Aragonite is calcite's best friend at the seafloor

Olivier Sulpis[1], Priyanka Agrawal[1], Mariette Wolthers[1], Guy Munhoven[2], Matthew Walker[3], Jack J. Middelburg[1]

[1]Utrecht University, The Netherlands
[2]Université de Liège, Belgium
[3]University of Lincoln, United Kingdom

vEGU21
OS3.1 – 'From the surface into the deep: advances in marine carbon dynamics with models and observations'
April 27, 2021 / 14:03-14:05

This display material gives some context and further details for my short vPICO presentation.

Results presented here are the object of a manuscript currently in preparation for publication.

Please contact me (Olivier) at o.j.t.sulpis@uu.nl for any question, comment or suggestion.

NeSSC
NETHERLANDS EARTH SYSTEM SCIENCE CENTRE

Although dominant, calcite is not the only $CaCO_3$ phase present in the pelagic ocean or in marine sediments.

Aragonite, about 50% more soluble than calcite in seawater (Mucci, 1983), and whose pelagic production is dominated by pteropods, **could account for 10 to 50% of global marine $CaCO_3$ export** (Bednaršek et al., 2012; Buitenhuis et al., 2019; Gangstø et al., 2008).
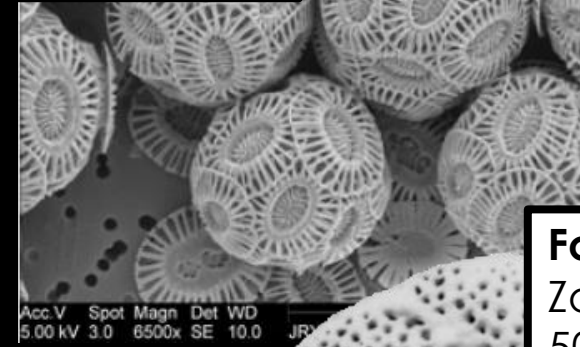
Yet, aragonite is neglected from most Earth System models used to reconstruct and predict Earth climates.

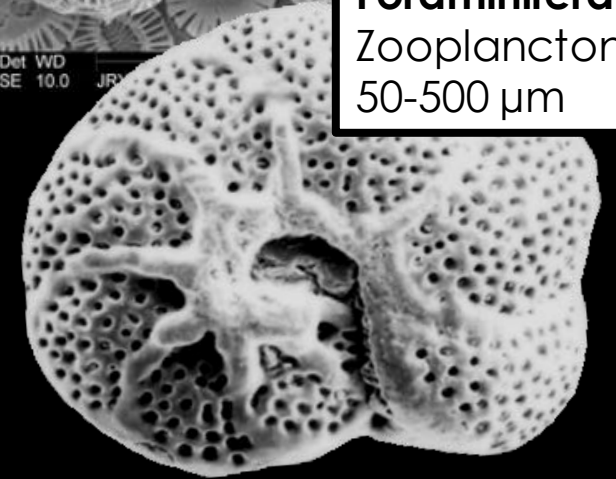Picture Dr. Nina Bednarsek
(Pacific Marine Environmental Laboratory)

Coccolithophores
Phytoplancton,
5-100 μm

Foraminifera
Zooplancton,
50-500 μm

Pteropods
'sea snails'
A few mm

Calcite

Aragonite

$$CaCO_3 \leftrightarrow Ca^{2+} + CO_3^{2-}$$

A Peijnenburg et al. 2021, *PNAS*
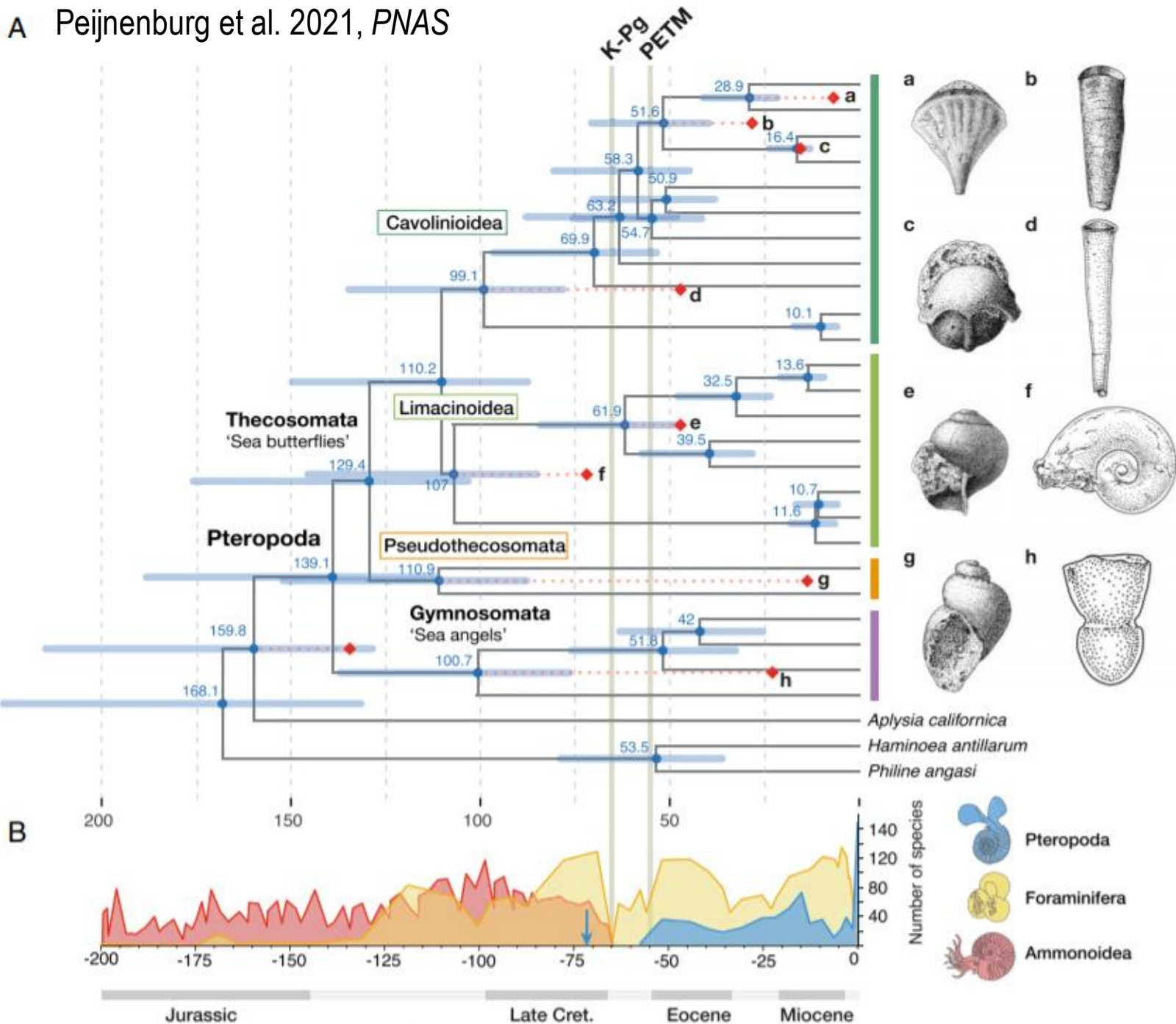
Pteropods, the main aragonite producers, have been around since the Jurassic. Even though they are abundant, they are rarely preserved in marine sediments. It is often assumed that aragonite disappears right below its saturation depth, unlike calcite which is preserved up to the calcite *compensation* depth (CCD), several kilometres below the calcite *saturation* depth.

Where are the pteropods?

CCD stands for calcite compensation depth: there are many different carbonate minerals, each with a different solubility.

Article Talk

Calcite

Read Edit View history Search Wikipedia

# ~~Carbonate~~ compensation depth

From Wikipedia, the free encyclopedia

Carbonate compensation depth (**CCD**) is the depth in the oceans below which the rate of supply of calcite (calcium carbonate) lags behind the rate of solvation, such that no calcite is preserved. Shells of animals therefore dissolve and carbonate particles may not accumulate in the sediments on the sea floor below this depth. **Aragonite compensation depth** (hence **ACD**) describes the same behaviour in reference to aragonitic carbonates. Aragonite is more soluble than calcite, so the aragonite compensation depth is generally shallower than the calcite compensation depth.

Contents [hide]
1 Solubility of carbonate
2 Variations in value of the CCD
3 See also
4 References

Solubility of carbonate [edit]

Calcium carbonate is essentially insoluble in sea surface waters today. Shells of dead calcareous plankton sinking to deeper waters are practically unaltered until reaching the lysocline, the point about 3.5 km deep past which the solubility increases dramatically with depth and pressure. By the time the CCD is reached all calcium carbonate has dissolved according to this equation:

$$CaCO_3 + CO_2 + H_2O \rightleftharpoons Ca^{2+}(aq) + 2\,HCO_3^-(aq)$$
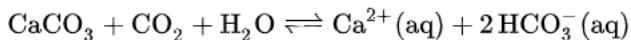
Calcareous plankton and sediment particles can be found in the water column above the CCD. If the sea bed is above the CCD, bottom sediments can consist of calcareous sediments called calcareous ooze, which is essentially a type of limestone or chalk. If the exposed sea bed is below the CCD tiny shells of $CaCO_3$ will dissolve before reaching this level, preventing deposition of carbonate sediment. As the sea floor spreads, thermal subsidence of the plate, which has the effect of increasing depth, may bring the carbonate layer below the CCD; the carbonate layer may be prevented from chemically interacting with the sea water by overlying sediments such as a layer of siliceous ooze or abyssal clay deposited on top of the carbonate layer.[1]

Variations in value of the CCD [edit]

The exact value of the CCD depends on the solubility of calcium carbonate which is determined by temperature, pressure and the chemical composition of the water – in particular the amount of dissolved CO_2 in the water. Calcium carbonate is more soluble at lower temperatures and at higher pressures. It is also more

Part of a series on the
Carbon cycle

Main page
Contents
Current events
Random article
About Wikipedia
Contact us
Donate

Contribute

Help
Learn to edit
Community portal
Recent changes
Upload file

Tools

What links here
Related changes
Special pages
Permanent link
Page information
Cite this page
Wikidata item

Print/export

Download as PDF
Printable version

Plots made using Berger (1978, *DSR*), Sulpis et al. (2018, *PNAS*) and GLODAPv2 data (Lauvset et al., 2016, *ESSD*).
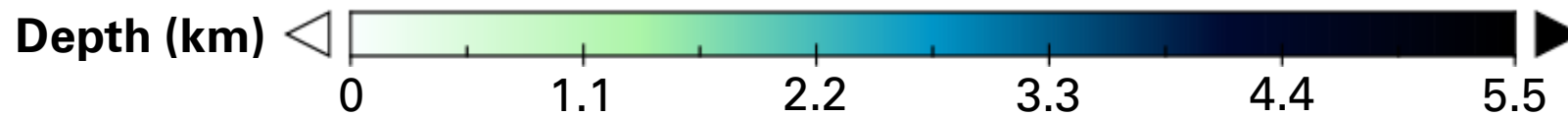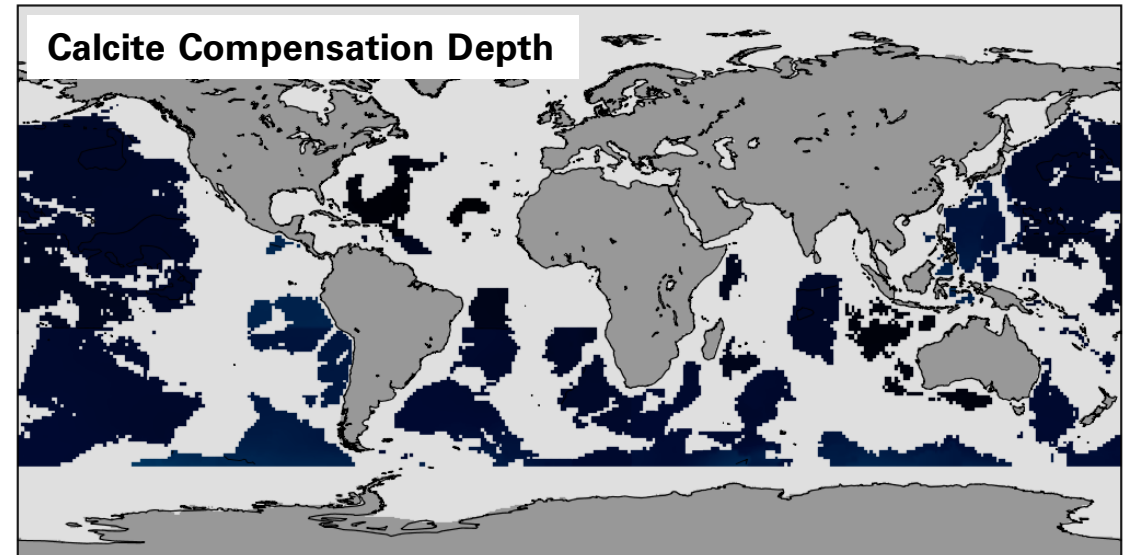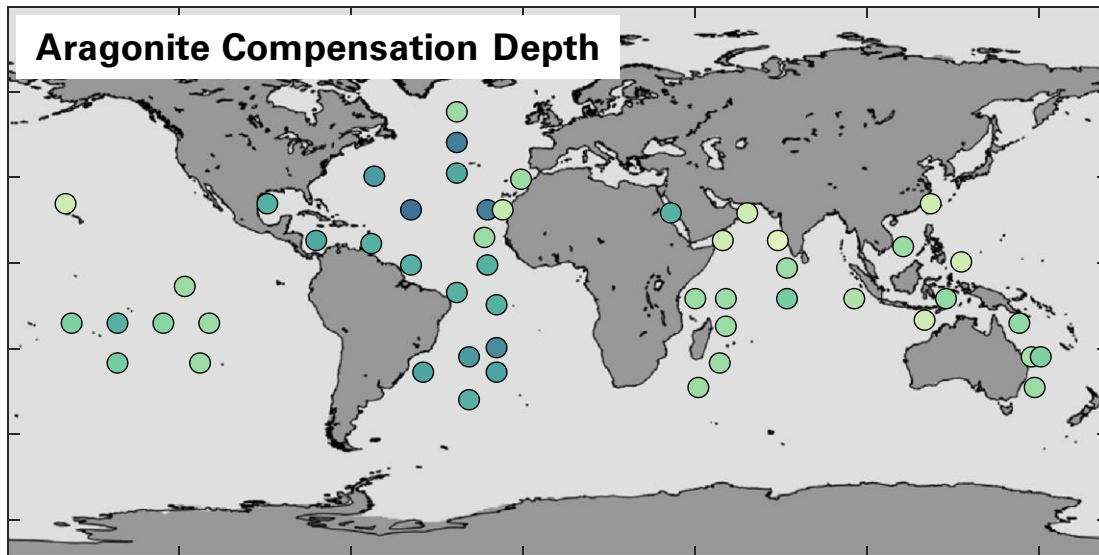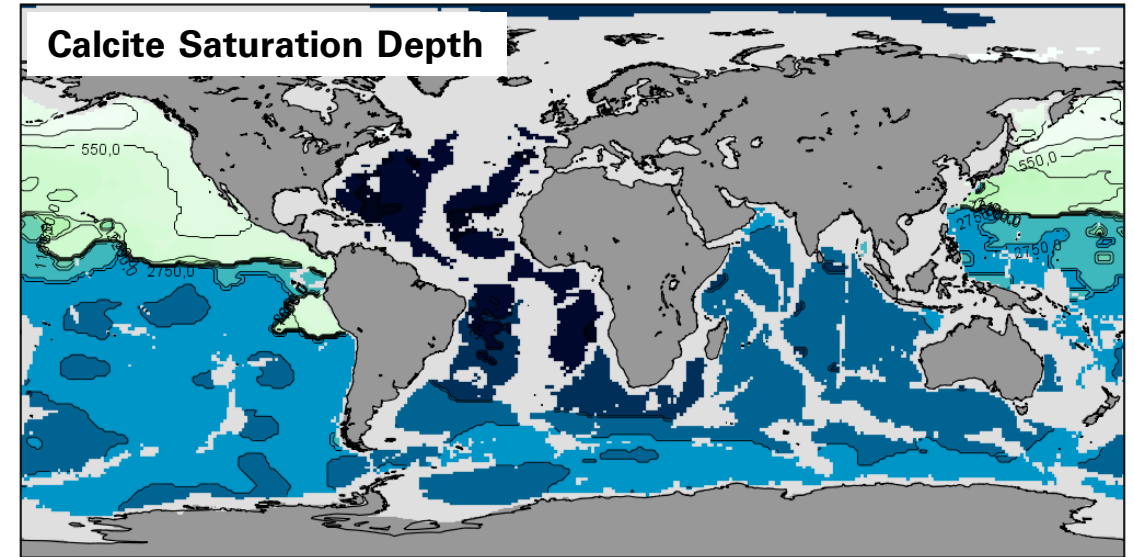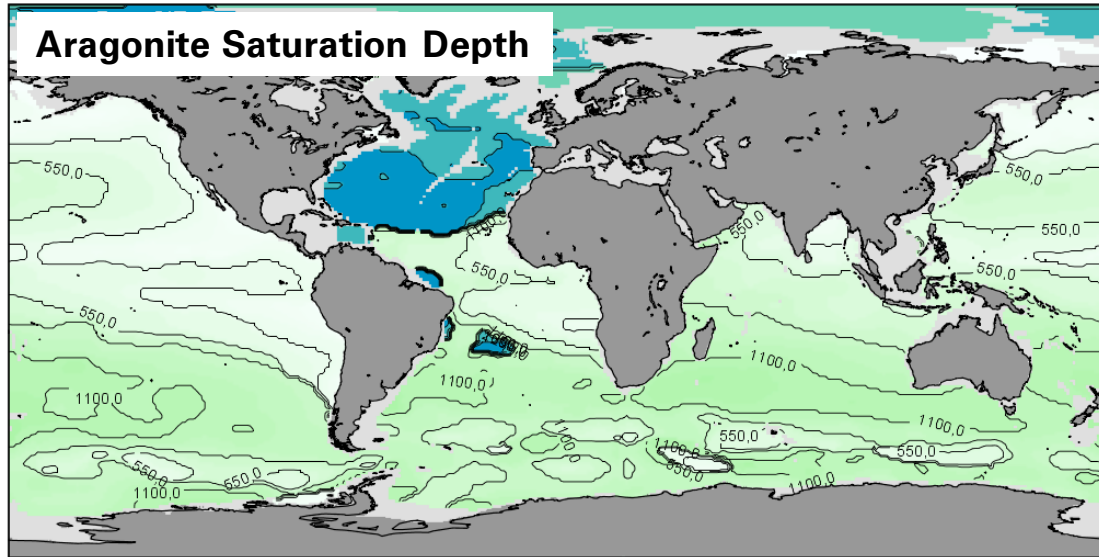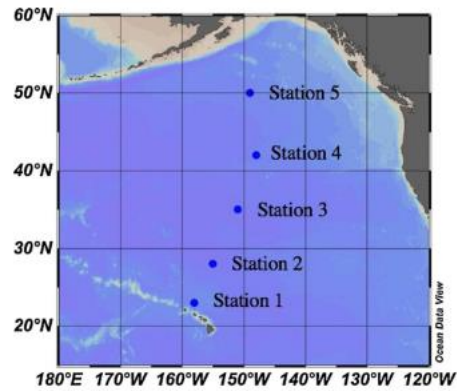
Dong et al. (2019, *EPSL*)

Why is it likely that aragonite reaches the seafloor even far below its saturation depth?

1) There is aragonite at abyssal depths (see plot on the left).

2) High concentrations of pteropod genetic material at >4 km-depth Boeuf et al. (2019, *PNAS*)

3) Aragonite pteropods sink with rates ranging from 80 to 1080 m per day (Noji et al., 1997 *JPR*).

4) Aragonite dissolution is not that fast in comparison with calcite's (Dong et al., 2019 *EPSL*, Adkins et al., 2021 *ARMS*).
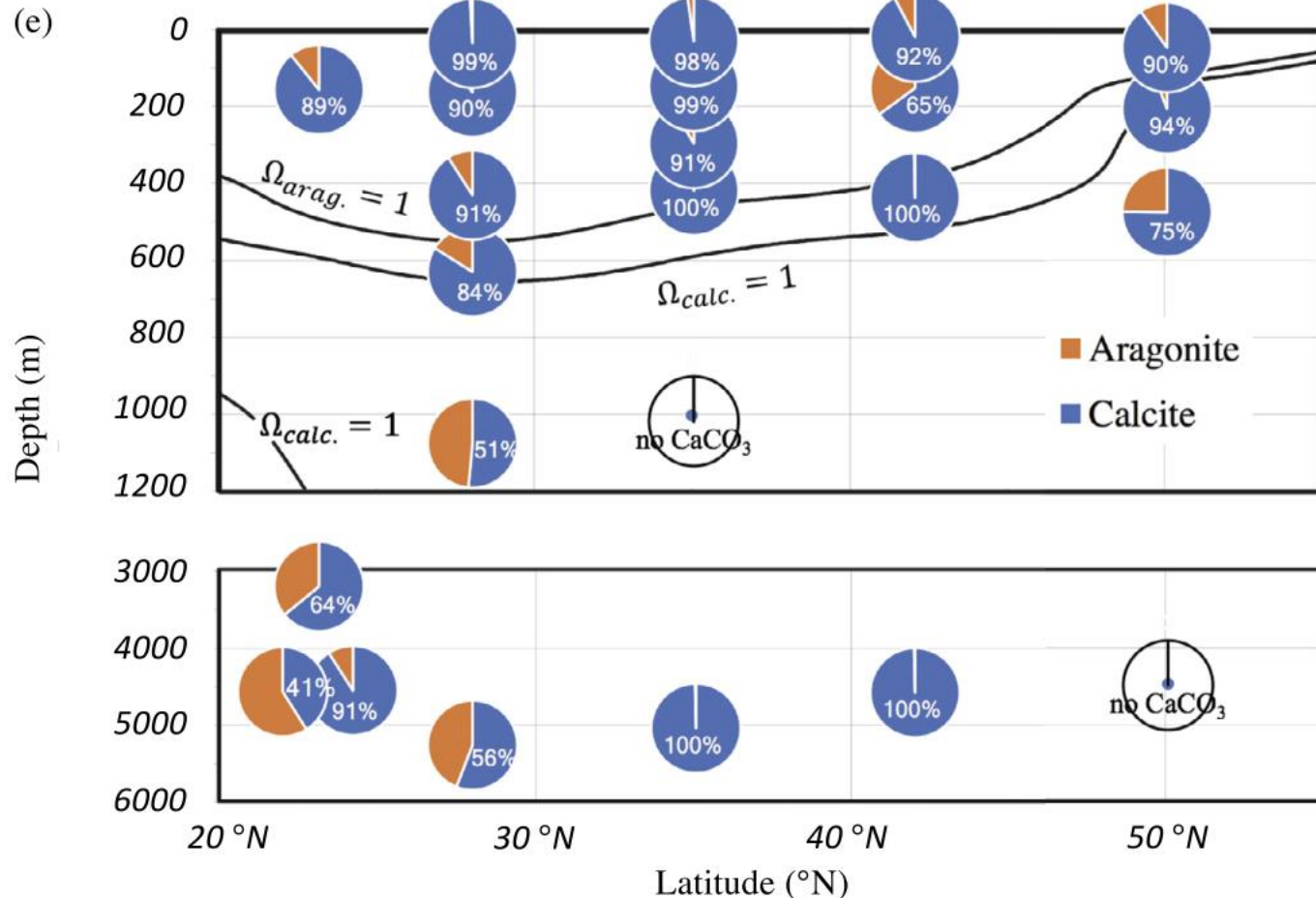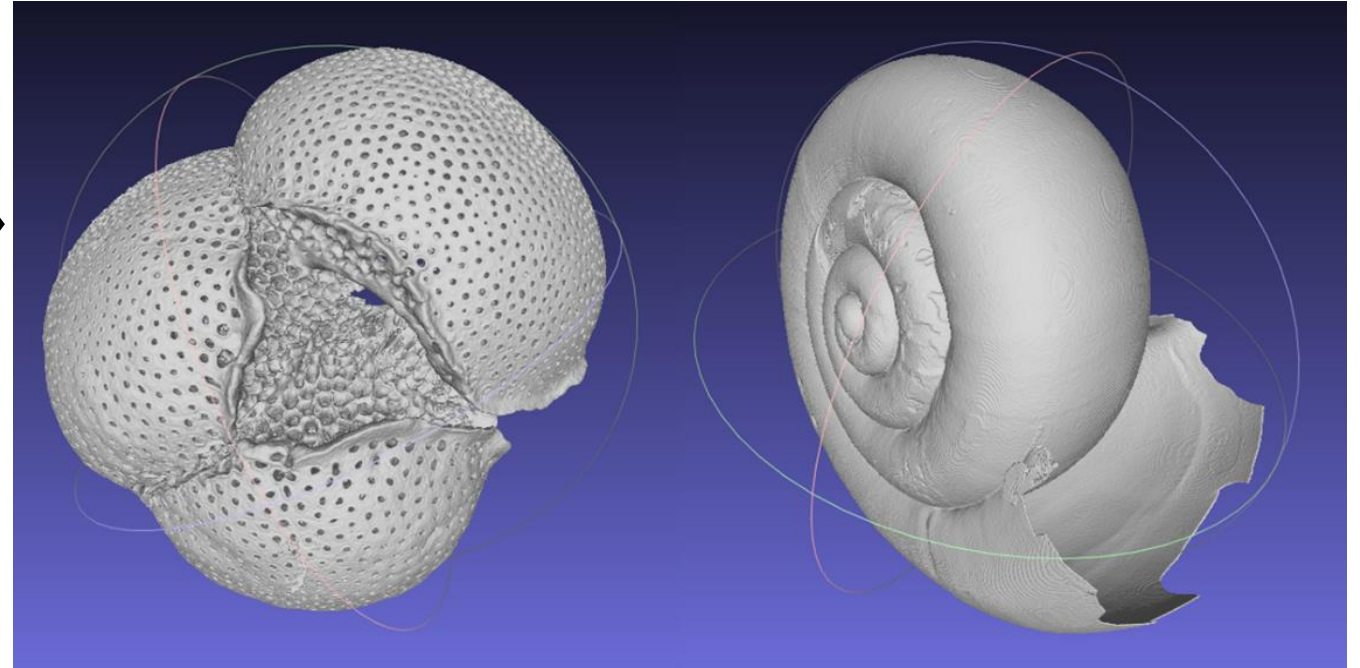
Methods

Import 3D scans of foraminifera, pteropods, etc.
⇒ Thanks to Dr. Rosie Oakes!
(request pteropods scans at rosieoakes.weebly.com)

1) Place the grains into a volume of undersaturated seawater

2) Simulate diffusion, advection and chemical reactions in water and at the surface of the grain

3) Simulate the shape changes caused by dissolution or precipitation

Methods (in more details)

All simulations were performed in COMSOL Multiphysics®, using the PARDISO solver and a Backward-Euler time stepping method. Eight dissolved species (H^+, OH^-, $H_2CO_3^*$, HCO_3^-, CO_3^{2-}, Ca^{2+}, Na^+, Cl^-) and 2 solid species (calcite, aragonite) were present. For each dissolved species, initial concentrations were chosen using PHREEQC, so that the initial saturation state of water ($\Omega_{calcite}$) with respect to calcite is about 0.6, a value typical of the deep sea

Calcite and aragonite dissolution (no precipitation) were implemented. The solubility constant of calcite was set at $10^{-8.48}$ and the solubility constant of aragonite set at $10^{-8.336}$. $CaCO_3$ reactions are not instantaneous, but instead occur with associated rates that depend on solution chemistry (thermodynamic driver) and on the nature of the mineral. For calcite and aragonite dissolution, we use kinetics from (Plummer et al., 1978).

A set of $CaCO_3$ particles were use in this study, some with shapes derived from natural grains, some more conceptual with simplified geometries. Planktonic foraminifera shell scans of Globoturborotalita nepenthes, a Miocene Pacific species (Todd, 1957), Menardella menardii, a Pleistocene Carribean specimen (Parker et al., 1865) and Bolliella adamsi, from the modern Pacific (Banner and Blow, 1959), were all obtained from the Tohoku University Museum e-foram database (http://webdb2.museum.tohoku.ac.jp/e-foram/). The Heliconoides inflatus pteropod shell, provided by Dr. Rosie Oakes, was obtained from a CT scan of a specimen caught at 150 m-depth in a sediment-trap located in the Cariaco Basin, in the Venezuelan shelf (Oakes and Sessa, 2020).

Simulations were performed in water with a density set to 1023.6 kg m^{-3} and a dynamic viscosity set to 9.59×10^{-4} Pa·s. To simulate the transport of each dissolved species, advection-diffusion-reaction equation is implemented.

Results

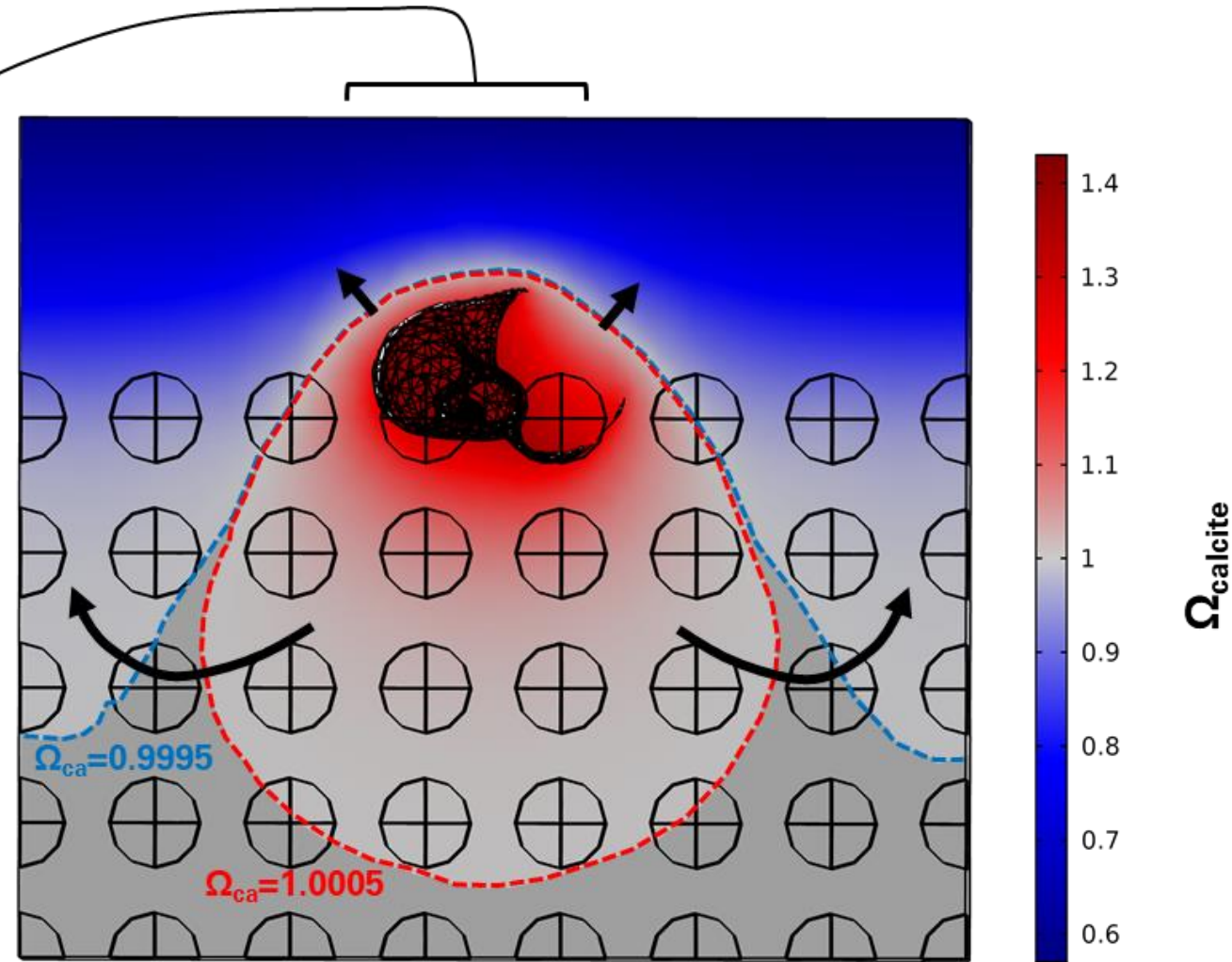**Specific surface area of biogenic minerals is a poor indicator of dissolution**

Globoturborotalita nepenthes *Menardella menardii* *Bolliella adamsi* *Heliconoides inflatus*
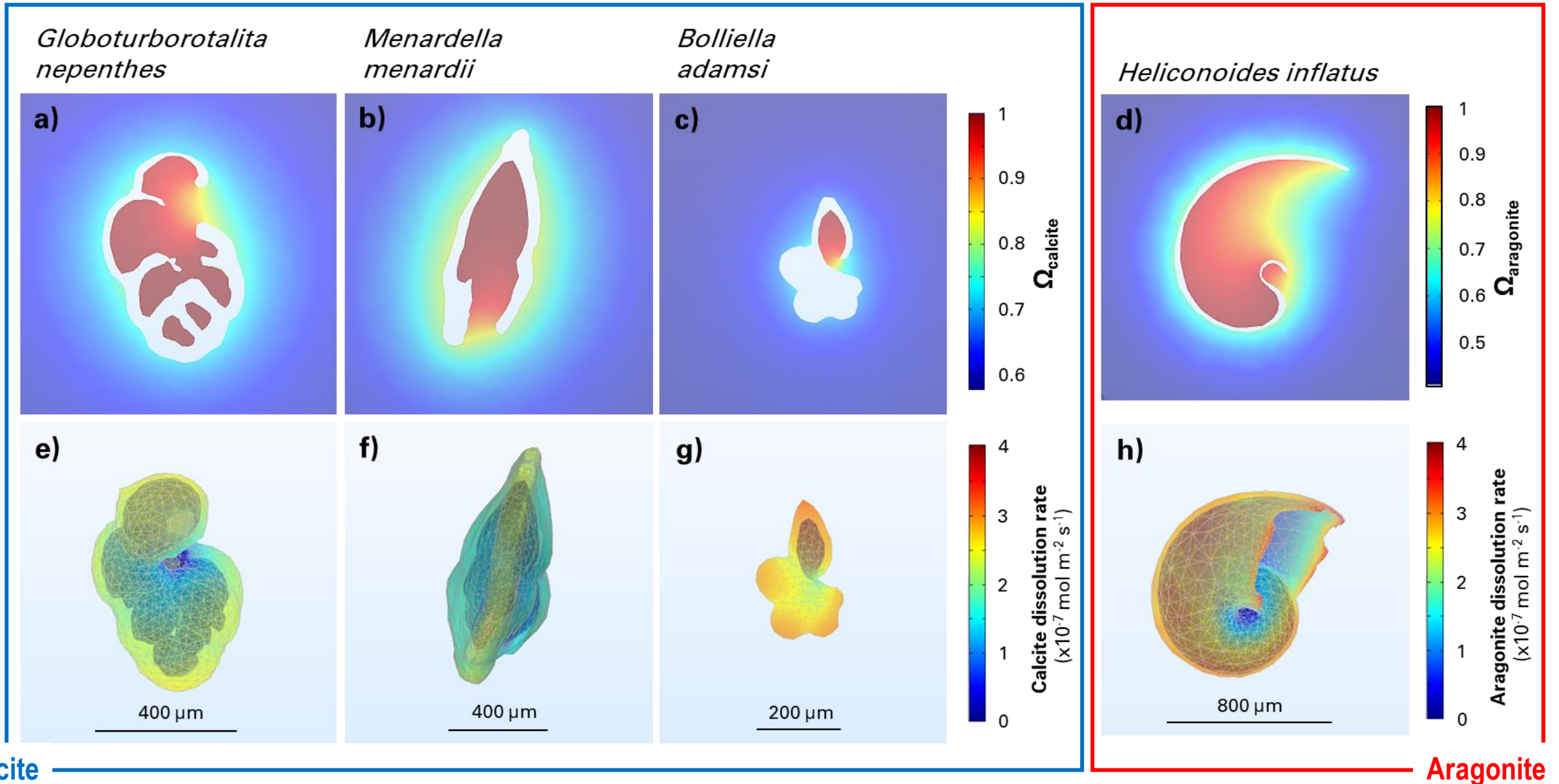
Calcite ——————————————————————————— Aragonite

Results

Pteropods atop a calcite sediment bed cause porewaters to be supersaturated with respect to calcite all the way up to the sediment-water interface.

Results

An aragonite pteropod shell sitting on a calcite sediment bed protects the calcite grains from dissolution.
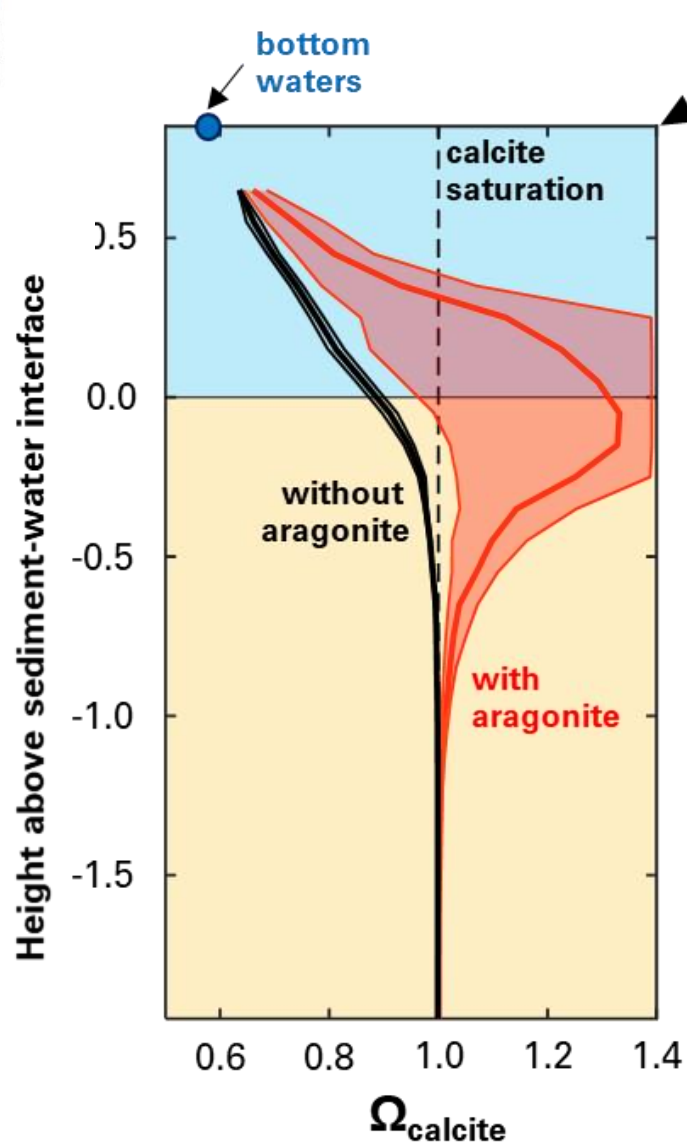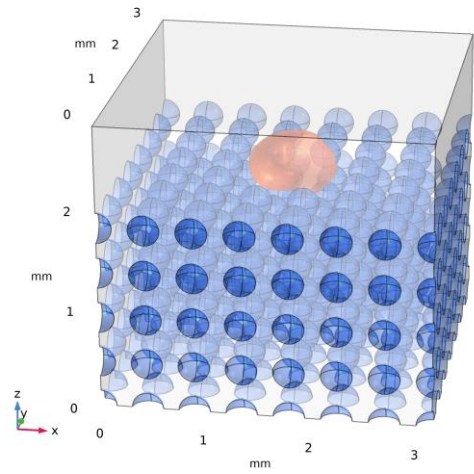
Calcite dissolution rate ($\times 10^{-8}$ mol m^{-2} s^{-1})

$\Omega_{ca}=1$

Conclusions and implications

Because of their fragility and their higher solubility, pteropods eventually disappear from the sediment-water interface. **Aragonite pteropods se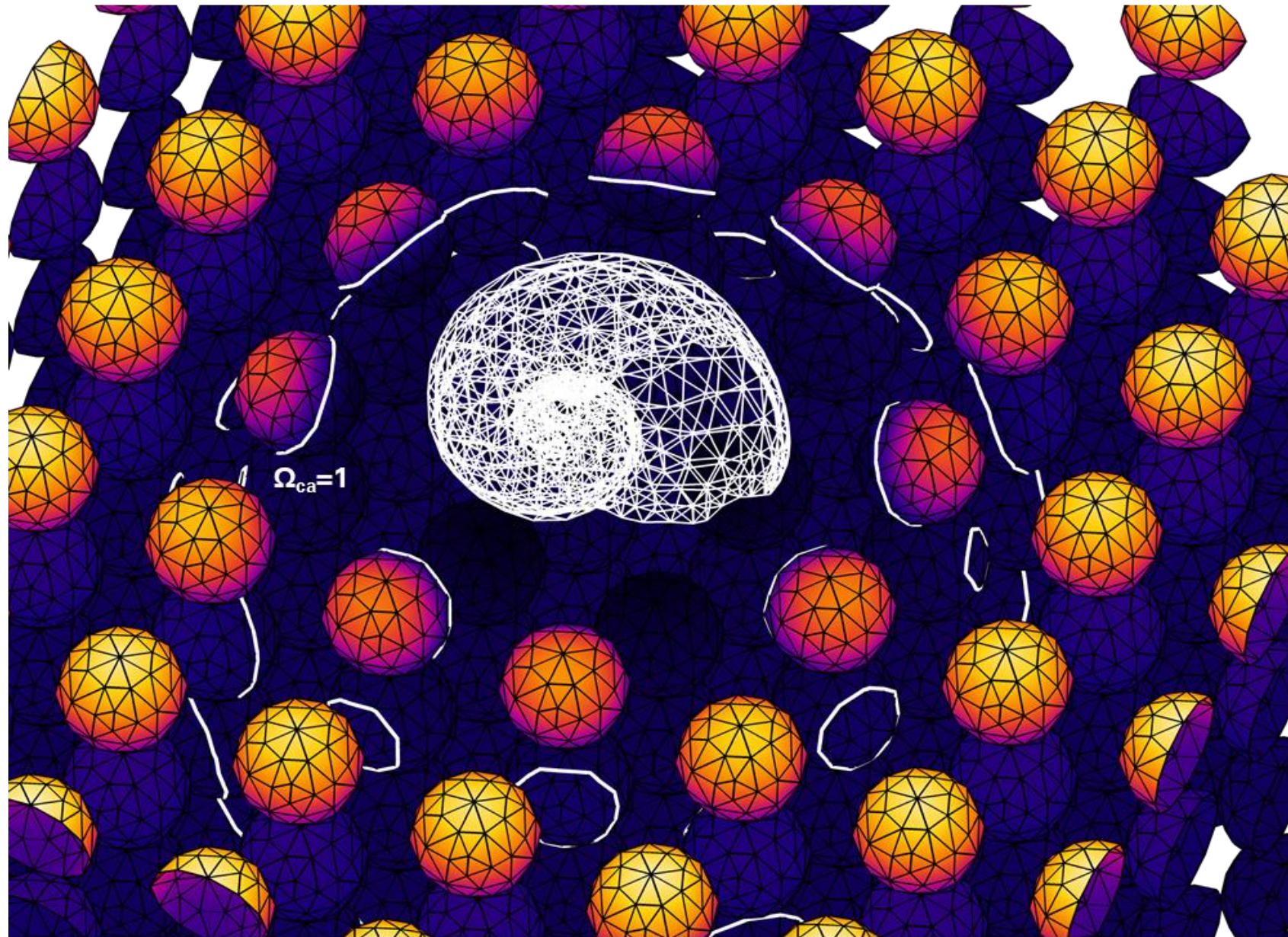ttling on a sediment subject to fast accumulation rates or intense bioturbation have better chances to be buried, and could serve as a buffering pill within the sediment**. Ultimately, this unidirectional interplay between aragonite and calcite, in which aragonite dissolution protects calcite, but nothing preserves aragonite from dissolution (except perhaps the presence of even more soluble minerals such as magnesian calcites), could partly account for the presence of thick calcite lysoclines in the ocean, while the ACD is generally much closer to its saturation depth.

Since aragonite producers are more vulnerable to ocean acidification (Orr et al., 2005), **an ocean acidification episode such as that of the Anthropocene could lead to a higher calcite to aragonite ratio in the $CaCO_3$ flux reaching the seafloor, hindering the proposed aragonite negative priming action, and favouring chemical erosion of calcite sediments**. As calcite dissolution at the seafloor neutralizes CO_2, this represents a negative feedback loop whose importance needs to be quantified and explored in further details.

Any question, comment or suggestion?
Please get in touch ☺ o.j.t.sulpis@uu.nl

References

● Adkins, J.F., Naviaux, J.D., Subhas, A.V., Dong, S. and Berelson, W.M. (2020) The Dissolution Rate of CaCO3 in the Ocean. Ann Rev Mar Sci.

● Banner, F.T. and Blow, W.H. (1959) The classification and stratigraphical distribution of the Globigerinaceae. Palaeontology. 2: 1-27.

● Bednaršek, N., Možina, J., Vogt, M., O'Brien, C. and Tarling, G.A. (2012) The global distribution of pteropods and their contribution to carbonate and carbon biomass in the modern ocean. Earth System Science Data 4, 167-186.

● Berger, W.H. (1978) Deep-sea carbonate: pteropod distribution and the aragonite compensation depth. Deep Sea Research 25, 447-452.

● Boeuf, D., Edwards, B.R., Eppley, J.M., Hu, S.K., Poff, K.E., Romano, A.E., Caron, D.A., Karl, D.M. and DeLong, E.F. (2019) Biological composition and microbial dynamics of sinking particulate organic matter at abyssal depths in the oligotrophic open ocean. Proc Natl Acad Sci U S A 116, 11824-11832.

● Buitenhuis, E.T., Le Quéré, C., Bednaršek, N. and Schiebel, R. (2019) Large Contribution of Pteropods to Shallow CaCO3 Export. Global Biogeochemical Cycles 33, 458-468.

● Dong, S., Berelson, W.M., Rollins, N.E., Subhas, A.V., Naviaux, J.D., Celestian, A.J., Liu, X., Turaga, N., Kemnitz, N.J., Byrne, R.H. and Adkins, J.F. (2019) Aragonite dissolution kinetics and calcite/aragonite ratios in sinking and suspended particles in the North Pacific. Earth and Planetary Science Letters 515, 1-12.

● Gangstø, R., Gehlen, M., Schneider, B., Bopp, L., Aumont, O. and Joos, F. (2008) Modeling the marine aragonite cycle: changes under rising carbon dioxide and its role in shallow water CaCO3 dissolution. Biogeosciences 5, 1057-1072.

● Lauvset, S.K., Key, R.M., Olsen, A., Heuven, S.v., Velo, A., Lin, X., Schirnick, C., Kozyr, A., Tanhua, T., Hoppema, M., Jutterström, S., Steinfeldt, R., Jeansson, E., Ishii, M., Perez, F.F., Suzuki, T. and Watelet, S. (2016) A new global interior ocean mapped climatology: the 1° × 1° GLODAP version 2. Earth System Science Data 8, 325-340.

● Mucci, A. (1983) The solubility of calcite and aragonite in seawater at various salinities, temperatures and one atmosphere total pressure. American Journal of Science 283, 780-799.

● Noji, T.T., Bathmann, U.V., Bodungen, B.v., Voss, M., Antia, A., Krumbholz, M., Klein, B., Peeken, I., Noji, C.I.-M. and Rey, F. (1997) Clearance of picoplankton-sized partides and formation of rapidly sinking aggregates by the pteropod, Limacina reiroversa. Journal of Plankton Research 19, 863-875.

● Oakes, R.L. and Sessa, J.A. (2020) Determining how biotic and abiotic variables affect the shell condition and parameters of <i>Heliconoides inflatus</i> pteropods from a sediment trap in the Cariaco Basin. Biogeosciences 17, 1975-1990.

● Orr, J.C., Fabry, V.J., Aumont, O., Bopp, L., Doney, S.C., Feely, R.A., Gnanadesikan, A., Gruber, N., Ishida, A., Joos, F., Key, R.M., Lindsay, K., Maier-Reimer, E., Matear, R., Monfray, P., Mouchet, A., Najjar, R.G., Plattner, G.K., Rodgers, K.B., Sabine, C.L., Sarmiento, J.L., Schlitzer, R., Slater, R.D., Totterdell, I.J., Weirig, M.F., Yamanaka, Y. and Yool, A. (2005) Anthropogenic ocean acidification over the twenty-first century and its impact on calcifying organisms. Nature 437, 681-686.

● Parker, W.K., Jones, T.R. and Brady, H.B. (1865) On the nomenclature of the Foraminifera. Part X. (continued). The species enumerated by D'Orbigny in the 'Annales des Sciences Naturelles,' 1826, vol. vii. - III. The species illustrated by models. Annals and Magazine of Natural History. (3) 16 (91): 15-41.

● Peijnenburg, K., Janssen, A.W., Wall-Palmer, D., Goetze, E., Maas, A.E., Todd, J.A. and Marletaz, F. (2020) The origin and diversification of pteropods precede past perturbations in the Earth's carbon cycle. Proc Natl Acad Sci U S A 117, 25609-25617.

● Plummer, L.N., Wigley, T.M.L. and Parkhurst, D.L. (1978) The kinetics of calcite dissolution in CO2-water systems at 5° to 60°C and 0.0 to 1.0 atm CO2. American Journal of Science 278.

● Sulpis, O., Boudreau, B.P., Mucci, A., Jenkins, C.J., Trossman, D.S., Arbic, B.K. and Key, R.M. (2018) Current CaCO3 dissolution at the seafloor caused by anthropogenic CO2. Proceedings of the National Academy of Sciences 115, 11700-11705.

● Todd, R. (1957) Smaller foraminifera, in: Paper, U.G.S.P. (Ed.), Geology of Saipan, Mariana Islands. Part 3, Paleontology, pp. 265-320.

NESSC

NETHERLANDS EARTH SYSTEM SCIENCE CENTRE