

Exponential crystallization in corals

Corresponding Author: Professor Pupa Gilbert

This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The manuscript presents highly interesting and novel results concerning the mineral phases of the newly forming *Stylophora* skeleton. However, one important issue requires clarification. The authors state that “the forming skeleton subject of this study is at the top of the nubbin, its growth is most active,” yet the regions analyzed (e.g., Fig. 1) do not allow unambiguous determination of whether the studied areas corresponds to rapid accretion deposits (RADs; traditional centers of calcification) or to thickening deposits (TDs), where growth dynamics are lower. For example, Fig. S1:B may represent the skeleton near the nubbin tip, but it clearly shows both small projections corresponding to RADs and directly adjacent TD regions (compare also Malik et al. 2020, *Acta Biomater.* 108: 314–329). In RADs, the skeleton is characterized by a nanogranular structure, recognizable even deeper in the skeleton (thus formed earlier in ontogeny), whereas this feature is not as evident in TDs (cf. Bezerara et al. 2011, *Ultramicroscopy* 111: 1268–1276). This structural heterogeneity at the growing edges of the skeleton makes it unclear whether the reported “fast crystallization rate of precursor phases” refers to RADs or TDs. This distinction is important in the context of other studies using EBSD (Coronado et al. 2019, *Nat. Commun.* 10: 2496) and Raman spectroscopy (Stolarski et al. 2021, *PNAS* 118: e2013316117), which show that RADs can retain a disordered character long after deposition, possibly reflecting a distinct mechanism of non-crystalline phase stabilization. The revised version of the manuscript should explicitly address this interpretative uncertainty.

(Remarks on code availability)

Reviewer #2

(Remarks to the Author)

Rechav et al describe a study of the mechanism of formation of the skeleton of corals, where they use PhotoEmission Electron Microscopy to monitor the composition of the mineral adjacent to the growth front. Using this technique the authors are able to map the change in composition of the mineral at the growth front over time. The principal results are that all precursors exhibit a consistent exponential decay from the growth front, and that calcium carbonate hemihydrate is the principal precursor material. The work is carefully done, and is clearly reported.

However, I just do not find these results significant enough to warrant publication in *Nat Comms*. In particular, the authors have already published an article in which they report the existence of calcium carbonate hemihydrate in coral (ref 4 “Myriad Mapping of nanoscale minerals reveals calcium carbonate hemihydrate in forming nacre and coral biominerals”).

I have a few comments:

(1) The authors have decided to call calcium carbonate hemi-hydrate “pre-aragonite”. I think this is a bit dangerous. Although there are no current examples of it converting to calcite/ vaterite, to-date there have not been very many studies on this phase. So, at this stage, I would not like to make the statement that it cannot convert to phases other than aragonite.

(2) I think the article would benefit from discussion of how the current results fit with the authors previous findings. In ref 3 “Amorphous calcium carbonate particles form coral skeletons” it is stated that “We show direct spectromicroscopy evidence in *Stylophora pistillata* corals that two amorphous precursors exist, one hydrated and one anhydrous amorphous calcium carbonate (ACC); that these are formed in the tissue as 400-nm particles; and that they attach to the surface of coral skeletons, remain amorphous for hours, and finally, crystallize into aragonite”

The current paper seems to contradict these findings, saying that there is actually much more hemihydrate than hydrated ACC. This needs to be discussed.

P2, line 40. I do not know what “Eight areas, 5 and 3” refers to. What does the 5 and 3 mean?

P8, line 18. “Yet the exponential crystallization behavior observed here may reflect a more general mechanism shared across abiotic contexts.”

Again, not enough information exists to make this statement.

(3) The authors place huge emphasis on the “exponential crystallization behavior”. More discussion is required of the significance of this observation. Why is it so important that coral shows this behavior rather than following another growth model?

(Remarks on code availability)

I do not have the expertise to review this.

Reviewer #3

(Remarks to the Author)

Review of Crystallization fast and slow

By Zoe Rechav et al.,

Overall Comments:

This work is a very interesting analysis of the composition and rates of transformation of carbonate precursor phases that mature into aragonite at the edge of coral skeletons. The use of PEEM-based myriad mapping (MM) to gain insights into the rate of transformations is novel and has the potential to be applied to other biomineral and materials research. It builds on recent work from Prof. Gilbert's group in 2024.

My main critique of the article is also a word of caution to the authors about using the term “mineral” to describe CCHH. I would strongly suggest that they keep the established nomenclature over trying to rename it as “pre-aragonite.”

This article also assumes that the author already have a thorough knowledge of the surrounding literature regarding PEEM and MM. As MM is still a new approach, I would recommend that the authors present some representative spectra of the reported precursor phases and quickly walk us through the defining features before diving into their growth rate and maturation analyses.

Specific comments:

Title. This title is not particularly descriptive and shows no indication that the authors are exclusively looking at corals in this work. I would suggest adding “in corals” at the end. Otherwise, there are other scientists who specialize in crystal growth and might think that this is a review paper on this topic.

ABSTRACT

Page 1, line 27. Very cool observation!

Page 1, line 28. I would strongly suggest that the authors refrain from renaming CCHH as “pre-aragonite.” See further discussion as to why below (Page 7, line 26).

INTRODUCTION

Page 2, line 6. This distinction of an ECF and ICF and the model with the hypothetical vesicles is only one interpretation for coral biomineralization. As the precise biomineralization mechanism is not the primary goal of this particular work, I would suggest that the authors stick to a more generalized description of biomineralization in corals—that corals crystallize aragonite using a calcifying fluid between the skeleton and the organism (e.g., Tambutté et al. 2011).

Tambutté, S., et al. (2011). Coral biomineralization: From the gene to the environment. *J. Exp. Mar. Bio. and Eco.*, 408(1–2), 58–78.

Page 2, line 28. It might be a good idea to add “Expanding on recent work by Schmidt et al., 2024, for this work...” As someone reading this through the first time, it took me a while to realize that there is already a lot of MM work published by this group and that this is not the first work to look at corals. Having this introductory phrase will help readers refer to this initial work before sitting down to digest the current work.

RESULTS

Page 2, line 37. Before diving into the distributions of these precursor phases, as a reader, I would like to see the Ca L-edge spectra of these different precursor phases and how the authors identified the presence of this new CCHH phase in their system. As this is a new technique, I think that it is fair to show some representative spectra from this work next to some reference spectra, even if similar results are already presented in recent papers by other authors.

Page 3, Fig. 1. I would just like to note that the pink and red colors are very difficult to distinguish in these maps (and even in the graphs), even though I am not color blind. May I suggest switching one of them to an orange or yellowish color that would stand out better? I realize that this group has already used this color scheme before, but figured I'd make this note.

Page 3, line 15. As there is no added section for a discussion, could the authors please expand on the analyses comparing the two pH treatments? Why are the precursor proportions different? What is the significance of having the two different pHs? This feels glossed over.

Page 4, line 29. That is very interesting that the authors are able to present a skeletal growth velocity per day. As corals skeletons are known to grow with visible growth bands that represent day vs. night, could the authors comment on how this would impact the results? I see that your average rate is still constant on the macro-scale (great test!), but how does that account for day-night variability? Is the deposition of new precursor phase truly constant, or does it occur in spurts where there is a constant velocity during a particular growth spurt? Something to consider. I like the idea of exploring how this method could be applied to coral cores.

Page 6, line 20. Could the authors suggest a physiochemical explanation as to why the 1/e lengths and times are distinct for the different precursors? Does water have a strong impact? Bond distances? This would be very interesting for predicting the maturation behaviors of these precursors in future engineered materials.

Page 6, line 26. Just to clarify, does this mean that you would expect to see these precursor phases in a coral that has been dead for up to 6 months? In other words, are you suggesting that someone studying these phases using other techniques (high-res IR, Raman, TEM) be able to potentially "see" these phases as well? This would be a very interesting follow-up. Also, out of curiosity, is it possible to prepare a fresh sample directly at the synchrotron?

Page 7, line 26. I think that it would be scientifically irresponsible to call this a mineral if the authors do not have the necessary crystallographic data (e.g., crystal structure data by XRD and/or TEM with accompanying cif files)--in addition to this excellent spectroscopic data (which focuses on the bonding environment around Ca)--to define the new mineral species and submit it for consideration to the commission on new mineral names at the International Mineralogical Association (IMA). Furthermore, this example would likely not pass the criteria for becoming a mineral (per the IMA definition of a mineral), since it is biogenically formed, as opposed to being formed through a geological process—interesting, I know. Perhaps this may change in the future, but for now, as the goal of this work does not appear to be the description of a new mineral species, please do not call this a mineral or try to rename this compound that has already been adopted in the literature as "CCHH." It is common knowledge that many precursor phases will mature into specific mineral species, so I really do not see the added value of calling it "pre-aragonite" over CCHH.

CONCLUSIONS

Page 7, line 46. Very cool!

Page 8, line 6. It may be worth comparing to deep water corals that grow very slowly at low aragonite saturation states (and very low pHs)--sometimes below a seawater saturation state that is below 1!

METHODS

I cannot speak to the PEEM mapping details as I have never used it before, but I would reiterate my comment above that I would like to see some raw spectra of the Ca L-edge presented next to reference spectra.

(Remarks on code availability)

I did not review the code as that is not my area of expertise.

Version 2:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

I appreciate the authors' revisions and the additional clarification regarding the identification and treatment of RAD/CoC versus TD regions. I remain uncertain, however, about the conclusion that "the particle accretion mechanisms are the same" in RADs and TDs.

While the authors describe their inclusion/exclusion criteria, the revised manuscript still does not explicitly state whether the reported "fast crystallization rate of precursor phases" applies strictly to TDs or also to surface RADs. Given the different stabilization dynamics of RADs/CoCs described in previous EBSD and Raman studies, this clarification would be valuable.

The authors argue that RADs and TDs must share the same accretion mechanism because AFM shows similar nanoparticulate textures at the nanoscale. However, Benzerara et al. explicitly noted a discrepancy between AFM and TEM imaging of RAD and TD regions: AFM highlights surface nanodomains, whereas TEM indicates that TD fibers behave as genuine micron-scale single crystals. As Benzerara et al. wrote, the nanodomains seen by AFM may reflect surface defect ordering, not necessarily the underlying growth mechanism. Because TEM does not show nanogranular structure within TDs, AFM similarity alone does not imply identical accretion pathways.

In light of this, it remains uncertain whether RADs and TDs indeed form by the same particle accretion mechanism, particularly below the surface where crystallographic continuity differs.

(Remarks on code availability)

Reviewer #2

(Remarks to the Author)

"Exponential crystallization in corals" by Professor Gilbert and colleagues

The authors have made significant improvements to their manuscript, which have greatly improved its quality and impact. They have managed to convince me of the importance of their results (the reason for my initial rejection from Nat Comms).

Based on their further discussions I do have a few more queries, however.

(1) From my understanding, the authors state that each of the phases identified crystallizes at an identical rate.

What could give rise to this effect? What is the transformation sequence of the phases? It really does seem very strange that a crystalline phase (CCHH) would crystallize at the same rate as an amorphous one. If indeed ACC.H₂O, ACC and CCHH are indeed distinct and not just a continuum of phases.

(2) They also state that the rate of crystallization is independent of the environment of the domains of each phase. This really does not seem to make any physical sense (and it has to ... even if crystallization occurs within an organism).

For example, crystallization of ACC will undoubtedly be faster if the ACC is deposited on calcite or aragonite (heterogeneous nucleation) as compared if homogeneous nucleation occurs with the ACC. Heterogeneous nucleation is always – by definition – faster than homogeneous nucleation.

So how can this observation be valid?

(Remarks on code availability)

Reviewer #3

(Remarks to the Author)

I appreciated the authors' efforts in improving their manuscript per the comments from all three reviewers. They sufficiently addressed all of my concerns. Thank you!

(Remarks on code availability)

Version 3:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

I have reviewed the authors' revisions, which seem to explain my concerns sufficiently clearly. At this point, I have no further comments.

(Remarks on code availability)

Reviewer #2

(Remarks to the Author)

I am happy that the authors have addressed my remaining queries to the best of their ability.

(Remarks on code availability)

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REVIEWER COMMENTS

Reviewer #1 (Remarks to the Author):

The manuscript presents highly interesting and novel results concerning the mineral phases of the newly forming *Stylophora* skeleton.

Thank you!

However, one important issue requires clarification. The authors state that “the forming skeleton subject of this study is at the top of the nubbin, its growth is most active,” yet the regions analyzed (e.g., Fig. 1) do not allow unambiguous determination of whether the studied areas corresponds to rapid accretion deposits (RADs; traditional centers of calcification) or to thickening deposits (TDs), where growth dynamics are lower. For example, Fig. S1:B may represent the skeleton near the nubbin tip, but it clearly shows both small projections corresponding to RADs and directly adjacent TD regions (compare also Malik et al. 2020, *Acta Biomater.* 108: 314–329). In RADs, the skeleton is characterized by a nanogranular structure, recognizable even deeper in the skeleton (thus formed earlier in ontogeny), whereas this feature is not as evident in TDs (cf. Bezerara et al. 2011, *Ultramicroscopy* 111: 1268–1276).

We thank the reviewer for this useful suggestion. We re-read with great interest both papers and agree that one of the 8 areas analyzed, (Fig. S2 area 5 and Fig. S6), are indeed RADs. We added a comment to this effect on [page 3 lines 1-4](#): “These are small regions from 2 of 8 total areas analyzed. Fig. S2 presents the 8 areas in their entirety, seven of which are at the forming edge of bulk skeletons, sometimes termed thickening deposits (TD) and one (area 5) is on a spine, sometimes termed rapid accretion deposit (RAD) or Centers of Calcification (CoCs)^{16, 17}. Despite different morphology and crystal orientations, TDs, RADs or CoCs form by particle attachment and precursor phases³.”

We respectfully disagree that Benzerara et al. say that RADs and TDs are distinct. At the nanoscale, which is the scale at which we analyzed all precursor phases, they look identical, as shown for example by comparing the AFM images in Benzerara et al. Fig. 3 B and C. They are nanoparticulate, and the nanoparticles are the same size. The particle accretion mechanisms, therefore, must be the same. Our data in this and many other papers before also show that they are the same spectroscopically. We cited the papers by Malik and Benzerara for the nomenclature and Mass et al. to show that particle attachment and precursor phases are the same.

This structural heterogeneity at the growing edges of the skeleton makes it unclear whether the reported “fast crystallization rate of precursor phases” refers to RADs or TDs. This distinction is important in the context of other studies using EBSD (Coronado et al. 2019, *Nat. Commun.* 10: 2496) and Raman spectroscopy (Stolarski et al. 2021, *PNAS* 118: e2013316117), which show that RADs can retain a disordered character long after deposition, possibly reflecting a distinct mechanism of non-crystalline phase stabilization. The revised version of the manuscript should explicitly address this interpretative uncertainty.

Excellent idea! Thank you for suggesting it! We have now clarified that, if the CoCs occur at the surface we include them in the analysis (e.g. Fig. S2, area 5 and Fig. S6), but if they are in the bulk of the skeleton they are excluded, because, as the reviewer says, all precursor phases are stabilized in the CoCs. We have cited the Coronado 2019 and Stolarski 2021 papers, and our own by DeVol 2015 and Mass et al. 2017, where we showed that the CoCs stay amorphous longer. See page 13 lines 36-37: “CoCs are known to contain amorphous precursors for a decade *post-mortem*^{3,30,40,41}.”

We stress that inclusion criterion 3 (page 13 line 31-37) excludes CoCs in the bulk from the analysis, thus, they were not analyzed here in 7 out of 8 areas, because they would interfere with the exponential decays that are the goal of this analysis. This was already explained before, on page 13 lines 31-37.

Reviewer #2 (Remarks to the Author):

Rechav et al describe a study of the mechanism of formation of the skeleton of corals, where they use PhotoEmission Electron Microscopy to monitor the composition of the mineral adjacent to the growth front. Using this technique the authors are able to map the change in composition of the mineral at the growth front over time. The principal results are that all precursors exhibit a consistent exponential decay from the growth front, and that calcium carbonate hemihydrate is the principal precursor material. The work is carefully done, and is clearly reported.

Thank you!

However, I just do not find these results significant enough to warrant publication in Nat Comms. In particular, the authors have already published an article in which they report the existence of calcium carbonate hemihydrate in coral (ref 4 “Myriad Mapping of nanoscale minerals reveals calcium carbonate hemihydrate in forming nacre and coral biominerals”).

We agree. The question is not anymore about the existence of precursors phases and the dominance of CCHH. The discovery here is that they decay exponentially in space and time, as now highlighted in the title. Overall, we hope we have improved the clarity of the paper enough that reviewer will agree that this is a significant discovery. The new title is on page 1 line 1: “Exponential crystallization in corals

I have a few comments:

(1) The authors have decided to call calcium carbonate hemi-hydrate “pre-aragonite”. I think this is a bit dangerous. Although there are no current examples of it converting to calcite/ vaterite, to-date there have not been very many studies on this phase. So, at this stage, I would not like to make the statement that it cannot convert to phases other than aragonite.

We thank the reviewer for raising concern regarding our choice to call calcium carbonate hemihydrate (CCHH) ‘pre-aragonite’ based only on our observations from the PEEM data. Another reviewer had a similar concern. Additionally, we applied at the International Mineral Association (IMA), but they have not yet approved the new name. This may change very soon, so we will

call it by the new name in a future publication. We thought it would be cool to name it here, because CCHH is the super-star precursor on coral skeletons, but there is no rush. We now removed pre-aragonite from everywhere and only use CCHH. See the abstract on [page 1 line 28](#), main text on [page 8 lines 2-7](#), and methods on [page 12 line 47](#).

(2) I think the article would benefit from discussion of how the current results fit with the authors previous findings. In ref 3 “Amorphous calcium carbonate particles form coral skeletons” it is stated that “We show direct spectromicroscopy evidence in *Stylophora pistillata* corals that two amorphous precursors exist, one hydrated and one anhydrous amorphous calcium carbonate (ACC); that these are formed in the tissue as 400-nm particles; and that they attach to the surface of coral skeletons, remain amorphous for hours, and finally, crystallize into aragonite”

The current paper seems to contradict these findings, saying that there is actually much more hemihydrate than hydrated ACC. This needs to be discussed.

We thank the reviewer for noticing this apparent discrepancy, which we had not previously discussed in this paper. We now explain this on [page 8 line 12-24](#): “The relative paucity of ACCH_2O , expected to be the first deposited and most abundant surface phase for *Stylophora pistillata*³, has only 2% abundance. This is surprising, as ACCH_2O was expected to be the first deposited and most abundant surface Mass et al.³.

The Mass et al. 2017³ paper discusses only ACC and $\text{ACC-H}_2\text{O}$ precursors because with component mapping or myriad mapping one can only find phases that one is looking for, that is, phases for which one has the x-ray absorption near-edge structure spectrum (Fig. 1B) and fits the unknown spectrum from each pixel with a linear combination of known spectra. CCHH was not discovered by Zou et al. until 2019⁸, thus, one could not have suspected its existence in 2017. Once we noticed that some spectra from coral skeletons were not well fit by either ACCH_2O , ACC, or any combinations thereof, we broadened the search, included CCHH, MHC, and vaterite, then excluded vaterite because the fits are not significantly improved by fitting with 6 rather than 5 component spectra, and vaterite was the worst fitting of the 3 metastable crystalline precursors⁴.”

P2, line 40. I do not know what “Eight areas, 5 and 3” refers to. What does the 5 and 3 mean?

Thank you for spotting this. We now explain on [page 2 line 31-33](#): “Eight areas of skeleton surfaces were acquired from corals grown in seawater at pH 8.05 (5 areas) or pH 7.2 (3 areas). Minimal radiation damage was done to these areas during the PEEM data first and repeat acquisitions¹⁵.”

P8, line 18. “Yet the exponential crystallization behavior observed here may reflect a more general mechanism shared across abiotic contexts.” Again, not enough information exists to make this statement.

Thank you! We greatly softened the statement on [page 11 lines 21-25](#): “Whether or not the exponential crystallization behavior observed here reflects a more general mechanism, occurring in other biominerals and geologic minerals remains unknown. Our findings, however, provide the methods and the software to broaden spatial decay analysis to reveal exponential crystallization decays in other biogenic, geologic, and synthetic materials, if they exist.”

(3) The authors place huge emphasis on the “exponential crystallization behavior”. More discussion is required of the significance of this observation. Why is it so important that coral shows this behavior rather than following another growth model?

We thank the reviewer for stimulating us to improve the paper, and our thinking, on this very important point. Thanks to this stimulus, we developed a new model, described in the new session “**Grand canonical model**” on [pages 8-10](#), which includes the [new Fig. 4](#).

We also mention the grand canonical model in the abstract on [page 1 lines 28-30](#): “Exponential crystallization inspired a grand canonical model that closely matches experimental data and thus suggests that the skeleton conditions in which crystallization occurs are constant.”, and in the conclusions, on [page 11 lines 19-21](#): “The close match of the grand canonical model data with experimental data provides a theoretical framework to describe exponential crystallization in stable coral skeletons.”

Reviewer #2 (Remarks on code availability):

I do not have the expertise to review this.

Reviewer #3 (Remarks to the Author):

Review of Crystallization fast and slow

By Zoe Rechav et al.,

Overall Comments:

This work is a very interesting analysis of the composition and rates of transformation of carbonate precursor phases that mature into aragonite at the edge of coral skeletons. The use of PEEM-based myriad mapping (MM) to gain insights into the rate of transformations is novel and has the potential to be applied to other biomineral and materials research. It builds on recent work from Prof. Gilbert's group in 2024.

Thank you!

My main critique of the article is also a word of caution to the authors about using the term “mineral” to describe CCHH. I would strongly suggest that they keep the established nomenclature over trying to rename it as “pre-aragonite.”

We thank the reviewer for this criticism, which we have taken at heart. We now removed pre-aragonite from everywhere and only use CCHH. See the abstract on [page 1 line 28](#), main text on [page 7 lines 44-46](#), and methods on [page 12 line 40](#).

This article also assumes that the author already have a thorough knowledge of the surrounding literature regarding PEEM and MM. As MM is still a new approach, I would recommend that the authors present some representative spectra of the reported precursor phases and quickly walk us through the defining features before diving into their growth rate and maturation analyses.

We thank the reviewer for this useful suggestion. We added the reference spectra obtained to produce the myriad maps to Fig. 1B page 3, mentioned them on page 2 lines 45-47: “The component spectra are also shown in Fig. 1B, acquired from synthetic ACCH₂O, ACC, CCHH, MHC, and aragonite.”

We briefly explained how myriad maps are obtained. See page 2 lines 36-44: “To generate an MM, the unknown spectrum at each pixel is fitted by a linear combination of five known component spectra. The resulting coefficients, constrained between 0 and 1, are the proportion of each component spectrum. This procedure yields five “proportion maps (pMaps), one per spectral component, where pixel values correspond to the local abundance of that phase. These maps are then merged into a single MM using five distinct colors. To ensure quantitative fidelity, we restrict the display to dominant phases by omitting proportions below 0.5. Each pixel is assigned a single color, with brightness encoding the proportion (e.g., dark to bright cyan corresponds to 0.5 to 1.0). While information on mixed phases is not retained, the displayed pixels are fully quantitative.”

Specific comments:

Title. This title is not particularly descriptive and shows no indication that the authors are exclusively looking at corals in this work. I would suggest adding “in corals” at the end. Otherwise, there are other scientists who specialize in crystal growth and might think that this is a review paper on this topic.

Thank you! We changed the title to “**Exponential crystallization in corals**”

Which is short but more informative. We removed fast and slow because it was not informative and it unnecessarily complicated the title. The salient point of this paper are the exponential decays and rises of all phases vs. space and time, thus, we highlighted “exponential” as the first word of the title.

ABSTRACT

Page 1, line 27. Very cool observation!

Thank you! We fully agree! The predominance of CCHH is very exciting but that could be seen even statically in the 2024 *Nature Communications* paper. The fact that decay constants in space or time are phase independent is even more surprising and exciting.

Page 1, line 28. I would strongly suggest that the authors refrain from renaming CCHH as “pre-aragonite.” See further discussion as to why below (Page 7, line 26).

We fully agree, thus, we have now removed pre-aragonite from everywhere and use only CCHH. See the abstract on page 1 line 28, main text on page 8 lines 2-7, and methods on page 12 line 47.

INTRODUCTION

Page 2, line 6. This distinction of an ECF and ICF and the model with the hypothetical vesicles is only one interpretation for coral biomineralization. As the precise biomineralization mechanism is not the primary goal of this particular work, I would suggest that the authors stick to a more

generalized description of biomineralization in corals—that corals crystalize aragonite using a calcifying fluid between the skeleton and the organism (e.g., Tambutté et al. 2011).

Tambutté, S., et al. (2011). Coral biomineralization: From the gene to the environment. *J. Exp. Mar. Bio. and Eco.*, 408(1–2), 58–78.

We thank the reviewer for this very useful suggestion. We have now removed all references to ECF and ICF, and simply state on [page 2 lines 8-9](#) that “Corals form crystalline aragonite from a calcifying fluid between the skeleton and the organism ^{7,9,10}.” Ref. 7 is Tambutté et al. 2011.

Page 2, line 28. It might be a good idea to add “Expanding on recent work by Schmidt et al., 2024, for this work...” As someone reading this through the first time, it took me a while to realize that there is already a lot of MM work published by this group and that this is not the first work to look at corals. Having this introductory phrase will help readers refer to this initial work before sitting down to digest the current work.

Excellent suggestion! Thank you! We have now changed on [page 2 line 20](#) to read: “Expanding on recent work by Schmidt et al. 2024 ⁴, for this work, we used the MM method to explore how and where the known CaCO₃ precursor and mature phase, ACCH₂O, ACC, CCHH, ... ”

RESULTS

Page 2, line 37. Before diving into the distributions of these precursor phases, as a reader, I would like to see the Ca L-edge spectra of these different precursor phases and how the authors identified the presence of this new CCHH phase in their system. As this is a new technique, I think that it is fair to show some representative spectra from this work next to some reference spectra, even if similar results are already presented in recent papers by other authors.

We thank the reviewer for this useful suggestion. We preferred not to insert spectra as a standalone new figure, because, as the reviewer says, they are not new to this work. We have therefore added them to the new [Fig. 1B](#). See the new figure and caption on [page 3 lines 12-14](#): “The x-ray absorption near-edge structure spectra (345-355 eV) of 4 precursors and aragonite are also shown in B, color coded as MM pixels, except for the aragonite spectrum, which is plotted in white rather than blue.”.

Page 3, Fig. 1. I would just like to note that the pink and red colors are very difficult to distinguish in these maps (and even in the graphs), even though I am not color blind. May I suggest switching one of them to an orange or yellowish color that would stand out better? I realize that this group has already used this color scheme before, but figured I’d make this note.

We appreciate the concern of the reviewer about the color scale used to differentiate ACCH₂O from MHC, red and magenta, respectively. We understand that red and magenta placed side by side are difficult or impossible to distinguish for red-green colorblindness. We have thought about this in the past and opted for all precursor phases to be off-blue and mature phase to be blue, so colorblind people can see that the precursors are localized at the surface.

Regarding changing the color scheme to, say, orange instead of magenta, we could easily do this, but prefer not, so the data are consistent across multiple publications, not only for us, but for all readers and presenters at conferences that show our data.

In the spectra, we changed the style of MHC datapoints to be magenta-outlined empty circles, so they are easily distinguishable from the red solid circles used for ACCH₂O. The caption explains this on [page 4 line 4](#): “Magenta datapoints are open circles to distinguish them from red.”. This cosmetic change is extended to other figures as well. See [new Figures 1, 3, and S5](#). S5 caption also reads: “Magenta MHC datapoints are open symbols to distinguish them from solid red ACCH₂O.”

Page 3, line 15. As there is no added section for a discussion, could the authors please expand on the analyses comparing the two pH treatments? Why are the precursor proportions different? What is the significance of having the two different pHs? This feels glossed over.

Thank you for noticing this omission. We originally set out to study the effect of seawater acidification, but we did not observe any difference, so we did not extensively comment about it. We have now done better on [page 5 line 37](#) “At both pH 7.2 and 8.05 there is a spread of initial precursor proportions at the edge ([Fig. S4](#)).” and [page 5 line 39-42](#): “This is not surprising, because Venn et al. 2019 showed that across the same range of seawater pH used here, the calcification rate in *Stylophora pistillata* corals remains constant as pH decreases, especially during the day when most of the skeleton deposition happens ¹⁹.”

Page 4, line 29. That is very interesting that the authors are able to present a skeletal growth velocity per day.

Thank you!

As corals skeletons are known to grow with visible growth bands that represent day vs. night, could the authors comment on how this would impact the results? I see that your average rate is still constant on the macro-scale (great test!), but how does that account for day-night variability? Is the deposition of new precursor phase truly constant, or does it occur in spurts where there is a constant velocity during a particular growth spurt? Something to consider. I like the idea of exploring how this method could be applied to coral cores.

We thank the reviewer for these interesting and intriguing suggestions and questions. We have no idea what the instantaneous growth rate is, and how it varies during the day or the night. We see from Venn et al. 2019 that day calcification is considerably greater than night calcification, and this is, presumably, what generates the well-known daily banding that the reviewer mentions. We looked, but do not see this banding with PEEM at any of the elemental edges (Ca, C, O) or in the crystallographic orientation of aragonite spherulites, thus, we can't say how the banding correlates with precursor phases or crystal organization. A correlative study done with soft-x-rays to see the precursors and hard-x-rays to see daily banding on precisely the same areas would be very desirable, but it has never been done.

Page 6, line 20. Could the authors suggest a physiochemical explanation as to why the 1/e

lengths and times are distinct for the different precursors? Does water have a strong impact? Bond distances? This would be very interesting for predicting the maturation behaviors of these precursors in future engineered materials.

We thank the reviewer for this question, which made us realize that we had not explicitly said that the decay constants are the same for all phases and phase transitions. We have now fixed this omission, and therefore removed the confusion, by adding point iv on [page 6 lines 25-27](#): “(iv) All decay constants are the same, within the uncertainty, despite dramatic differences in phase transitions: dehydration, and/or crystallization, and/or crystal structure transformation.”

We hope it is now clear that “the 1/e lengths and times are NOT distinct for the different precursors”. As to the “physiochemical explanation” we think that the equal 1/e lengths and times suggest a physical rather than physiological mechanism. We also come to this conclusion on [page 10 line 45](#).

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We thank the reviewer for these questions and suggestions. Indeed! We added a paragraph to this effect on [page 7 lines 29-32](#): “Importantly, having now demonstrated that fixed, dehydrated, and embedded coral samples can be as old as 6 months and still have some precursor phases, many other methods can be used to analyze precursors, including high-resolution infrared⁴ or Raman spectroscopies, or transmission electron microscopy (TEM), or nanoscale x-ray diffraction (nano-XRD).”

Page 7, line 26. I think that it would be scientifically irresponsible to call this a mineral if the authors do not have the necessary crystallographic data (e.g., crystal structure data by XRD and/or TEM with accompanying cif files)--in addition to this excellent spectroscopic data (which focuses on the bonding environment around Ca)--to define the new mineral species and submit it for consideration to the commission on new mineral names at the International Mineralogical Association (IMA). Furthermore, this example would likely not pass the criteria for becoming a mineral (per the IMA definition of a mineral), since it is biogenically formed, as opposed to being formed through a geological process—interesting, I know. Perhaps this may change in the future, but for now, as the goal of this work does not appear to be the description of a new mineral species, please do not call this a mineral or try to rename this compound that has already been adopted in the literature as “CCHH.” It is common knowledge that many precursor phases will mature into specific mineral species, so I really do not see the added value of calling it “pre-aragonite” over CCHH.

We thank the reviewer for their concern, along with another reviewer. We have already presented the XRD data and cif files for synthetic CCHH in Zou et al. 2019. At that time, CCHH was a material not a mineral, because it had never been observed in nature. Now it has.

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CONCLUSIONS

Page 7, line 46. Very cool!

Thank you!

Page 8, line 6. It may be worth comparing to deep water corals that grow very slowly at low aragonite saturation states (and very low pHs)--sometimes below a seawater saturation state that is below 1!

This is a great idea, for which we thank the reviewer. The experiment is certainly feasible, although we do not have access to deep-sea corals at present. It will take years to plan and do these experiments thus, we will keep them for another paper. We added a comment in the manuscript to this effect. See [page 11 line 9-11](#): “The deep-sea corals that form their skeletons at lower seawater pH values are of particular interest. How does their crystallization rate compare to surface corals?”

METHODS

I cannot speak to the PEEM mapping details as I have never used it before, but I would reiterate my comment above that I would like to see some raw spectra of the Ca L-edge presented next to reference spectra.

We added spectra to the existing figure. See [new Fig. 1B on page 3](#).

Reviewer #3 (Remarks on code availability):

I did not review the code as that is not my area of expertise.

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RESPONSE TO REVIEWER COMMENTS

Below, all text from the reviewers is in black font, ours in response is in blue font. In the manuscript as well, the modified text is in blue font.

Reviewer #1 (Remarks to the Author):

The manuscript presents highly interesting and novel results concerning the mineral phases of the newly forming *Stylophora* skeleton.

Thank you!

However, one important issue requires clarification. The authors state that “the forming skeleton subject of this study is at the top of the nubbin, its growth is most active,” yet the regions analyzed (e.g., Fig. 1) do not allow unambiguous determination of whether the studied areas corresponds to rapid accretion deposits (RADs; traditional centers of calcification) or to thickening deposits (TDs), where growth dynamics are lower. For example, Fig. S1:B may represent the skeleton near the nubbin tip, but it clearly shows both small projections corresponding to RADs and directly adjacent TD regions (compare also Malik et al. 2020, *Acta Biomater.* 108: 314–329). In RADs, the skeleton is characterized by a nanogranular structure, recognizable even deeper in the skeleton (thus formed earlier in ontogeny), whereas this feature is not as evident in TDs (cf. Benzerara et al. 2011, *Ultramicroscopy* 111: 1268–1276).

We thank the reviewer for this useful suggestion. We re-read with great interest both papers and agree that one of the 8 areas analyzed, (Fig. S1 area 5 and Fig. S5), are indeed RADs. We added a comment to this effect on page 3 lines 1-4: “These are small regions from 2 of 8 total areas analyzed. Fig. S1 presents the 8 areas in their entirety, seven of which are at the forming edge of skeletons, sometimes termed thickening deposits (TDs) and one (area 5) is on a spine, sometimes termed rapid accretion deposits (RADs) or centers of calcification (CoCs)^{16, 17}. Despite different morphology and crystal orientations, all TDs, RADs, and CoCs form by particle attachment and precursor phases³.”

We respectfully disagree that Benzerara et al. say that RADs and TDs are distinct. At the nanoscale, which is the scale at which we analyzed all precursor phases, they look identical, as shown for example by comparing the AFM images in Benzerara et al. Fig. 3 B and C. They are nanoparticulate, and the nanoparticles are the same size. The particle accretion mechanisms, therefore, must be the same. Our data in this and many other papers before also show that they are the same spectroscopically. We cited the papers by Malik and Benzerara for the nomenclature and Mass et al. to show that particle attachment and precursor phases are the same.

This structural heterogeneity at the growing edges of the skeleton makes it unclear whether the reported “fast crystallization rate of precursor phases” refers to RADs or TDs. This distinction is important in the context of other studies using EBSD (Coronado et al. 2019, *Nat. Commun.* 10: 2496) and Raman spectroscopy (Stolarski et al. 2021, *PNAS* 118: e2013316117), which show that RADs can retain a disordered character long after deposition, possibly reflecting a distinct mechanism of non-crystalline phase stabilization. The revised version of the manuscript should explicitly address this interpretative uncertainty.

Excellent idea! Thank you for suggesting it! We have now clarified that, if the CoCs occur at the surface we include them in the analysis (e.g. Fig. S1, area 5 and Fig. S5), but if they are in the bulk of the skeleton they are excluded, because, as the reviewer says, all precursor phases are stabilized in the CoCs. We have cited the Coronado 2019 and Stolarski 2021 papers, and our own by DeVol 2015 and Mass et al. 2017, where we showed that the CoCs stay amorphous longer. See [page 13 lines 36-37](#): “CoCs are known to contain amorphous precursors for a decade *post-mortem*^{3,30,40,41}.”

We stress that inclusion criterion 3 ([page 15 line 8-14](#)) excludes CoCs in the bulk from the analysis, thus, they were not analyzed here in 7 out of 8 areas, because they would interfere with the exponential decays that are the goal of this analysis. This was already explained before, on [page 15 line 8-14](#).

Reviewer #2 (Remarks to the Author):

Rechav et al describe a study of the mechanism of formation of the skeleton of corals, where they use PhotoEmission Electron Microscopy to monitor the composition of the mineral adjacent to the growth front. Using this technique the authors are able to map the change in composition of the mineral at the growth front over time. The principal results are that all precursors exhibit a consistent exponential decay from the growth front, and that calcium carbonate hemihydrate is the principal precursor material. The work is carefully done, and is clearly reported.

Thank you!

However, I just do not find these results significant enough to warrant publication in Nat Comms. In particular, the authors have already published an article in which they report the existence of calcium carbonate hemihydrate in coral (ref 4 “Myriad Mapping of nanoscale minerals reveals calcium carbonate hemihydrate in forming nacre and coral biominerals”).

We agree. The question is not anymore about the existence of precursors phases and the dominance of CCHH. The discovery here is that they decay exponentially in space and time, as now highlighted in the title. Overall, we hope we have improved the clarity of the paper enough that the reviewer will agree that this is a significant discovery. The new title is on [page 1 line 1](#): “Exponential crystallization in corals

I have a few comments:

(1) The authors have decided to call calcium carbonate hemi-hydrate “pre-aragonite”. I think this is a bit dangerous. Although there are no current examples of it converting to calcite/ vaterite, to-date there have not been very many studies on this phase. So, at this stage, I would not like to make the statement that it cannot convert to phases other than aragonite.

We thank the reviewer for raising concern regarding our choice to call calcium carbonate hemihydrate (CCHH) ‘pre-aragonite’ based only on our observations from the PEEM data. Another reviewer had a similar concern. Additionally, we applied at the International Mineral Association

(IMA), but they have not yet approved the new name. This may change very soon, so we will call it by the new name in a future publication. We thought it would be cool to name it here, because CCHH is the super-star precursor on coral skeletons, but there is no rush. We now removed pre-aragonite from everywhere and only use CCHH. See the abstract on [page 1 line 28](#), main text on [page 9 lines 46-48 and page 10 lines 1-3](#), and methods on [page 14 line 23](#).

(2) I think the article would benefit from discussion of how the current results fit with the authors previous findings. In ref 3 “Amorphous calcium carbonate particles form coral skeletons” it is stated that “We show direct spectromicroscopy evidence in *Stylophora pistillata* corals that two amorphous precursors exist, one hydrated and one anhydrous amorphous calcium carbonate (ACC); that these are formed in the tissue as 400-nm particles; and that they attach to the surface of coral skeletons, remain amorphous for hours, and finally, crystallize into aragonite”

The current paper seems to contradict these findings, saying that there is actually much more hemihydrate than hydrated ACC. This needs to be discussed.

We thank the reviewer for noticing this apparent discrepancy, which we had not previously discussed in this paper. We now explain this on [page 8 line 12-24](#): “The relative paucity of ACCH_2O , expected to be the first deposited and most abundant surface phase for *Stylophora pistillata*³, has only 2% abundance. This is surprising, as ACCH_2O was expected to be the first deposited and most abundant surface by Mass et al.³.

The Mass et al. 2017³ paper discusses only ACC and $\text{ACC-H}_2\text{O}$ precursors because with component mapping or myriad mapping one can only find phases that one is looking for, that is, phases for which one has the x-ray absorption near-edge structure spectrum ([Fig. 2B](#)) and fits the unknown spectrum from each pixel with a linear combination of known spectra. CCHH was not discovered by Zou et al. until 2019⁸, thus, one could not have suspected its existence in 2017. Once we noticed that some spectra from coral skeletons were not well fit by either ACCH_2O , ACC, or any combinations thereof, we broadened the search, included CCHH, MHC, and vaterite, then excluded vaterite because the fits are not significantly improved by fitting with 6 rather than 5 component spectra, and vaterite was the worst fitting of the 3 metastable crystalline precursors⁴.”

P2, line 40. I do not know what “Eight areas, 5 and 3” refers to. What does the 5 and 3 mean?

Thank you for spotting this. We now explain on [page 2 line 31-33](#): “Eight areas of skeleton surfaces were acquired from corals grown in seawater at pH 8.05 (5 areas) or pH 7.2 (3 areas). Minimal radiation damage was done to these areas during the PEEM data first and repeat acquisitions¹⁵.”

P8, line 18. “Yet the exponential crystallization behavior observed here may reflect a more general mechanism shared across abiotic contexts.” Again, not enough information exists to make this statement.

Thank you! We greatly softened the statement on [page 11 lines 21-25](#): “Whether or not the exponential crystallization behavior observed here reflects a more general mechanism, occurring in other biominerals and geologic minerals remains unknown. Our findings, however, provide the

methods and the software to broaden spatial decay analysis to reveal exponential crystallization decays in other biogenic, geologic, and synthetic materials, if they exist.”

(3) The authors place huge emphasis on the “exponential crystallization behavior”. More discussion is required of the significance of this observation. Why is it so important that coral shows this behavior rather than following another growth model?

We thank the reviewer for stimulating us to improve the paper, and our thinking, on this very important point. Thanks to this stimulus, we developed a new model to understand if the exponential decay of precursors into aragonite is sufficient to generate the results observed. The model is described in the new section “**kinetic model**” on pages 10-11, and it produced the new Fig. 5, showing that the simulated results are in pretty good agreement with the experimental data. We also added a new section about the “**Implications of exponential crystallization in coral skeletons**” on pages 11-12.

Reviewer #2 (Remarks on code availability):
I do not have the expertise to review this.

Reviewer #3 (Remarks to the Author):

Review of Crystallization fast and slow
By Zoe Rechav et al.,

Overall Comments:

This work is a very interesting analysis of the composition and rates of transformation of carbonate precursor phases that mature into aragonite at the edge of coral skeletons. The use of PEEM-based myriad mapping (MM) to gain insights into the rate of transformations is novel and has the potential to be applied to other biomineral and materials research. It builds on recent work from Prof. Gilbert's group in 2024.

Thank you!

My main critique of the article is also a word of caution to the authors about using the term “mineral” to describe CCHH. I would strongly suggest that they keep the established nomenclature over trying to rename it as “pre-aragonite.”

We thank the reviewer for this criticism, which we have taken at heart. We now removed pre-aragonite from everywhere and only use CCHH. See the abstract on page 1 line 28, main text on page 9 lines 46-48 and page 10 lines 1-3, and methods on page 14 line 23.

This article also assumes that the author already have a thorough knowledge of the surrounding literature regarding PEEM and MM. As MM is still a new approach, I would recommend that the authors present some representative spectra of the reported precursor phases and quickly walk us through the defining features before diving into their growth rate and maturation analyses.

We thank the reviewer for this useful suggestion. We added the reference spectra obtained to produce the myriad maps to Fig. 2B page 5, mentioned them on page 4 lines 9-11: “The component spectra are also shown in Fig. 2B, acquired from synthetic ACCH₂O, ACC, CCHH, MHC, and aragonite.”

We briefly explained how myriad maps are obtained. See page 3 line 25 and page 4 lines 1-8: “To generate an MM, the unknown spectrum at each pixel is fitted by a linear combination of five known component spectra. The resulting coefficients, constrained between 0 and 1, are the proportion of each component spectrum. This procedure yields five “proportion maps (pMaps), one per spectral component, where pixel values correspond to the local abundance of that phase. These maps are then merged into a single MM using five distinct colors. To ensure quantitative fidelity, we restrict the display to dominant phases by omitting proportions below 0.5. Each pixel is assigned a single color, with brightness encoding the proportion (e.g., dark to bright cyan corresponds to 0.5 to 1.0). While information on mixed phases is not retained, the displayed pixels are fully quantitative.”

Specific comments:

Title. This title is not particularly descriptive and shows no indication that the authors are exclusively looking at corals in this work. I would suggest adding “in corals” at the end. Otherwise, there are other scientists who specialize in crystal growth and might think that this is a review paper on this topic.

Thank you! We changed the title to “**Exponential crystallization in corals**”

Which is short but more informative. We removed fast and slow because it was not informative and it unnecessarily complicated the title. The salient point of this paper are the exponential decays and rises of all phases vs. space and time, thus, we highlighted “exponential” as the first word of the title.

ABSTRACT

Page 1, line 27. Very cool observation!

Thank you! We fully agree! The predominance of CCHH is very exciting but that could be seen even statically in the 2024 *Nature Communications* paper. The fact that decay constants in space or time are phase independent is even more surprising and exciting.

Page 1, line 28. I would strongly suggest that the authors refrain from renaming CCHH as “pre-aragonite.” See further discussion as to why below (Page 7, line 26).

We fully agree, thus, we have now removed pre-aragonite from everywhere and use only CCHH. See the abstract on page 1 line 28, main text on page 9 lines 46-48 and page 10 lines 1-3, and methods on page 14 line 23.

INTRODUCTION

Page 2, line 6. This distinction of an ECF and ICF and the model with the hypothetical vesicles is only one interpretation for coral biomineralization. As the precise biomineralization mechanism

is not the primary goal of this particular work, I would suggest that the authors stick to a more generalized description of biomineralization in corals—that corals crystalize aragonite using a calcifying fluid between the skeleton and the organism (e.g., Tambutté et al. 2011).

Tambutté, S., et al. (2011). Coral biomineralization: From the gene to the environment. *J. Exp. Mar. Bio. and Eco.*, 408(1–2), 58–78.

We thank the reviewer for this very useful suggestion. We have now removed all references to ECF and ICF, and simply state on [page 2 lines 6-7](#) that “Corals form crystalline aragonite from a calcifying fluid between the skeleton and the organism ^{7, 9, 10}” Ref. 9 is Tambutté et al. 2011.

Page 2, line 28. It might be a good idea to add “Expanding on recent work by Schmidt et al., 2024, for this work...” As someone reading this through the first time, it took me a while to realize that there is already a lot of MM work published by this group and that this is not the first work to look at corals. Having this introductory phrase will help readers refer to this initial work before sitting down to digest the current work.

Excellent suggestion! Thank you! We have now changed on [page 2 line 18](#) to read: “Expanding on recent work by Schmidt et al. 2024 ⁴, for this work, we used the MM method to explore how and where the known CaCO₃ precursor and mature phase, ACCH₂O, ACC, CCHH, ... ”

RESULTS

Page 2, line 37. Before diving into the distributions of these precursor phases, as a reader, I would like to see the Ca L-edge spectra of these different precursor phases and how the authors identified the presence of this new CCHH phase in their system. As this is a new technique, I think that it is fair to show some representative spectra from this work next to some reference spectra, even if similar results are already presented in recent papers by other authors.

We thank the reviewer for this useful suggestion. We preferred not to insert spectra as a standalone new figure, because, as the reviewer says, they are not new to this work. We have therefore added them to the new [Fig. 2B](#). See the new figure and caption on [page 5 lines 6-8](#): “The x-ray absorption near-edge structure spectra (345-355 eV) of 4 precursors and aragonite are also shown in B, color coded as MM pixels, except for the aragonite spectrum, which is plotted in white rather than blue.”

Page 3, Fig. 1. I would just like to note that the pink and red colors are very difficult to distinguish in these maps (and even in the graphs), even though I am not color blind. May I suggest switching one of them to an orange or yellowish color that would stand out better? I realize that this group has already used this color scheme before, but figured I’d make this note.

We appreciate the concern of the reviewer about the color scale used to differentiate ACCH₂O from MHC, red and magenta, respectively. We understand that red and magenta placed side by side are difficult or impossible to distinguish for red-green colorblind people. We have thought about this in the past and opted for all precursor phases to be non-blue and the mature phase to be blue, so colorblind people can see that the precursors are localized at the surface.

Regarding changing the color scheme to, say, orange instead of magenta, we could easily do this, but prefer not, so the data are consistent across multiple publications, not only for us, but for all readers and presenters at conferences that show our data.

In the spectra, we made the magenta spectrum dashed rather than solid line (Fig. 2B). In the decays (Fig. 2C,D), we changed the style of MHC datapoints to be magenta-outlined empty circles, so they are easily distinguishable from the red solid circles used for ACCH₂O. The caption explains this on page 5 lines 13-14: “Magenta datapoints are open circles to distinguish them from red.”. This cosmetic change is extended to other figures as well. See new Figures 2,4 and S4. Fig. S4 caption also reads: “Magenta MHC datapoints are open symbols to distinguish them from solid red ACCH₂O.”

Page 3, line 15. As there is no added section for a discussion, could the authors please expand on the analyses comparing the two pH treatments? Why are the precursor proportions different? What is the significance of having the two different pHs? This feels glossed over.

Thank you for noticing this omission. We originally set out to study the effect of seawater acidification, but we did not observe any difference, so we did not extensively comment about it. We have now done better on page 7 lines 31-36 “At both pH 7.2 and 8.05 there is a spread of initial precursor proportions at the edge (Fig. S3). However, the decay constants are consistent across all areas, pH values, and precursors, within the standard deviation error. Table S5 shows that even separating by pH they are consistent. This is not surprising, because Venn et al. 2019 showed that across the same range of seawater pH used here, the calcification rate in *Stylophora pistillata* corals remains constant as pH decreases, especially during the day when most of the skeleton deposition happens¹⁹.”

Page 4, line 29. That is very interesting that the authors are able to present a skeletal growth velocity per day.

Thank you!

As corals skeletons are known to grow with visible growth bands that represent day vs. night, could the authors comment on how this would impact the results? I see that your average rate is still constant on the macro-scale (great test!), but how does that account for day-night variability? Is the deposition of new precursor phase truly constant, or does it occur in spurts where there is a constant velocity during a particular growth spurt? Something to consider. I like the idea of exploring how this method could be applied to coral cores.

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Page 6, line 26. Just to clarify, does this mean that you would expect to see these precursor phases in a coral that has been dead for up to 6 months? In other words, are you suggesting that someone studying these phases using other techniques (high-res IR, Raman, TEM) be able to potentially “see” these phases as well? This would be a very interesting follow-up. Also, out of curiosity, is it possible to prepare a fresh sample directly at the synchrotron?

We thank the reviewer for these questions and suggestions. Indeed! We added a paragraph to this effect on [page 9 lines 31-34](#): “Importantly, having now demonstrated that fixed, dehydrated, and embedded coral samples can be as old as 6 months and still have some precursor phases, many other methods can be used to analyze precursors, including high-resolution infrared⁴ or Raman spectroscopies, or transmission electron microscopy (TEM), or nanoscale x-ray diffraction (nano-XRD).”

Preparing samples near a synchrotron is possible, in principle, but we had very inconsistent results before we started collaborating with the CSM group in Monaco. Excellent marine biologists with stable and reliable aquarium conditions are absolutely necessary to compare results from coral preparations done at different times as presented here.

Page 7, line 26. I think that it would be scientifically irresponsible to call this a mineral if the authors do not have the necessary crystallographic data (e.g., crystal structure data by XRD and/or TEM with accompanying cif files)--in addition to this excellent spectroscopic data (which focuses on the bonding environment around Ca)--to define the new mineral species and submit it for consideration to the commission on new mineral names at the International Mineralogical Association (IMA). Furthermore, this example would likely not pass the criteria for becoming a mineral (per the IMA definition of a mineral), since it is biogenically formed, as opposed to being formed through a geological process—interesting, I know. Perhaps this may change in the future, but for now, as the goal of this work does not appear to be the description of a new

mineral species, please do not call this a mineral or try to rename this compound that has already been adopted in the literature as “CCHH.” It is common knowledge that many precursor phases will mature into specific mineral species, so I really do not see the added value of calling it “pre-aragonite” over CCHH.

We thank the reviewer for their concern, along with another reviewer. We have already presented the XRD data and cif files for synthetic CCHH in Zou et al. 2019. At that time, CCHH was a material not a mineral, because it had never been observed in nature. Now it has. We applied at the International Mineral Association (IMA), but they have not yet approved the new name. This may change very soon, so we will call it by the new name in a future publication. We thought it would be cool to name it here, because CCHH is the super-star precursor on coral skeletons, but there is no rush. We will first settle with IMA, by showing that CCHH forms in at least another geologic system, they will have to accept that it is a mineral. For now, we removed pre-aragonite from everywhere and only use CCHH. See the abstract on [page 1 line 28](#), main text on [page 9 lines 46-48](#) and [page 10 lines 1-3](#), and methods on [page 14 line 23](#).

CONCLUSIONS

Page 7, line 46. Very cool!

Thank you!

Page 8, line 6. It may be worth comparing to deep water corals that grow very slowly at low aragonite saturation states (and very low pHs)--sometimes below a seawater saturation state that is below 1!

This is a great idea, for which we thank the reviewer. The experiment is certainly feasible, although we do not have access to fresh deep-sea corals at present. It will take years to plan and do these experiments thus, we will keep them for another paper. We added a comment in the manuscript to this effect. See [page 12 line 32-34](#): “The deep-sea corals that form their skeletons at lower seawater pH values are of particular interest. How does their crystallization rate compare to surface corals?”

METHODS

I cannot speak to the PEEM mapping details as I have never used it before, but I would reiterate my comment above that I would like to see some raw spectra of the Ca L-edge presented next to reference spectra.

We added spectra to the existing figure. See [new Fig. 2B on page 3](#).

Reviewer #3 (Remarks on code availability):

I did not review the code as that is not my area of expertise.

Response to reviewers

Reviewer #1 (Remarks to the Author):

I appreciate the authors' revisions and the additional clarification regarding the identification and treatment of RAD/CoC versus TD regions. I remain uncertain, however, about the conclusion that "the particle accretion mechanisms are the same" in RADs and TDs. While the authors describe their inclusion/exclusion criteria, the revised manuscript still does not explicitly state whether the reported "fast crystallization rate of precursor phases" applies strictly to TDs or also to surface RADs. Given the different stabilization dynamics of RADs/CoCs described in previous EBSD and Raman studies, this clarification would be valuable.

The authors argue that RADs and TDs must share the same accretion mechanism because AFM shows similar nanoparticulate textures at the nanoscale. However, Benzerara et al. explicitly noted a discrepancy between AFM and TEM imaging of RAD and TD regions: AFM highlights surface nanodomains, whereas TEM indicates that TD fibers behave as genuine micron-scale single crystals.

As Benzerara et al. wrote, the nanodomains seen by AFM may reflect surface defect ordering, not necessarily the underlying growth mechanism. Because TEM does not show nanogranular structure within TDs, AFM similarity alone does not imply identical accretion pathways. In light of this, it remains uncertain whether RADs and TDs indeed form by the same particle accretion mechanism, particularly below the surface where crystallographic continuity differs.

We thank the reviewer for highlighting the importance of identifying which regions are analyzed in this work. As part of the inclusion/exclusion criteria, all areas in which precursor proportion increases deeper into the skeleton are removed. Precursor proportion increases deeper into the skeleton may indicate CoCs, shown to remain amorphous even 10 years after the death of the animal (DeVol et al. 2015). Of the 8 areas used in the analysis, seven are TDs. The remaining area, area 5, includes mostly TDs and some CoCs more than 4 micron from the edge of the skeleton. Pixel information was only collected up to the first 4 micron in this work. Thus, no pixel information from the CoCs in area 5 was collected for this work. We now specify that no CoCs are analyzed in this work. See [page 4 line 13-18](#): "One area (area 5) on a spine contains several centers of calcification (CoCs), sometimes termed rapid accretion deposits (RADs)^{16, 17} or centers of rapid accretion (CRAs) and TDs¹⁸, more than 4 micron from the fresh forming surface of the skeleton. The CoCs in area 5 are far enough away from the surface that no pixels from CoCs are included in this work. This is a relevant distinction, as CoCs and fibers are known to form with different amounts of organics, and different kinetics^{16, 18, 19}."

Reviewer #2 (Remarks to the Author):

"Exponential crystallization in corals" by Professor Gilbert and colleagues

The authors have made significant improvements to their manuscript, which have greatly improved its quality and impact. They have managed to convince me of the importance of their results (the reason for my initial rejection from Nat Comms).

Thank you.

Based on their further discussions I do have a few more queries, however.

(1) From my understanding, the authors state that each of the phases identified crystallizes at an identical rate.

What could give rise to this effect? What is the transformation sequence of the phases? It really does seem very strange that a crystalline phase (CCHH) would crystallize at the same rate as an amorphous one. If indeed ACC.H₂O, ACC and CCHH are indeed distinct and not just a continuum of phases.

We thank the reviewer for these important questions regarding the decay rate of each of the precursors. We are as surprised as you are that the decay rates are all the same. This is why we now use the word “Unexpectedly” in the abstract, and in the results and discussion.

We now speculate about potential causes on [page 11 lines 39-45](#): “Speculative explanations for consistent decay rates include physical constraints on coral skeleton growth, such as, for example the effect of confinement on crystal formation ³⁵. Confinement changes the kinetics or thermodynamics of crystallization by restricting the dimensions of the system in one, two, or three directions ³⁵. Speculative organic examples include generalist catalysts or inhibitors, such as protons doing acid/base catalysis, or water, or ions or molecules that regulate reaction rates for multiple, diverse reactions or phase transitions. Generalist enzymes are well-known in bacteria ³⁶, but have rarely been reported in corals ³⁷.”

(2) They also state that the rate of crystallization is independent of the environment of the domains of each phase. This really does not seem to make any physical sense (and it has to ... even if crystallization occurs within an organism).

For example, crystallization of ACC will undoubtedly be faster if the ACC is deposited on calcite or aragonite (heterogeneous nucleation) as compared if homogeneous nucleation occurs with the ACC. Heterogeneous nucleation is always – by definition – faster than homogeneous nucleation. So how can this observation be valid?

We thank the reviewer for highlighting this concern. We explain on [page 11 line 24-26](#): “Since nucleation happens within the already deposited solid, it must be heterogenous nucleation of aragonite on the surface of the precursor phases ³⁴.”

Reviewer #3 (Remarks to the Author):

I appreciated the authors' efforts in improving their manuscript per the comments from all three reviewers. They sufficiently addressed all of my concerns. Thank you!

We thank the reviewer for their previous comments!

Response to reviewers Round 3

Reviewer #1 (Remarks to the Author):

I have reviewed the authors' revisions, which seem to explain my concerns sufficiently clearly. At this point, I have no further comments.

Thank you!

Reviewer #2 (Remarks to the Author):

I am happy that the authors have addressed my remaining queries to the best of their ability.

Thank you!