RESPONSE TO THE REFEREES AND REPORT ON CHANGES MADE IN MANUSCRIPT bg-2017-305

Additional/general changes made (*for direct responses to Referees #1 and #2, see further below*):

MODEL RUNS:

All model runs have been repeated on the basis of a slightly improved preindustrial reference run. The newly introduced comparison with the observed Atlantic dissolved ^{230}Th section revealed somewhat too low values in the upper 1000 m. The changes with respect to the original reference run are: A stronger reduction of biological particle production through reducing V_{max} (nutrient uptake velocity) increasing see ice thickness, a reduction of the clay flux for ^{230}Th scavenging (from atmospheric dust input which may have been overestimated for the Atlantic originally) to 25% (a sensitivity experiment with 100% dust flux was also added see below), and a change in the equilibrium coefficient k_d between dissolved and particle attached phases taking particle specific scavenging rates into account (following Hayes et al., Marine Chemistry 170 (2015) 49–60).

As compared to the original manuscript, a suite of sensitivity experiments has been added to the analysis. These experiments address:

A) With respect to the new preindustrial control run:

- A general slight increase in the scavenging equilibrium coefficient k_d.

- A strong increase of the scavenging equilibrium coefficient k_d in the grid cells directly above the ocean floor (to test the effect of resuspension of particles and hydrothermal vents).

- An increase of the clay flux to 100% of the prescribed dust input at the ocean surface.

- Scavenging to $CaCO_3$ and clay only, not to POC.

- Scavenging to clay and POC only, not to $CaCO_3$.

B) With respect to the RCP8.5 moderate calcification projection (changes scaled by the decadal change resulting from the fully-fledged Earth system model NorESM):

- A reduction/variation in ocean overturning.

- A reduction/variation in V_{max} (nutrient uptake velocity).

- A reduction/variation in particle sinking velocity.

- A simultaneous reduction/variation of overturning, V_{max}, and particle sinking velocity.

C) With respect to the RCP8.5 extreme calcification projection (changes scaled by the decadal change resulting from the fully-fledged Earth system model NorESM):

- A simultaneous reduction/variation of overturning, V_{max}, and particle sinking velocity.

FIGURES:

In order to account for the wishes of the referees and to keep a good balance between text and figures, we introduced some new figures and modified some original figures. A part of the figures was moved to a newly established Supplementary material.

Figure 3: Newly drawn with new reference run and using a somewhat different "cruise track" for the Atlantic section.

Figure 4: Newly added Atlantic section from observations and model minus observations section.

Original Figure 4 has become new Figure 5: The single station profiles have been removed (because we added the observed section), and the scatter diagram has been redrawn.

Original Figure 5 has become new Figure 6: The biological production maps have been redrawn using the new reference run data.

New Figure S1: Atlantic and Pacific meridional cross sections have been added for the scavenging equilibrium coefficient k_d in the Supplementary Material.

Newly added Figure 7: Cross sections documenting the results of the sensitivity experiments with respect to the preindustrial control run.

Original Figure 6 on RCP scenarios has been moved to Figure S2 in the Supplementary Material.

Original Figure 7 has become new Figure 8 and was redrawn using the data from the new runs.

Original Figure 8 has become new Figure S3 in the Supplementary Material: Figure S3 shows a higher sensitivity in dissolved ^{230}Th with at 700 m depth with respect to a decrease in $CaCO_3$ production due to the revised scavenging formulation. The y-axis resolution was changed so that the cross over points for the theoretical detection level are better resolved. The control run values are now shown for the respective control run using the RCP atmospheric CO_2 concentrations, but no change in $CaCO_3$ production (originally only the RCP8.5 control run values have been shown; this has been corrected now).

Original Figure 9 has been redrawn: The y-axis resolution was changed so that the cross over points for the theoretical detection level are better resolved. The control run values are now shown for the respective control run using the RCP atmospheric CO_2 concentrations, but no change in $CaCO_3$ production (originally only the RCP8.5 control run values have been shown; this has been corrected now).

Original Figure 10 has become new Figure S4 in the Supplementary Material: The y-axis resolution was changed so that the cross over points for the theoretical detection level are better resolved. The control run values are now shown for the respective control run using the RCP atmospheric CO_2 concentrations, but no change in $CaCO_3$ production (originally only the RCP8.5 control run values have been shown; this has been corrected now).

New Figure 10 replaces the original Figures 11 and 12: Figure 10 was draw using the results from the revised model runs.

Newly added Figure 11: Cross sections on dissolved ^{230}Th have been added which show the change due to decadal variability in various model parameters relative to a scenario run with calcification reduction effect only. The data are from the new sensitivity experiments concerning the projections.

Newly added Figure 12: The time of signal emergence has been shown now also for the runs with simultaneous decadal changes in model parameters.

Newly added Figure 13: Maps of surface and deep changes in alkalinity and dissolved ^{230}Th during 2040-2010 as for the RCP8.5 projection have been drawn using moderate calcification changes. This illustrates the difference in reactions to $CaCO_3$ production changes for the two tracers alkalinity and dissolved ^{230}Th.

Response to Anonymous Referee #1

(Referee's comments in italics. Our references to figures, page/line numbers etc. in the response to the referees refer to the originally submitted manuscript except where it is explicitly stated otherwise.)

Our response 1.0:

We would like to thank the referee for the very valuable comments and suggestions.

This modelling study seeks to test whether the oceanic distribution of dissolved ^{230}Th could serve as an indicator of reduced biogenic $CaCO_3$ formation as the ocean acidifies due to anthropogenic CO_2 emissions. It proposes that ^{230}Th concentrations, particularly in the deep ocean, may be a more sensitive indicator of such change than direct observations of changing alkalinity in the surface ocean. In some ways, the modelling work described is a rather incremental advance relative to earlier work assessing the ^{230}Th response to change in the $CaCO_3$:POC ratio presented in Heinze et al. 2006. The present manuscript, however, focuses specifically on testing how this ratio might be influenced by future ocean acidification, and whether this could be detected by ^{230}Th measurements.

The ability to detect systematic change in the production of biogenic $CaCO_3$ in response to ocean acidification would be a useful tool, making this modelling endeavour potentially useful. The idea that ^{230}Th may allow such detection is not intuitive, but interesting and worthy of consideration. Therefore, the general direction of this contribution is welcome. I am, however, unsure from the present manuscript that the utility of ^{230}Th to assess $CaCO_3$ flux has been demonstrated.

Our response 1.1:

This study here goes beyond the work of Heinze et al. (2006), where only the effect of an instantaneous switch in $CaCO_3$ rain ratio for one single grid point time series has been shown and only a few lines of text were devoted to ocean acidification (Figure 8 and pages 10-11 of Heinze et al. (2006)). In our study here, we investigate the global ocean ^{230}Th reaction for a series of realistic CO_2 emission scenarios, we employ an improved model with respect to simulation of the $CaCO_3$:POC rain ratio pattern, have recalibrated the scavenging rate constants, and add an analysis of the time of emergence of a clearly identifiable signal in ^{230}Th. Further, we test the ^{230}Th reaction for different sensitivities of $CaCO_3$ to ocean acidification (based on the option as used in the study by (Ilyina et al., 2009). In addition, there seems some urgency to establish methods for detecting large-scale ocean acidification impacts as the respective integrated effect on ecosystems is not well known (see Gattuso et al. (2015), citation: "*Most studies have investigated the effects of ocean acidification on isolated organisms; far less is known about the effects on communities and ecosystems.*"). Therefore, our study here is fully justified. We address possible improvements of the assessment of $CaCO_3$ fluxes through ^{230}Th below.

1. Threshold for detection: The authors assume that detection of change in ^{230}Th depends only on the analytical uncertainty of measurement. Measurements of ^{230}Th in seawater shows significant spatial and temporal variation, however, which far exceed measurement uncertainty. Some of this variation reflects known processes, such as productivity or large-scale circulation, which cause consistent spatial patterns. But other variation is akin to 'noise', caused by seasonality of particle flux, eddying circulation, variability in boundary scavenging etc. To assess the possibility to detect change in the profile of ^{230}Th due to variation in the composition of settling particles requires consideration of the natural variability of the ^{230}Th field. One way to consider this might be to statistically compare closely spaced samples in the ever-growing observational ^{230}Th dataset to assess small-scale natural

variability. My guess is that a more realistic detection threshold is likely to be 2 to 3 times higher than the value assumed in this study. That would not prevent detection in the deep ocean (e.g. in Fig 9) but would delay the date of detectability in that setting, and would prevent detection at shallower depths. Intuitively that seems realistic given that intermediate depths typically show quite large (and presently poorly explained) temporal changes in ^{230}Th concentrations.

Our response 1.2:

We agree with the referee that the detection levels shown in Figures 8, 9, and 10 would be the earliest possible (assuming that the preindustrial levels would be known as well). This has also been written in the text (page 10, line 22). If other factors than changes in $CaCO_3$ would occur this could change. However, Figures 8-10 show large-scale averages for entire oceans within the model world. It should be legitimate to show this earliest possible detection threshold for the average of a large region. Figures 8-10 do not make a judgement on how good an observing system should be to fully exploit the potential of ^{230}Th to diagnose large-scale changes in $CaCO_3$ flux. Figures 8-10, however, demonstrate the potential of ^{230}Th to detect such changes. For large-scale averages, the noise should cancel out. We have carried out a number of additional sensitivity experiments concerning the reference run without anthropogenic rising CO_2 and with rising pCO_2. These sensitivity experiments are described under section 4 (renamed to "4 Control run, scenario experiments, and sensitivity experiments") and discussed in section 5. Table 2 has been added as an overview about the various experiments. The impact of the sensitivity experiments is illustrated in the new figures 7, 11, and 13 and discussed in sections 5 and 6.

2. Sensitivity to other changes: To be a useful monitor for $CaCO_3$ flux change, future ^{230}Th concentrations must be more responsive to that process than to other possible changes. There is very little consideration in the manuscript of other likely controls on the ^{230}Th distribution. These might include future changes in circulation driven by changing wind fields or freshwater inputs; changing productivity of organic carbon due to circulation changes; changing remineralisation of organic carbon due to altered O_2 levels; changing fluxes of silicate dust due to changing winds and continental aridity; or changing ballasting related to ecosystem change. I do not have an instinct about whether any such changes are likely to generate substantial changes in the ^{230}Th field, but this seems a fundamental issue for a modelling study such as this one to address. Can the authors do more to assess whether $CaCO_3$ fluxes are really the dominant control on ^{230}Th change? Or only one of several global changes that will alter the field?

Our response 1.3:

Our paper focuses on ^{230}Th as a tool for detecting $CaCO_3$ production changes. We have discussed the limitation of our approach on page 16, lines 10-22, including the use of a constant velocity field. In the revised manuscript, we have added a series of sensitivity experiments also with respect to the preindustrial reference run (runs P1-P5, see new Table 2). These runs address uncertainties in the equilibrium coefficient k_d in general and specifically in view of hydrothermal vents, the strength of the clay flux, and the effect of omitting POC or $CacO_3$ as carrier phases for ^{230}Th. The experiments are described in sections 4 and discussed in section 6. The new figure 7 was added illustrating the results. In addition, the sensitivity experiments relative to the projections (S1-S5, Table 2) show the effects of circulation changes, changes in nutrient uptake velocity, and particle sinking speed. The set-up for these experiments S1-S5 mimicking interannual/decadal variability through scaling of parameter changes to the overturning change time series from a fully-fledged Earth system model is presented in section 4.

3. Accuracy of the model: The ^{230}Th model used is well established and has been thoroughly documented in the literature before, but there are some presentational issues in the present manuscript that limit the reader's ability to assess its prediction of future ^{230}Th change:

i. Since Heinze 2006, there are significantly more ^{230}Th observations, including long ocean sections (see http://www.egeotraces.org/?group=Dissolved%20Natural%20Radionuclides,variable=Th%20230%20dissolved). It is now possible to directly compare modelled sections (e.g. Fig 3) with observations, and this should be done in this manuscript. Doing so reveals some quite important discrepancies, particularly in the deep ocean, which is being touted here as a sensitive indicator for changing CaCO$_3$ fluxes. These discrepancies include deviations related to scavenging at the seafloor and in MOR plumes. If these processes are not considered, the deep-ocean sensitivity of ^{230}Th to downward particle flux may well be overestimated.

Our response 1.4:

We have added a meridional Atlantic cross section of dissolved ^{230}Th for both model and observations and discussed the discrepancies and their potential implications for diagnosing CaCO$_3$ flux changes through ^{230}Th. To this end, new Figures 3, 4, and 7 have been added and discussed. Because the reference run of the original manuscript showed somewhat too low ^{230}Th values in the upper North Atlantic (representing a large relative error) we reformulated and retuned the model, and repeated all model experiments. The changes in the new model are a partial further reduction of particle production under ice (scaled with the ice thickness), using only 25% of the clay flux for scavenging, and adjusting the k_d value with respect to particle composition. The model description has been updated accordingly.

ii. Perhaps I have misunderstood, but Figures 8-10 indicate that even the control run shows a significant change in deep ^{230}Th, despite the lack of CaCO$_3$ change in this run. This is puzzling, and seems to suggest a problem with the long-term handling of ^{230}Th in the model?

Our response 1.5:

We explain this already in the submitted manuscript on page 11, lines 1-4: "For constant CaCO$_3$ production, the intermediate and deep water ^{230}Th activities start to rise around year 2100 as well (see black curves in Figures 8-10). This effect is due to the increasing dissolution of CaCO$_3$ particles in the water column in parallel with downward mixing of waters that carry anthropogenic loads of dissolved organic carbon and hence subsurface and deep acidification." We expanded the text in order to explain this more clearly: "For constant CaCO$_3$ production, the intermediate and deep water ^{230}Th activities start to rise around year 2100 as well (see black curves in Figures S3, 9, and S4). This effect is due to the increasing dissolution of CaCO$_3$ particles in the water column in parallel with downward mixing of waters that carry anthropogenic loads of dissolved organic carbon and hence subsurface and deep acidification. The effect is most important in areas, where anthropogenic carbon is mixed down quickly and induces a significant shoaling of the CaCO$_3$ saturation level and CaCO$_3$ lysocline as well the Carbonate Compensation Depth through deep-water acidification. Parts of the deep Pacific are not as much influenced by this as compared to the Atlantic within the 21st century. The control run in the figures does not represent the reference run with constant preindustrial atmospheric pCO$_2$ but the run with constant CaCO$_3$ production and rising pCO$_2$ according to the RCP scenarios."

iii. Less significant, but it would also be good to see how the model predicts change as a profile or section, rather than as a time series at a single depth. As you go to greater depth in the ocean, the

residence time of ^{230}Th increases, so change might be slower, but the flux of organic carbon decreases so the influence of a CaCO$_3$ change will be more important. Seeing how such depth-related effects compete in the model would be interesting, and help to assess how realistic it is in representing the natural cycle.

Our response 1.6:

We have added respective cross sections on how the Atlantic and Pacific meridional ^{230}Th distribution changes if we assume decadal variability in selected parameters relative to a case with constant biological production (new Figure 11). These cross sections show that also the effects of decadal variability will increase with depth for changes in biological carbon cycling and strength of ocean overturning.

Overall, these three concerns leave me unconvinced that this study is ready for publication. The idea of using ^{230}Th to assess CaCO$_3$ fluxes is interesting, however, so I'd encourage the authors to seek to address these issues. A revised version of the work could then be a useful contribution.

Our response 1.7:

Our results for this revised version show that for strong changes in CaCO$_3$ production, the ^{230}Th signal in deep waters still is a promising respective indicator. For more moderate changes in CaCO$_3$ production, the ^{230}Th signal in deep waters may be masked by other effects such as changes in particle sinking velocity and circulation. Sections 5 and 6, and the abstract have been updated respectively.

Other comments:

P4-6: The description of the model set up could be reduced, given that this is a previously described model, and that some aspects (e.g. C isotopes) are not relevant to this study.

Our response 1.8:

In reviews of previous publications, where we omitted a detailed model description, the respective referees asked us to include a more detailed description so that readers would not have to read another (or more) articles in parallel. We, therefore, would like to keep the model description but will remove those elements, which are not relevant for this manuscript. We have added a description of the revised scavenging formulation for the experiments shown in this revised version.

P7: It's good to see the GEOTRACES data used, but the source of this data is strangely attributed. Neither de Baar nor Boyle were involved in collection of ^{230}Th data. Please cite the relevant papers directly for this data (e.g. Hayes et al., Deng et al) in addition to the Mawji et al. paper.

Our response 1.9:

We have corrected the references for the GEOTRACES data set – many thanks for pointing this out.

Are any spatial changes expected because of changing rain-ratio? High latitude waters will decrease saturation faster than mid-latitude, so changes may be more acute there. I wonder if looking at the relative change in ^{230}Th between regions may be a more sensitive indicator of the specific response to changing carbonate saturation than the general deep-ocean response?

Our response 1.10:

This is an interesting metric for analysis – many thanks. We have looked at this. Indeed we could detect a faster rain ratio change $CaCO_3$/POC at high latitudes than in lower latitudes. However, this signal was not directly translated into a simple deep ^{230}Th change pattern.

Response to Anonymous Referee #2

(Referee's comments in italics. Our references to figures, page/line numbers etc. in the response to the referees refer to the originally submitted manuscript except where it is explicitly stated otherwise.)

Our response 2.0:

We would like to thank the referee for the very useful suggestions and comments.

In this manuscript Heinze et al. explore the feasibility of using measurements of dissolved ^{230}Th in the deep ocean to detect changes in calcification as a result of ocean acidification. The idea being it would be nice to be able to "check" the response of carbonate export/calcification to ocean acidification with observations of changes in both parameters. They argue that this approach is complementary to using measurements of alkalinity in the surface ocean to detect changes in calcification. This is an intriguing idea, especially the idea that surface changes are 'magnified' in the deep water through ^{230}Th. And I fully agree with the authors' concluding sentence that the full potential of ^{230}Th has yet to be realised. However, I have some reservations about this manuscript.

First, the idea is not actually new, having been proposed over 10 years ago by the first author (Heinze et al, 2006).

Our response 2.1:

The idea was brought up by Heinze et al. (2006). This study follows up on it and pursues it in greater detail focusing now on the possibility of detecting changes in carbonate production through the monitoring of deep-water dissolved ^{230}Th levels. See also our detailed response 1.1 in reply to Referee #1.

More importantly, and particularly as the current work can be considered a 'follow up' on the initial work, this work is missing a key sensitivity analysis. Stepping back, the authors have shown that it's quite possible that changes in carbonate production and export will result in measureable changes in ^{230}Th concentrations in the deep sea in coming decades or at least centuries. However, they have not adequately demonstrated that it will be possible to distinguish between the different 'parameterisations', or 'sensitivities' of calcification to OA, using the ^{230}Th measurements, which is the premise of this work. In their experiments, where only CO_2 and calcification change, yes there are clear differences in the time of emergence for the different parameterisations. However, in the real world there will almost certainly be changes in POC, $CaCO_3$ and opal that are independent of OA, driven by changes in stratification, temperature, dust deposition, even anthropogenic nutrient input. Do the different Th trajectories and times of emergence stay distinctly different when you add in these other changes? Furthermore, ocean circulation will likely change and that will change ^{230}Th distributions independent of changes in particle flux and composition. Again, can you distinguish between different OA sensitivities once you factor in a range of ocean circulations? It all comes down to the sensitivity of ^{230}Th distributions to OA compared to their sensitivity to other perturbations.

Our response 2.2:

We have added two sets of additional sensitivity experiments (a) with respect to the preindustrial reference run (experiments P1-P5, new Table 2) and (b) relative to the projections including time dependent change (experiments S1-S4, new Table 2). We think that our study has a value even without such additional sensitivity experiments, but agree that these experiments strengthen the manuscript. Please, see our detailed responses 1.2, 1.3, and 1.4 in reply to Referee #1.

The authors mention that changes in deep ocean ^{230}Th concentration emerge at about the same time as changes in alkalinity, and point out that the two tracers offer complementary information. I think this is an excellent point. My feeling is a study that combines these two tracers, together with a sensitivity analysis as suggested here, could potentially be quite useful in showing how the two tracers together (or perhaps just one or the other) can be used to distinguish, on the basis of time of emergence, between different sensitivities of carbonate export to OA.

Our response 2.3:

This is an interesting point – thank you. We have tried to identify a systematic interdependence between alkalinity changes and ^{230}Th changes, but so far could not find out how this could possibly lead to a new tracer for acidification impacts. We have added the new Figure 13 to illustrate this and describe the idea/issue in the discussion.

So my recommendation is to conduct some more model simulations to assess sensitivity to these other changes, and if possible to also consider a study that combines both ^{230}Th and alkalinity.

Our response 2.4:

See our responses 2.2 and 2.3 for this.

Other comments:

- The model does not include hydrothermal particles, which are important scavengers for Th (e.g. recent papers by Hayes)

Our response 2.5:

Regionally too high modelled ^{230}Th deep water values in the Atlantic section have been found (new Figure 4). We have added a sensitivity experiment, where we increased the equilibrium coefficient for k_d for partitioning between dissolved and particle attached phases in the grid cells directly above the ocean floor. According to this, adding hydrothermal vents could be a means of reducing the discrepancy between model results and observations. See also the new Figure 7 and the updated discussion section.

- Although the authors cite Heinze et al. 2006 as evidence for a lack of sensitivity to the choice of particle phases scavenging Th, it would be good to actually show that result in the context of the present study, as part of the sensitivity analysis.

Our response 2.6:

We have added sensitivity experiments with omitting the scavenging to (a) POC, and (b) CaCO3, and further have carried out a run with changes in the clay flux for scavenging. Sections 4 and 5 have been updated accordingly and the new Figure 7 has been inserted.

- I don't think figure 6 is necessary - Section plots would be more useful for the model-data comparison than the station by station comparisons.

Our response 2.7:

We have kept Figure 6, as not every biogeochemical trace element researcher is fully familiar with the greenhouse gas scenarios, but moved Figure 6 to the Supplementary Material as Figure S2. Plots of observations and model results have been added for an Atlantic meridional cross section (see also our response to Referee #1).

The potential of ^{230}Th for detection of ocean acidification impacts on pelagic carbonate production

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Abstract. Concentrations of dissolved ^{230}Th in the ocean water column increase with depth due to scavenging and downward particle flux. Due to the ^{230}Th scavenging process, any change in the calcium carbonate ($CaCO_3$) fraction of the marine particle flux due to changes in biological $CaCO_3$ hard shell production as a consequence of progressing ocean acidification would be reflected in the dissolved ^{230}Th activity. Our prognostic simulations with a biogeochemical ocean general circulation model using different scenarios for the reduction of $CaCO_3$ production under ocean acidification and different greenhouse gas emission scenarios (RCPs 8.5 to 2.6) reveal the potential for deep ^{230}Th measurements to detect reduced $CaCO_3$ production at the sea surface. The time of emergence of an acidification induced signal on dissolved ^{230}Th is of the same order of magnitude as for alkalinity measurements. Interannual and decadal variability in other factors than a reduction in $CaCO_3$ hard shell production may mask the ocean acidification induced signal in dissolved ^{230}Th and make detection of the pure $CaCO_3$ induced signal more difficult so that only really strong changes in marine $CaCO_3$ export would be unambiguously identifiable soon. Nevertheless, the impact of changes in $CaCO_3$ export production on marine ^{230}Th are stronger than those for changes in POC (particulate organic carbon) or clay fluxes. Yet, deep ocean ^{230}Th concentrations are less affected by seasonal and multiyear variability than surface alkalinity. Thus, deep ocean ^{230}Th observations could be advantageous to guide monitoring and detection campaigns. Furthermore, given that the precision of ^{230}Th measurements may potentially improve in the near future, earlier detection of ocean acidification impact signals would be possible. Our results indicate that the deep Pacific Ocean and the deep Southern Ocean are the most suitable regions for selected regular reoccupations of deep reaching ^{230}Th stations.

1 Introduction

Progressing ocean acidification is a fact. It can be directly seen from measurements at Eulerian time series stations (e.g., Bates, (2007); Dore et al., (2009); Santana-Casiano et al., (2007)) and also at larger depth from high quality deep hydrography data (Olafsson et al., 2009). Depending on the emission scenario for CO_2, the decrease in ocean pH and the decrease in carbonate saturation will continue and become more pressing during this century (e.g., Orr et al., (2005); Steinacher et al., (2009); Bopp et al., (2013)). Temporal and regional patterns of changes in pH and carbonate saturation are can be relatively straightforwardly to projected by Earth system models including marine inorganic carbon chemistry formulations (e.g. Bopp et al., (2013)). They also can be monitored through long-term high quality measurements of the inorganic carbon system. However, monitoring impacts of ocean acidification on biological processes remains challenging. While for some organisms, especially corals (Kleypas et al., 1999),

detrimental effects due to decreasing pH and carbonate saturation have been determined, the various physiological impacts of ocean acidification on specific organisms and ecosystem functioning are still under investigation (e.g., Iglesias-Rodriguez et al., (2008); Kroeker et al., (2013); Meyer and Riebesell, (2015); Riebesell et al., (2007)). At present, a series of possible pH-dependencies of governing marine carbon cycle parameters (such as elemental stoichiometric ratios and nutrient uptake kinetics under biological particle production) are discussed. So far, the potential decrease in calcification due to the lowering of carbonate saturation under high pCO_2 is among the key changes which may be expected to occur, especially when it comes to organisms building aragonite shells (the meta-stable form of $CaCO_3$, calcite has a lower solubility than aragonite) (Raven et al., 2005). Two important questions emerge: 1. If changes in biological calcification would indeed occur in the ocean during the coming years – how can they be detected and monitored by observational frameworks (through which methodology and through which variable)? 2. In which oceanic region could one observe early signals of these changes unambiguously at the earliest possible stage?

Development of such early warning systems is vital in order to check the validity of parameterisations of pH-dependent processes in ocean models and to take appropriate mitigation/adaptation measures to diminish the consequences of potential considerable ecosystem changes due to ocean acidification. Such changes could affect the marine food chain. In a global modelling study, Ilyina et al. (2009) quantified the detection thresholds for changes in alkalinity due to changes in a series of possible formulations for the reduction of calcification (with the term "calcification" we mean here the production of $CaCO_3$ hard parts by marine biota) with pH decrease. The logic behind the approach of Ilyina et al. (2009) is as follows: If ocean acidification leads to a decrease in calcification, more CO_3^{2-} ions would be retained in the surface water and not become incorporated into $CaCO_3$ shell material. Changes in CO_3^{2-} ion concentration would induce a change in ocean total alkalinity, which could eventually be measured against an earlier baseline. According to that study, the tropical Pacific (with high $CaCO_3$ production rates) would be the region for detecting such alkalinity changes first, as the anticipated change in $CaCO_3$ production would be largest there in absolute terms. For intermediate dependencies of $CaCO_3$ production on pH/carbonate saturation, a reduction in biological calcification could unequivocally only be diagnosed from ca., year 2035 on. In the Arctic Ocean, where pH changes are expected to be most pronounced, large scale changes in calcification would be detectable even later on the basis of alkalinity measurements due to the overall lower biological production rates. Likewise, detection may be additionally complicated due to signals from natural seasonal and interannual variations in surface total alkalinity (Carter et al., 2016). There is thus a need for the development of novel detection methods. Heinze et al. (2006) investigated the impact of varying rain ratios $CaCO_3:C_{org}$ on the distribution of the radionuclides thorium (^{230}Th), protactinium (^{231}Pa), as well as beryllium (^{10}Be). As the rain ratio describes the average amount of carbon atoms incorporated into $CaCO_3$ shell material relative to the amount of carbon atoms incorporated into organic matter by plankton, a reduction in calcification would lead to a rain ratio decrease. Indeed, especially for ^{230}Th, due to its affinity for scavenging to $CaCO_3$ particles, a considerable increase in the concentration of dissolved ^{230}Th with depth and time was obtained in a sensitivity experiment with strong rain ratio reduction. In this paper here, we explore the option of using radionuclides for diagnosing changes in calcification and respectively reduced downward marine particle flux in more detail.

2 The concept - radionuclides and particles

We focus here on ^{230}Th, a ~~long lived~~long-lived radionuclide (half-life $7.5 \cdot 10^4$ yr) and a highly particle reactive metal. ^{230}Th is produced in the uranium decay series. As uranium has a very long residence time in the ocean and quasi-homogenous concentrations in seawater, the present natural marine ^{230}Th source is constant everywhere in

5 the ocean water column and thus ideally suited for using it as a tracer in modelling studies. ^{230}Th is strongly particle reactive and is removed from the water column quickly through scavenging by the vertical particle flux in the ocean (for a summary, please, see Henderson et al., ~~(~~1999~~)~~). The majority of ^{230}Th is removed from the water column and will not re-enter the bottom waters, e.g., through sediment pore water diffusion (though resuspension may potentially cause some re-release). In spite of its strong particle reactivity, concentrations of dissolved ^{230}Th

10 show horizontal as well as vertical gradients in the water column which are induced by the oceanic current field and differential particle fluxes as well as particle concentrations (e.g., Henderson et al., ~~(~~1999~~)~~; Yu et al., ~~(~~1996~~)~~). The distribution of particle bound ^{230}Th follows the particle concentrations and particle fluxes. Both, the dissolved ^{230}Th and the particle bound ^{230}Th show nutrient type vertical profiles with low values at the surface and increasing concentrations with depth. Dissolved ^{230}Th increases with depth as particles continuously carry ^{230}Th downwards

15 and new equilibria between the dissolved phase and the ~~particle attached~~particle-attached phase establish as illustrated in Figure1. The equilibrium between the concentration of the dissolved phase [^{230}Th$_{diss}$] and the concentration of the ~~particle attached~~particle-attached phase [^{230}Th$_{part}$] can be described in an analog way to a chemical reaction equation:

$$^{230}Th_{diss} \quad \leftrightarrow \quad ^{230}Th_{part}$$
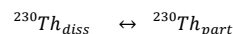
20 The respective analog for the mass action law constant describing to which extent the reaction from left to right is carried out is then given through the k_d value governing the equilibrium between the dissolved and particle bound phases for the radionuclide:

$$k_d = \frac{\left[^{230}Th_{part}\right]}{\left[^{230}Th_{diss}\right]}$$

Often, k_d values are formulated to account for a shift of the equilibrium towards the ~~particle attached~~particle-

25 attached phase at low particle mass concentrations assuming that low particulate concentrations occur in parallel to low particle sizes with correspondingly high reactive surface areas when compared to large particles (e.g. Honeyman et al., ~~(~~1988~~)~~). Respective formulations have been used successfully in ^{230}Th modelling studies (Heinze et al., 2006; Henderson et al., 1999).

30 How would then the distribution of dissolved ^{230}Th in the ocean reflect changes in marine calcification at the sea surface? There are indications, that ^{230}Th is attached first of all to CaCO$_3$ and clay particles in the water column as preferential carrier phases (Chase et al., 2002, 2003; Luo and Ku, 1999, Hayes et al., 2015b). Indeed, Heinze et al. (2006) reproduced the ~~large scale~~large-scale ^{230}Th distribution in the world ocean with a coarse resolution biogeochemical ocean general circulation model based on a formulation allowing ^{230}Th scavenging only by CaCO$_3$

35 and clay particles. Other studies have indicated that preferential carrier phases may vary regionally in the ocean (Scholten et al., 2005). However, Heinze et al. (2006) could demonstrate that rain ratio changes (CaCO$_3$:Corg) in marine biological particle export production could also be recorded, if ^{230}Th became in addition attached to particulate organic carbon (POC). A weakening of CaCO$_3$ particle production would result in a less efficient ^{230}Th scavenging as less particles (in terms of mass) would be available to carry ^{230}Th to larger depths and finally the

3

sediment. Changes in the strength of $CaCO_3$ production and the respective downward particle flux are reflected increasingly better in the ^{230}Th distribution with increasing depth (see Heinze et al., (2006)) due to two reasons. First, $CaCO_3$ particles get less well degraded as POC (which is remineralised mostly in the upper 1000 m of the water column) and thus reach larger depth; this is also corroborated from sediment trap measurements (e.g., (Honjo, 1996)). Second, due to the scavenging of ^{230}Th by particles, the vertical downward particle flux, and the equilibration between dissolved and particle bound phases, ^{230}Th is continuously transferred from shallower layers to larger depths. Thus temporal changes in ^{230}Th scavenging in the upper ocean become enlarged in the deep ^{230}Th distribution as in a kind of "magnifying glass" (see Figure 1). We investigate here, whether this feature can be exploited for an early detection method of ~~large scale~~large-scale reductions in calcification and correspondingly reduced rates in $CaCO_3$ particle export and $CaCO_3$ particle fluxes through the water column.

3 Model description

In this ~~study~~study, we use the Hamburg ocean carbon cycle circulation model HAMOCC (Maier-Reimer, 1993) in its annually averaged version (time step 1 yr, Heinze and Maier-Reimer, (1999); Heinze et al., (2009); Heinze et al., (2016)) with a horizontal resolution of 3.5°x3.5°. This coarse resolution model is computationally very efficient and useful when multiple integrations are needed such as for the testing and adjusting of scavenging codes. An advantage of this fast model ~~is,~~is that it includes a fully equilibrated early diagenesis module (10 layers) under each grid point and thus can account for alkalinity changes induced by dissolution of $CaCO_3$ from the seafloor. The model version employed here corresponds to the version as used in Heinze et al. (2009) and Heinze et al. (2016) with a slightly updated ~~the~~ scavenging module of Heinze et al. (2006) with resepct to the formulation of the equilibrium coefficient governing the distribution of ^{230}Th between the dissolved and particle attached phase (see below). For details, please, see these publications. The model uses a fixed ocean velocity field (and thus provides no dynamical computation of the ocean currents; velocities, temperature, salinity and ice cover are rather read from an input file). The model includes an atmospheric compartment ("slab atmosphere") which allows for prognostic computation of the atmospheric CO_2 concentration as well as meridional atmospheric CO_2 transport. We describe here only briefly features of specific relevance for this study. The water column is structured into 11 layers (centred at 25, 75, 150, 250, 450, 700, 1000, 2000, 3000, 4000, and 5000 m). The bioturbated top sediment zone of the early diagenesis module is divided into 10 layers which are separated by interfaces at 0, 0.3, 0.6, 1.1, 1.6, 2.1, 3.1, 4.1, 5.1, 7.55, and 10 cm ''downcore.'' We make the simplifying assumption that no pore water reactions take place below 10 cm depth in the sediment (see, e.g., Smith and Rabouille, (2002); Boudreau, (1997)). The biogeochemical model includes the processes of air-sea gas exchange, biogenic particle export production out of the ocean surface layer, particle flux through the water column and particle degradation by dissolution as well as ~~remineralization~~remineralisation, transport of dissolved substances with the ocean currents, deposition of particulate constituents on the ocean floor, pore water chemistry and diffusion, advection of solid sediment weight fractions (organic carbon, organic phosphorus, $CaCO_3$, opal, and clay), bioturbation, and sediment accumulation (export out of the sediment mixed layer). The model predicts the following tracer concentrations in the atmosphere, the ocean water column and in the sediments. Atmospheric tracers include the concentrations of ~~$^{12}CO_2$~~ (carbon dioxide)~~, $\delta^{13}CO_2$,~~ and O_2. In the water column, concentrations of DIC (dissolved inorganic carbon), POC (particulate organic carbon), POP (particulate organic phosphorus), DOC (dissolved organic carbon), $CaCO_3$

4

(calcium carbonate or particulate inorganic carbon) ~~all for 12C as well as ¹²C~~, dissolved oxygen O_2, dissolved PO_4^{3-} as biolimiting nutrient, silicic acid $Si(OH)_4$ and opal (biogenic particulate silica BSi) are calculated. In the sediment pore waters, the same dissolved substances as in the water column, as well as solid sediment constituents such as clay, $CaCO_3$, opal, and organic carbon are simulated. The inorganic carbon chemistry is computed following Dickson et al. (2007). In the advection scheme and for the other chemical reactions, DIC and TAlk are used as ''master tracers'' form which derived quantities such as the CO_3^{2-} concentration and the pH value are computed through a Newton-Raphson algorithm. In the annually averaged model as employed in this study, only export production of biogenic particles is modelled (and no explicit phytoplankton and zooplankton concentrations). Particle production takes place in the model surface layer representing the euphotic zone. Phosphate serves as biolimiting nutrient. POC and opal export productions are simulated following Michaelis Menten kinetics for nutrient uptake (e.g., Sarmiento and Gruber, (2006)) (where the phytoplankton concentration is replaced by the phosphate concentration as ecosystem processes as such are not explicitly modelled):

$$P_{POC} = \frac{V_{max}^{POC} \cdot [PO_4^{3-}]^2}{K_s^{POC} + [PO_4^{3-}]} \; ;$$

and

$$P_{opal} = \frac{V_{max}^{opal} \cdot [Si(OH)_4]^2}{K_s^{PopalC} + [Si(OH)_4]} \; ;$$

where P_{POC} and P_{opal} are the POC and opal export production rates (mol l^{-1} yr^{-1}), Red(C:P) is the Redfield ratio C:P, V_{max}^{POC} and V_{max}^{opal} are the maximum uptake rate of phosphate and silicic acid from the water column (yr-1), and K_s^{POC} as well as K_s^{opal} are the respective half saturation constants. V_{max}^{POC}, V_{max}^{opal}, K_s^{POC}, and K_s^{opal} are simulated as a function of sea surface temperature as described by Heinze et al. (2003). POP production follows POC production with a constant stoichiometry here. The export production of $CaCO_3$ is coupled to the local production ratio P_{opal}/P_{POC}. It starts to increase gradually (parameter R see below) if P_{opal}/P_{POC} sinks below a threshold value S_{opal}, i.e., when not enough silicic acid is available in the ocean surface layer to fuel full diatom growth:

$$P_{CaCO3} = P_{POC} \cdot R \cdot a \cdot \left(1 - \frac{\frac{P_{opal}}{P_{POC}}}{S_{opal}} \right) for \; \frac{P_{opal}}{P_{POC}} < S_{opal}; \quad (1)$$

$$P_{CaCO3} = 0 \; for \; \frac{P_{opal}}{P_{POC}} \geq S_{opal} \; .$$

Parameter R is the maximum possible rain ratio C(CaCO$_3$):C(POC), a is the CaCO$_3$ saturation dependent factor to account for an ocean acidification impact (see Figure 2, following Ilyina et al., (2009)), and S$_{opal}$ is the threshold value of P_{opal}/P_{POC} for gradual onset of CaCO$_3$ production. Particle fluxes and particle degradation are simulated through balance equations for sinking particulate matter as in Heinze et al. (2009) and Heinze et al. (2016) taking the saturation state for CaCO$_3$ and biogenic silica into account.

Scavenging of ^{230}Th is simulated according the reversible first-order scavenging reaction (Gehlen et al., 2003; Heinze et al., 2006):

$$\frac{dc_{part}}{dt} = K \cdot [c_{part}^{EQ} - c_{part}]; \quad c_{part}^{EQ} = k_d \cdot c_{diss} \cdot M;$$

c_{part} is the concentration of particle bound ^{230}Th, c_{diss} the concentration of dissolved ^{230}Th, c_{part}^{EQ} the equilibrium concentration of particle bound ^{230}Th. The first-order rate constant K (in [yr^{-1}]) is set here to 10^4 yr^{-1} thus assuming a quasi-instantaneous equilibration. Concentration of suspended particulate material is represented by M. For the partitioning coefficient k_d between the dissolved and particle attached phases of ^{230}Th we follow the formulation of (Honeyman et al., 1988), which accounts implicitly for the changing reactive surfaces of particles with particle size:

$$log_{10}k_d^{first\ guess}k_d = A + B \cdot log_{10}M$$

where M is the particle concentration (here taken in mg particles per ~~liter~~litre) and A as well as B are ~~tunable~~tuneable parameters. In addition to ^{230}Th we carry also ^{231}Pa as well as ^{10}Be in our model (see Heinze et al., (2006)), but focus here on ^{230}Th only. For each of these radionuclides, the preferential carrier phase can be selected in a dedicated switchboard. ~~(the particle masses of the different particle species are then cumulatively summed up for computing the equilibrium between particle attached and dissolved ^{230}Th phases using the respective k_d value).~~ For ^{230}Th scavenging, we used here CaCO$_3$, POC, and clay as carrier phases. With introducing a particle specific scavenging following Hayes et al. (2015b), the final formulation for the scavenging equilibrium coefficient then becomes:

$$k_d = \left(C_{CaCO3} \cdot F_{CaCO3} + C_{POC} \cdot F_{POC} + C_{clay} \cdot F_{clay}\right) \cdot k_d^{first\ guess}$$

Where C and F are the weighting coefficients and fractions of total local particle mass. The A, B, and C values are included in Table 1. Atlantic and Pacific cross sections with the k_d values for the control simulation without CO$_2$ emissions is given in Figure S1 (in the Supplementary Material).

The clay flux is computed according to the modern dust deposition from Mahowald et al. (1999) assuming that respective clay particles are chemically quasi-inert in seawater. Particle bound ^{230}Th phases never get to zero, even if all biogenic particles may get degraded, because at each grid point there is – at least a tiny – dust flux consisting of inert clay. Therefore, particle concentrations as such never go to zero (a minimum concentration could be prescribed, but this was not necessary in our case). Because the Atlantic dust deposition may be overestimated (Gehlen et al., 2003), we assumed for the ^{230}Th scavenging only 25% of the respective clay flux strength in order to avoid too strong scavenging in Atlantic surface waters (see also our sensitivity experiment assuming 100% in comparison below). We allow biological production under sea ice scaled with the local sea ice thickness.

4 Control run, ~~and~~ scenario experiments, and sensitivity experiments

The model was spun-up re-starting from an earlier integration and computed into quasi-equilibrium including the sediment over 40,000 years. The equilibrium coefficient k_d was determined through a visual fit to observations of dissolved ^{230}Th taken from the literature (Bacon and Anderson, 1982; Bacon et al., 1989; Chase et al., 2002; Cochran et al., 1995; Cochran et al., 1987; Colley et al., 1995; Guo et al., 1995; Huh and Beasley, 1987; Moore, 1981; Moran et al., 1997; Moran et al., 1995; Nozaki and Horibe, 1983; Nozaki and Yang, 1987; Nozaki et al., 1987; RoyBarman et al., 1996; Scholten et al., 1995; Vanderloeff and Berger, 1993; Vogler et al., 1998) and combined with the data as given in the GEOTRACES Intermediate Data Product Version 3 (Mawji et al. , (2015)~~;,~~ ~~where especially the southern hemisphere data by Hein de Baar and Edward Boyle have been used~~ Hayes et al.,

2015a,b; Deng et al., 2014). Important global bulk numbers and the parameters for the partitioning coefficient k_d resulting from an optimal linear fit to observed data are listed in Table 1.

Key variable as simulated	unit	Control run value
Atmospheric CO_2 mixing ratio	[ppm]	281.9
POC export production (pre-industrial)	[Gt C yr^{-1}]	9.76
$CaCO_3$ export production (pre-industrial)	[Gt C yr^{-1}]	1.16
Coefficient A for k_d	-	6.39
Coefficient B for k_d	-	0.4

Table 1: Summary of control run results.

Meridional sections of dissolved ^{230}Th concentrations for the Atlantic and Pacific Oceans are given in Figure 3. The vertical distribution clearly shows the increase of concentrations with depth due to the downward transfer of ^{230}Th with the marine particle flux. A comparison of simulated and observed dissolved ^{230}Th values in the water column along a meridional Atlantic cross section (Figure 4) indicates that the model dissolved ^{230}Th is in fairly good agreement with observations regarding vertical distributions of ^{230}Th in selected locations, except for a strong overestimation in some bottom water locations. This could be due to deficiencies in the flow field and corresponding problems or due to the lack of explicit simulations of hydrothermal vents and sediment resuspension. We carried out a respective sensitivity experiment (see discussion further below). A scatter plot of modelled and observed ^{230}Th values and the locations of stations with observed data are shown in Figure 5. The standard-run export production rates for POC and $CaCO_3$ are given as maps in Figure 65.

An overview concerning the model all model simulations is given in Table 2. We carried out a total of 12 different model projections under fourthree different scenarios for changes in calcification (deviating from the including control runs with constant calcification but rising atmospheric CO_2) and four different scenarios of the future development of the atmospheric CO_2 concentration (C8.5-2.6, L8.5-2.6, M8.5-2.6, and E8.5-2.6, see Table 2). All scenarios were restarted from the same previously performed spin-up model run reflecting a preindustrial biogeochemical state of the ocean. Throughout the experiments, the ocean circulation field was not changed. The model was integrated during the calendar years 12700-2300 spanning a the time period of 11600 years. In the model spin-up simulation, the atmospheric CO_2 concentration was a prognostic variable. For the computations from 1700 onwards, we prescribed the atmospheric CO_2 concentration according to the Representative Concentration Pathways (RCPs) including their extension to year 2300 (van Vuuren et al., 2011) as used in CMIP5 (Coupled Model Intercomparison Project Phase 5). Our simulations follow scenarios RCP 2.6, RCP 4.5, RCP 6.0, and RCP8.5 designed to spanning a range of radiative forcing between 2.6 and 8.5 W/m^2 by the year 2100. The respective atmospheric CO_2 concentrations are shown in Figure S26. For the decrease in calcification with decreasing pH as well as carbonate saturation, functional relationships between $CaCO_3$ export production and carbonate saturation were chosen which correspond to the respective experiments in Ilyina et al. (2009). For each RCP, we carried out a control simulation with constant calcification, a moderate decrease of $CaCO_3$ production with decreasing saturation, a linear dependency simulation with respectively stronger decrease in $CaCO_3$ production) and an extreme scenario (Figure 2). To date, no clear bulk formulation for the dependency of $CaCO_3$ export on $CaCO_3$ saturation exists. Therefore, the scenarios carried out here are only sensitivity experiments and

not overall exhaustive simulations in order to reproduce the entire range of possible changes in ocean biogeochemistry.

As an indication for the robustness of our results, a suite of sensitivity experiments was carried out. In a first set of sensitivity experiments (P1-P5, Table 2), we investigated how much the preindustrial control simulation depends on selected parameter choices. In P1, parameter A for $k_d^{\text{first guess}}$ was slightly increased from 5.8 to 6.0 in order to test the dependency of the result from small changes in the still not very precisely know k_d value for ^{230}Th. The effect of release of material from hydrothermal vents and resuspension of material from the sediments, we carried out experiment P2 with a strong increase in scavenging in the lower most wet model grid cells (directly over the ocean floor). To this end, parameter A for $k_d^{\text{first guess}}$ was increased by 0.5 units in these grid boxes. In our general reference run P0 we applied scavenging to clay, as if the clay flux would only be 25% of its prescribed value. Therefore, we added also run P3, where 100% clay flux was assumed also for the ^{230}Th scavenging. Finally, in experiments P4 and P5, we switched off the scavenging to POC and $CaCO_3$ respectively in order to see the importance of these two biogenic particle species on the ^{230}Th distribution.

In a second set of sensitivity experiments, we tested how sensitive the future projection of dissolved ^{230}Th is in view of other factors than changes in $CaCO_3$ production (S1-S5, see Table 2). Because we use an annually averaged model without seasonal cycle and also employed fixed annul mean velocity field, we have to use approximations in order to see the effect of a change in the velocity field or other changes involving interannual/decadal variability. We use here the time series of the Atlantic Meridional Overturning from the fully fledged Earth system model NorESM for a historic ramp-up and subsequent RCP8.5 forcing (Tjiputra et al., 2016; see Figure 2 therein). In experiment S1, we scaled the three-dimensional velocity field (and also the convective mixing representation) of our simplified model with this time series, leading to an overall reduction in circulation strength. The formulation for this scaling is:

$$Y^{scaled} = (1 + \Delta Overturning(t)) \cdot Y^{reference}$$

with Y being a scalar variable (such as the velocity components in the x-, y-, and, z-directions, the convective adjustment, or other specific biogeochemical parameters), Y^{scaled} the value as updated for the sensitivity experiments, $Y^{reference}$ the original value as used in the reference run, and $\Delta Overturning$ the relative change in Atlantic meridional overturning between a specific year after year 1850 and year 1850 itself ($\Delta Overturning$ would be zero until 1850). Using this scaling, we also investigated separately from a circulation change the consequences of variations in the maximum nutrient uptake velocity V_{max} in our simple trophic model (a reduction in V_{max} could be seen as a deterioration of growth conditions for plankton under climate change) (run S2), and in the sinking velocity of particles (corresponding to, e.g., a loss in ballast material) (run S3). In experiments S4 and S5 finally, the simultaneous effects of changes in the circulation, V_{max}, and the particle sinking velocity were explored for the moderate (S4) and the extreme (S5) calcification scenarios. The list of potential factors with an influence on ^{230}Th is much longer, however, our choice of factors covers at least the physical forcing through the velocity field, surface biogeochemistry through V_{max}, and three-dimensional biogeochemistry through the particle sinking speed.

5 Results and discussion

The results from the sensitivity experiments relative to the preindustrial control run are summarised in Figure 7. Increasing the scavenging equilibrium coefficient in general (run P1, Figure 7a-b) or over the ocean bottom (run P2, Figure 7c-d) corrects to a substantial degree the too high bottom water vales for dissolved ^{230}Th in the southern Atlantic, but leads to high relative errors in the upper few hundred meters (where ^{230}Th concentrations are generally

5   low). Too low upper ocean ^{230}Th concentrations occur also for increasing the scavenging to 100% of the clay flux (run P3, Figure 7 e-f). Omitting, the scavenging to POC has only minor influence on the ^{230}Th distribution because of the relatively shallow recycling of POC (run P4, Figure 7g-h). In contrast, cancelling the scavenging to $CaCO_3$ (and only retaining that to POC and clay) leads to a completely unrealistic dissolved ^{230}Th distribution with at least a fivefold overestimation (run P5, Figure 7i-j; note change of colour code in Figure 7i-j). These results demonstrate

10   that the choice of critical parameters for our preindustrial reference simulation (run P0) results in a reasonable dissolved ^{230}Th distribution. The crucial role of $CaCO_3$ particles for determining water column ^{230}Th has been confirmed.

We discuss now the results for the projections. According to the various scenarios applied, considerable changes

15   in surface alkalinity (not shown) and corresponding changes in $CaCO_3$ export production evolve at high CO_2 (Figure 87). The effect is on the average larger in the Pacific than in the Atlantic due to the overall higher modelled biological production rates of $CaCO_3$ in the Pacific Ocean. The extreme calcification scenario would lead to vastly reduced $CaCO_3$ export production after year 2100 in all RCPs except the most moderate RCP2.6 where even a partial recovery occurs.

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For dissolved ^{230}Th, we show here time series for depth levels 700 m, 2000 m, and 4000 m (Figures S38, 99, and S410, respectively). According to recent intercalibration experiments, still sizable discrepancies exist between the absolute values in ^{230}Th measurements from different laboratories, though these measurements show a smaller scatter for replicates within a single laboratory. Intercalibration experiments reveal a standard deviation for

25   measurements on one sample by different laboratories of about 0.07-0.08 dpm/1000l (Anderson et al., 2012). We take 0.075 dpm/1000l as an approximate indicative value for the detection level for changes in dissolved ^{230}Th concentrations in seawater in (Figures S3, 9, and S48 10;, see orange lines therein). This may be a somewhat optimistic estimate for samples of past decades, but future developments of measuring techniques could possibly reduce measurement errors and the spread across analyses from different laboratories and application of different

30   measurement methods. The detection level is shown here relative to the modelled preindustrial values. The time of emergence as indicated by the orange line in Figures S3, 9, and S48 10 is, therefore, the earliest possible time of detection if preindustrial ^{230}Th would be known. Figures S3, 9, and S48 10 show the increase of dissolved ^{230}Th activities with depth from 700 m (Figure S38), over 2000 m (Figure 9) to finally 4000 m (Figure S410). At 700 m the increase in ^{230}Th activities due to the assumed ocean acidification effect is too small to unambiguously show

35   an effect for RCP2.6 (Figure S38). This picture changes when going down to 2000 m and below, where an effect would be detectable within this century at least for the stronger forcing scenarios RTCP8.5 and RCP6.0 (Figures 9 and S4). At 4000 m depth finally, the effect would be measurable quite soon for all RCPs and a moderate impact of ocean acidification on the calcification (Figure 10). For constant $CaCO_3$ production, the intermediate and deep waterdeep-water ^{230}Th activities start to rise around year 2100 as well (see black curves in Figures S3, 9, and S48

40   10). This effect is due to the increasing dissolution of $CaCO_3$ particles in the water column in parallel with

downward mixing of waters that carry anthropogenic loads of dissolved organic carbon and hence subsurface and deep acidification. The effect is most important in areas, where anthropogenic carbon is mixed down quickly and induces a significant shoaling of the $CaCO_3$ saturation level and $CaCO_3$ lysocline as well the Carbonate Compensation Depth through deep-water acidification. Parts of the deep Pacific are not as much influenced by this as compared to the Atlantic within the 21st century. The control run in the figures does not represent the reference run with constant preindustrial atmospheric pCO_2 but the run with constant $CaCO_3$ production and rising pCO_2 according to the RCP scenarios.

In order to look for most suitable regions for detection of ocean acidification effects on $CaCO_3$ particle fluxes using modern [230]Th data, we plotted the year of emergence for different reference years and different assumed detection levels (Figures 10[1 and 12]). The year of emergence is defined here as the earliest possible year of a potential detection in case that the [230]Th signal (rate of change over time) is only influenced by a decrease in calcification and not any other processes (such as potential shifts in circulation and associated changes in biological particle production). We choose 2010[two different pairs of] as reference year[s], to which the [230]Th activity at a later stage would be compared to[.,] and 0.075 dpm/1000l as [two different] limit[s] for the detection of a signal. For the moderate calcification scenario, the time of emergence at least at 4000 m would be comparable to the time of emergence as potentially inferable through repeat surface alkalinity measurements (Ilyina et al., 2009) (Figure 10a-b). For the extreme scenario the signal would be identifiable considerably earlier. The signal emerges earliest in deep Pacific waters. [: (1) Year 2000 and 0.075 dpm/1000l and (2) year 2020 and 0.0325 dpm/1000l. Case (1) should reflect high quality observations of the first decade of the 21th century while case (2) should reflect hopefully further increased precision in the measurements in the few years to come next. We first looked at these two cases for the moderate calcification scenario (Figure 11). The deeper one goes down in the water column the younger the year of emergence becomes. For case (1) with reference year 2000 and detection limit 0.075 dpm/1000l earliest years would be around 20 years from now at 4000 m depth in the North Pacific (Figure 11 a,b). For case (2) even some earlier thresholds would occur where the shorter difference to the reference year would be more than made up by a higher precision of the measurements (Figure 11 c,d).]

[For the extreme calcification impact scenario, earlier strong changes in calcification and [230]Th activity occur and suitable detection limits would be available over large parts of the Pacific Ocean and in general at southern high latitudes latest by year 2025 for case (1) (Figure 12 a,b). For newer measurements to come (reference year 2020 and detection limit 0.0325 dpm/1000l, case (2)), the earliest years of emergence are a bit later than for case (1) in contrast to the situation for the moderate calcification scenario. This behaviour can be explained by the lower baseline level for $CaCO_3$ production at year 2020 where it is already strongly reduced as compared to the preindustrial values. But still large parts of the Pacific Ocean would have an earlier detection level than 2025.]

The results on the early warning indicator as shown in Figure 10 are based on the simplifying assumption, that only changes in calcification caused by ocean acidification influence the water column [230]Th concentrations under progressing acidification and climate forcing. We, therefore, also mimicked the effect of interannual/decadal variability in circulation and biogeochemical parameters (run S1-S5, Table 2). Comparing the projections under RCP8.5 and the moderate calcification scenario for the case without interannual/decadal variability (run M8.5,

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Table 2) with the one including variability (run S1-3, Table 2) for the middle of this century reveals differences in the order of the assumed detection level for changes in the velocity field and the particle sinking velocity and smaller changes for varying V_{max} (Figure 11a-f). The effect on modulating water column ^{230}Th can be quite variable for different oceanic domains. Deviations can add-up or compensate each other locally. For simultaneous changes of circulation, V_{max}, and particle sinking velocity, the overall deviations from the run without variability amount to 2-3 times the theoretical detection limit (Figure 11g-h). We repeated the analysis of the time of emergence with the runs including interannual variability for the moderate (S4) and also the extreme (S5) scenario. For this analysis, we again chose 2010 as the reference year but increased the detection limit to 2.5*0.075 dpm/1000l. Under these more realistic conditions, the time of emergence would be shifted to the end of the century for the moderate calcification scenario and to the middle of the century for the extreme scenario (Figure 12).

The question arises, whether surface alkalinity and deep ^{230}Th measurements possibly could be combined successfully in order to detect ocean acidification impacts on calcification. We could, so far, not detect any simple relationship between surface changes in $CaCO_3$ export production, surface alkalinity, and ^{230}Th in spite of the conceptually clear interdependencies. In order to illustrate this, we plotted changes in surface alkalinity and 3000 m ^{230}Th over time for the run with moderate calcification scenario and RCP8.5 forcing between 2040 and 2010. The distributions show a somewhat consistent picture without interannual/decadal variability (run M8.5, Figure 13a-b) with general rises in both surface alkalinity and deep ^{230}Th. For the case including interannual/decadal variability (run S4, Figure 13c-d) the temporal gradients in both variables become smaller and the deep ^{230}Th even may reverse. This does not mean that it would be impossible to construct a combined Alk-^{230}Th tracer, only that such a tracer cannot be derived from this study..

As compared to the detection approach for ocean acidification impacts through total alkalinity measurements as pursued by Ilyina et al. (2009), the ^{230}Th method presented here results in similar time of emergence of a signal reflecting changes in biocalcification if one omits interannual/decadal variability and other possible influence factors. While for alkalinity, surface measurements would primarily be involved, for ^{230}Th one would use deep ocean measurements. For very deep depth levels below 4000 m and very high precision measurements of ^{230}Th one could presumably shorten the time of emergence. Possibly, for the deep measurements some averaging effect over the water column would occur and results from a few stations may be representative for a larger area. The deep Pacific Ocean and to some degree the deep Southern Ocean look as the best areas for detecting ocean acidification impacts through ^{230}Th. The dust deposition onto the Atlantic Ocean surface originating from mobilisation in the Saharan desert – and the hence strong clay particle flux – blur the imprint of ocean acidification induced changes in $CaCO_3$ flux onto ^{230}Th.

The probably most important limitation of the approach here is the fixed velocity field which does not vary realistically with seasons, interannual variability, climatic variability modes (such as El Niño Southern Oscillation or North Atlantic Oscillation). In reality, the distribution of ^{230}Th depends also on variations in the flow field and resulting changes in nutrient availability, and consequently changes in particle production as well as flux. Also the effect of boundary scavenging (Anderson et al., 1983; Roy-Barman et al., 2009), i.e. the transport of dissolved ^{230}Th from areas of low particle concentrations to those with high particle concentrations (especially at ocean

margins at shelf seas) is not spatially resolved in our model. ~~Our results concerning the time of emergence may, therefore, be somewhat optimistic. On the other hand, given a larger amount of vertical observed ^{230}Th profiles, still a common effect due to reduced CaCO$_3$ production should be detectable through statistical analysis even in the presence of shorter term natural variability in circulation and particle fluxes.~~ Further uncertainties are associated with the choice of the k$_d$ values and particle specific reactivity. ~~Concerning the latter, another study did not reveal a substantial change in results, if different combinations of particle specific scavenging were applied in the model (Heinze et al., 2006).~~

The extreme scenario on pH-dependent CaCO$_3$ production is likely to be an overestimation. According to the results from this study and Ilyina et al. (2009) a respective large change in the real world would probably have been detected through the alkalinity signal and other methods such as remote sensing and sediment trap measurements already. ~~Also~~In addition, the reaction of CaCO$_3$ shell producing organisms to sinking carbonate saturation levels is not a simple function and can vary between taxa (Kroeker et al., 2013).

The detection method for ocean acidification impacts through ^{230}Th would work best, if the preindustrial values for dissolved oceanic ^{230}Th activities could reliably be reconstructed. From core top samples and ~~corals~~corals, one could possibly determine whether the particle attached ^{230}Th activities and hence those of the dissolved fraction would have undergone any variations over the last centuries and millennia. However, the overall uncertainties associated with the formation and analysis of the paleo-record values may be too high to provide an accurate enough baseline for comparisons with modern water column measurements.

6 Conclusions

In this study, we investigated the potential of the particle reactive radionuclide ^{230}Th for detection of reduced calcification by biota due to progressing ocean acidification. The time of emergence of a dissolved ^{230}Th activity signal with respect to a reference year and reference activity is about the same as for detection approaches employing alkalinity if one disregards effects of interannual/decadal variability in the flow field and other influence factors than ocean acidification induced changes in CaCO$_3$ export production. Taking into account interannual/decadal variability including ocean circulation changes may delay the signal emergence by several decades. Nevertheless, regular selected reoccupations of a series of deep stations in the Pacific Ocean and Southern Ocean with highest quality ^{230}Th measurements would be helpful to accompany alkalinity measurements that are easier to do in order to see whether both tracers give consistent results. Surface alkalinity measurements include signals of natural variability on seasonal and multiyear scales. Likewise, changes in ocean circulation and changes in biological particle production due to other processes than ocean acidification may lead to changes in the marine ^{230}Th distribution (and alkalinity). As the deep ocean is less prone to effects of natural variability and the quality of observations does not change with depth, deep ocean observations of ^{230}Th could be advantageous for monitoring and detecting ocean acidification effects on calcification. ~~Furthermore, substantial improvements in the overall precision of water column ^{230}Th measurements could potentially lead to earlier detection years than using alkalinity measurements.~~ In any case, ^{230}Th represents a fascinating magnifying glass for changes in ocean surface processes seen through the deep ocean signal. Its potential has not yet been fully exploited.

12

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Tables:

Key variable as simulated	unit	Control run value
Atmospheric CO_2 mixing ratio	[ppm]	277.6
POC export production (pre-industrial)	[Gt C yr^{-1}]	9.25
$CaCO_3$ export production (pre-industrial)	[Gt C yr^{-1}]	1.07
Coefficient A for $k_d^{first\ guess}$	-	5.8
Coefficient B for $k_d^{first\ guess}$	-	0.4
Coefficient C_{CaCO3}	-	3.0
Coefficient C_{POC}	-	0.3
Coefficient C_{clay}	-	2.3

Table 1: Summary of control run results (run P0, see Table2).

Name	CO_2-scenario	Calcification Scenario	Sensitivity experiment description
P0	Preindustrial	Constant	Pre-industrial control run, all variables in quasi-equilibrium
P1	Preindustrial	Constant	Coefficient A for $k_d^{first\ guess}$ increased from 5.8 to 6.0
P2	Preindustrial	Constant	Coefficient A for $k_d^{first\ guess}$ increased by 0.5 in bottom grid cells
P3	Preindustrial	Constant	Clay flux increased from 25% to 100% dust input
P4	Preindustrial	Constant	No scavenging to POC
P5	Preindustrial	Constant	No scavenging to $CaCO_3$
C8.5	RCP8.5	Constant	RCP8.5 control, only change is atmospheric CO_2
C6.0	RCP6.0	Constant	RCP6.0 control, only change is atmospheric CO_2
C4.5	RCP4.5	Constant	RCP4.5 control, only change is atmospheric CO_2
C2.6	RCP2.6	Constant	RCP2.6 control, only change is atmospheric CO_2
L8.5	RCP8.5	Linear	Calcification reduction
L6.0	RCP6.0	Linear	Calcification reduction
L4.5	RCP4.5	Linear	Calcification reduction
L2.6	RCP2.6	Linear	Calcification reduction
M8.5	RCP8.5	Moderate	Calcification reduction
M6.0	RCP6.0	Moderate	Calcification reduction
M4.5	RCP4.5	Moderate	Calcification reduction
M2.6	RCP2.6	Moderate	Calcification reduction
E8.5	RCP8.5	Extreme	Calcification reduction
E6.0	RCP6.0	Extreme	Calcification reduction
E4.5	RCP4.5	Extreme	Calcification reduction
E2.6	RCP2.6	Extreme	Calcification reduction
S1	RCP8.5	Moderate	As M8.5, but overturning reduced with rising CO_2
S2	RCP8.5	Moderate	As M8.5, but V_{max} for nutrient uptake reduced with rising CO_2
S3	RCP8.5	Moderate	As M8.5, but particle sinking velocity reduced with rising CO_2
S4	RCP8.5	Moderate	As M8.5, but changes as in S1M8.5, S2M8.5, S3M8.5 together
S5	RCP8.5	Extreme	As E8.5, but changes as in S1M8.5, S2M8.5, S3M8.5 together

Table 2: Model runs overview.

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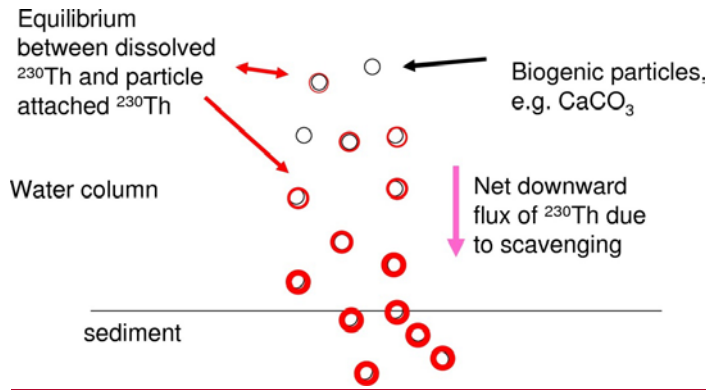
Figures:

Figure 1: Schematic illustration of the equilibration process between the dissolved and particle-attached phases of ^{230}Th and the increasing concentrations downward in the water column.
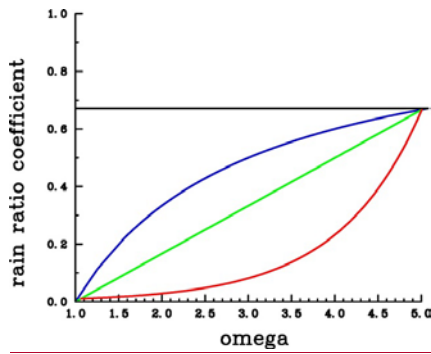
Figure 2: Assumed sensitivities of CaCO$_3$ export production in response to changes in calcite saturation. The rain ratio coefficient is used as factor "a" applied to the right hand side of the equation for CaCO$_3$ production (see eq. 1). For the control run, "a" was fixed at each grid point according to the prevailing pre-industrial carbonate saturation (following the moderate sensitivity). Blue: Moderate sensitivity. Green: Linear sensitivity. Red: Extreme sensitivity. The shape of the curves would look similar at each grid point; only the pre-industrial cross-over point would be different.

18
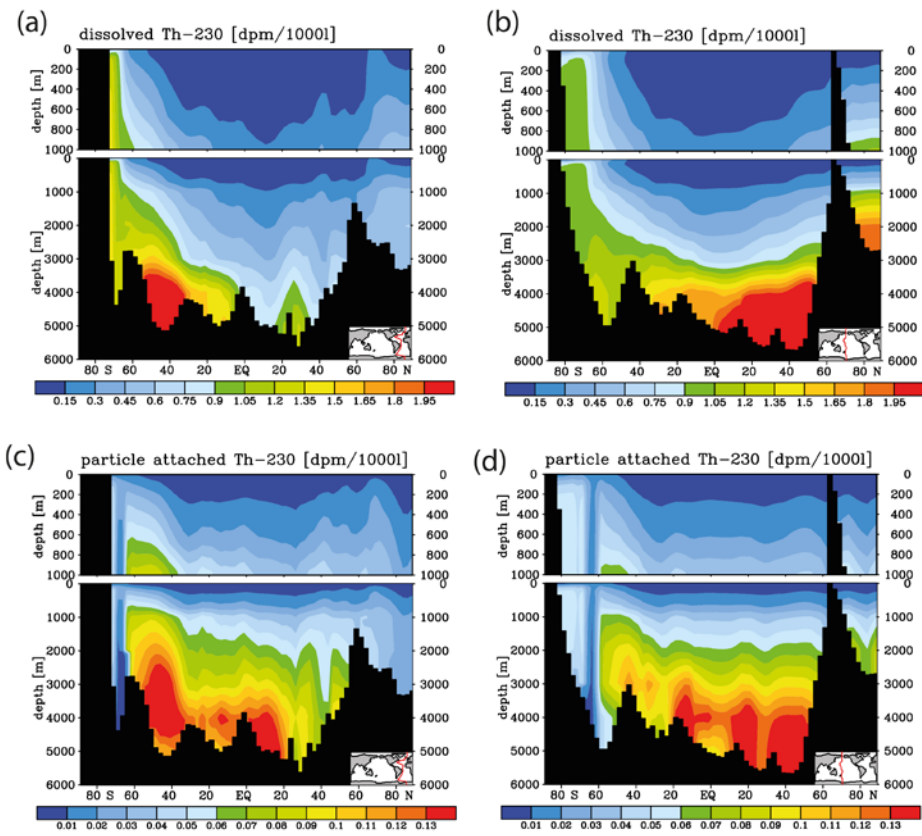
Figure 3: Meridional [230]Th cross sections in [dpm/1000l] (dpm = disintegration per minute) for the model control run under pre-industrial atmospheric CO_2. (a) Dissolved, Atlantic. (b) Dissolved, Pacific. (c) Particle attached, Atlantic. (d) Particle attached, Pacific.
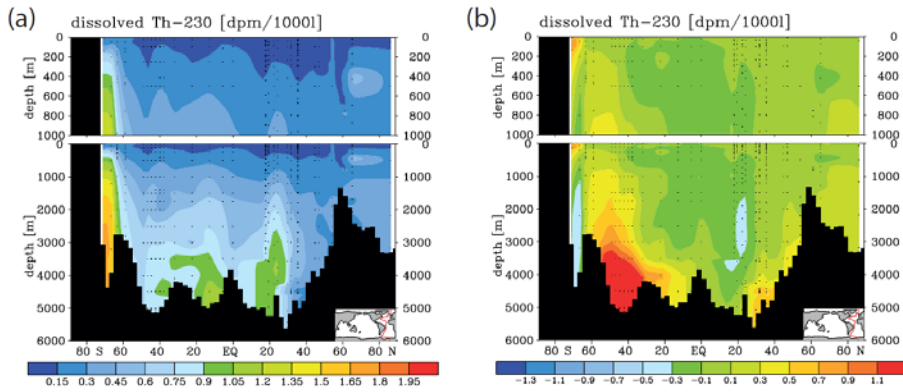
Figure 4: Meridional dissolved [230]Th Atlantic Ocean cross section in [dpm/1000l] (dpm = disintegration per minute): (a) Interpolation from observations (data from the GEOTRACES intermediate data product; for references, please see text). (b) Difference between the model values from the control run without CO_2 emissions and the observations.
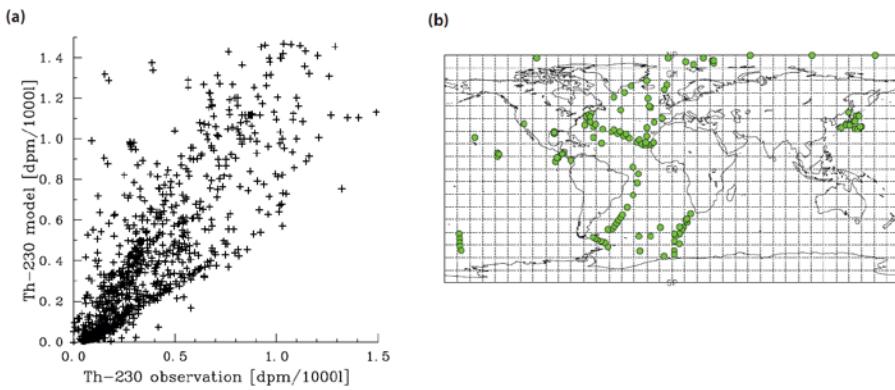
Figure 5: Comparison of dissolved [230]Th model results with observations (for references of observations see text). (a) Correlation between observations and modelled values. (b) Location of all vertical profiles as used in this work.
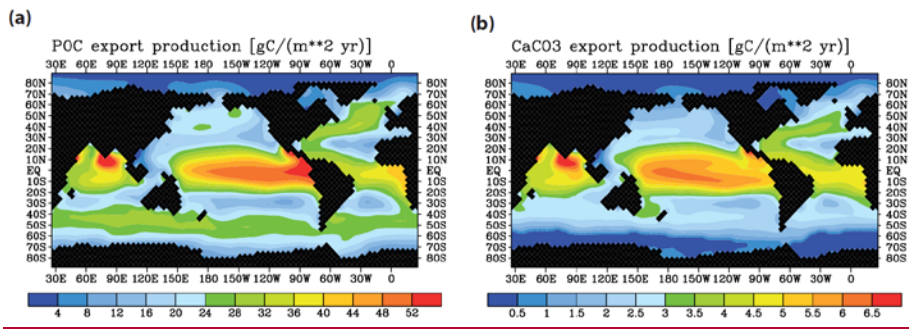
Figure 6: Model control run results for (a) biological export production of particulate organic carbon and (b) CaCO$_3$ export.

22

23

Figure 8: Temporal evolution of Atlantic (left column) and Pacific (right column) annual mean CaCO$_3$ export production under the different scenarios for the sensitivity of calcification under high CO$_2$ (unit: GtC yr^{-1}). From top to bottom for greenhouse gas scenarios RCP8.5. RCP 6.0, RCP4.5, and RCP2.6.
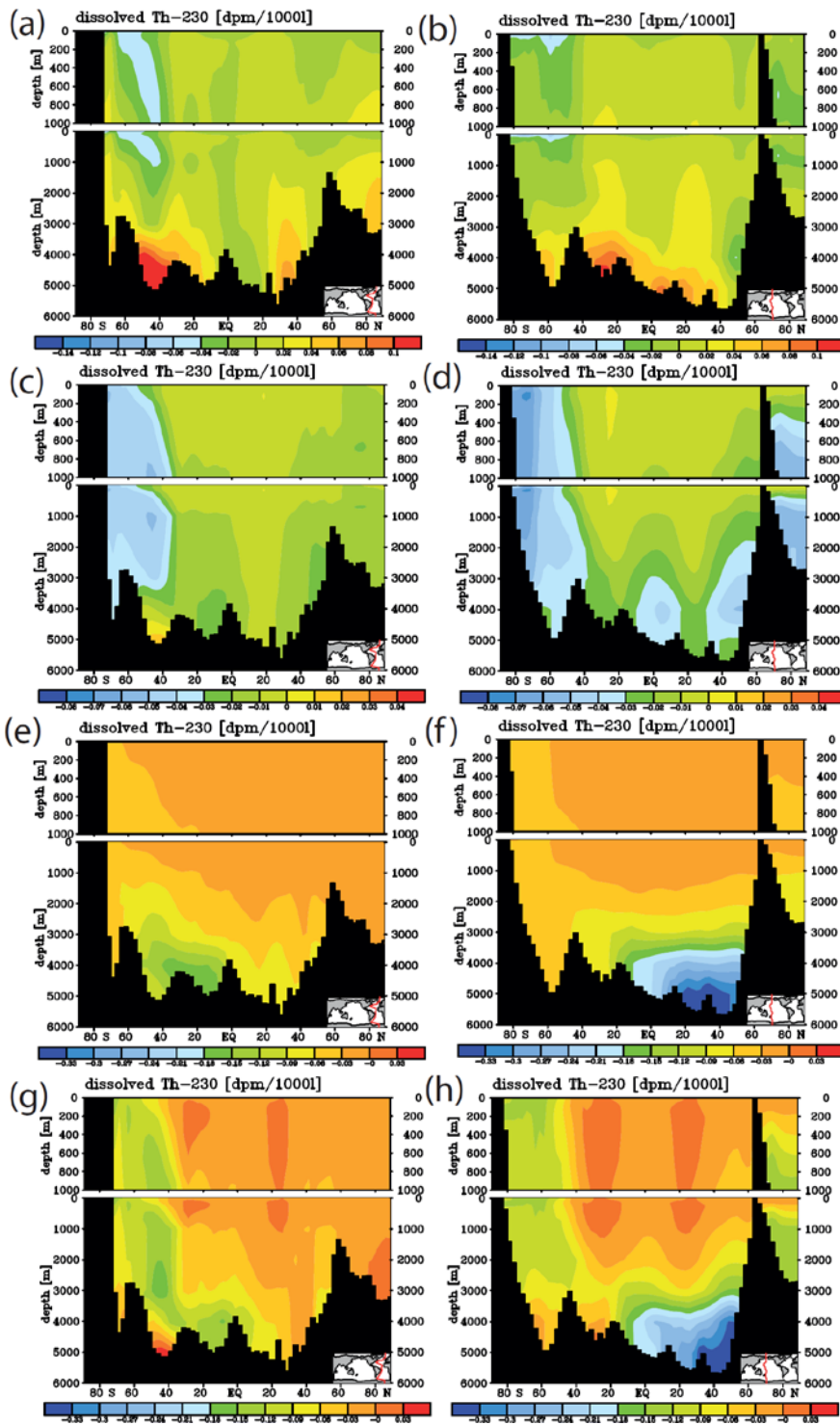
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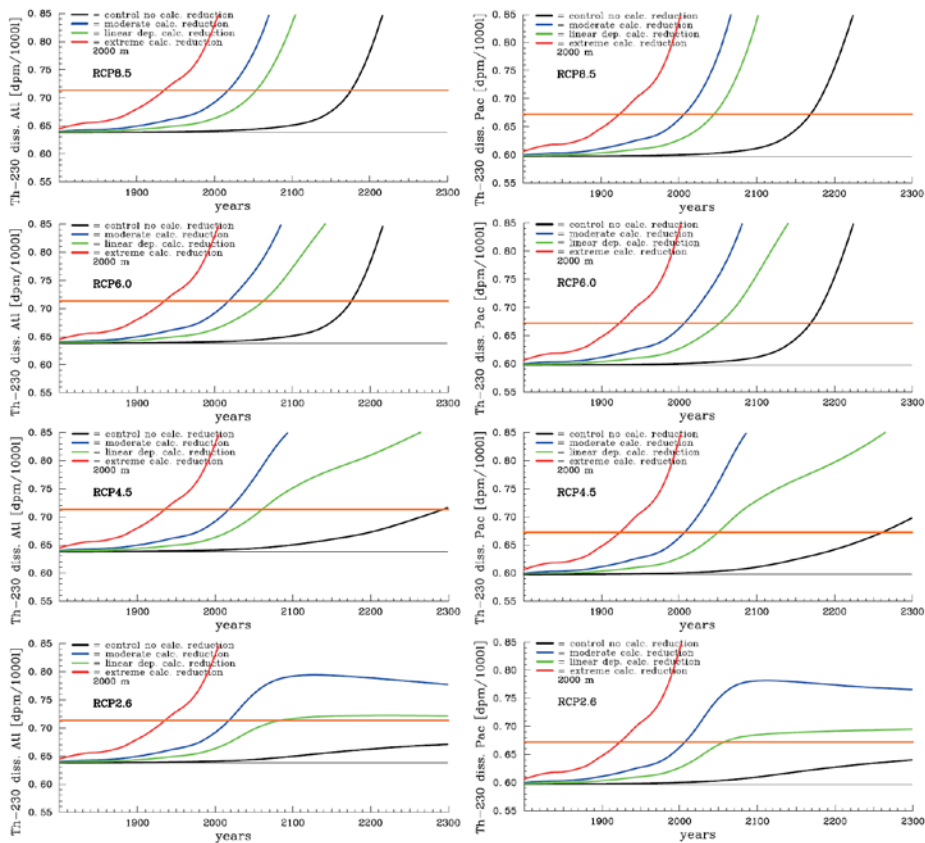
Figure 9: Time series for the evolution of mean Atlantic (left column) and Pacific (right column) dissolved ^{230}Th concentrations at 2000 m under the different scenarios for reduction of calcification under high CO_2 (unit: dpm/1000l). From top to bottom for greenhouse gas scenarios RCP8.5. RCP 6.0, RCP4.5, and RCP2.6. The orange line indicates the theoretical detection limit for changes with respect with respect to the pre-industrial. (Respective diagrams for depth levels 700 m and 4000 m are given in Figures S3 and S4.)
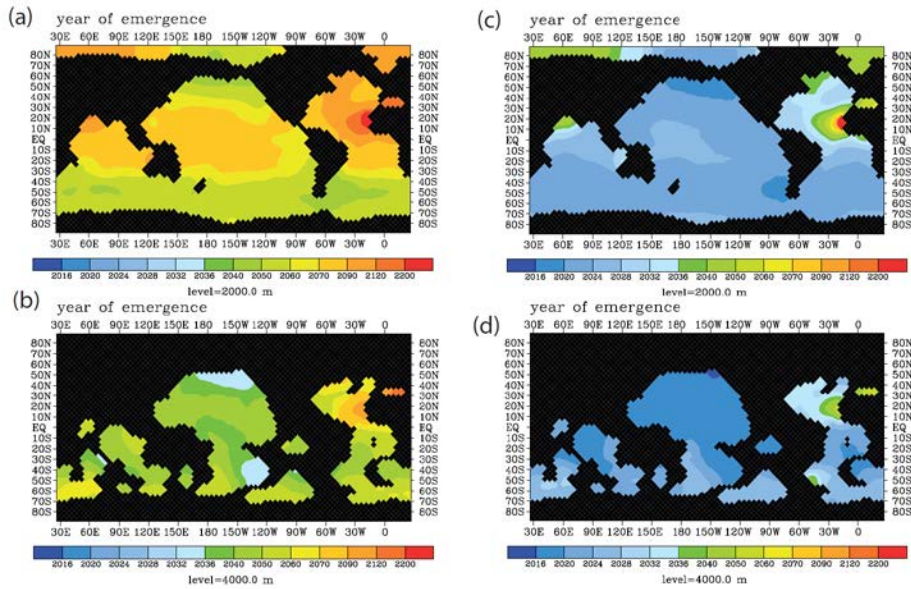
Figure 10: Prospective year of emergence for an ocean acidification induced signal in dissolved [230]Th activity as derived from the model runs. Shown are the calendar years of emergence for the depth levels 2000m and 4000m. All figures are shown for the strong RCP8.5 scenario concerning atmospheric CO_2 concentration and the moderate scenario of calcification decrease with saturation state, year 2010 as reference year for [230]Th activity and 0.075 dpm/1000l as analytical threshold between different samples. (a) For the moderate calcification scenario, at 2000 m depth. (b) Same as (a) but for depth level 4000 m. (c) For the extreme calcification scenario, at 2000 m depth. (d) Same as (c) but for depth level 4000 m.

(a) dissolved Th-230 [dpm/1001]
(b) dissolved Th-230 [dpm/1001]
(c) dissolved Th-230 [dpm/1001]
(d) dissolved Th-230 [dpm/1001]
(e) dissolved Th-230 [dpm/1001]
(f) dissolved Th-230 [dpm/1001]
(g) dissolved Th-230 [dpm/1001]
(h) dissolved Th-230 [dpm/1001]

Figure 11: Meridional cross sections for sensitivity experiments concerning the projections including a representation of interannual/decadal variability. Shown are differences in dissolved [230]Th for forcing relative to the normal run with RCP8.5 and the moderate calcification scenario for year 2050. (a) Change in velocity field (for details see text). (b) As (a) but for the Pacific. (c) Change of V_{max} for phosphate uptake (for details see text), Atlantic. (d) As (c) but for the Pacific. (e) Change of the sinking velocity of particulate matter (for details see text). (f) As (e) but for the Pacific. (g) Simultaneous change of velocity field, V_{max}, and sinking velocity.
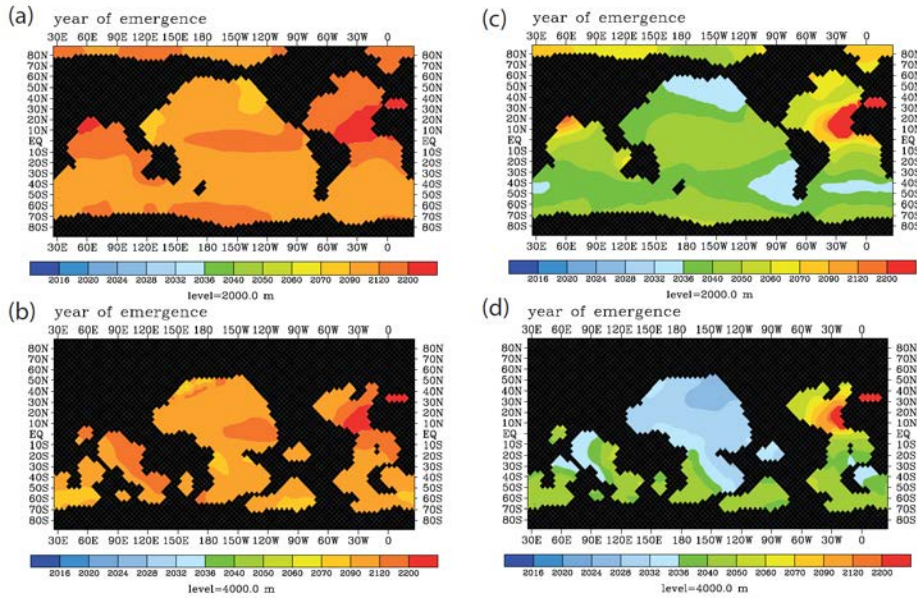
Figure 12: Prospective year of emergence for an ocean acidification induced signal in dissolved ^{230}Th activity as derived from the model runs. Shown are the calendar years of emergence for the depth levels 2000m and 4000m. All figures are shown for the strong RCP8.5 scenario concerning atmospheric CO_2 concentration and the moderate scenario of calcification decrease with saturation state, year 2010 as reference year for ^{230}Th activity and 2.5·0.075 dpm/1000l as analytical threshold between different samples. In contrast to Figure 11, here an analysis including interannual/decadal variability in selected biogeochemical parameters is shown. (a) For the moderate calcification scenario, at 2000 m depth. (b) Same as (a) but for depth level 4000 m. (c) For the extreme calcification scenario, at 2000 m depth. (d) Same as (c) but for depth level 4000 m.
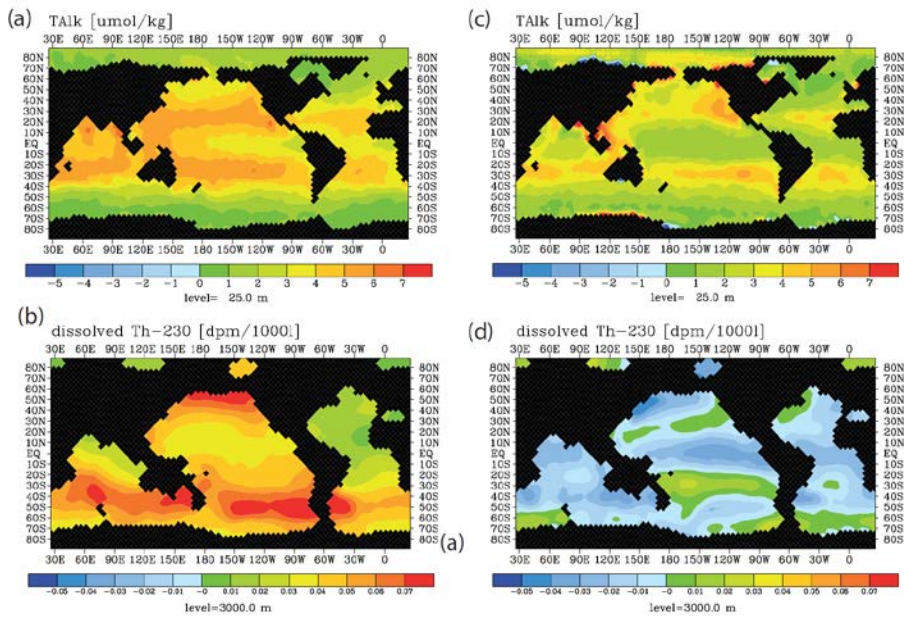
Figure 13: Surface alkalinity changes and deep ^{230}Th changes during 2040-2010 as for the RCP8.5 projection using moderate calcification changes. Left column without variability, (a) at the sea surface, (b) at 3000 m. Right column with decadal parameter variability, (c) at the sea surface, (b) at 3000 m.
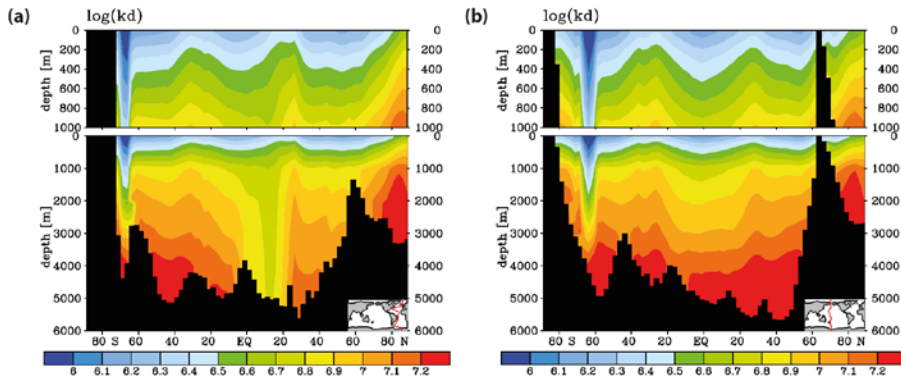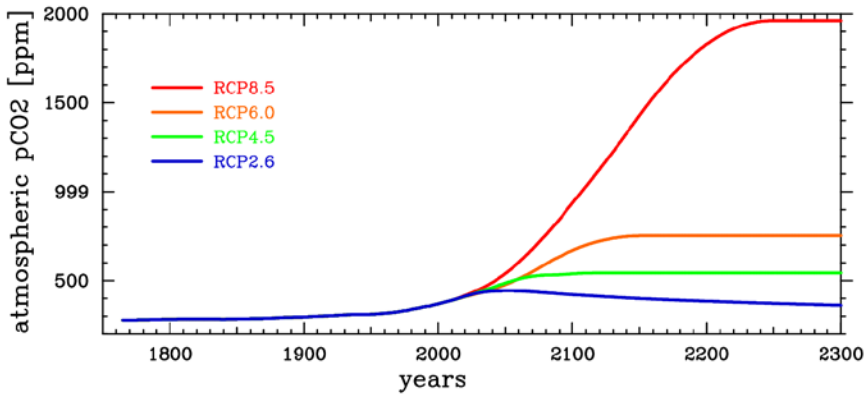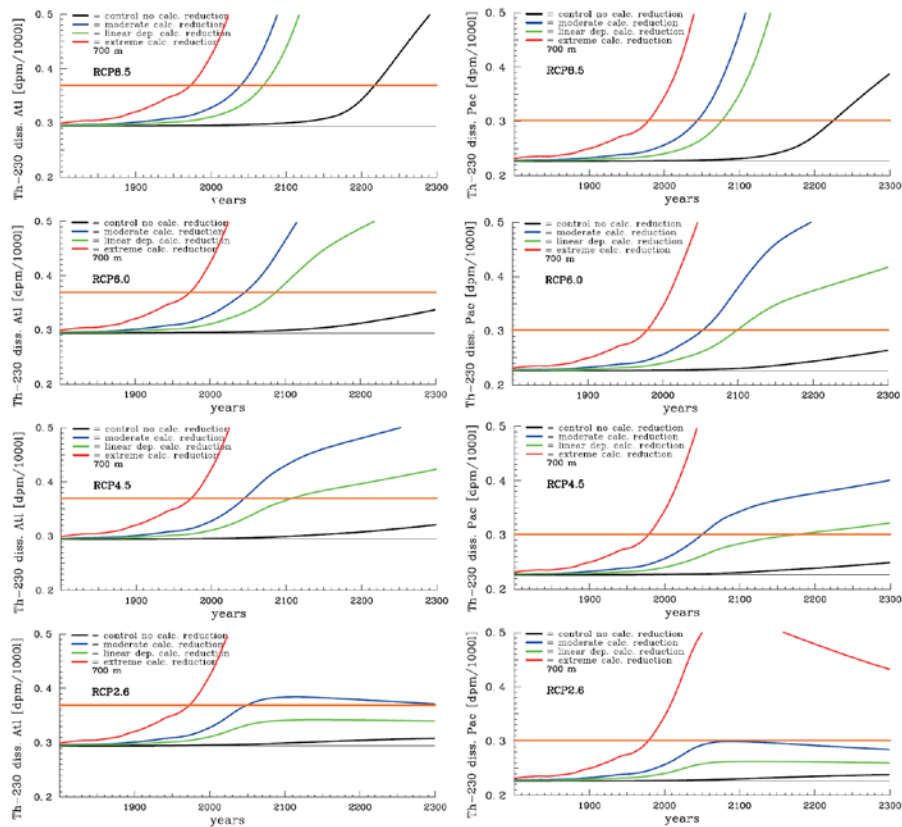
Supplementary Material:

Figure S1: Meridional cross sections of the scavenging equilibrium coefficient k_d as used for the control runs and the standard future scenarios. (a) Atlantic. (b) Pacific.


Figure S2: CO_2 concentrations according to the Representative Concentration Pathways (RCPs, van Vuuren et al., 2011) as prescribed in the predictive model runs.

Figure S3: Time series for the evolution of mean Atlantic (left column) and Pacific (right column) dissolved ^{230}Th concentrations at 700 m under the different scenarios for reduction of calcification under high CO_2 (unit: dpm/1000l). From top to bottom for greenhouse gas scenarios RCP8.5. RCP 6.0, RCP4.5, and RCP2.6. The orange line indicates the theoretical detection limit for changes with respect with respect to the pre-industrial.
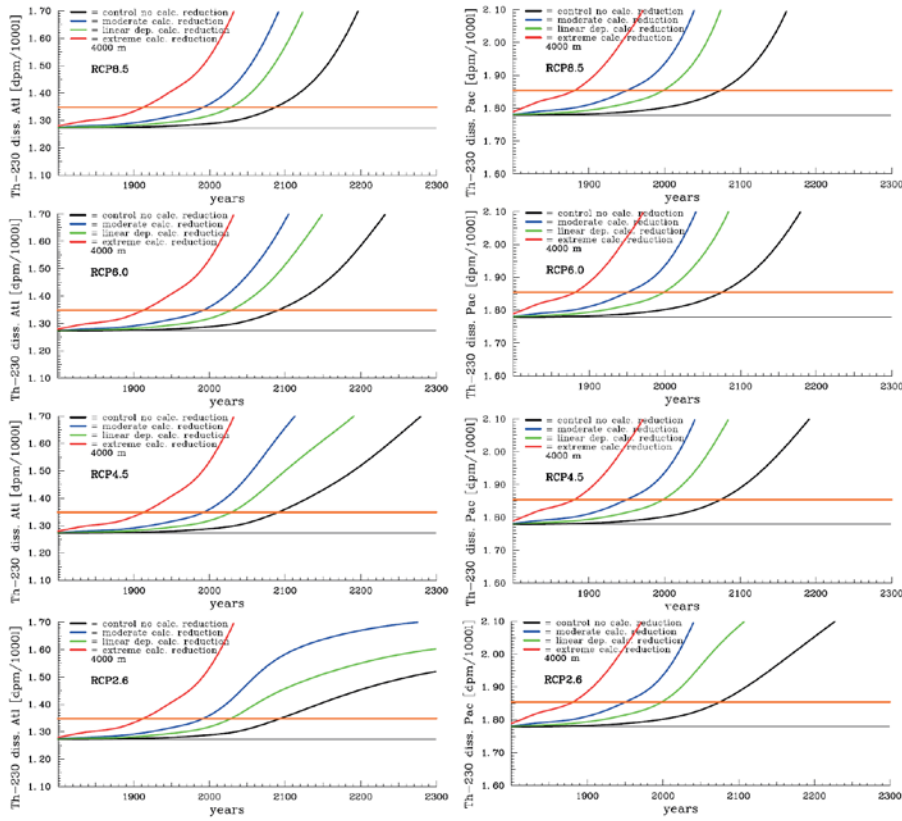
Figure S4: Time series for the evolution of mean Atlantic (left column) and Pacific (right column) dissolved ^{230}Th concentrations at 4000 m under the different scenarios for reduction of calcification under high CO_2 (unit: dpm/1000l). From top to bottom for greenhouse gas scenarios RCP8.5. RCP 6.0, RCP4.5, and RCP2.6. The orange line indicates the theoretical detection limit for changes with respect with respect to the pre-industrial.