Uranium and strontium isotope study of late-stage speleothems from lava tube caves in El Malpais National Monument, New Mexico

Zachary LaPointe, Victor Polyak, and Yemane Asmerom

2013, pp. 223-228. https://doi.org/10.56577/FFC-64.223

in:

Geology of Route 66 Region: Flagstaff to Grants, Zeigler, Kate; Timmons, J. Michael; Timmons, Stacy; Semken, Steve, New Mexico Geological Society 64th Annual Fall Field Conference Guidebook, 237 p.
https://doi.org/10.56577/FFC-64

This page is intentionally left blank to maintain order of facing pages.

URANIUM AND STRONTIUM ISOTOPE STUDY OF LATE-STAGE SPELEOTHEMS FROM LAVA TUBE CAVES IN EL MALPAIS NATIONAL MONUMENT

ZACHARY LAPOINTE, VICTOR POLYAK, AND YEMANE ASMEROM
Earth and Planetary Sciences, University of New Mexico, Albuquerque, New Mexico, 87131

ABSTRACT—Strontium isotope values measured for six calcite and opal speleothem samples from five lava tube caves, formed in three different >15,000 year-old basalt flows in El Malpais National Monument, western New Mexico, reveal a combined soil- and bedrock-related origin. All speleothem growth was several thousand years after the lava tube caves formed. Uranium-series ages of all six samples shows that speleothem growth likely coincided with wetter periods of the Holocene. Four of the six samples formed during the late Holocene between 4,000 and 1,000 years ago, consistent with previous reconstructions of a wetter Late Holocene in the southwestern United States. Growth of a middle Holocene sample is coincident with a brief wetter period in northern Mexico and central New Mexico defined by lacustrine sediment studies, and growth of an early Holocene sample crudely matches a wetter period defined by Carlsbad area stalagmite growth.

INTRODUCTION

Lava tube caves host 40% of the known cave minerals globally, 10% of which are unique to lava tube caves (Forti, 2005). Chemical and isotopic studies of lava tube cave speleothems can provide important information about the geologic mechanisms responsible for such speleothem formations and may reveal valuable paleo-environmental information (Lee et al., 2005; Woo et al., 2008). However, few studies have employed isotope analysis on lava tube cave speleothems to explore these topics (Hill and Forti, 1997; Pint, 2006). Here, we present uranium-series chronology and strontium (Sr) isotope data from speleothems collected from caves in El Malpais National Monument, as well as a soil sample above one of the caves.

Lava-tube caves are unique speleothem-forming environments due to their insoluble bedrock, extreme temperature variation, drip water chemistry, and cave atmosphere composition and ventilation (Rogers and Mosch, 1997; Forti, 2005). As these conditions vary, so do the mineral-forming processes and resultant minerals that form the speleothems (Onac and Forti, 2011). This study focuses on the timing and mechanisms behind the formation of lava tube speleothems from El Malpais National Monument caves with an emphasis on paleoclimate.

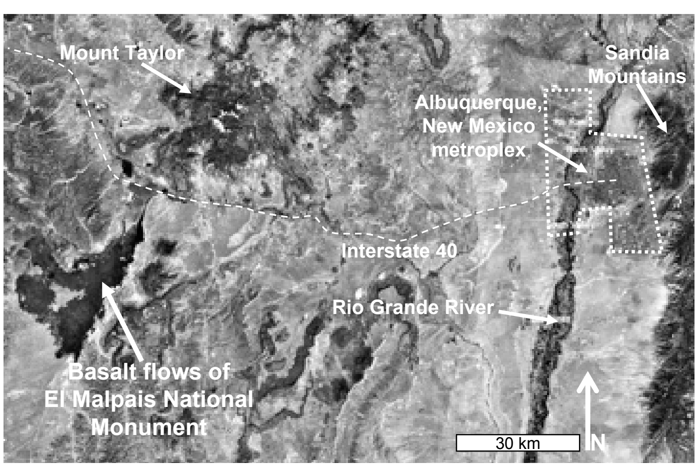

FIGURE 1. Location of study area.

Lava tube systems of the El Malpais National Monument are within the Zuni-Bandera volcanic field southeast of the Zuni uplift located in west central New Mexico (NPS, 2012) (Fig. 1). Zuni-Bandera-eruption events occurred between 115,000 and 3,900 years ago (Laughlin et al., 1993; Dunbar and Phillips, 2004). Precambrian igneous and metamorphic rocks and Permian, Triassic, Jurassic and Cretaceous sedimentary rocks make up the immediate geologic surroundings of the Bandera volcanic field (Laughlin and West, 1976; NPS, 2012). The Monument contains some of the most impressive lava tube caves in the continental United States (Fig. 2). Speleothem formations for this study were collected from ELMA Cave #61, ELMA Cave #110, ELMA Cave #150, and ELMA Cave #319 within the Bandera volcanic field and within El Malpais National Monument. These caves are located in three basalt flows, the Hoya de Cibola (ELMA Caves #110 and 150), La Tetra (ELMA Cave 319), and El Calderon (ELMA Cave #61) flows, all of which are older than 15,000 years (Laughlin et al., 1993; Van der Hoven and Quade, 2002).

Speleothem-forming processes in lava tube caves

Forti (2005) provides a detailed summary of six secondary mineral-forming processes observed during and after formation of lava tubes. Of these, degassing and solubilization are the two processes that form minerals during terminal lave tube cave genesis, in the cooling stage. These processes require high cave temperatures and abundant concentrations of magma volatiles lingering in the cave atmosphere. Minerals formed from the degassing processes are formed when fumarole gases cool and form sublimates on the cave wall and are commonly sulfur, oxides, hydroxides and sulfates (Forti, 2005). The solubilization process occurs when penetrating meteoric waters charged with soluble substances, leached from the bedrock, rapidly evaporate upon entering the cave leaving behind sulfate and chloride deposits (Forti, 2005). A mineral deposit survey by Rogers and Mosch (1997) indicates that El Malpais lava tube systems probably contained speleothems formed by these early processes and that they likely consisted primarily of gypsum, halite, and calcite. However, most of the minerals/speleothems formed by

FIGURE 2. Lava tube cave passages in El Malpais National Monument. Top photograph is a large entrance to a large lava tube cave passage. Bottom photograph is un-collapsed lava tube cave. Note secondary (lighter colored) coatings on the cave walls and floor. (See also Color Plate 11A)

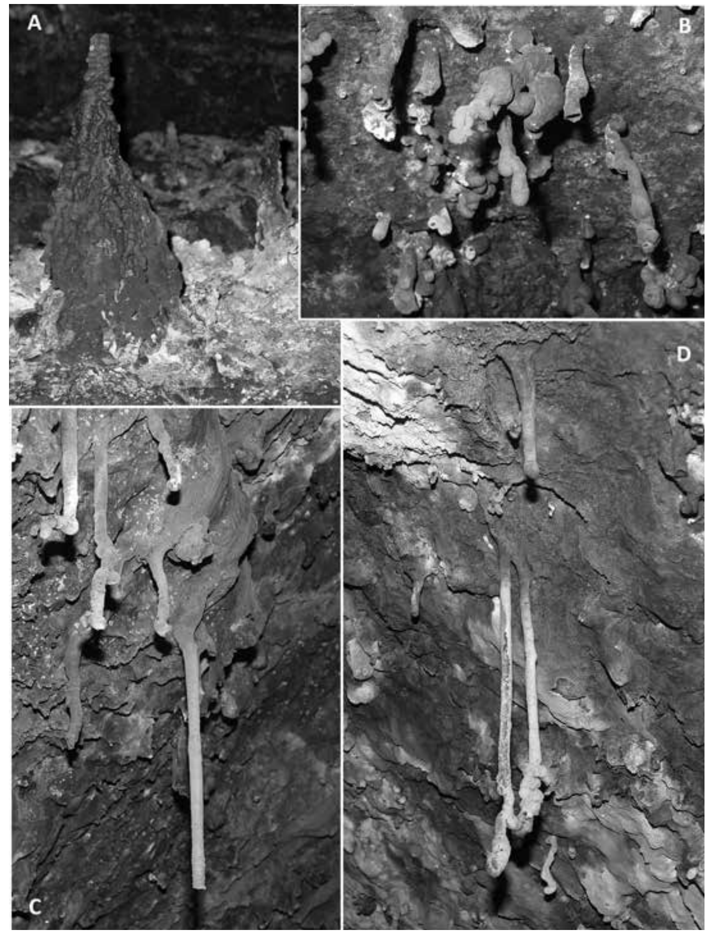

FIGURE 3. Various lava formations that mimic speleothems. These include A) lava stalagmites, B) lava helictites and soda straws, C) lava stalactites, and D) lava stalactites with helictites on their tips.

these processes appear to be too unstable to survive more than a few decades after tube system cooling and hydrologic conditions (Rogers and Mosch, 1997; Forti, 2005).

A later mineral-forming process known to deposit more stable minerals is termed the alteration process (Forti, 2005), which is the alteration and transportation of ions from mineral constituents of lava bedrock by seeping or condensate meteoritic waters. Forti (2005) notes that the minerals formed from this process are more resilient to weathering and can remain stable long after the cooling event. Minerals associated with this process include gypsum crusts, opal coralloids, and carbonates (Forti, 2005). Late-stage speleothem-forming processes are karst, biogenic, and phase change processes and occur hundreds to thousands of years after the cooling event. These processes require biogenic production of CO_2 in overlying soils, seeping meteoritic waters, diatom colonies, and equilibrated cave temperatures with the outside atmosphere upon cessation of volcanic activity. Mineral groups associated with these processes primarily include carbonates, silicates, nitrates, phosphates, sulfates, halides, and oxides (Forti, 2005). Of these, the most common are carbonates and silicates composed of calcite and opal (Hill and Forti, 1997; Rogers and Mosch, 1997; Forti et al., 2004; Forti, 2005; White, 2010; Woo et al., 2008). Calcite moonmilk and coralloids, opal coralloids, and an opal/calcite soda straw are among the speleothems collected in the El Malpais lava tube caves for this study. Figures 3 and 4 show examples of lava-formations and speleothems that decorate these caves. Lava formations, which are not speleothems, mimic speleothems and formed while the lava tube caves were forming. We have measured the U-Th ages of these speleothems, as well as Sr isotope values to develop a better understanding of the processes responsible for their origin.

METHODS

Six speleothem samples were collected from four different lava tube caves in three distinct lava flows within EL Malpais National Monument for uranium-series age and Sr isotopic analyses. Samples collected from lava tubes of the Hoya de Cibola flow consist of calcium carbonate moonmilk (sample 110-EM-2) and an opal coralloid (110-EM-3) from ELMA Cave #110, and opal coralloid (150-2a) and a calcium carbonate and opal soda straw (150-Soda) from ELMA Cave #150. Samples from El Calderon flow consist of an opal coralloid (61-2) and surface soil (61-S) from ELMA

Cave #61. Two pieces of opal coralloids (319-T and 319-B) were collected from ELMA Cave #319 in the La Tetera flow.

Two separate powders were extracted from what was observed to be the top and bottom portions of 110-EM-2 moonmilk (Fig. 5) and 319-coralloid. Powders were also extracted from 110-EM-3, 150-2a, 150-Soda and 61-2. Sample powders were subjected to acid digestion in a 7N HNO_3 solution. The insoluble residue of the coralloid samples in the acid solution confirmed the presence of opal. Additional digestion by adding 22.6N HF acid was required to dissolve the silicate fractions. Dissolved samples were spiked with a mixed synthetic ^{229}Th-^{233}U-^{236}U tracer for uranium-series analysis. Ion exchange columns were used to flush elemental calcium and silicon from the sample solutions and to separate clean fractions of uranium and thorium. Uranium and thorium isotopes were analyzed separately on a Thermo NEPTUNE multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS). The analytical procedures used for the uranium-series analysis are similar to those described by Shen et al. (2002). Detrital ^{230}Th was removed and ages corrected by assuming the average global silicate ^{230}Th/^{232}Th ratio of 4.4x10-6 (±100%) ppm.

Samples 61-2, 61- S (surface soil), 110-EM-3, 110-EM-2 Top, 110-EM-2 Bottom, and 319-B were selected for Sr isotope analysis. The samples were dissolved in 15N HNO_3 and spiked with a synthetic ^{84}Sr solution. The spiked sample solutions were added to ion exchange columns to flush major cations from the sample solution and to collect Sr only. Isotopic Sr was measured on the NEPTUNE MC-ICP-MS.

RESULTS

Uranium-series analyses of the collected samples revealed that these speleothems grew intermittently during the early to late Holocene, between 10,000 and 1,600 years ago. The 61-2 coralloid is the oldest of the collected mineral samples with a uranium-series date of 10,320 ± 630 years in ELMA Cave #61, in the El Calderon basalt flow, which is reported to be 115,000 years old (Cascadden et al., 1997). Uranium-series analysis of a second powder drilled from the 61-2 coralloid produced an age of 10,000 ± 330 years, supporting this result. All other results are from speleothems formed in caves younger than 20,000 years. The 110-EM-3 coralloid yielded a middle Holocene age of 6,190 ± 140 years. All other samples are late Holocene in age and cluster between 3,800 and 1,600 years ago.

110-EM-2 moonmilk growth is representative of this late Holocene time period. Age analysis of two powders extracted from the top and bottom portions of 110-EM-2 moonmilk revealed growth between 3,870 ± 190 to 1,090 ± 120 years ago (Fig. 5). The other three sample ages fall within the period of 110-EM-3 moonmilk growth. The ELMA Cave #150 soda straw sample has an age of 2,960 ± 120 years ago and the 150-2a coralloid sample formed 1,850 ± 130 years ago. Two powders were extracted from the 319-coralloid, 319-B and 319-T, and yielded ages of 1,630 ± 50 and 2,900 ± 120 years ago, respectively. Due to the nature of thin banding and shape of the coralloid, top and bottom could not be determined, and we consider that these two ages probably represent an approximate range of growth (Fig. 5; Table 1).

The ^{87}Sr/^{86}Sr value measured from the soil above ELMA Cave #61 was measured to be 0.71310 (total dissolution), and an ^{87}Sr/^{86}Sr value of 0.71132, measured from sample 61-2 coralloid, closely resembles this soil value. The ^{87}Sr/^{86}Sr values measured from the ELMA CAVE #110 samples (EM series) falls between the host bedrock value and the pedogenic carbonate soil values reported by Van der Hoven and Quade (2002). The ^{87}Sr/^{86}Sr values of 110-EM-3 coralloid and 110-EM-2 moonmilk top and bottom are 0.70728, 0.70743, and 0.70723, respectively, and are close to the Hoya de Cibola bedrock ^{87}Sr/^{86}Sr value of 0.7060. These values are closer to the pedogenic soil carbonate average value of 0.7078 reported by Van der Hoven and Quade (2002). The 319-coralloid ^{87}Sr/^{86}Sr value of 0.70589 also falls between the La Tetra bedrock value of 0.7047 (Van der Hoven and Quade, 2002), and the pedogenic average carbonate soil value of 0.7078 reported by Van der Hoven and Quade (2002). Sr isotopes from the 319-coralloid are closer to the bedrock values and indicate that incorporation of bedrock ions into the opal and calcite occurred during its formation. A similar mixed ion source is proposed by Rogers and Mosch (1997) for El Malpais speleothems and confirmed by our study. White (2010) also notes the weathering of anorthite feldspars in basalt bedrock in lava tube caves from Hawaii is likely an important source of calcium in secondary calcite formations. All results are included in Table 2.

TABLE 1. Uranium-series data for lava tube caves speleothems. All errors are 2-sigma absolute. Ratios are activity ratios, and yrs BP is years before present.

Sample	^{238}U (ng/g)	^{232}Th (pg/g)	^{230}Th/^{232}Th activity ratio	^{230}Th/^{238}U activity ratio	meas σ^{234}U (‰)	initial σ^{234}U (‰)	uncorr age yrs BP	corrected age
yrs BP	2402 ±15	19106 ±107	8.8 ±0.3	0.023 ±8.3E-4	226 ±7.6	227 ±7.7	2065 ±76	1850 ± 131
319-B	4996 ±39	13105 ±162	20.3 ±0.4	0.017 ±3.5E-4	132 ±5.2	133 ±5.2	1692 ±35	1625 ±48
319-T	2165 ±18	18311 ±110	11.5 ±0.2	0.032 ±5.3E-4	133 ±6.6	134 ±6.6	3121 ±56	2904 ±121
150- Soda	2669 ±19	16818 ±84	15.7 ±0.4	0.032 ±7.7E-4	144 ±4.9	145 ±5.0	3143 ±77	2961 ±119
110-EM-2 bottom	1472 ±4	18959 ±85	10.2 ±0.1	0.043 ±3.4E-4	126 ±1.3	127 ±1.3	4246 ±35	3868 ± 192
110-EM-2 Top	878 ±2	6903 ±75	5.3 ±0.1	0.014 ±2.9E-4	124 ±2.0	124 ±2.1	1323 ±28	1091 ± 119
110-EM-3	2814 ±9	23007 ±75	22.5 ±0.2	0.060 ±4.5E-4	51 ±0.8	52 ±0.8	6450 ±50	6190 ±139
61-2	4155 ±12	161724 ±686	8.7 ±0.2	0.111 ±2.1E-4	111 ±1.1	115 ± 1.1	11494 ±224	10321 ±625
61-2 2nd run	4940 ±13	107208 ±254	14.5 ±0.1	0.103 ±4.3E-4	109 ±0.6	112 ±0.6	10661 ±47	10001 ±333

DISCUSSION

Measured Sr isotope values for all of these samples suggest the speleothem samples are a mixture of soil and bedrock sources, thereby suggesting that these lava tube cave speleothems formed from both the alteration process and from soil-derived processes (karst and biogenic). Sr isotope results for sample 61-2, however, show that it formed almost exclusively from overlying soil components, which may be due to this older basalt flow having a much thicker and more mature soil. The multiple millennia time lag between lava flow formation and secondary speleothem formation indicated by our uranium-series results is in agreement with the latter karst and alteration processes responsible for speleothem development described by Forti (2005).

Our uranium-series chronology from these six speleothem samples coincide with periods of elevated precipitation during the Holocene, suggesting that periods of enhanced moisture resulted in an increase in dripping, seeping, and condensing water in these lava tube caves. The time lag between the lava tube cave origin and the secondary mineral speleothems is greater than 10,000 years, so surface vegetation and soil had time to develop, and lack of these are not likely interfering with speleothem growth mechanisms although it is also possible that our sampling missed older speleothems in these caves. Polyak and Asmerom (2001) provide a high resolution late-Holocene speleothem climate record which indicates a wetter than present moisture regime prevailed from 4,000 to 800 years ago. This period in the late Holocene was cooler and wetter than average middle and late-early Holocene conditions in the southwestern United States (Polyak and Asmerom, 2001, Polyak et al., 2001, Polyak et al., 2004), and coincides with six of the eight speleothem ages reported here. It also coincides with the age of the ice deposit in

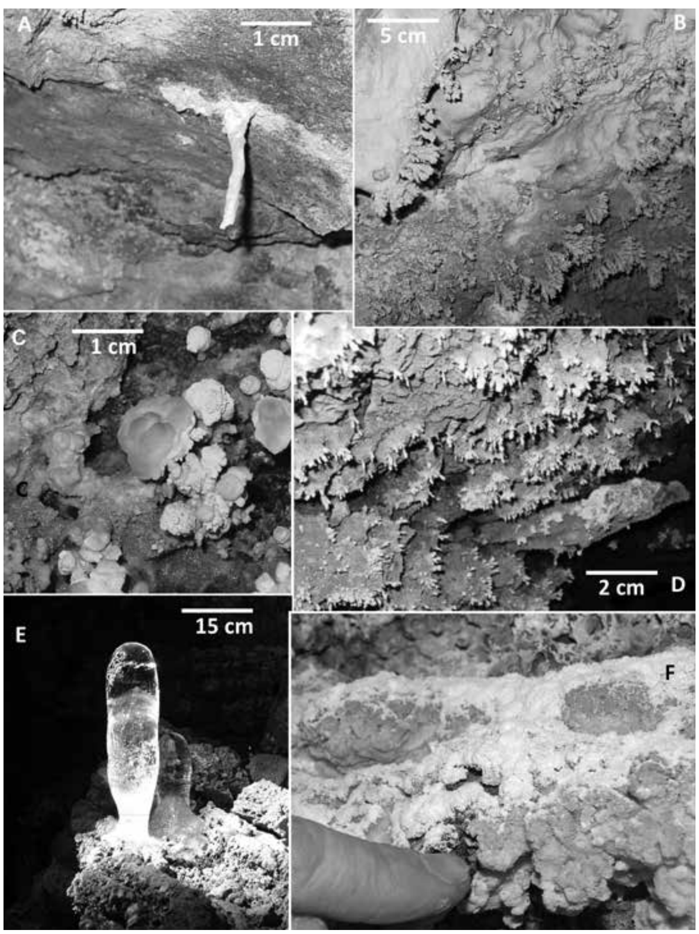

FIGURE 4. Examples of speleothems in the lava tube caves of our study area. A) Soda straws are rare in these caves. The sample collected consisted of both calcite and opal. B) Directional coralloids indicate air flow. C) Mushroom-like coralloids that probably consist primarily of calcite. D) Rod-like coralloids probably consist primarily of opal. E) Ice stalagmites form seasonally in winter in several of the caves in the study area. F) Gypsum crusts are common in the youngest lava tube caves and probably have an origin that relates to the terminal cave genesis. Yellow deposits on the gypsum are probably elemental sulfur. All samples collected were already damaged/detached. (See also Color Plate 11B)

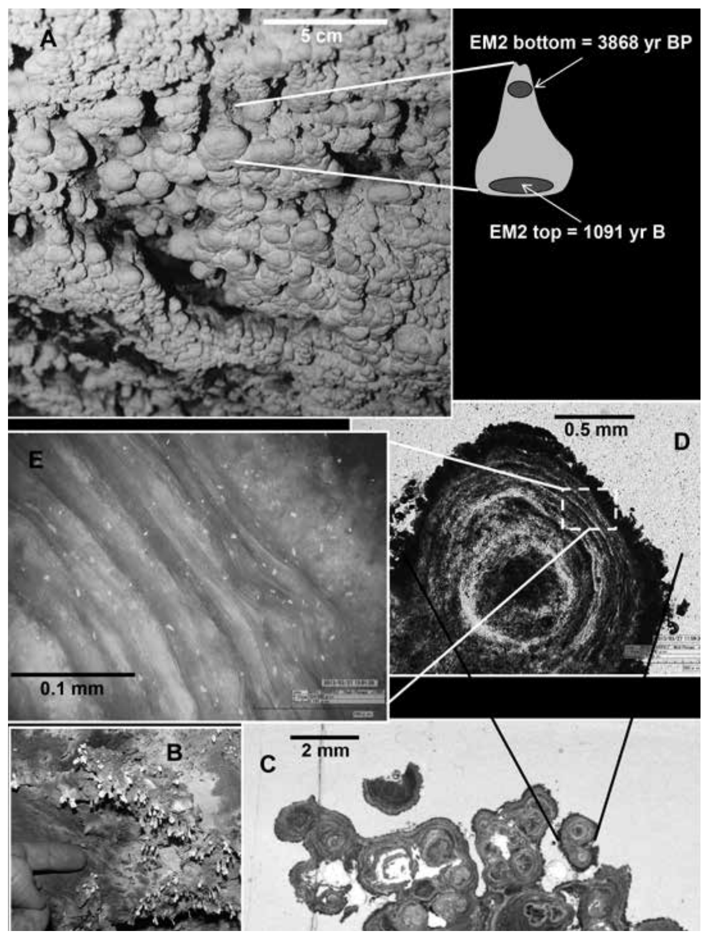

FIGURE 5. Samples 110-EM-2 and 110-EM-3 were two of the six samples analyzed. A) Sample 110-EM-2 is calcite moonmilk on the cave ceiling. One cauliflower-like body of moonmilk was collected, and top and bottom dates on this sample indicate that the moonmilk grew during the late Holocene. B) Sample 110-EM-3 was a coralloid frond similar to those shown in this figure. C) A thin section micrograph shows the complexity of growth of 110-EM-3, further illustrated in D) in transmitted light. E) A closer look at part of the coralloid in reflected light shows that the interior exhibits lamina or microlayers that are approximately 1 μm thick.

TABLE 2. Strontium isotope data for lava tube caves speleothems. Errors are 1-sigma percent.

Sample	$^{87}Sr/^{86}Sr$ ratio	Basalt Bedrock	$^{87}Sr/^{86}Sr$ ratio
61-2 (coralloid)	0.711320 ±0.00075%	El Calderon	0.7056 (Van der Hoven, S., et al., 2002)
61-S (soil) Total dissolution	0.713102 ±0.000493%	El Calderon	0.7056 (Van der Hoven, S., et al., 2002)
110-EM-3 (coralloid)	0.707280 ±0.000408%	Hoya de Cibola	0.7060 (Van der Hoven, S., et al., 2002)
110-EM-2 Top (moonmilk)	0.70743237 ±0.00022%	Hoya de Cibola	0.7060 (Van der Hoven, S., et al., 2002)
110-EM-2 Bottom (moonmilk)	0.70723876 ±0.0013%	Hoya de Cibola	0.7060 (Van der Hoven, S., et al., 2002)
319-B (coralloid)	0.705886 ±0.0009%	La Tetera	0.7047 (Van der Hoven, S., et al., 2002)

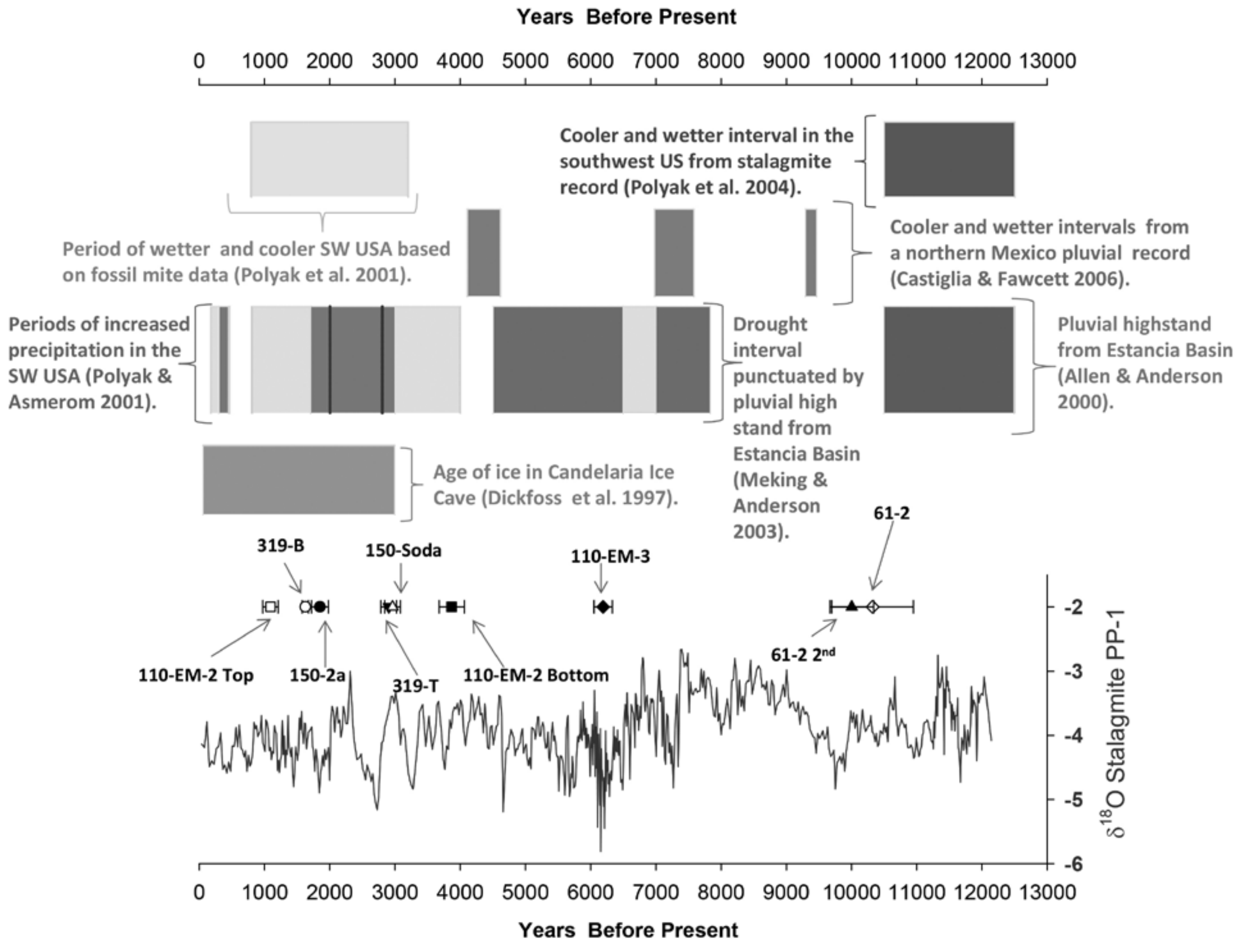

FIGURE 6. Plot of sampled speleothem ages from lava tube caves in El Malpais National Monument and paleoclimate data from the southwestern United States (SW USA), all in calendar years before present. The top left gray bar represents a period of wetter and cooler conditions in the SW USA from the study of fossil mites preserved in three Carlsbad area stalagmites (Polyak et al., 2001). The top right bar represents a time of wetter conditions in the SW USA from the growth record of several Carlsbad area stalagmites from Polyak et al. (2004). The second row of bars represent reconstructed pluvial periods from Laguna El Fresnal and Laguna Santa Maria subbasins in northern Mexico (Castiglia and Fawcett, 2006). The third row down (left side) alternating lighter and darker bars represent periods of increased precipitation in the SW USA relative to current conditions from the study of the growth history of several Carlsbad area stalagmites by Polyak and Asmerom (2001). The lighter bars represent periods of greater than present precipitation, the darker bars the wettest periods of the record, and the dark black stripes represent two pulses of heavier precipitation periods. The box in the center of the third row represents a pronounced dry period punctuated by a wetter interval represented by the lighter center bar as recorded in the Estancia Basin from Menking and Anderson (2003). The box to the far right in the third row represents a pluvial high stand from the Estancia Basin from Allen and Anderson (2000). In the fourth row down, the bar represents the measured interval of ice growth from the Candelaria Ice Cave within El Malpais National Monument from Dickfoss et al. (1997). The point plots with horizontal error bars represent the ages of the lava tube cave spelethems (this study). The bottom blue curve is a continuous $\delta^{18}O$ record from a Carlsbad area stalagmite from Pink Panther Cave from the SW USA from Asmerom et al. (2007). See Fairbanks et al. (2005) for radiocarbon to calendar age conversion.

Candelaria Ice Cave (Dickfoss et al., 1997). The 10,000-year-old 61-2 coralloid overlaps a wetter period in the early Holocene 10,000 to 12,000 years ago reported by Polyak et al. (2004) from southeast New Mexico caves and a pluvial highstand measured in the Estancia Basin, central New Mexico, between 10,000 to 12,000 years before present (Allen and Anderson, 2000). One exception to this model is the 6,190-year-old coralloid which grew during the middle Holocene, a period that has been interpreted in many studies to be the driest sustained period of the Holocene. However, the timing of growth of coralloid coincides with a short, wet period identified in the Estancia Basin record and that probably represented a break between an early and late phase of middle Holocene aridity (Menking and Anderson, 2003), and roughly coincides with a wet period indicated by a lacustrine record in northern Mexico (Castiglia and Fawcett, 2006). Comparison of lava tube cave speleothem growth episodes with wet periods interpreted by others is included in Figure 6. This small sampling and preliminary study shows that the growth history of lava tube cave speleothems could be developed into a useful climate proxy.

CONCLUSIONS

The Sr isotope values of six Holocene-age, lava tube speleothem samples from El Malpais National Monument reveal that the calcite and opal making up these speleothems has both a soil- and bedrock-related origin. Our study is consistent with a correspondence between speleothem deposit ages and known intervals of wetter climates in the southwestern United States which support, to some degree, the notion that speleothem growth, and probably soil development, are related to periods of wetter climate in the southwestern United States.

ACKNOWLEDGMENTS

Samples were collected by permit issued by El Malpais National Monument. We thank Monument personnel Herschel Schulz, Dana Sullivan, David Hays and Andrew Bundshuh for their help with permits and logistics. Paula Provencio, Sam Bono, and other members of the Sandia Grotto of the National Speleological Society helped in the field.

REFERENCES

Allen, B. and Anderson, R., 2000, A continuous, high-resolution record of late Pleistocene climate variability from the Estancia Basin, New Mexico: Geological Society of America Bulletin, v. 112, p. 1444-1458.

Asmerom, Y., Polyak, V., Burns, S. and Rassmussen, J., 2007, Solar forcing of Holocene climate: New insights from a speleothem record, southwestern United States: Geological Society of America, v. 35, p. 1-4.

Cascadden, T. E., Geissman, J. W., Kudo, A. M., and Laughlin, A. W., 1997, El Calderon cinder cone and related basalt flows, in Mabery, K., ed., Natural history of El Malpais National Monument: New Mexico Bureau of Mines and Mineral Resources Bulletin 156, p. 41–52.

Castiglia, P.J. and Fawcett, P.J., 2006, Large Holocene lakes and climate change in the Chihuahuan Desert: Geology, v. 34, p. 113-116.

Dickfoss, P.V., Betancourt, J.L., Thompson, L.G., Turner, R.M., and Tharnstrom, S., 1997, History of ice at Candelaria Ice Cave, New Mexico: New Mexico Bureau of Mines and Mineral Resources, Bulletin 156, p. 91-112.

Dunbar, N. and Phillips, F. 2004, Cosmogenic 36Cl ages of lava flows in the Zuni-Bandera volcanic field, north-central New Mexico, U.S.A.: New Mexico Bureau of Geology and Mineral Resources, Bulletin 160, p. 309-317.

Fairbanks, R.G., Mortlock, R.A., Tzu-Chien, C., Cao, L., Kaplan, A., Guilderson, T.P., Fairbanks, T. W., and Bloom, A. L., 2005, Marine Radiocarbon Calibration Curve Spanning 0 to 50,000 Years B.P. Based on Paired $^{230}Th/^{234}U/^{238}U$ and ^{14}C Dates on Pristine Corals: Quaternary Science Reviews, v. 24, p. 1781-1796.

Forti, P., Galli, E., Rossi, A., Pint, J. and Pint, S., 2004, The Hibashi Lava Tube: The Best Site in Saudi Arabia for Cave Minerals: International Symposium on Vulcanospeleology, Azores, Oral Presentations program, p. 30-31.

Forti, P., 2005, Genetic Processes of Cave Minerals in Volcanic Environments: An Overview: Journal of Cave and Karst Studies, v. 67, p. 3-13.

Hill, C., and Forti, P., 1997, Cave Minerals of the World: Huntsville, National Speleology Society, 464 p.

Laughlin, A. and West, F., 1976, The Zuni Mountains, New Mexico, as a potential dry hot rock geothermal energy site: Los Alamos National Laboratory, Report 6197, pp. 1-13.

Laughlin, A., Charles. R., Reid, K. and White, C., 1993, Field-trip guide to the geochronology of the EL Malpais Monument and the Zuni-Bandera volcanic field, New Mexico: New Mexico Bureau Mines Mineral Resources, Bulletin 149, p. 1-23.

Lee, K., Choi, D. and Woo, K., 2005, Origin and diagenesis of the cave corals in the lava tubes of Jeju Islands, Korea Hellenic Speleological Society, v. ,p. 622-624.

Menking, K. and Anderson, R., 2003, Contributions of La Nina and El Nino to middle Holocene drought and late Holocene moisture in the American Southwest: Geology, v. 31, p. 937-940.

National Park Service (NPS), 2012, El Malpais National Monument: Geologic Inventory Report: Natural Resource Report NPS/NRSS/GRD/NRR-2012/578.

Onac, B. and Forti, P., 2011, Minerogenetic mechanisms occurring in the cave environment: an overview: International Journal of Speleology, v. 40, p. 79-98.

Pint, J., 2006, Vulcanospeleology in Saudi Arabia: Acta Carsologica, v. 35, p. 107-119.

Polyak, V. and Asmerom, Y., 2001, Late Holocene Climate and Cultural Changes in the Southwestern United States: Science, v. 249, p. 148-151.

Polyak, V., Cokendolpher, J., Norton, R. and Asmerom, Y., 2001, Wetter and cooler late Holocene climate in the southwestern United States from mites preserved in stalagmites: Geology, v. 29, p. 643-646.

Polyak, V. J. Rasmussen, J.B.T., and Asmerom, Y., 2004, Prolonged wet period in the southwestern United States through the Younger Dryas: Geology, v. 32, p. 5-8.

Rogers, B. and Mosch, C., 1997, Snowballs in the underground—Lava-tube deposits and morphology: Natural history of El Malpais National Monument: New Mexico Bureau of Mines and Mineral Resources Bulletin 156, p. 83-90.

Shen, C., Edwards, L., Cheng, H., Dorale, J., Thomas, R., Moran, S., Weinstein, S. and Edmonds, H., 2002, Uranium and thorium isotopic compositions and concentration measurements by magnetic sector inductively coupled plasma mass spectrometry: Chemical Geology, v. 185, p. 165-178.

Van der Hoven, S.J., and Quade, J., 2002, Tracing spatial and temporal variations in the sources of calcium in pedogenic carbonates in a semiarid environment: Geoderma, v. 108, p. 259-276.

White, W., 2010, Secondary Minerals in Volcanic Caves: Data from Hawai'I: Journal of Cave and Karst Studies, v. 72, p. 75-85.

Woo, K., Choi, D. and Lee, K., 2008, Silicification of cave corals from some lava tube caves in the Jeju Island, Korea: Implications for speleogenesis and a proxy for paleoenvironmental change during the Late Quaternary: Quaternary International, v. 176-177, p. 82-95.