

Supplementary Information

Material

The nannofossils were collected from rock samples from 3 drill-sites (Supplementary Tab. 1): i) DSDP Site 463 in the Pacific Ocean, ii) ODP Site 1049 in the proto-North Atlantic Ocean, and iii) the Cismon Core in the north eastern Italy corresponding to the western margin of the Cretaceous Tethys Ocean.

Site and sample	Ma	Age	Lithology	Preservation	SAMPLE CODE	SPECIMEN CODE	Species	Mn/Ca (mmol/mol)	Mn vs Ca (r)
ODP 1049-12R-2, 89-90 (141.69 mbsf)	111	Early Albian	clayish brown nannofossil chalk	good	141	141_Bc_D1	<i>Biscutum constans</i>	1.44	0.87
						141_Bc_D2	<i>Biscutum constans</i>	1.45	0.91
						141_Wb_D1	<i>Watznaueria bamesiae</i>	1.46	0.79
						141_Wb_N1	<i>Watznaueria bamesiae</i>	1.6	0.78
						141_Wb_N2	<i>Watznaueria bamesiae</i>	1.56	0.81
						141_Ze_E1	<i>Zeugrhabdotus erectus</i>	1.31	0.81
						141_Ze_E2	<i>Zeugrhabdotus erectus</i>	1.23	0.72
						141_Ze_N1	<i>Zeugrhabdotus erectus</i>	1.6	0.79
ODP 1049-12R-3, 66-67 (142.96 mbsf)	112	Early Albian	laminated black shale (OAE 1b)	good	142	141_Ra_N2	<i>Rhagodiscus asper</i>	1.5	0.81
						142_Bc_D1	<i>Biscutum constans</i>	2.28	0.70
						142_Bc_D2	<i>Biscutum constans</i>	2.06	0.58
						142_Bc_D4	<i>Biscutum constans</i>	2.12	0.60
						142_Wb_D1	<i>Watznaueria bamesiae</i>	1.52	0.66
						142_Wb_E1	<i>Watznaueria bamesiae</i>	1.59	0.57
						142_Wb_E2	<i>Watznaueria bamesiae</i>	2.03	0.71
						142_Wb_N1	<i>Watznaueria biporta</i>	1.66	0.81
						142_Wb_N6	<i>Watznaueria fossacinta</i>	1.86	0.64
						142_Ra_E1	<i>Zeugrhabdotus erectus</i>	1.3	0.69
						142_Ze_D2	<i>Zeugrhabdotus erectus</i>	1.5	0.35
						142_Ze_D5	<i>Zeugrhabdotus erectus</i>	1.96	0.31
						142_Ze_N2	<i>Zeugrhabdotus erectus</i>	1.55	0.69
ODP 1049-13R-2, 60-62 (151 mbsf)	116	Late Aptian	clayish red nannofossil chalk	moderate	151	151_Bc_D1	<i>Biscutum constans</i>	1.59	0.81
						151_Wb_D1	<i>Watznaueria bamesiae</i>	1.59	0.78
						151_Wb_D2	<i>Watznaueria manivitiae</i>	1.58	0.93
						151_Wb_N1	<i>Watznaueria bamesiae</i>	1.54	0.75
						151_N_D1	<i>Nannoconus truittii</i>	2.1	0.73
						151_N_D6	<i>Nannoconus truittii</i>	3.01	0.90
DSDP 463-60R-1, 40-42 (528.4 mbsf)	117	Late Early Aptian	nannofossil chalk	moderate	463	151_N_E1	<i>Nannoconus truittii</i>	3.1	0.85
						463_c8_Wb_D1	<i>Watznaueria bamesiae</i>	1.75	0.75
Cismon core 32.39 m	122	latest Barremian	limestone	moderate	Cis met	cis_met_Wb_D1	<i>Watznaueria bamesiae</i>	1.77	0.82

Table 1. Ma/Ca average values are reported for all specimens analysed. On the left, details on the sample provenance (well site, stratigraphic depth, age, lithology) is provided. Mn vs Ca Pearson correlation coefficient (r) calculated on all data points is also reported.

DSDP Site 463 was drilled at a water depth of 2525m on the ancient structural high of the western Mid-Pacific Mountains (21° 21.010' N, 174° 40.070' E) during DSDP Leg 62. During the Early Cretaceous, Site 463 was located at a palaeolatitude of 20° S, with a paleo-depth between a few hundred meters¹ and 1 km².

The studied sample is DSDP 463-60R-1, 40-42 (528.4 mbsf) (here named DSDP 463), being a nannofossil chalk of late early Aptian age (ca. 117 Ma). It corresponds to an interval marked by moderate surface water fertility (Bottini et al., 2015).

ODP Site 1049 was drilled on Blake Plateau at 2670 m water depth about 530 km east of Jacksonville, Florida (30°8.53'N, 76°6.72'W). The site is positioned at Blake Nose which lies at the outer flank of a gently sloping ramp with Paleogene and Cretaceous strata. During the late Aptian–early Albian the site was located at a paleolatitude of 25°N³ about 60 km seaward of a large carbonate platform that ran parallel to the present-day Florida coast⁴. Paleodepth estimates range from middle bathyal⁴ to outer shelf to upper slope⁵.

The Upper Aptian–Lower Albian at Site 1049 is 32m thick and composed dominantly of rhythmically alternating red, white and green bioturbated calcareous clay and clayrich chalk^{4,6}. The sequence includes the sedimentary expression of OAE 1b, a finely laminated, 46 cm thick black shale containing up to 12.3 wt % total organic carbon⁷.

The studied samples are:

- ODP 1049-12R-2, 89-90 (141.69 mbsf) (here named 141), being a clayish brown nannofossil chalk of Early Albian age (ca. 111 Ma). It corresponds to an interval marked by relatively high surface water fertility⁸.
- ODP 1049-12R-3, 66-67 (142.96 mbsf) (here named 142), being a black shale of the OAE 1b interval of Early Albian age (ca. 111.5 Ma). It corresponds to an interval marked by high surface water fertility⁸. This sample also corresponds to an interlude of intense volcanism responsible for CO₂ and trace metals emissions⁹.
- ODP 1049-13R-2, 60-62 (151 mbsf) (here named 151), being a clayish red nannofossil chalk of Late Aptian age (ca. 115.5 Ma). It corresponds to an interval marked by low surface water fertility¹⁰. It was also an interval characterized by relatively abundant *N. truittii* (*N. truittii* acme) which flourished under relatively cooler and low fertility conditions as well as temporary absence of intense volcanic activity.

The Cismon Core, drilled in the Italian Southern Alps, north-eastern Italy (46°02'N, 11°45'E; 398m altitude), is represented by a total stratigraphic thickness of 131.8m with 100% recovery. The site was located on the southern margin of the Mesozoic Tethys, on the eastward deepening slope between the Trento Plateau (a pelagic submarine high) and the Belluno Basin¹¹. The Cismon sequence was deposited at an estimated palaeo-depth of 1000–1500m during the Early Cretaceous¹²⁻¹⁴. The studied sample is at 32.39 m (here named Cis-met), being a limestone of Latest Barremian age (ca. 122 Ma). It corresponds to an interval marked by low to moderate surface water fertility¹⁰.

Nannofossil preservation.

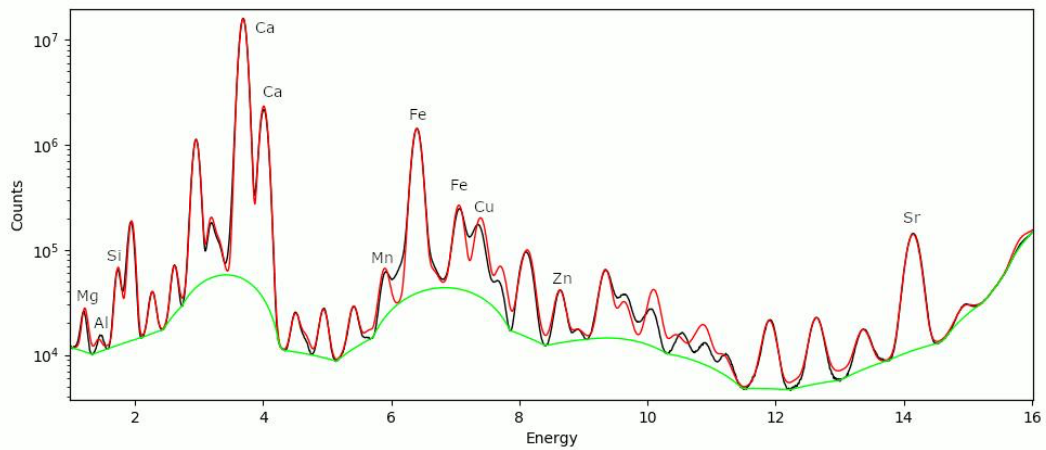
The nannofossil preservation state was evaluated under optical microscope and scanning electron microscope. Specimens from ODP Site 1049 (samples 141, 142) have good preservation. Specimens from ODP Site 1049 (sample 151), DSDP Site 463 and Cismon Core have moderate preservation with minor to moderate signs of overgrowth (Supplementary Plates I-VIII).

Remarks on studied nannofossil species.

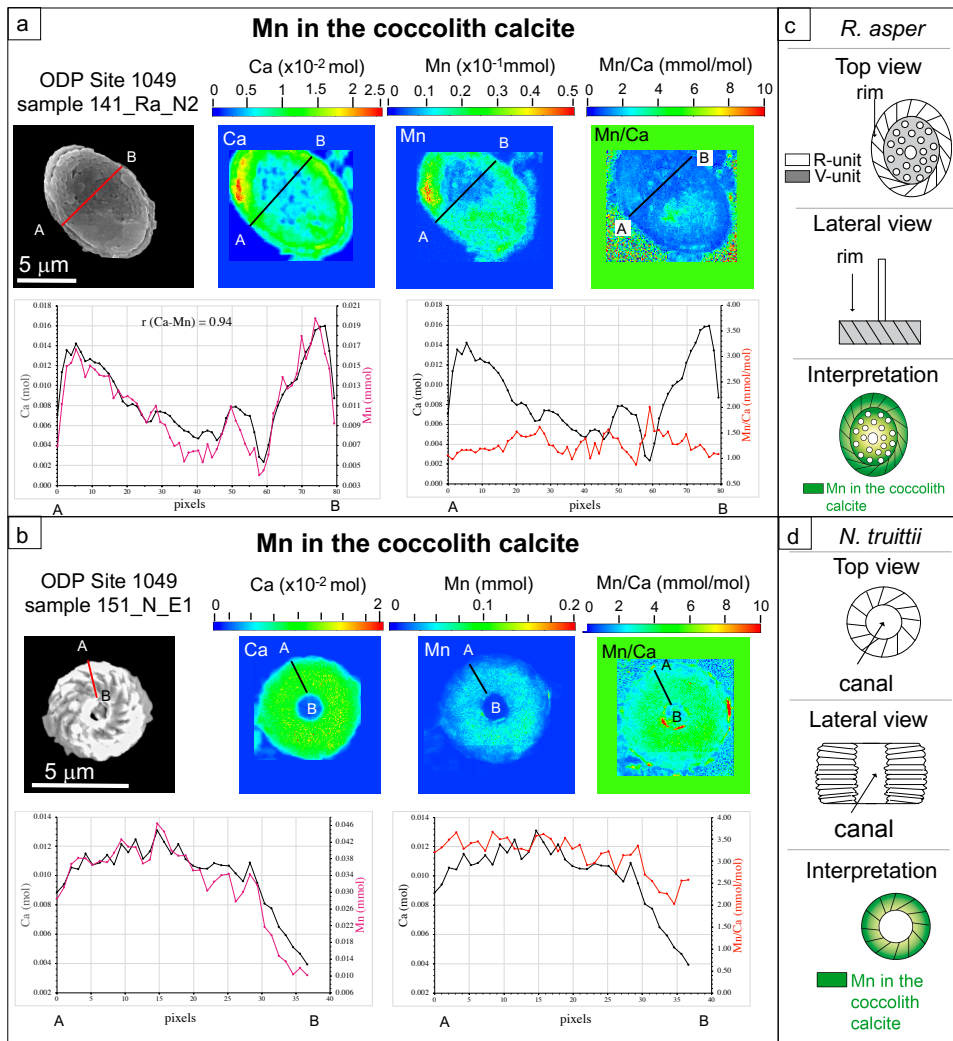
The majority of the studied *Watznaueria* specimens are *W. barnesiae*, the most common Cretaceous taxon, but there is also one specimen of *W. fossacinta*, one *W. biporta* and one *W. manivitiae* (Supplementary Tab. 1). *W. fossacinta* and *W. biporta* differ from *W. barnesiae* because of the shape

of the central coccolith area: *W. fossacinta* has a narrow central area opening and *W. biporta* has two well-defined pores separated by a conjunct transverse bar (Supplementary Plates VI). Conversely, *W. barnesiae* central area is closed or very narrow, with no structures (Fig. 2a; Supplementary Plates I, II, III, VI). *W. manivitiae* resemble *W. barnesiae* but it is represented by larger specimens (length > 9 μm), (Supplementary Plates II).

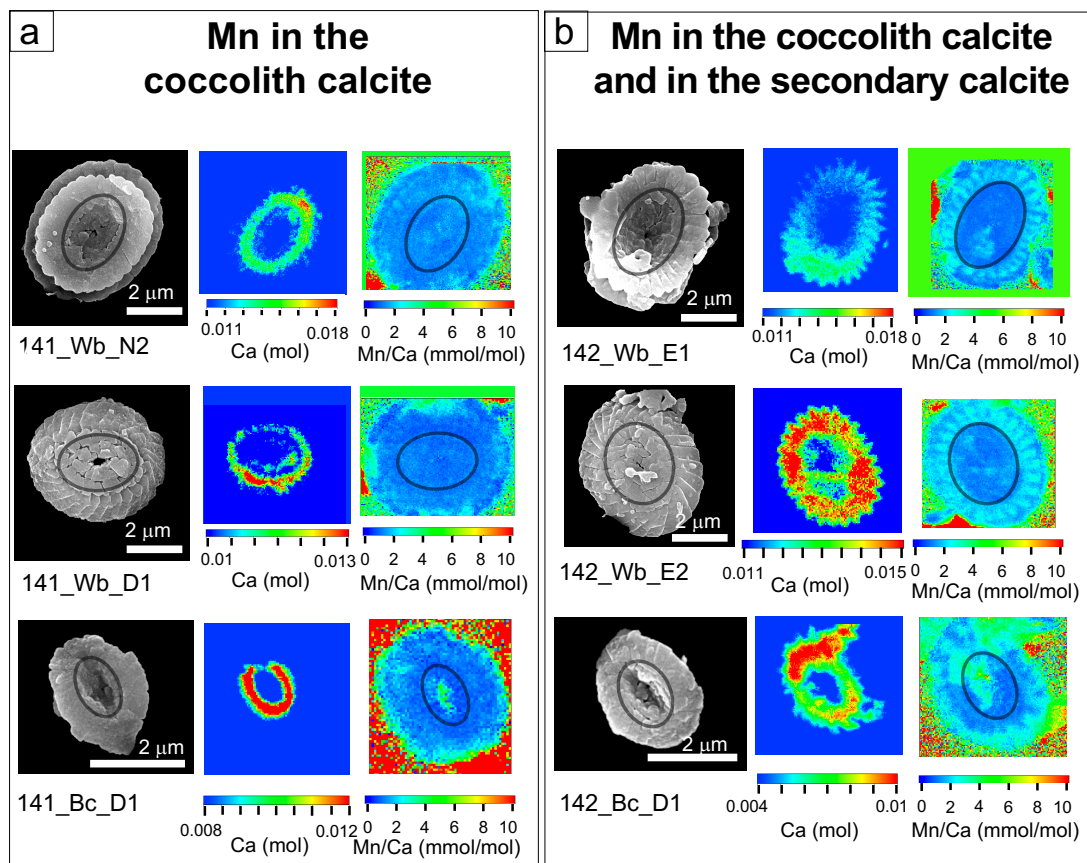
Results



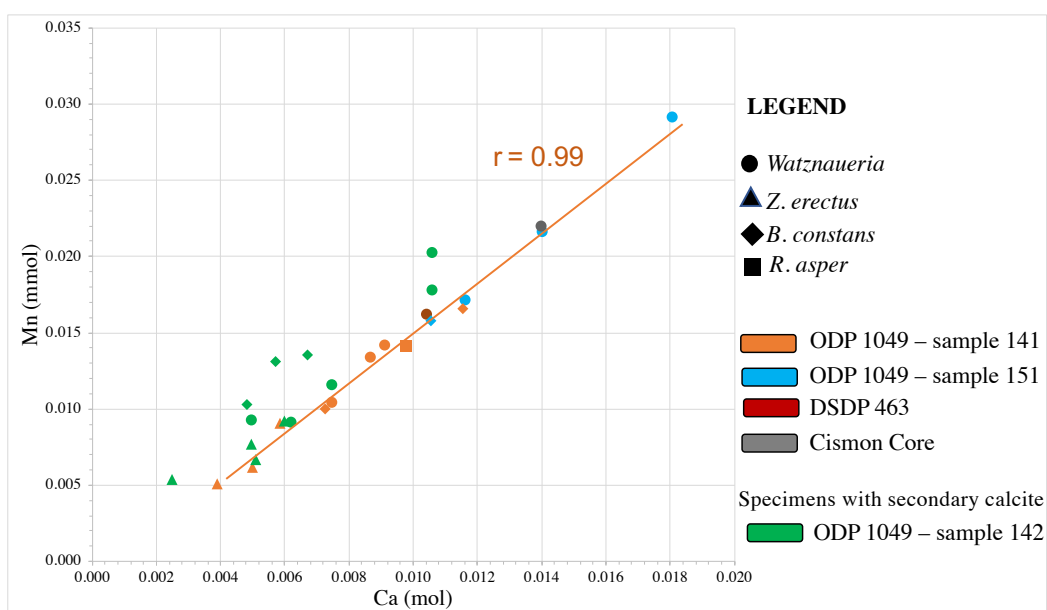
Supplementary Figure_1. X-ray fluorescence (XRF) spectra obtained for the coccolith specimens analysed in this study. The fits are calculated with PyMCA¹ and used to derive i/Ca.



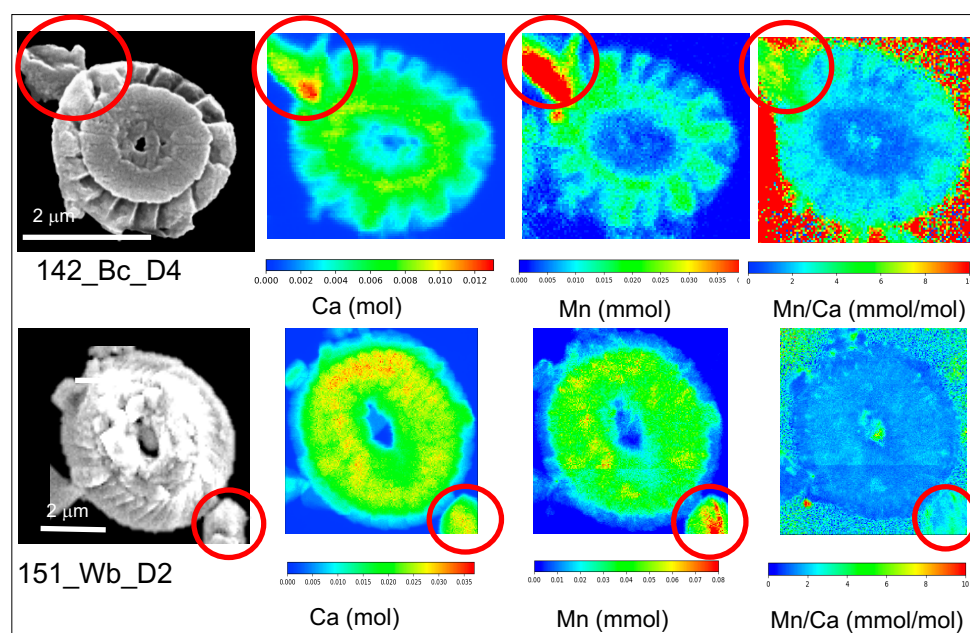
Supplementary Figure 2. Manganese distribution in *Rhagodiscus asper* (muroliths) and *Nannoconus truittii* (nannolith). **a.** Scanning electron microscope (SEM) image and Ca, Mn and Mn/Ca XRF maps of *R. asper* specimen from ODP Site 1049, sample 141 (141_Ra_N2). Mn has a relatively homogenous distribution and mimics the Ca pattern. The Ca, Mn and Mn/Ca values across the transect A-B are reported. **b.** SEM image and Ca, Mn and Mn/Ca XRF maps of *N. truittii* specimen from ODP Site 1049, sample 151 (151_N_E1). Mn has a relatively homogenous distribution and mimics the calcium pattern. **c.** Top and lateral view sketches of *R. asper*. R and V units indicate the direction of the *c*-axis in the calcite crystals composing the V = sub-vertical *c*-axis; R = sub-radial *c*-axis. **d.** Top and lateral view sketches of *N. truittii*.



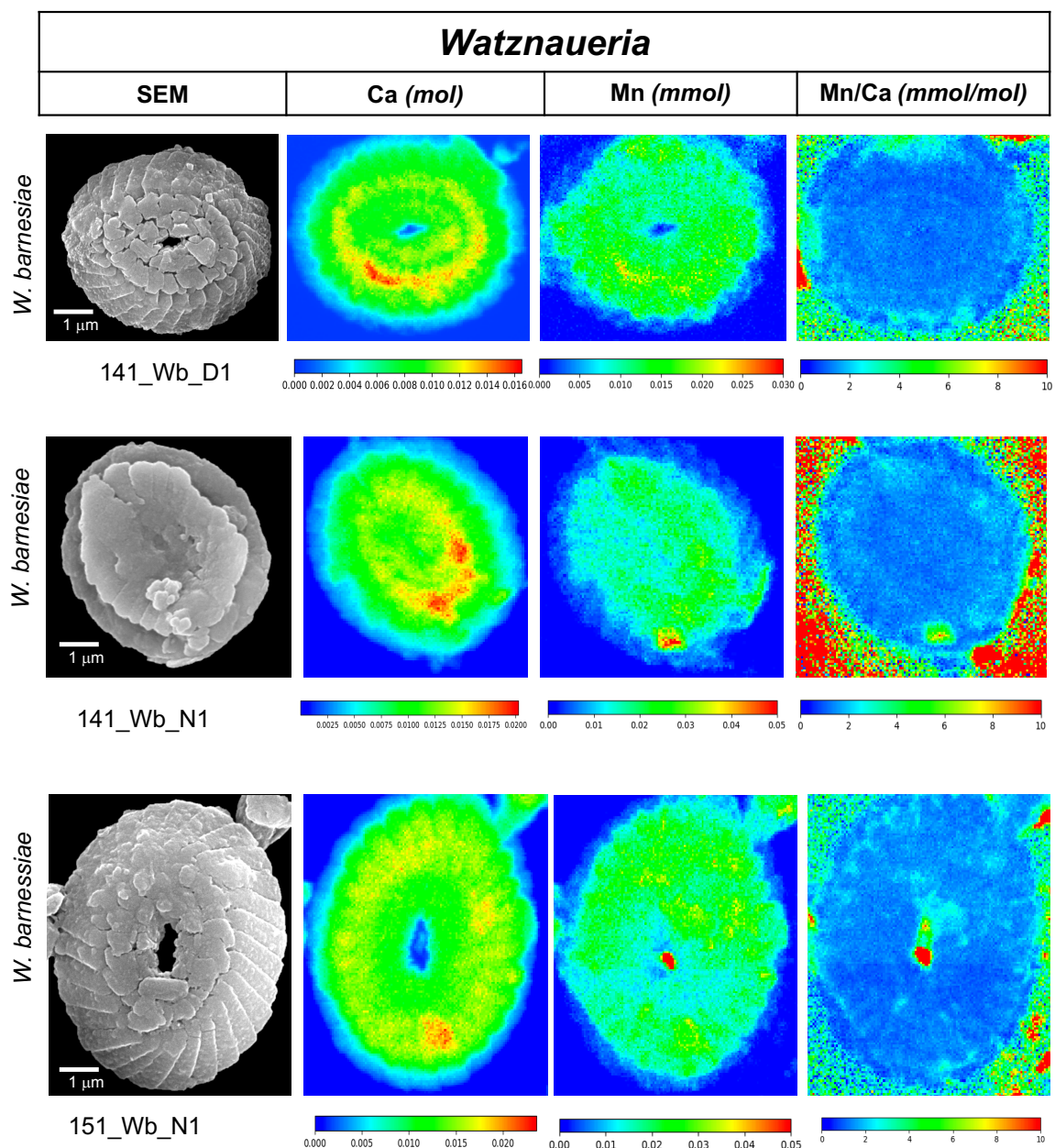
Supplementary Figure 3. **a.** SEM image, Ca and Mn/Ca maps of three placolith specimens (from top to bottom, *W. barnesiae* 141_Wb_N2; *W. barnesiae* 141_Wb_D1; *B. constans* 141_Bc_D1) characterized by Mn in the primary calcite. For each specimen, the tube position (where the distal and proximal shields are sealed) is indicated with a black oval line on the SEM image and Mn/Ca map. The Ca map is forced to highlight the thicker part of the coccolith corresponding to the tube. **b.** SEM image, Ca and Mn/Ca maps of three placolith specimens (from top, *W. barnesiae* 142_Wb_E1; *W. barnesiae* 142_Wb_E2; *B. constans* 142_Bc_D1) characterized by Mn in the primary and secondary calcite. For each specimen, the tube position is indicated with a black oval line on the SEM image and Mn/Ca map. The Ca map is forced to highlight the thicker part of the coccolith corresponding to the tube but also to the outer rim suggesting that these coccoliths have thicker outer rim. The calcite deposits in the outer rim are enriched in Mn.



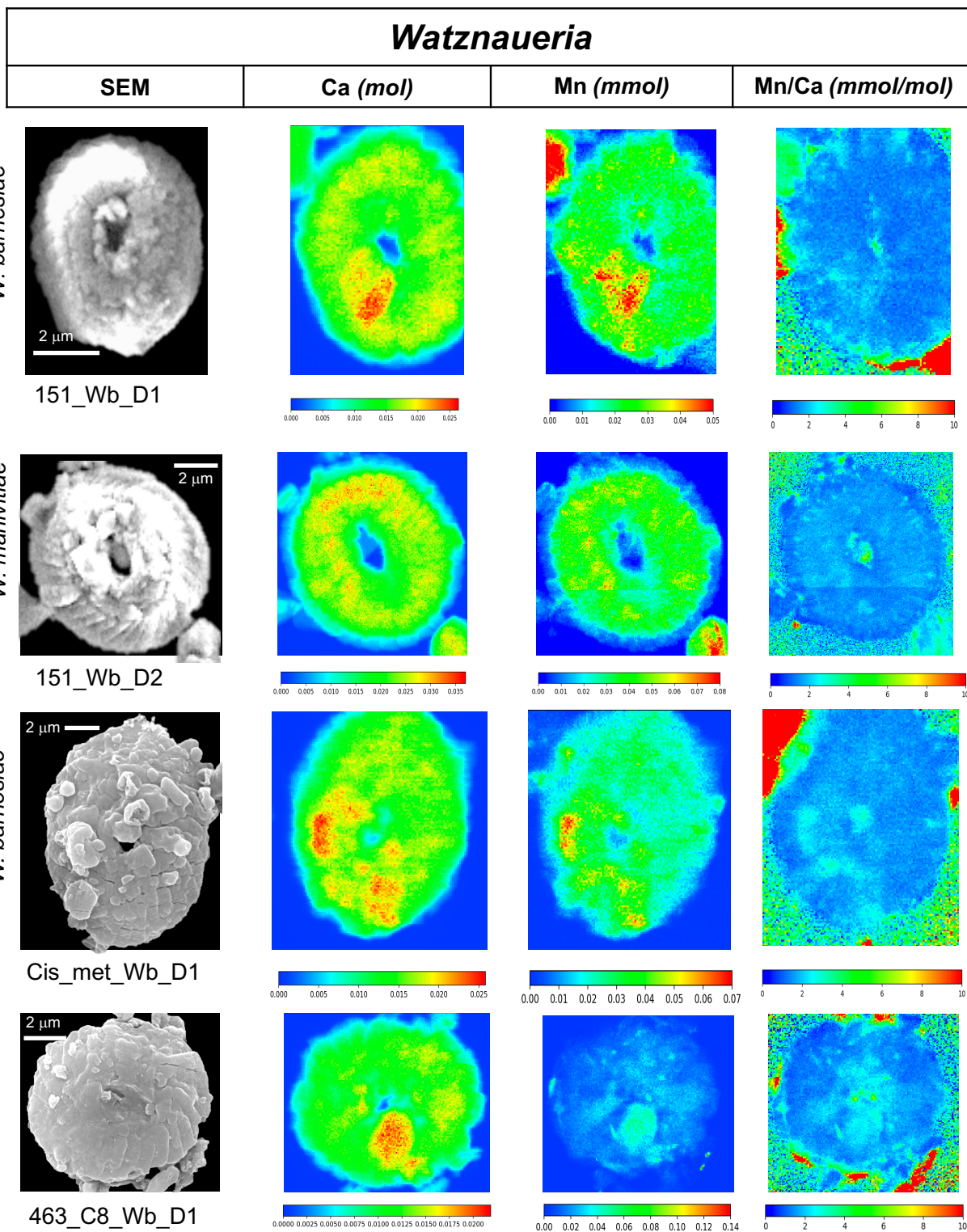
Supplementary Figure 4. Scatter plot of nannofossil average Ca (mol) and Mn (mmol). There is a positive correlation ($r = 0.99$) between the average Ca and Mn of the specimens from samples 141, 151 (ODP Site 1049), Cismon Core and DSDP Site 463. Specimens from sample 142 (ODP Site 1049) are not fitting with this correlation. Colors refer to different samples: orange = ODP Site 1049, sample 141; green = ODP Site 1049, sample 142; blue = ODP Site 1049, sample 151; bordeaux = DSDP Site 463; grey = Cismon Core. Squares = *R. asper*; diamonds = *B. constans*; triangles = *Z. erectus*; dots = *Watznaueria*.



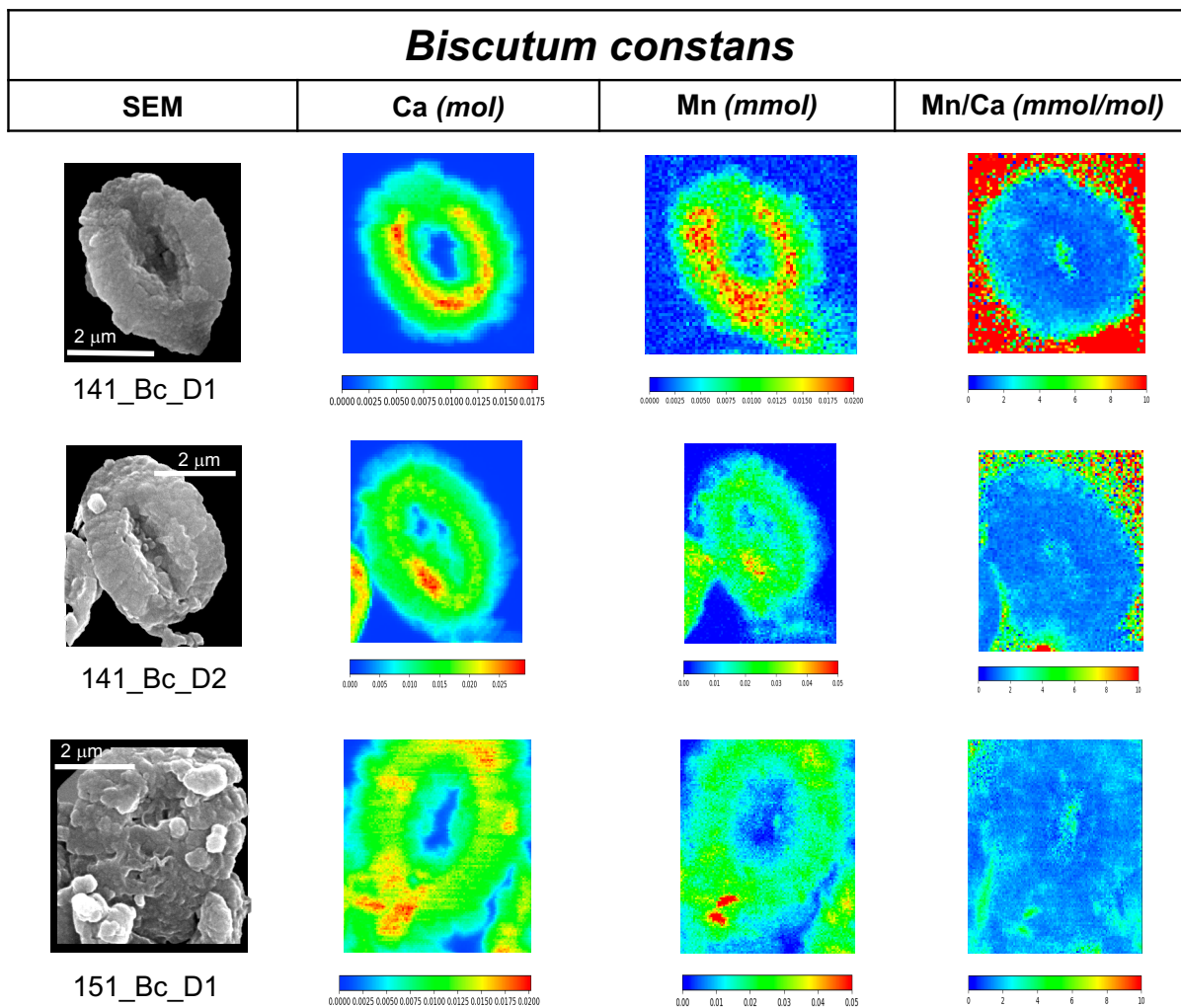
Supplementary Figure 5. Abiogenic calcite fragments highlighted in the red circles. SEM, Ca, Mn and Mn/Ca maps are reported and show that the abiogenic calcite has higher Mn (mmol) and Mn/Ca ratios (mmol/mol).



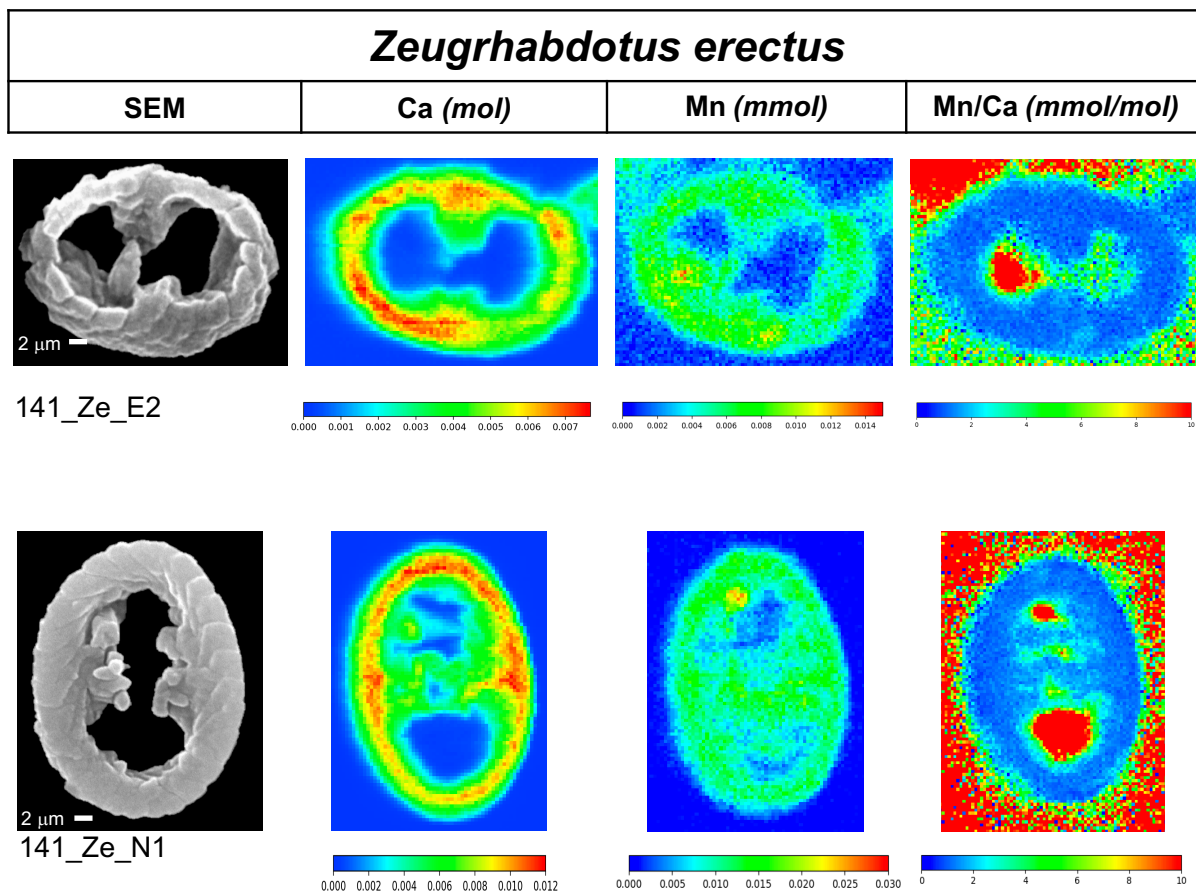
Supplementary Plate I. Coccoliths of *W. barnesiae* showing Mn in the coccolith calcite.



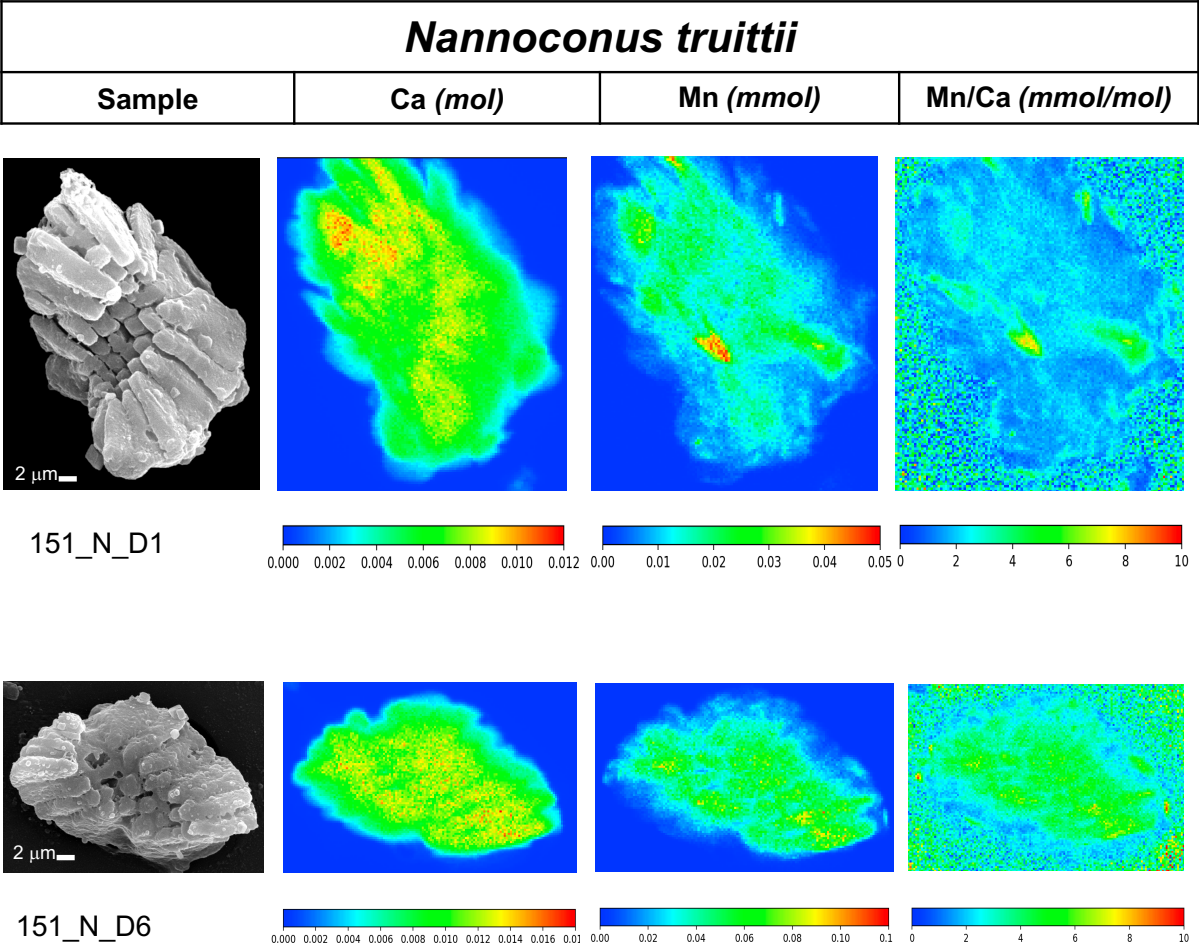
Supplementary Plate II. Coccoliths of *Watznaueria* showing Mn in the coccolith calcite.



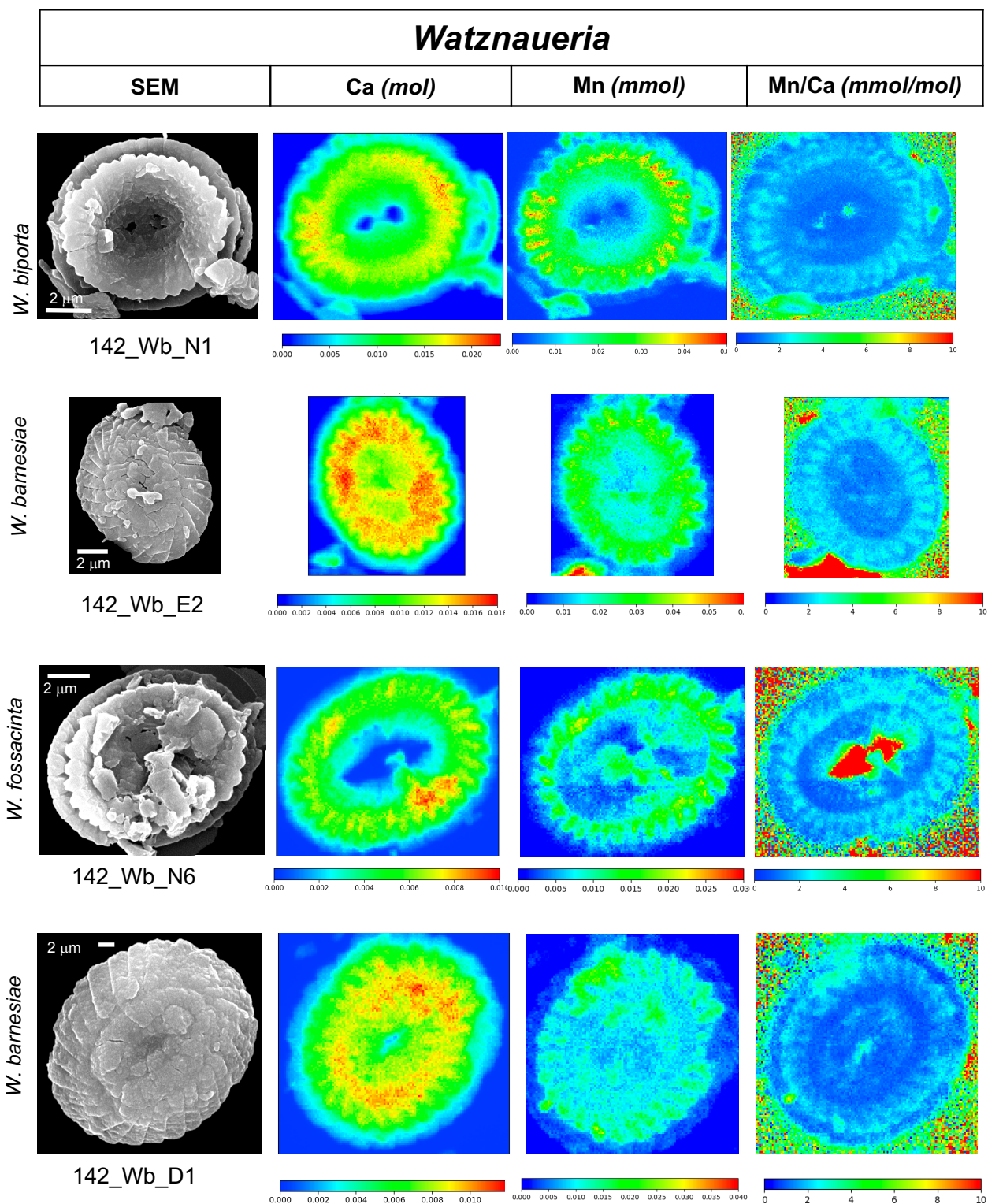
Supplementary Plate III. Coccoliths of *Biscutum constans* showing Mn in the coccolith calcite.



Supplementary Plate IV. Coccoliths of *Zeugrhabdodus erectus* showing Mn in the coccolith calcite.

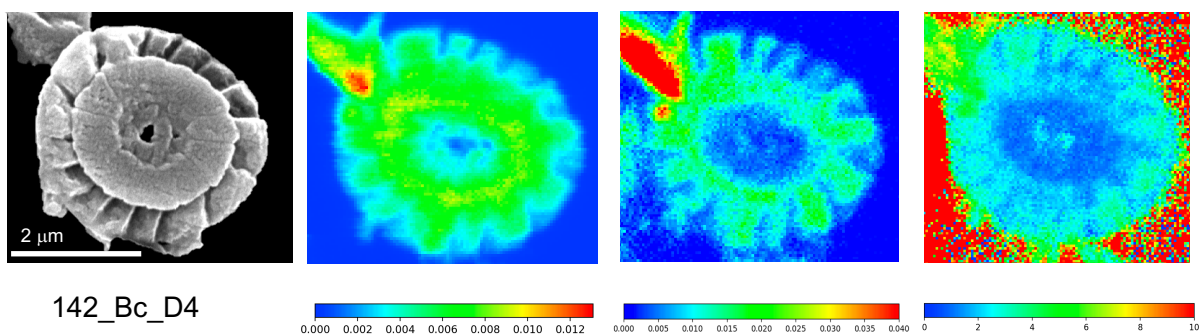
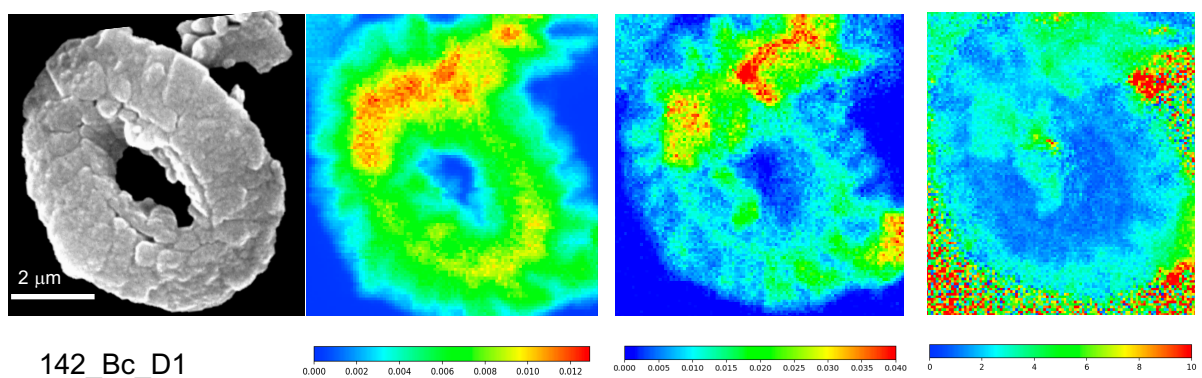
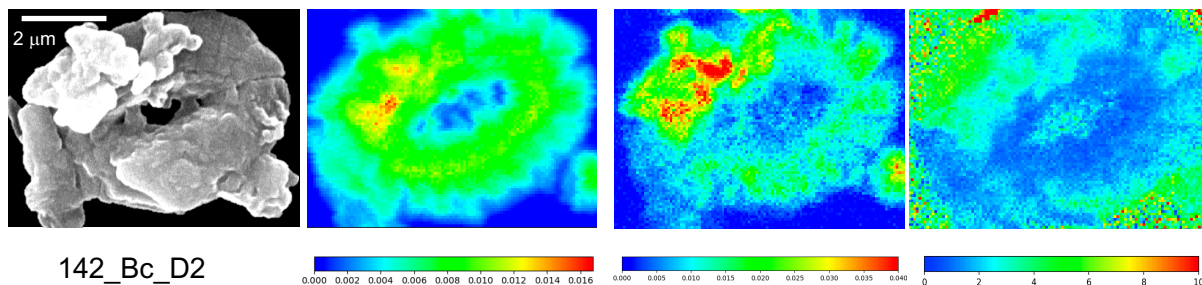


Supplementary Figure_Plate V. Nannoliths of *Nannoconus truittii* showing Mn in the coccolith calcite.



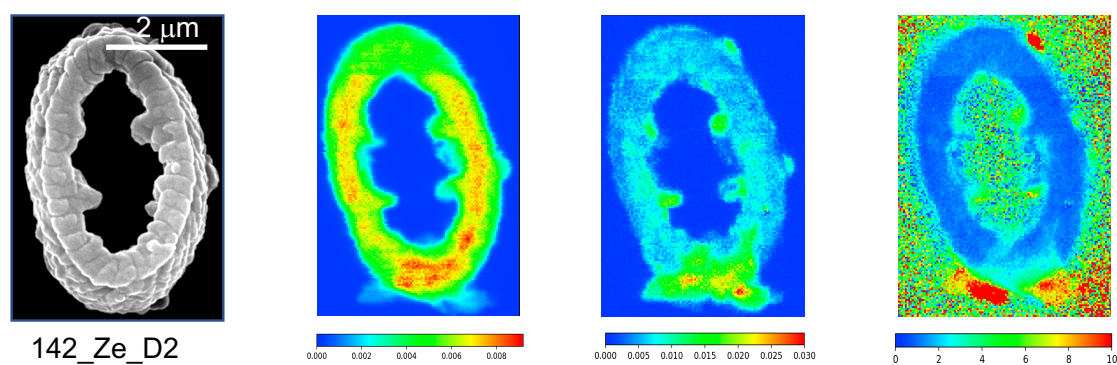
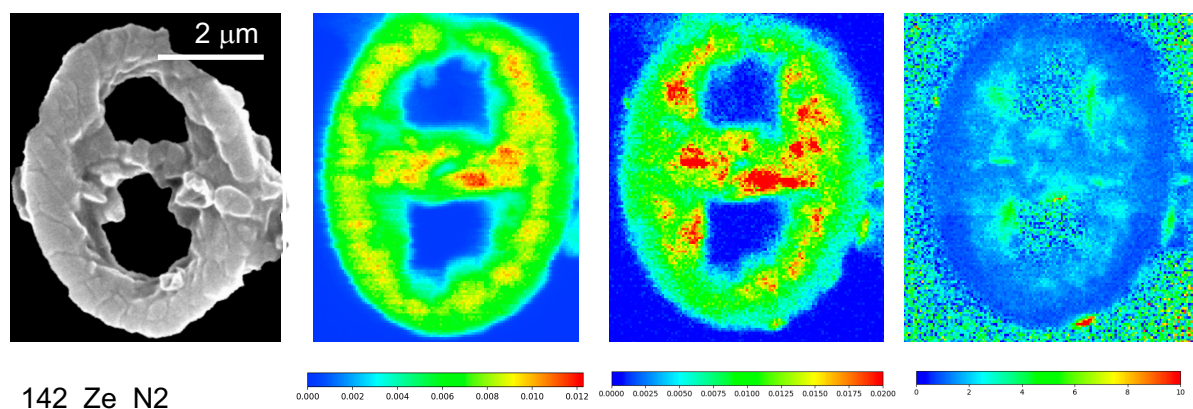
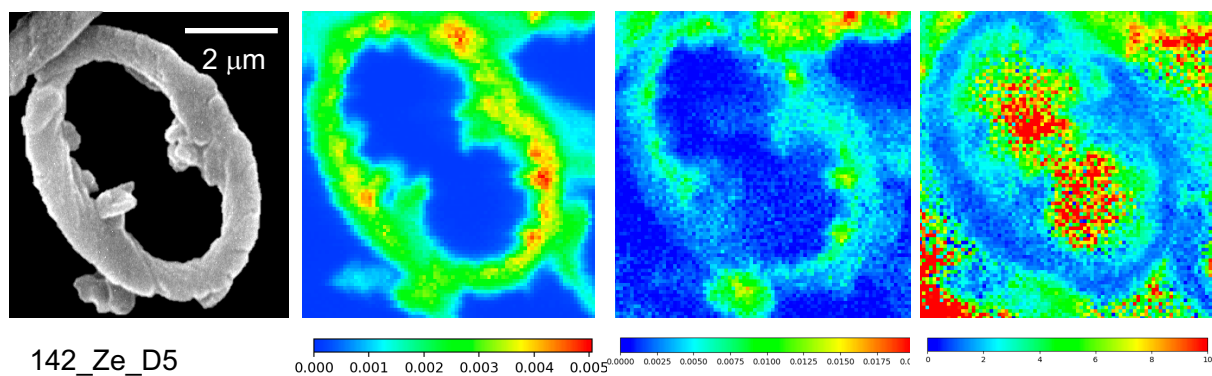
Supplementary Plate VI. Coccolith of *Watznaueria* showing Mn in the coccolith calcite and secondary calcite deposits enriched in Mn.

<i>B. constans</i>			
SEM	Ca (mol)	Mn (mmol)	Mn/Ca (mmol/mol)



Supplementary Plate VII. Coccoliths of *B. constans* showing Mn in the coccolith calcite and secondary calcite deposits enriched in Mn.

<i>Zeugrhabdodus erectus</i>			
SEM	Ca (mol)	Mn (mmol)	Mn/Ca (mmol/mol)



Supplementary Plate VIII. Coccoliths of *Zeugrhabdodus erectus* showing Mn in the coccolith calcite and secondary calcite deposits enriched in Mn.

References

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