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Supplementary Materials for

A nanocrystalline monoclinic $CaCO_3$ precursor of metastable aragonite

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The PDF file includes:

Other Supplementary Material for this manuscript includes the following:

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Section S1. Crystallographic relationship between mAra and aragonite

Orthogonal aragonite (a= 4.96 Å, b= 7.97 Å, c= 5.74 Å) can be converted to monoclinic-1 aragonite (a= 4.96 Å, b= 5.74 Å, c= 9.39 Å, and β=121.9) by applying the following conversion matrix (determined from 3D EDT data):

$$\begin{pmatrix} -1 & 0 & 0 \\ 0 & 0 & 1 \\ 1 & 1 & 0 \end{pmatrix}$$

The best fit to the mAra diffraction data is monoclinic-6 (fig. S5), which can be derived from orthogonal aragonite by applying the following conversion matrix (determined from 3D EDT data):

$$\begin{pmatrix} -6 & 0 & 0 \\ 0 & 0 & 1 \\ 1 & 1 & 0 \end{pmatrix}$$

The application of this matrix gives a= 29.76 Å, b= 5.74 Å, c= 9.39 Å, and β=121.9°. The unit cell refinement of this data results in the proposed monoclinic unit-cell parameters for mAra: a= 28.6(7) Å, b= 5.7(1) Å, c= 9.2(1) Å, and β= 120.2(5)°.

Fig. S1. Sample collection sites. Aragonite occurs as a thin white flowstone covering the dolomite bedrock of the cave wall. White arrow points to the TEM grid box placed under a small stalactite (1 cm thick, 5 cm long, grey arrow). Water from this active speleothem dripped onto the TEM grid box for 20 hours. Black arrow marks the flowstone surface that was also sampled**.** Photo credit: Christoph Spötl (Institute of Geology, University of Innsbruck).

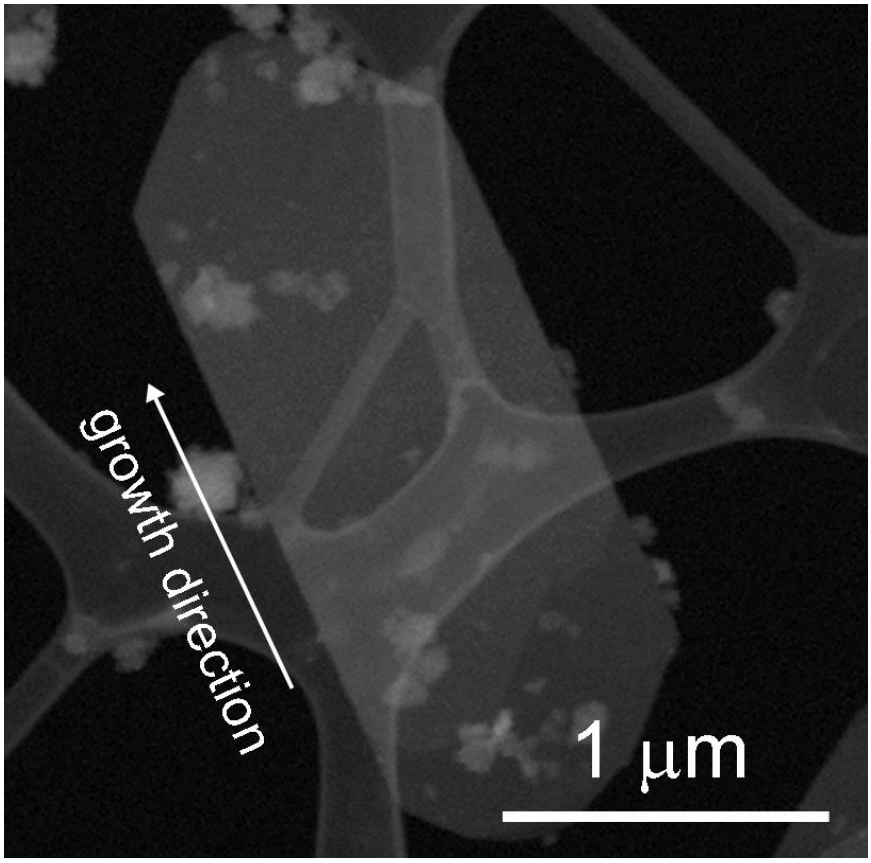

Fig. S2. The EDT measured hydromagnesite grain from the drip water sample.

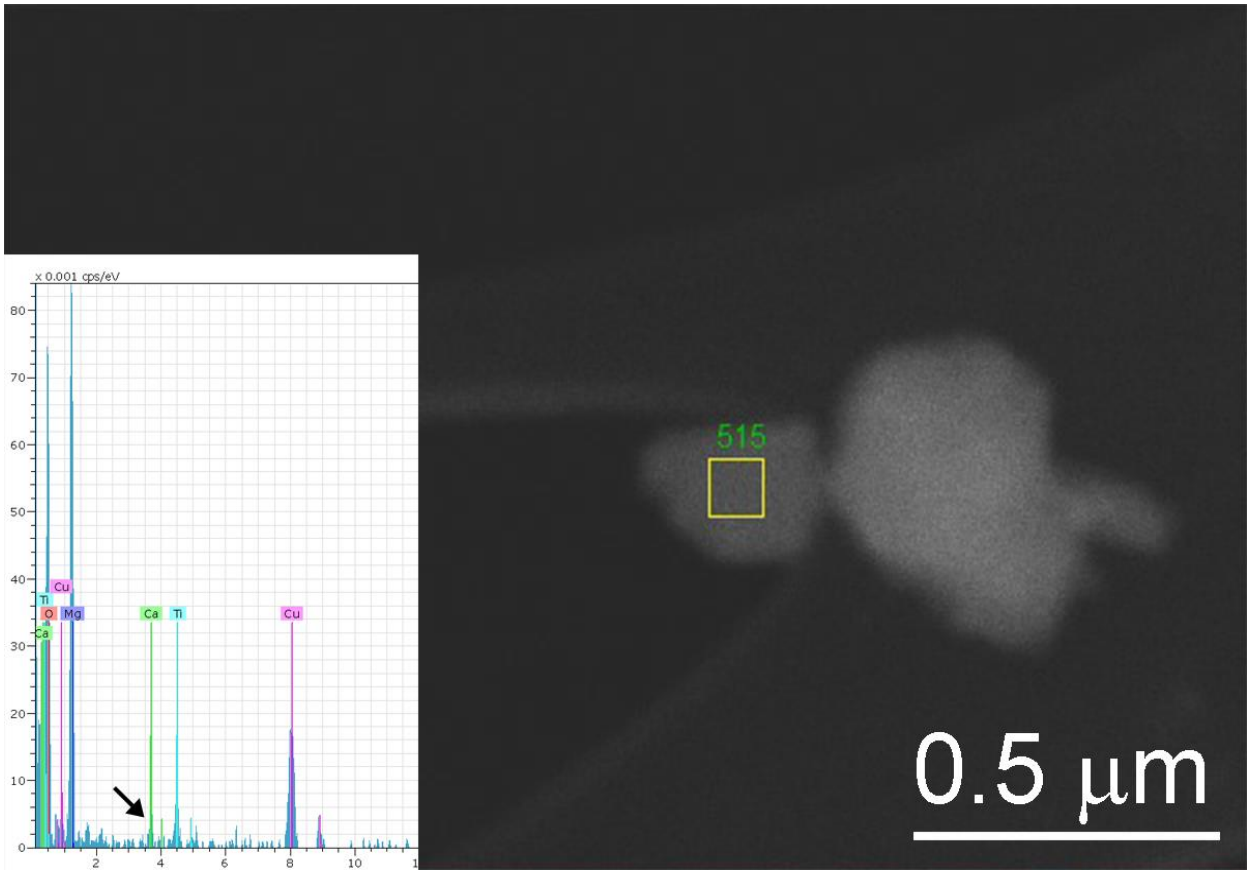

Fig. S3. Magnesite coexisting with mAra in the sample collected from the surface of the aragonite flowstone. Black arrow points to the Ca Kα peak and indicates ~5 at% Ca. Ti and Cu originate from the sample holder.

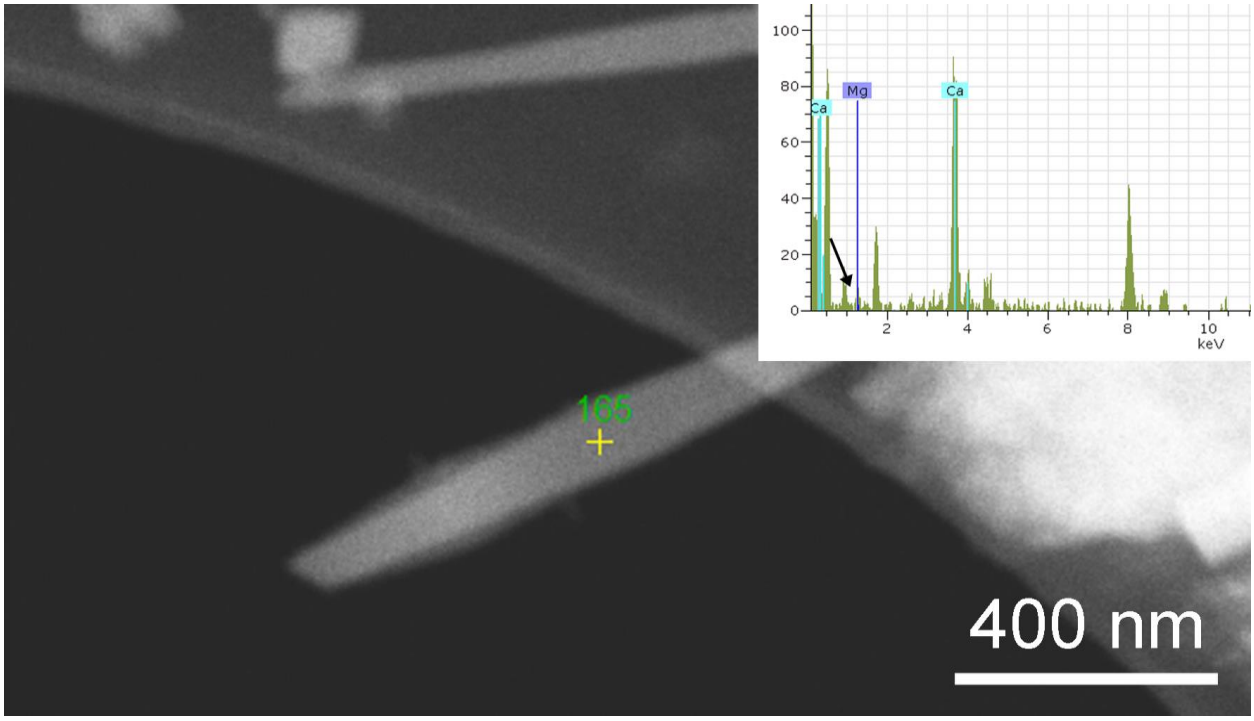

Fig. S4. Chemical analysis of the mArа crystal measured by EDT (Fig. 3) indicates ~2 at % Mg. Black arrow points to the Mg Kα peak. Unlabelled peaks originate from the sample holder.

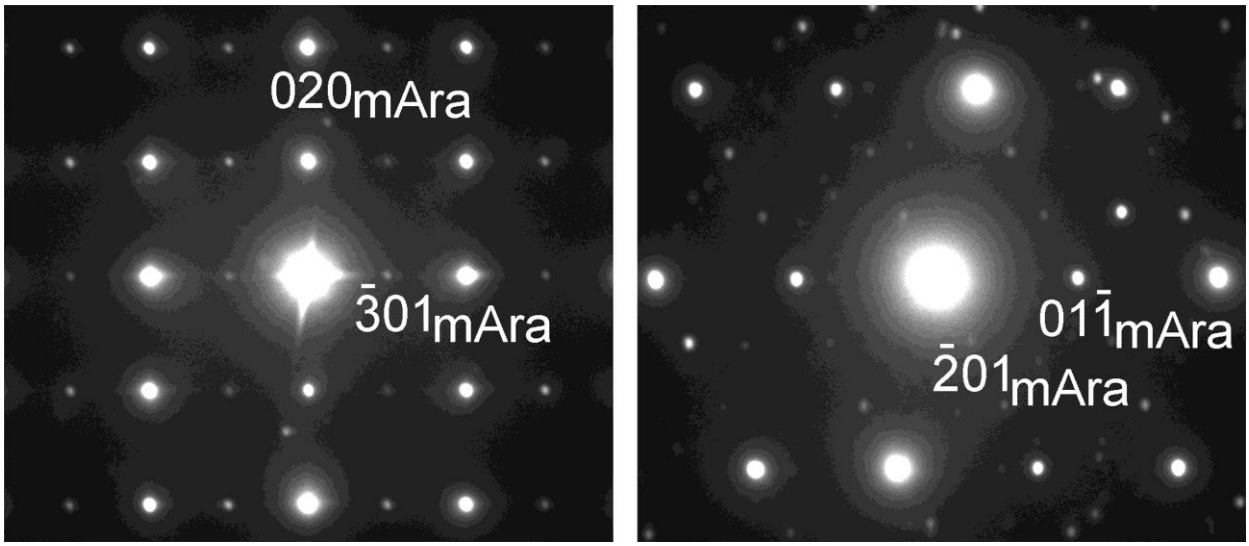

Fig. S5. Satellite reflections of the SAED patterns (2 and 3 of Fig. 2) can be indexed with the mAra (monoclinic-6) unit cell. Sample thickness gives rise to {010} mAra reflections.

Table S1. Summary of EDT data for hydromagnesite and mAra.

	$Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$	$CaCO_3$
Morphology	Plate	Needle
Cell setting	Monoclinic	Monoclinic
Space group (Herman-Mauguin)	P 1 2_1/c 1	P 1 2_1/c 1
Cell dimensions		
***a, b, c* (Å)**	9.9(1), 8.9(1), 8.5(1)	28.6(7), 5.7(1), 9.2(1)
α, β, γ (°)	90, 114.4(5), 90	90, 120.2(5), 90
***V* ($Å^3$)**	682	1296.2
Z	4	4
Stoichiometric formula	$Mg_5O_{18}C_4H_{10}$	$Ca_6C_6O_{18}$
Formula weight M_r	233.83	600.53
Density (g/cm3)	2.277	3.077
Temperature (K)	293(2)	293(2)
Data collection wavelength (Å)	0.0335	0.0335
Cell measurement θmin	0.152	0.173
Cell measurement θmax	1.066	0.872
Number of measured reflections	2430	2210
Rint	0.2549	0.4271
hmin – hmax	-10 - 10	-24 - 25
kmin – kmax	-9 - 9	-5 - 5
lmin – lmax	-9 - 9	-8 - 8
Number of independent reflections	824	827
Number of observed reflections	689	624
Observed criterion	$I > 2\sigma(I)$	$I > 2\sigma(I)$
Number of frames collected	116	121
Exposure time/frame (s)	1	1

Table S2. Summary of structure refinements of hydromagnesite and mAra.

	Hydromagnesite*	**Missing-atoms** mAra**	**All-atoms mAra*****
Parameters Refined	54	101	121
Number of restraints	17	0	159
Rall	0.3082	0.4908	0.3861
Robs	0.3026	0.4436	0.3173
wRall	0.6412	0.6966	0.6054
wRobs	0.6383	0.6847	0.5775
Goodness of fit (S)	3.702	3.292	2.774
Restrained S all	3.677	3.292	2.566
Max e-/Å3 in final diff. map	0.232	0.349	0.307
Min e-/Å3 in final diff. map	-0.278	-0.317	-0.474

*H positions excluded

**Missing 3C and 2O atoms

***restraints for 3C and 2O positions

Table S3. EDT-measured and SHELXL-refined hydromagnesite atomic coordinates (*x*1, *y*1, *z*1) versus literature data (*x*2, *y*2, *z*3) of (*30*). Maximum errors are 0.07 Å for Mg and 0.03 Å for light atoms. Similarity parameters were determined using the Bilbao Crystallographic Server (**http://www.cryst.ehu.es**).

	x1	***x2***	***y1***	***y2***	***z1***	***z2***	**atomic displacements**
Mg	0.3493	0.34502	0.0637	0.06865	0.3557	0.35897	0.0740
Mg	0.3501	0.34474	0.438	0.43518	0.4914	0.49177	0.0599
Mg	0	0	0	0	0	0	0
C	0.0737	0.08223	0.2495	0.26599	0.287	0.27463	0.2169
C	0.4699	0.47277	0.3362	0.33128	0.2364	0.23558	0.0542
OH	0.2152	0.22455	0.9843	0.97967	0.102	0.11721	0.1307
OW	0.226	0.24791	0.589	0.61189	0.286	0.30117	0.2865
OW	0.234	0.23813	0.8947	0.92381	0.45	0.45921	0.2688
O	0.024	0.00878	0.143	0.17176	0.18	0.16220	0.3038
O	0.017	0.01677	0.3598	0.37440	0.329	0.30587	0.2349
O	0.211	0.22288	0.2453	0.25692	0.37	0.35464	0.2329
O	0.4408	0.43075	0.1981	0.19566	0.213	0.21587	0.1139
O	0.4854	0.49221	0.4011	0.40165	0.3739	0.37848	0.0626
O	0.4809	0.49778	0.3971	0.39688	0.1084	0.11400	0.1537

*H positions excluded

**Missing 3C and 2O atoms

***restraints for 3C and 2O positions

Table S4. Atomic coordinates and equivalent isotropic displacement parameters (U_{iso} in Å^2) for the ab initio determined, missing-atoms ($x1$, $y1$, $z1$, $U_{iso}1$) and all-atoms refined ($x1$, $y1$, $z1$, $U_{iso}2$) mAra structures.

	x1	*x2*	*y1*	*y2*	*z1*	*z2*	$U_{iso}1$	$U_{iso}2$
Ca1	0.7240	0.7216	0.7430	0.7562	1.1216	1.1170	0.0801	0.0308
Ca2	0.6145	0.6102	0.2528	0.2383	0.9468	0.9419	0.0811	0.0443
Ca3	0.5576	0.5570	0.7550	0.7475	0.6039	0.5997	0.0802	0.0384
Ca4	0.7789	0.7751	0.2493	0.2502	0.9578	0.9425	0.0748	0.0506
Ca5	0.8866	0.8900	0.7614	0.7506	1.1081	1.1027	0.0829	0.0486
Ca6	0.9426	0.9432	0.2400	0.2326	1.4395	1.4284	0.1527	0.0598
O1	0.6929	0.7107	0.5546	0.6059	0.8297	0.8631	0.1051	0.0508
O2	0.5315	0.5435	0.9530	0.9308	0.8088	0.8319	0.0502	0.0051
O3	0.6504	0.6358	0.8964	0.9421	1.1530	1.1128	0.1289	0.0718
O4	0.6991	0.6964	0.0854	0.0756	0.9730	0.9505	0.0519	0.0763
O5	0.6431	0.6341	0.5855	0.6011	0.8661	0.8436	0.1191	0.1645
O6	0.8078	0.7981	0.6035	0.6032	0.8457	0.8160	0.0835	0.0885
O7	0.5202	0.5301	0.4286	0.4275	0.9089	0.9122	0.0867	0.0507
O8	0.8719	0.8619	0.4525	0.4038	1.2282	1.2011	0.0807	0.0874
O9	0.8723	0.8622	0.4349	0.3888	1.4558	1.4228	0.0863	0.0784
O10	0.9800	0.9729	0.9197	0.9037	1.3021	1.3183	0.1432	0.0878
O11	0.7069	0.6939	0.0525	0.0852	0.7394	0.7319	0.0742	0.1787
O12	0.7881	0.7831	0.3460	0.4266	1.2302	1.1870	0.1160	0.1023
O13	0.5354	0.5251	0.0700	0.0891	1.1989	1.1680	0.0457	0.0753
O14	0.9714	0.9500	0.3601	0.4160	1.2388	1.1920	0.0972	0.1037
O15	0.7975	0.7993	0.9165	0.8963	1.1522	1.1109	0.1679	0.0472
O16	0.9701	0.9614	0.5944	0.6143	1.6082	1.5968	0.2056	0.1019
O17		0.8790		0.9571		1.3193		0.0988
O18		0.6150		0.4323		1.1952		0.0857
C1	0.6415	0.6638	0.0364	0.0758	0.7609	0.7958	0.0563	0.0212
C2	0.8523	0.8300	0.9211	0.9182	1.3027	1.2619	0.0406	0.0846
C3	0.8190	0.8334	0.4169	0.4092	1.2733	1.2715	0.0425	0.0120
C4		0.9993		0.9043		1.2432		0.0583
C5		0.6611		0.9122		1.2704		0.0594
C6		0.5055		0.0774		1.2589		0.0697

Table S5. Ca–O bond distances (in angstrom units) for the all-atoms refined mAra structure. The Ca-O bond distances vary between 2.419 Å and 2.653 Å for standard aragonite. The unusually long bond distance of Ca6-O16 is shown in bold**.**

	Bond1	**Bond2**	**Bond3**	**Bond4**	**Bond5**	**Bond6**	**Bond7**	**Bond8**	**Bond9**
Ca1	-O1	-O1	-O3	-O4	-O5	-O6	-O11	-O12	-O15
	2.358	2.559	2.656	2.251	2.653	2.180	2.523	2.427	2.387
Ca2	-O2	-O3	-O4	-O5	-O7	-O11	-O13	-O18	-O18
	2.406	2.170	2.595	2.483	2.420	2.729	2.659	2.518	2.537
Ca3	-O2	-O3	-O3	-O5	-O7	-O7	-O13	-O13	-O18
	2.576	2.509	2.446	2.370	2.645	2.383	2.565	2.342	2.323
Ca4	-O1	-O4	-O6	-O8	-O9	-O11	-O12	-O12	-O15
	2.586	2.497	2.569	2.578	2.705	2.345	2.369	2.672	2.424
Ca5	-O6	-O8	-O9	-O10	-O14	-O15	-O16	-O17	-O18
	2.757	2.469	2.503	2.363	2.416	2.761	2.208	2.464	2.736
Ca6	-O8	-O9	-O10	-O10	-O14	-O14	-O16	**-O16**	-O17
	2.417	2.458	2.477	2.486	2.506	2.483	2.565	**2.983**	2.236

Additional datasets (separate files)

Data file S1. (Hydromagnesite.cif) cif file of the measured hydromagnesite.

Data file S2. (Hydromagnesite.hkl) hkl file of the measured hydromagnesite.

Data file S3. (Missing-atoms mAra.cif) cif file of the missing-atoms mAra.

Data file S4. (All-atoms mAra.cif) cif file of the all-atoms mAra.

Data file S5. (mAra.hkl) hkl file of the measured mAra.