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Supplemental Material for "Manganese stromatolites in caves: El Soplao (Cantabria, Spain)"

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Analytical methods

The macroscopic features of the Mn-oxide-rich deposits were observed and recorded in situ. 20 samples of laminated Mn-oxides were collected from three sites (Fig. 1B). The samples were slabbed with a diamond saw and scanned. Double-polished thin sections were obtained from epoxy-impregnated blocks, and examined using a petrographic microscope. Freshly broken surfaces were observed using a JEOL 6400 scaning electron microscope (SEM) equipped with a energy-dispersive X-ray microanalyzer. The mineralogy of 34 powdered subsamples was investigated by x-ray diffaction (XRD), using a Bruker D8 diffractometer. Subsamples for XRD represent discrete layers (4 to 10 mm thick) and concentrates of the Mn-oxide-rich material obtained using a Frantz magnetic separator. Total organic carbon (TOC) of bulk samples was determined using a LECO SC-144 analyzer. The infrared (IR) spectra of 9 samples were obtained by the KBr pellet technique using a Nicolet Magna-IR 750 spectrometer.

145 elemental analysis of the Mn-oxide-rich material were performed on five carbon-coated thin sections by wavelength dispersive spectrometry using a JEOL JXA 8900 electron microprobe (EMP) operating at 15kV, 20nA, and 5 to 15 µm beam diameter. Oxygen was measured using a LDE1 multilayer diffracting crystal, yielding a statistical precision similar to heavier elements. Synthetic Mn2O was used as a standard for O and

Mn. The EMP analysis totals are low (averages per sample ranging from 78 to 93%), due to the presence of H in structural water, C (not measured), and especially of microporosity (Harrisson, A.M., Winter, N.B., and Taylor, H.F.W., 1987, X-ray microanalysis of microporous materials: Journal of Materials Science Letters, v. 6, p. 1339–1340, doi:10.1007/BF01794611.). No normalization has been applied, therefore real element abundances are slightly higher than those reported here. Average compositions was calculated for each sample and for the entire sample set. The EMP also served to obtain backscattered electron (BSE) images to reveal small-scale chemical variations.

The speleothems retrieved For U-series dating were slabbed and scanned, and seven ~20 mg aragonite sub-samples were microdrilled from layers free of visible detrital material. U-Th isotope ratios were measured in a Nu Instruments multicollector inductively coupled plasma mass spectrometer (Hellstrom, J.C., 2003, Rapid and accurate U/Th dating using parallel ion-counting multi-collector ICP-MS. Journal of Analytical Atomic Spectrometry 18, 1346-1351).

Table DR1: Uranium-series analyses (brackets denote activity ratios; i = initial). U-Th ages and [234U/238U]i were calculated assuming an initial [230Th/232Th] of 1.5±1.5. The analyses conducted following Hellstrom (2003). Ages and initial [234U/238U] were calculated using the Monte Carlo method implemented in Isoplot/Ex (K. R. Ludwig, Berkeley Geochron. Center Spec. Pub., 1999, 2, 47). All uncertainties are two-sigma.

U-Th ages could have been calculated only for the two samples of stalagmite BO-2. Both the ages and calculated [234U/238U]i are very close to each other, suggesting no significant U loss from these samples. Samples FS63K-11, FS63M-13, FS61D-15 and COL1-18, when plotted in a [234U/238U] vs. [230Th/238U] isochron diagram, all line up along the infinite age U-Th isochon, indicating U-Th secular equilibrium and thus true ages older than ~500ka. The data from the flowstone sample COC3AE-20 indicate significant post-crystallization uranium loss; therefore a U-Th age cannot be obtained.

Based on the similarity of the calculated [234U/238U]initial for the two youngest samples, 234U-238U ages were calculated assuming an initial [234U/238U] of 3 plus or minus a factor of two of the excess 234U. Given the relatively large range of assumed [234U/238U]i (i.e. from 2 to 5), the uncertainty of the U-U ages is high (~250ka), but still the ages are useful for the purposes of this study. Because of post-depositional uranium loss, the U-U age of sample COC3AE-20 is an overestimate of the true age, as U loss should have altered the measured 234U/238U ratio through preferential leaching of 234U from alpha-recoil-damaged lattice sites.

The U-series results indicate that the stromatolites are most likely older than ~1 Ma BP. However, the oldest U-U speleothem date in the low-gradient canyon is ~1.7 Ma +-0.25 Ma. Because the stromatolites and the low-gradient canyon both formed at the water table, it is then feasible that the stromatolites formed prior to ~1.45 Ma. After the formation of the epiphreatic low-gradient canyon, the water table has fallen ~400 m (Fig. 1b). In a nearby karst massif (~20 km to the east), Smart (Smart, P.L., 1986, Origin and development of glacio-karst closed depressions in the Picos de Europa, Spain: Zeitschrift fur Geomorphologie, v. 30, p. 423–443.) estimated a long-term rate of

base level lowering of ~0.3 m/ka based on spelothem U-Th dates. If we extrapolate this rate to the Arnedo karst, the main relict canyon of El Soplao would have been active ~1.2 Ma ago. This estimation must be taken with caution, but is consistent with the minimum age of the stromatolites derived from our 238U-234U dates.

Table DR1: Uranium-series analyses

Sample ID	Analysis no.	U(ngg^{-1})	±95%	$[^{230}Th/^{238}U]$	±95%	$[^{234}U/^{238}U]$	±95%	$[^{232}Th/^{238}U]$	±95%	U-Th age ka	±95%	$[^{234}U/^{238}U]_i$	±95%	234U age Ma	±95%
BO2-6	UMA02697 Apr-2009	3768	345	1.9286	0.0046	1.7130	0.0037	0.00008821	0.0000031	406	9	3.25	.05	0.36	0.25
BO2-7	UMA02787 Jul-2009	6157	492	1.9366	0.0054	1.7368	0.0037	0.00002806	0.0000084	377	8	3.14	.04	0.35	0.25
FS63K-11	UMA02698 Apr-2009	1744	206	1.1893	0.0118	1.1356	0.0064	0.00041005	0.0001187	629	+inf./– 150	1.8	+inf/- 0.9	0.95	0.25
FS63M-13	UMA02699 Apr-2009	3811	476	1.1789	0.0048	1.1237	0.0020	0.00017910	0.0000063	>654	–	>3.3	–	0.98	0.25
FS61D-15	UMA02700 Apr-2009	5158	504	1.1730	0.0055	1.1208	0.0033	0.00029809	0.0000164	806	+inf./– 220	2.2	+inf/- 0.9	0.99	0.25
COL1-18	UMA02701 Apr-2009	63278	6032	1.0271	0.0034	1.0176	0.0021	0.00001048	0.0000006	>655	–	>1.3	–	1.67	0.25
COC3AE-20	UMA02702 Apr-2009	11027	1029	1.6792	0.0056	1.1739	0.0037	0.00515004	0.0001430		–	–	–	0.86	0.25