0.362 ± 0.091	-2.30 ± 1.00
A3	61.43 ± 0.14	65.06 ± 0.12	0.617 ± 0.153	-0.77 ± 1.00
Sub-Sample	$^{230}\text{Th}/^{238}\text{U}$	$^{238}\text{U}/^{204}\text{Pb}$	$^{206}\text{Pb}/^{204}\text{Pb}$	Model Age (Ma)
A1	0.992 ± 0.013	29517.0 ± 0.4	24.34 ± 0.18	0.73 ± 0.44
A2	1.000 ± 0.008	13077.0 ± 0.2	24.56 ± 0.15	1.76 ± 0.72
A3	1.001 ± 0.005	6698.1 ± 0.3	25.22 ± 0.18	4.06 ± 1.25

All errors are absolute 2 σ except for errors of $^{238}\text{U}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$, which are 2 σ percent. The $^{206}\text{Pb}/^{204}\text{Pb}$ is adjusted for an initial $\delta^{234}\text{U}$ of $1500 \pm 500 \text{‰}$. The model ages are $^{238}\text{U}/^{204}\text{Pb}$ - $^{206}\text{Pb}/^{204}\text{Pb}$ ages.

DISCUSSION

The trend in Fig. 7 distinctly shows anomalously younger ages in the two subsamples that are interpreted from their negative $\delta^{234}\text{U}$ values to be altered.

The trend suggests that U has probably migrated in parts of the crust after the crust formed, and/or that quartz as a second phase and perhaps younger than the dolomite, was present in subsamples A1 and A2, and has altered the pristine dolomite crust and interfered with measurement of an accurate dolomite U-Pb age. The negative $\delta^{234}\text{U}$ values in the two subsamples suggest that some U was removed from those sites, and perhaps precipitated as tyuyamunite on the surface of the dolomite crust with quartz long after speleogenesis. A quartz phase also may not have fully dissolved in the nitric treatment and/or may have a younger formation age than the dolomite, which may have interfered with the isotope system. Later-stage evaporative deposits of dolomite and quartz on speleogenetic dolomite rinds are clearly

identified by Palmer & Palmer (2012). An isochron age will require further analyses of additional pieces that do not contain quartz.

At least three possible dolomite types exist in the sulfuric acid caves of the Guadalupe Mountains. Dolomite in the host rock, dolomite in speleothems, and dolomite as a speleogenetic byproduct. The host rock is Permian in age, and in the case of Left Hand Tunnel, it is probably reef limestone (as in Palmer & Palmer, 2012, their Fig. 11) rather than dolostone. Based on provenance, and XRD and TEM results, we interpret sample 94044 to be a speleogenetic dolomite crust. Regardless, the U-Pb age of crust that contains host rock dolomite will produce an anomalously high age, millions of years older than the period of speleogenesis and up to the age of the Permian limestone, ~265 Ma. Speleothemic dolomite will yield ages less than the age of speleogenesis. Our U-Pb model age of 4 Ma for the dolomite crust that we have interpreted to be speleogenetic strongly supports our interpretation and provides additional insight

Fig. 7. Graph showing ^{238}U - ^{206}Pb model ages from three subsamples of sample 94044 relative to the measured $\delta^{234}\text{U}$ values for those subsamples. One subsample, 94044-A3, in secular equilibrium, produces a model age of 4.1 ± 1.3 Ma, consistent with the argon-age of 4 Ma for the Big Room level. The other two subsample results show evidence of alteration and produce seemingly anomalously young ages. The subsample 94044-A3 results support that the dolomite is primary speleogenetic.

into the process of SAS. The XRD and TEM results provide a further characterization of these crusts. As Palmer & Palmer (2012, their Figs. 11 & 12) have described, micritized rinds of dolomite and calcite form during SAS. The active sulfuric acid cave, Cueva de Villa Luz, Mexico, has a gypsum and anhydrite rind covering the bedrock, and the micritized calcite/dolomite rind forms between the sulfate rind and the bedrock (Palmer & Palmer, 2012, their Fig. 12). This is a likely analog for the fossil sulfuric acid caves such as Carlsbad Cavern. In many cases, over millions of years, the more soluble sulfate rind is removed, leaving a dolomite/calcite rind on the surface of the bedrock such as exemplified by sample 94044. The crinkle morphology and desiccation cracks in these crusts suggest that in many cases they formed as pastes as Palmer and Palmer (2012) have described. Once characterized, a benefit of speleogenetic dolomite is that it might survive longer than the speleogenetic sulfate minerals. For example, sulfuric acid caves in the Guadalupe Mountains that no longer contain alunite might have dateable speleogenetic dolomite crusts that can be used to determine the timing of speleogenesis of those caves.

CONCLUSION

Dolomite crust (sample 94044) from Carlsbad Cavern interpreted to be speleogenetic was characterized using XRD, SEM, TEM, and U, Th, Pb isotopic analyses. XRD and TEM show that this dolomite is as well-ordered crystallographically as the Permian bedrock dolomite. While the U, Th, Pb isotopic results were complicated by presence of authigenic quartz and/or post-depositional migration of U, one of three subsample analyses, subsample 94044-A3 yielded a $\delta^{234}\text{U} = -0.8 \pm 1.0$ ‰ and $^{230}\text{Th}/^{238}\text{U} = 1.001 \pm 0.005$, showing that this subsample is likely well-preserved. The ^{238}U - ^{206}Pb model age of 94044-A3 is 4.1 ± 1.3 Ma,

which is consistent with the $^{40}\text{Ar}/^{39}\text{Ar}$ alunite age of 4.0 ± 0.2 Ma for the Big Room level. Our results show that it is possible to determine the absolute timing of hypogene SAS by U-Pb dating of speleogenetic dolomite. This is particularly applicable to SAS caves that no longer contain the sulfate byproduct alunite.

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