

30 April 2019 Addendum to response:

For Lyle et al. "Late Miocene to Recent High Resolution Eastern Equatorial Pacific Carbonate Records: Stratigraphy linked by dissolution and paleoproductivity"

Following editorial instructions about how to proceed, we have copied the revised abstract into the web portal and a clean pdf of the revised manuscript. We have also attached our response to review file from March 2019 to the "track changes" version of the revised text.

Response to reviewers of “Late Miocene to Recent High Resolution Eastern Equatorial Pacific Carbonate Records: Stratigraphy linked by dissolution and paleoproductivity

5 Mitchell Lyle, Anna Joy Drury, Jun Tian, Roy Wilkens, and Thomas Westerhold

In this response the original critique is in black and responses by the authors to the reviews are written in blue. We thank the reviewers for their thorough critiques of our paper “Late Miocene to Recent High Resolution Eastern Equatorial Pacific Carbonate Records: Stratigraphy linked by dissolution and paleoproductivity”. We have revised the paper substantially in response to the comments. We have added information to the abstract to better explain the objective of the paper. We have rearranged and rewritten the introduction with this goal in mind as well. We have recombined the original section 4 with the discussion so it is now below results. And we have followed advice to clarify the writing and add material to the supplemental material. One major addition was a better explanation of how the CaCO₃ MAR gradient method worked to determine the CCD, and tables of the CCD determination by this method, as well as estimates of paleodepth to the sea floor through time. Because of the reorganization, figure numbers in the revision have changed order, as listed below:

	<i>Figure # in Submission</i>	<i>Figure # in Revision</i>
20	<i>Fig 1</i>	<i>Fig 1</i>
	<i>Fig 4</i>	<i>Fig 2</i>
	<i>Fig 5</i>	<i>Fig 3</i>
	<i>Fig 6</i>	<i>Fig 4</i>
	<i>Fig 7</i>	<i>Fig 5</i>
25	<i>Fig 2</i>	<i>Fig 6</i>
	<i>Fig 3</i>	<i>Fig 7 (figure revised and repurposed)</i>
	<i>Fig 10</i>	<i>Fig 8</i>
	<i>Fig 8</i>	<i>Fig 9</i>
	<i>Fig 9</i>	<i>Fig 10</i>

30

RESPONSE TO ANONYMOUS REVIEWER 1

Reference R1 requested extensive reorganization, and we felt that the R1 comments had merit. We added sentences to the abstract to define the objectives better, re-organized the introduction to give a broader outlook, and moved section 4 “Eastern Tropical Pacific Sedimentation since 10 Ma” back into the Discussion section. We reorganized the figures (see table) to match text changes. We added more discussion and tables to clarify how the CaCO₃ MAR gradient was used to establish the CCD. We have also addressed the specific comments in the R1 review, as shown below.

Anonymous Referee #1

10 Received and published: 3 January 2019

General comments

The manuscript of Mitchell Lyle et al. “Late Miocene to Recent High Resolution Eastern Equatorial Pacific Carbonate Records: Stratigraphy linked by dissolution and paleoproductivity” is supposed to be published in “CPD”. In their study, the authors critically discuss causes for the observed CaCO₃ deposition in the Eastern Equatorial Pacific over the past 8 Myr, i.e., production vs. dissolution. The study is based on XRF-derived bulk sediment composition data and mass accumulation rates from sites of IODP Expedition 320/321 and ODP Leg 138. The major outcome of the study is apparently the identification of five long-term low CaCO₃ intervals within the past 8 Myr – two of them as a result of CaCO₃ dilution through diatom production, and the other 3 as a result of enhanced CaCO₃ dissolution.

20

The overall story presented is based on an innovative approach and has the potential to be published in CPD. However, I recommend this paper for publication only with the revisions described below. Most importantly, the abstract and introduction lack a working hypothesis and a few sentences on the overall aim of the study. The discussion is thus not easy to follow in various parts and needs some re-structuring.

25

Specific comments

Abstract: I won't start the abstract with “We report: : :”. To me, there are 1-2 sentences missing at the beginning of the abstract summarizing the aim of your study (i.e., what are the scientific questions you want to solve). Page 1 Lines 12-14: Include information on locality of study sites, i.e., EEP.

30 *We added 3 sentences to the beginning of the abstract to explain the primary objective of the paper and to highlight the stratigraphic importance as well. We identified the sites as being in the eastern equatorial Pacific.*

Introduction (p. 1, l. 27 to p. 3, l. 7): In this part of the introduction you should make clear what's the aim of your study, i.e., what are yet unresolved scientific questions that you want to answer or what is your working hypothesis. From the introduction as it is now, the aim of your study is not clear to me.

5 *We revised the introduction to focus the objectives, to understand how CaCO₃ dissolution and production has shaped the regional stratigraphic record. In addition we have added context from the objectives of the Pacific Equatorial Age Transect (PEAT, IODP Expeditions 320 and 321).*

Page 3

10 Lines 5-7 and 26-29: These are results and therefore should not be part of the introduction.

These have been removed from the introduction.

Lines 9-12: Add the location where your records are from. You want to update the stratigraphy from 0-5.3 Ma, but work on the 0-8 Myr period. What about the 5.3-8 Myr stratigraphy? This should be mentioned here. “We
15 choose 5.3-0 Ma because it has good age control”: To me that's not an argument. You can mention that as an additional point but not as a reason of why this interval has been selected.

The paragraph has been revised to indicate that we have limited the discussion in this paper to the Pliocene and Pleistocene the LMBB has significant regional variation that needs further work to explore properly. A proper investigation of the LMBB must take into account the regional variability, both along the equator and across it.

20

Lines 20-23: This is no information relevant for the introduction. Please move this section together with l. 18-20, p. 4 into section 3.2. This will also avoid repetitions. To me it is also not clear why to generate a combined age model for all sites instead of using the original age models? Could you briefly explain that in the “age model section”?

25 *The sentences were moved. The brief reason that we needed to make a combined age model is that we found missing intervals in the Mix et al (1995) isotope record below where we joined the Site 849 and Site U1338 records. We added sentences to explain this in the text in section 3.2*

Page 4 (section 2)

30 Line 1-3: Include in parenthesis the ODP and IODP sites, respectively.

ODP and IODP were added.

Lines 3-7: I think this information is not relevant to your story, please delete.

We disagree—for Cenozoic studies it is critical to understand the time-geographic constraints on information from each drill site. We have revised the sentences to reflect the changes in the introduction.

5

Line 9: Change “All 7 sites have continuous orbital-resolving records of estimated CaCO₃: : :” to “We generated (correct?) continuous orbitally-resolved records of CaCO₃ for all 7 sites: : :”

These paragraphs have been moved to section 3.3 and have been revised to indicate who generated the records.

10

Lines 9-16: From this section it is not clear to me which records are new, and which records are already published. Please rephrase. Also, why are you mentioning records that go back to 24 Ma while you are only studying the 8-0 Ma interval?

These paragraphs have been moved to section 3.3 and are intended to show that additional data is available.

15

Lines 21-33: I suggest to move these sections to line 8.

We have moved the paragraph as suggested.

Page 5 (section 3)

20 Lines 12-13: Sites 848 and 850 where tied to the U1338-tied Site 849? Is that correct? Why were Sites 848 and 850 not also tied to U1338? And why have both Sites U1338 and 849 been selected as alignment sites?

We explain this better in the new text in Section 3.1. We found that correlations were less ambiguous by comparing Sites 848 and 850 first to Site 849 and then using the site to site correlation between Site U1338 and Site 849 to interpolate equivalent U1338 equivalent depth than to directly try to correlate those 2 sites to Site U1338. We have added text to this effect in Section 3.1.

25

Page 6 (section 3)

Lines 2-3: I don't understand: Are these already published data (because of the references) or are these new data?
Section 3.3 has been revised to better indicate the sources of the data. The intent of this paper is to synthesize the data.

30

Page 7 (section 3)

Line 7: “Unpublished opal analyses”: If you use these data to calibrate something, you have to publish them in this paper. Provide them at least in the supporting information.

5 *The Site 849 bio-SiO₂ analyses were included in the paper as Table SM-21 in the original draft. We have revised the text to make it clear that the data is in the Supplemental Material .*

Section 4: After the methods I expect the results, in which you just describe the data you have generated (i.e. sedimentation rates range from x-y, CaCO₃ fluctuates between x and y, MARs vary between x and y, etc.). However, Section 4 is more a discussion. Restructure sections 4-6 accordingly, i.e., either provide a section for the results and another section for the discussion, or provide a combined “results and discussion” section with several sub-sections. I would prefer the latter in order to avoid repetitions.

10 *Section 4 was moved to be after the results where it fits better. It has been incorporated into the revised paper as Section 5.1*

15 Line 19-21: I don’t understand.

The language of the section has been revised to make it clearer.

Page 8 (old section 5; new section 4)

20 Lines 31: “(1) the percentage profiles can be directly measured as the sediment sections are processed”: This is not an argument.

This is an important argument. Much of the science for a drilling expedition happens on board the ship. Most of the low resolution profiles as well as previous CCD reconstructions are based on these shipboard measurements. These shipboard measurements are the basis for Pälike et al (2012) as well. These points were added to the text.

25 Page 9 (section 5.1/5.2)

Line 1: “(3) the results are easily compared to earlier observations at other cores and drill sites”: I don’t get that point.

Most CCD reconstructions are based upon changes in the CaCO₃ % with depth to the sea floor, so of necessity are comparing CaCO₃ %.

30

Lines 3-5: Delete, because the same information is also given in the next sentence.

Sentence was removed

Lines 7-8: I think there is a third important factor you should also consider: What about a simple decrease in CaCO₃ production due to, e.g. Fe limitation, and thus reduced phytoplankton productivity?

5 *You are correct, which is why we worded this as “relative CaCO₃ dissolution”. We add a sentence to explain better.*

Line 14: Is there a better word for “defects”? What are the “defects”?

This was replaced with “...because of age errors for the timing of bio-events and magnetochrons used for the chronostratigraphy of the earlier age models...”

10

Lines 17-23: To me this paragraph does not belong to this section. Move to Section 6.2. Is the cyclicity of CaCO₃% described in this paragraph based on a visual evaluation or have you done some phase analysis (I guess you only show a wavelet analysis of the CaCO₃:BaSO₄ ratio)? “CaCO₃ % is high in Pleistocene glacial climate intervals”: Is the temporal resolution of your age model sufficient to determine whether CaCO₃% is highest during peak glacial conditions (as written now) rather than during glacial terminations as observed in previous studies?

15 *The 100-kyr carbonate cycles are a well-known feature of the Pleistocene equatorial Pacific, so it is appropriate to discuss this here. This variability is an observation from our records. We discuss timing later in Section 6.2. The statement has been revised somewhat to remove concerns about how we know the timing, but it is based on*
20 *studies ranging back to the Swedish Deep Sea expedition.*

Section 5.2: Why does such an anomaly not also occur at nearby Sites U1335 and U1338? Are they too far away from Site U1337?

25 *Sediment focusing that we can document tends to be a local phenomenon determined by local topography. We document additional evidence for focusing in Supplemental Material Section 7 and Figure SM-5. Since focusing is local, focusing at one site does not determine that there will be focusing in nearby basins. Furthermore, Site U1335 is roughly 400 km to the NW of Site U1337, and Site U1338 is about 600 km away to the SE. They could only be linked by very large-scale regional deposition.*

30 Page 10 (section 5.2/5.3)

Lines 9-10: Any explanation for that observation?

I added a reference to Lyle et al (2014) that found a similar result that CaCO₃ MAR was least affected by sediment focusing in the JGOFS region. Presumably this is because the CaCO₃ resides in a larger less transportable fraction.

5 Page 11 (section 5.3)

Line 1: This means that opal MAR is unrelated to glacial-interglacial change? It would be nice to highlight glacial or interglacial intervals in the figure.

Glacial intervals over PPLC-2 have been marked in the figure so that it is easier to identify the glacials in different time series. As described in the text, there is an association of opal MAR with glacials but the

10 *association is noisy.*

Line 21: I guess you mean three peaks by “CaCO₃ triplet”, correct? However, I cannot see them in the figure. Make sure that your figures are large enough in size and/or highlight special features such as the CaCO₃ triplet.

The triplet has been marked in both figures.

15

Page 13 (section 6)

Lines 10-15: This paragraph should go into the introduction section where you talk about the CCD.

The paragraph was moved to the introduction

20 Page 14 (section 6)

Lines 3-9: I can't follow. Please rephrase.

A paragraph was added to the text and the text was revised.

Line 11: You estimate the depth of the CCD based on CaCO₃ MAR. The latter you get from equation (1). But how do you transfer CaCO₃ MAR into the depth of the CCD? Also, can you provide a data table where you show all the values inserted into equation (1) to get CaCO₃ MAR? Provide link to figure.

25

We have added a paragraph to describe the CCD estimate better, and we added a more detailed description and tables to the supplemental material, along with tables of our CCD estimate and paleodepths for Sites U1338 and 851.

30 Section 6.1: How do your CCD estimates compare to that of Pálike et al. (2012)? Could you plot them together?

Their CCD is somewhere between 4.2 and 4.8 km for your study interval. How can you explain this difference?

Also you get a depth of the CCD of >6 km, how realistic is that?

We added the Pälike et al (2012) estimate to Figure 3 (MAR figure), and explained how the depth to the CCD for Pälike et al (2012) was controlled by a single site (U1334) during the Pliocene and Pliocene that was off axis and not really in the equatorial production regime. We agree that 6 km is deep, and discussed in the paper how local sedimentation vagaries leads to noise in the MAR/depth extrapolation.

Page 17 (section 6.3)

Lines 15-16: “In other words, attributing PPLC-4 to one cause is overly simplistic.” I don’t understand, please rephrase.

This has been reworded. At the present time there is no way to determine the direct link between higher dissolution in PPLC-4 and Central American Seaway closure. Other important changes were occurring in the global carbon system at that time.

Page 18 (section 6.4)

Section 6.4/Lines 25-26: I would not finish a paper like this. Since the paper is very long, I would delete the entire section.

The section has been reorganized and is now section 5.2. It has been better tied into the objective to understand changes in primary productivity.

Table 1: Change “Drill Sites in this study” to “Drill sites investigated in this study”. Add ODP and IODP to Sites. “Length of dated record”: Is that information relevant for your study? If not, please delete. “Data available”: Are these data sets that are already available and were worked on in this study (then references are missing), or are these data sets that were generated in this study? Please rephrase respectively.

Changed .

25

Table 2: “MIS at Site 849”: Delete “at Site 849”. Magnetic Chron: Not mentioned in the text. I would delete that column.

We changed “MIS at Site 849” to “Marine Isotope Stage”. We retained the Magnetic Chron column because this readily allows correlation to distant drill sites and is standard for Neogene work.

30

Figure 1: Start caption with something like “Overview of East Pacific drill sites”. “Sites U1335, U1337, U1338,

and 849 have XRF scanning chemical data, while Sites 848, 850, and 851 have CaCO₃% estimated from bulk density”: This information is not relevant for the figure. Delete. LMBB/Pliocene ratio: Not mentioned in the text. So if relevant, provide a discussion on this ratio in the main text, if not, delete.

Changes to caption have been done. A discussion of this ratio was already in the text; we have now made explicit
5 *mention of the LMBB/Pliocene ratio.*

Figure 3: This figure has not been mentioned in the main text; this doesn’t work. As I understand, the only aim of this figure is to show the higher temporal resolution of your new records compared to previously published data of Lyle and Baldauf (2015). So this figure does not contribute to the story presented in your paper. I suggest
10 either to delete this figure, or to move it into the supporting information, but including the data from Lyle and Baldauf as a comparison.

This figure has been eliminated, but the data have been repurposed as Fig 7 to show the relative invariance of clay MARs over the last 8 Myr.

15 Figure 4: a) I guess the black lines are a smooth, and the red and brown lines are raw data. Please add this information to the figure caption. b) Different colors refer to different sites? Please explain.

This is now Fig 2. In (a) the black lines are now explained in the caption. In (b) we have expanded the description to explain that each drill site is represented by a different color.

20 Figure 5: “MAR data are at 10 kyr intervals”: Delete, but make sure that this information is given in the methods. “Sites are arranged from south to north, at their modern position”: Delete. b) Maybe I missed it in the text: Why are these two sites used for CCD estimations? Please add information to the main text. “with two levels of smoothing”: Can you please also show the unsmoothed record? Delete “The 50 kyr smooth: :time of PPLC 4”. I suggest to remove the CCD record from that figure and to show it in a separate figure together with the CCD
25 record from Pālike et al. (2012).

Now figure 3. We think it is important, given that many people do not read the text thoroughly, to reiterate why the MAR data are smoother than the CaCO₃ % data.

Figure 6: b) Use different colors for opal MAR and opal:clay. c) Are these only the Mix et al. (1995) data? I don’t
30 get that from the figure caption. Please rephrase accordingly.

Now figure 4. The figure was changed to have different colors for bio-SiO₂ MAR and bio-SiO₂:clay. We have

also now consistently used bio-SiO₂ for biogenic silica. The caption was rephrased about the stable oxygen isotope data.

Figure 7: To make it easier for the reader, I suggest to add arrows, indicating that low (high) CaCO₃:BaSO₄ represents high (low) CaCO₃ dissolution. Is it possible to fill the 5-8 Ma gap in the CaCO₃:BaSO₄ record? If no data for Site 849 available, then only based on the records from the remaining sites? Then you can also extend the records shown in Fig. 8 back to 8 Ma.

(now Fig 5) We added arrows to show direction of low/high dissolution, added the 3-site stack to the 4-site stack record that ended at 5.2 Ma, so that a stacked record now goes back to 8.1 Ma.

10

Figure 8: See my comment to Fig. 7. a) Explain solid and thick lines. b) Enlarge labeling of “power” and “period”. Make dashed “period-lines” more prominent.

Labeling was enlarged, and the period lines are more prominent. Thick lines are explained in caption. We disagree with expanding the figure back to 8 Ma because it makes it more difficult to see the changes in the 100-kyr periods in the Pleistocene.

15

Figure 9: Explain solid and thick lines.

The explanation has been added to the figure

20 Technical corrections:

Several abbreviations are not introduced. Make sure to introduce all of them. *We believe we have now introduced all abbreviations.*

Versus vs vs. Remain consistent. *Fixed*

Bio-SiO₂: Do you mean biogenic SiO₂? Please rephrase. *Bio-SiO₂ is commonly used for biogenic SiO₂ and is more precise than opal when discussing chemistry and MAR. Researchers often add structural water to the formula of opal, which can change the mass. We discuss our usage at the beginning of the paper, and now use bio-SiO₂ throughout the paper.*

Labeling of sites: ODP Sites without “U”, IODP Sites with “U”. Please correct accordingly. *Corrected*

30 Page 1

Line 12: change “late Miocene-Recent” to “late Miocene to recent” *done*

Line 14: Add ODP *done*

Page 3

Line 15: Delete “The period between” and move “4.5 and 8 Ma” to “LMBB” in the
5 sentence before. *revised*

Line 20: Change “We use a combined age model: : :” to “We use a combined age model for all sites investigated
by joining: : :”. Delete “data from”. *The paragraph has been deleted in the revision*

Page 4

10 Line 22: Add reference to “At 5 Ma, the sites span from _4_S to _4_N” *We added how we did it; this is a
calculation for this paper. A table paleolocations for each drillsite could be added to the supplemental material if
needed.*

Page 5

15 Line 2: Delete “these” *done*

Page 6

Line 1: I guess Site 849 is missing in the heading *849 has been added to the heading.*

Lines 11 and 17-18: Remove, because this information is already given on p. 5, l. 2-3. *The paragraph has been
20 revised*

Lines 15-17: Change “Unfortunately, Hagelberg et al (1995) did not publish their CaCO₃ estimates for the Leg
138 Sites, so we redid the estimate for Sites 848, 850, and 851 along the revised splices presented here” to “Here
we provide CaCO₃ estimates for Sites 848, 850, and 851 along the revised splices”. *revised*

25 Page 7

Line 2: Remove “unfortunately”. *removed*

Page 9

Line 12-13: Repetition. Delete. *Lines were deleted*

30 Line 24: Change “CaCO₃ MAR records: : :” to “Except for Site U1337, CaCO₃ MAR records: : :” and remove
“however” in the following sentence. *revised*

Line 26: Change “: : :that is evidence: : :” to “: : : that is evident: : :” *the relevant phrase was changed to “may be caused by”*

Lines 27-28: Change “Most of the drill sites in this paper have variability in the bulk sediment MAR, but most of the bulk MAR variation is typically derived from changes CaCO₃ MAR. Site U1337 is unique: : :” to
5 “Variability in bulk sediment MARs of the sites investigated in this study is typically derived from changes in CaCO₃ MAR. However, Site U1337 is unique: : :” *the sentences are reworded as suggested*

Page 10

Line 2: Change “in addition to” to “our interpretation becomes supported by”. *The sentence is changed*

10 Line 12: Add “that we observe” to “intervals”. *added*

Line 23: Change “farther” to “further”. *Farther applies to distance, so fits better.*

Lines 25-27: Provide link to figure. *There is no figure of bio-SiO₂ MAR at different sites in the paper now. Sites U1335, 848, 850, and 851 do not have an estimate of bio-SiO₂, while Site U1337 has an anomalous bio-SiO₂ MAR because of the apparent sediment focusing. A figure could be made comparing MARs at Sites U1338 and
15 849, but this didn't seem needed.*

Lines 29-30: Delete “We infer: : :CaCO₃ content”. *The sentence was removed.*

Page 11

Line 20: Delete “: : :” *deleted*

20 Line 22: What do you mean by “they”? *Changed to PPLC-3*

Page 12

Line 9: Change “glacial carbonate cycles” to “glacial-interglacial carbonate cycles”. *changed*

25 Page 13

Line 31: Delete “for”. *Reworded*

Page 14

Lines 19-20: This information should be part of the figure caption and not of the main text. *The paragraph has
30 been reworded to make the levels of smoothing relevant*

Lines 31-34: Repetition of p. 13, l. 4-8. Please restructure. *The paragraphs have been combined and the*

redundancy has been eliminated.

Page 15

Line 2: Change “: :XRF scanning data are available, there: :” to “: :XRF scanning data are available (i.e.,
5 Sites XXX, YYY; ZZZ), there: :” and remove “at the four drill sites with XRF data” (l. 5-6). *These paragraphs were significantly reworded.*

Lines 30-34: This doesn’t work. You already provide a link to Fig 8 earlier. Delete this sentence, but make sure that the information about the smoothed d18O record is given in the figure caption. *fixed*

10 Page 16

Lines 2-3: Change “the correlation is still strong when CaCO₃:BaSO₄ is compared to the smoothed oxygen isotope record” to “that correlation is still strong”. *fixed*

Line 12: Add “Site” to 607. *fixed*

15 Page 17

Lines 6-9: Delete these sentences. *Sentences have been reworded.*

Page 21

Lines 1-2: Delete “In this paper: :work regionally”. *This has been reworded*

20 Lines 4-9: Restructure as follows: “We identified five long- term low CaCO₃ intervals within the 7 drill sites we investigated: PPLC-5 (4737-4465 ka), PPLC-4 (3 intervals between 4093 and 2915 ka), PPLC-3 (2 intervals on either side of a CaCO₃ high, between 2684 and 2248 ka), PPLC-2 (2135-1685 ka), and PPLC-1 (402-51 ka). With bulk chemical data and the geographic range of the investigated drill sites it is possible to distinguish between dissolution and production as causes of low CaCO₃ intervals in the Pliocene-Pleistocene record. We
25 found that PPLC-5 and PPLC-2 result from CaCO₃ dilution through diatom production, and the other 3 result from enhanced CaCO₃ dissolution.” *We used this guidance*

Line 16: Delete “whose 3: :and 3 Ma”. *Section has been reworded*

Line 21: Studies from 2016 are not really “new”. Replace “new” by “previous”. *Section has been reworded*

30 Page 33

Line 7: Remove “Late Miocene Biogenic Bloom”. *removed*

Line 7: Change “atandardized” to “standardized”. *fixed*

5

Reviewer 2 Comments (Daniele Reghellin):

- 10 *General response: Many of these comments overlap with that of R1. Distinct issues brought up by R2 are the lack of discussion about the inaccuracies of the GRA CaCO₃ estimate, the lack of information about how the CCD depth was calculated by the MAR method, and a need for better discussion about distinguishing a productivity event. We disagree with the comment that CaCO₃ cannot be estimated from GRA bulk density, since it has been adequately estimated this way for decades, albeit with about a 6% error when compared to discrete CaCO₃*
- 15 *measurements. We include a better discussion of the CaCO₃ MAR gradient method to estimate CCD.*

General Comments

I enjoyed reading and reviewing the Lyle et al. manuscript (MS No.: cp-2018-157). For most of the part, it is a

20 well written and structured manuscript, which presents high resolution sediment properties and compositional records from multiple locations of the eastern equatorial Pacific Ocean. The Results and their interpretation represent a fundamental contribution to the effort of understanding how this region and, more in general low latitude ocean areas, works as the ocean/climate system evolved to modern conditions. The Discussion mainly focuses on five Plio-Pleistocene intervals of low carbonate content. The causes of low carbonate content in the

25 EEP, dilution by biosilica particles versus dissolution of carbonate particles, are here examined using carbonate content, MAR of different sediment components, sedimentation rates, CaCO₃:BaSO₄ ratios and benthic foraminifera stable isotopes records from multiple locations of the EEP.

The main issues I found in the manuscript mostly concern parts of the Methods and Results and are listed in

30 “Specific comments”. The inaccuracies typical of carbonate content estimations from GRA density have not been discussed. It is not clear how CCD depth was calculated from CaCO₃ MAR and data are missing. In the Results/

Discussion it is not always clear how intervals of low carbonate content were interpreted as reflecting dilution by biosilica rather than greater carbonate dissolution or vice versa. The Biogenic bloom interval is improperly defined and its proposed end is imprecise. Given this, my overall evaluation is that this manuscript has the potential to be published in *Climate of the Past*, but I recommend to revise the manuscript according to all the
5 comments presented below before publication.

Specific comments

Abstract. At the beginning of the Abstract, add a couple of sentences introducing the problem(s) at the base of this study and the reasons for this study. Also, add a reference to the study area. There is no reference of the EEP
10 in the whole Abstract. *The abstract was changed by adding 3 sentences to the abstract, including a mention of the eastern equatorial Pacific*

Introduction. As for the Abstract, in the Introduction I couldn't find the unresolved questions that stay at the base of this study. Please add them together with the aims of this study.
15 *The introduction was revised to better communicate what we are reporting.*

Biogenic bloom. I think it is incorrect to refer to the Biogenic Bloom as “Late Miocene Biogenic Bloom (LMBB)” because this event did not occur only during the Miocene as it ended in the early Pliocene. This is stated in the manuscript several times and is reported in the literature. For
20 example, the studies cited on page 7 line 13 (Farrell et al., 1995, Lyle and Baldauf, 2015) refer to the biogenic bloom as “Biogenic Bloom” or as “late Miocene early Pliocene biogenic bloom”. In the paper it is also awkward to read that an early Pliocene interval (e.g. PPLC-5) is part of the LMBB. For example, on page 35 line 4 what is defined as a late Miocene event (LMBB) includes another event from the early Pliocene. It makes little sense to me. I strongly recommend to substitute “late Miocene Biogenic Bloom (LMBB)” with “Biogenic Bloom” or with
25 “late Miocene early Pliocene biogenic bloom” throughout the text, figures, figure captions and tables. Also change all the acronym “LMBB” accordingly, throughout the text, figures, figure captions and tables.

*Most of the Biogenic Bloom falls within the late Miocene, and LMBB is the best succinct description. “Biogenic Bloom” is too generic, and “LMEPBB” is too cumbersome. Similarly, the Miocene warm period is labeled the middle Miocene Climate Optimum (MMCO), even though it actually starts in the early Miocene. The LMBB is
30 made up of multiple high production intervals superimposed upon generally high sedimentation rates with respect to the Pleistocene. PPLC-5 is the last of these high production intervals.*

Data presented. In the text it is not so easy to keep track where the presented data come from (a previous study, this study, etc.) because of the important amount of data. It would make things easier for the reader to add some columns to Table 1 or even adding a new table in which is clearly listed type of data, drill site, data origin and time span of all the data presented in the study.

Papers where data are located are now included in Table 1; we also rewrote the sections discussing data to make data sources more clear.

CaCO₃ % estimates from GRA density (sections 3.4 and SM 5). There is no mention in the manuscript that carbonate content estimates calculated from GRA measured in EEP sediment have been demonstrated to lead to imprecise carbonate estimations. Reghellin et al. (2013) [Reghellin, D., G. R. Dickens, and J. Backman (2013), The relationship between wet bulk density and carbonate content in sediments from the Eastern Equatorial Pacific, Marine Geology, 344, 41-52] have shown that it is not possible to accurately describe the relationship between carbonate content using a single equation, like it was done in this study. The estimation errors are particularly evident at high CaCO₃ content (>60 %; the case of most of the records presented here) because of the wide range of WDB. Fig. SM-4 show that at Site 849 CaCO₃ estimation from GRA, XRF and discrete measurements give similar values but still differences are apparent between GRA and discrete measurements in the figure. On the basis of the results presented by Reghellin et al. (2013), new carbonate content records estimated from GRA density cannot be published without fully considering the uncertainties and inaccuracies of the method. In addition, the relationship varies significantly in the EEP from a site to another because of sediment composition differences (carbonate vs biosilica content and, within carbonate components, the type of them) at different locations. In the SM only one power law equation (5) is presented so I have the doubt that it was computed using all discrete CaCO₃ and density data from Sites 848, 849, 850 and 851 together. This can potentially bring to even greater errors in the CaCO₃ estimates than using different power law equations at different sites. If this is the case, I recommend to recalculate CaCO₃ estimates using different power law equations at different sites. Each power law equation should be computed using the data from that particular site only.

Carbonate in the eastern equatorial Pacific has been shown to be highly correlated with wet bulk density first in a 1979 paper by Larry Mayer (JSedPet 49,3, 819, now added to the references). Mayer measured grain size and fragments as well as carbonate content. He found that carbonate content accounted for 88% of the variance in wet bulk density, while mean grain size accounts for 0.5%, and percent fragments accounted for 0.01%.

Sediments lose porosity (gain wet bulk density) as they are buried. If this is not compensated for, there is a trend to higher density with depth and errors for higher CaCO₃ values. Most of the observations by Reghellin et al (2013) that GRA is unsuitable for estimating CaCO₃ probably arise because they did not decompact the GRA density. As for the CaCO₃ estimate being less certain at higher CaCO₃ percentages, see the supplemental material and see the plot by Hagelberg et al (1995, below), who found, as we did, that there was no trend of worse predictability with higher CaCO₃ contents. Hagelberg et al (1995), used essentially the same method as we did (we used a slightly different decompaction curve), and got root mean square (RMS) errors averaging 7% for estimated CaCO₃ % by GRA for all 8 sites, similar to the 6% we got for Site 849 versus ~4% for XRF estimates of CaCO₃ %. What we found, as discussed in the text are similar errors in the GRA method to Hagelberg et al. (1995). Figure SM-4 shows that the trends of discrete, XRF, and GRA estimates of CaCO₃ % are the same and reasonably fit the discrete measurements.

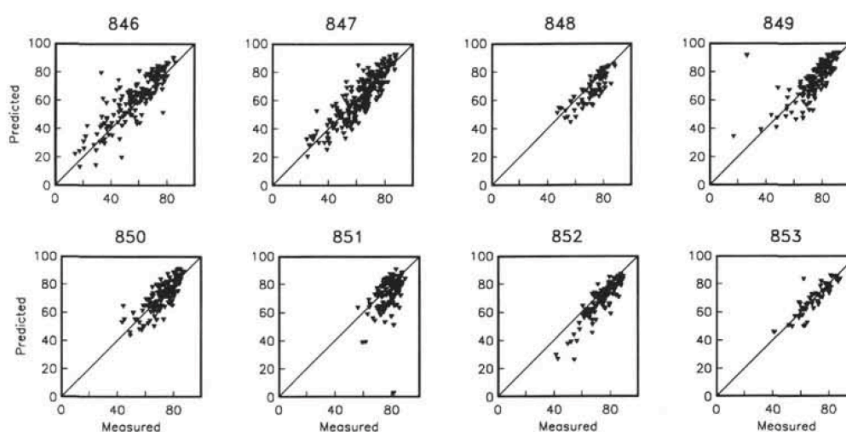


Figure 4. Scatter plots of predicted (from GRAPE) vs. measured %CaCO₃ from the top 6 m.y. of Sites 846 through 853.

MAR data (section 3.5). I tried to calculate some MAR for a few sediment components using the equation (6), with dry bulk density, sedimentation rates and CaCO₃ % data in the SM tables and the results were different from corresponding MAR data listed in your tables. Please verify if data presented in the tables are correct.

The data in the MAR tables are correct. I can only assume that R2 tried to calculate via individual samples, and not using the smoothed data found in tables SM-26 to SM-32. As explained in the text, the smoothing was done to minimize spikes caused by errors in sedimentation rate and individual bulk chemical analyses. Applying smoothed sedimentation rates to the unsmoothed data will result in erroneous results.

Biogenic bloom end. On page 7 line 16 is stated “is easily observed by the change in slope of the age-depth curves at about 4400 ka (Fig. 2)”. To me is evident that the most significant and clear change in the age-depth curves of Fig. 2 is a bit to the right of where the grey line is placed, which is at about 4600 ka. This is particularly evident in curves of Site U848, U1338, U851, U850 and U849. I would then strongly recommend to: i. move the end of the biogenic bloom line at 4600 ka in Fig. 2; ii. move green arrow tip to 4600 ka; iii. recalculate average sedimentation rates for the periods 0-4600 ka and 4600-7200 ka in Fig. 2; iv. modify all figures, figure captions and manuscript text according to the above reasoning.

This is now Fig 6 in the revised manuscript. We found that the end of PPLC-5, marking the last productivity interval in the LMBB, occurred at 4465 Ma. The figure is meant to be illustrative and the average sedimentation rates will change little if the dividing line is moved to 4600 ka. The figure was not used to determine the end of the LMBB since examination of sedimentation rates is a more useful measure. The R2 eyeball estimate of 4600 ka for the bend is probably older than the actual sedimentation rate changes. We propose to leave the figure alone.

Sediment focusing (page 10 line 6). “Surprisingly, the sediment: : : : strongly affect the CaCO₃ % profile” isn’t this because of moderate currents strength preferentially removes light-fine sediments as you say on lines 1 and 2? If this is the case it makes sense to me that sedimentation rates increase, CaCO₃ % decreases but leaving the CaCO₃ % profiles unaltered. And CaCO₃ MAR would increase because of higher sedimentation rates, even if dry density decreases because of the input of fine sediments. This is not anomalous to me.

We agree with this reasoning and it matches what we were trying to say in the text. The work we have done on sediment focusing (Lyle et al., 2014; Lovely et al., 2017) suggests that fine-grained materials are preferentially moved except at high current speeds where all the sediment moves.

Dilution vs dissolution. In the Results (sections 5.3-5.5) it is often missing a clear explanation of how it was distinguished between carbonate dilution by biosilica and carbonate dissolution. Section 5.3. The first paragraph (page 10 lines 12-19) is difficult to follow and needs rewriting because it is not clear how you interpreted some intervals (i.e. PPLC-5 and PPLC-2) as high production rather than high carbonate dissolution. Is it because carbonate% is low at on equator sites and not as much at off equator sites? or is it because of low carbonate% and relatively high carbonate MAR at on equator sites? The CaCO₃:BaSO₄ used to estimate carbonate dissolution is also very low at PPLC-2 at all sites (Fig. 7). Couldn’t it be that high production also generated greater carbonate dissolution? How is it possible to completely exclude carbonate dissolution in this interval? I recommend to

clearly state in which way it is possible to distinguish between dilution and dissolution. Section 5.4. Lines 14-15: it is not clear how data at PPLC-4 indicate dissolution rather dilution by biosilica. Provide clear explanation. Section 5.5. Here it is easier to follow your rationale because you introduce the CaCO₃:BaSO₄ proxy. I strongly recommend to add references to this proxy in the interpretation of the other PPLC intervals (so in sections 5.3 and 5.4). It would make your interpretation of low carbonate intervals much stronger and easier to follow by the reader.

These are now sections 4.3 to 4.5. We have revised the section to make it more clear. As explained in the paragraph in question a combination of MAR and percentage data marks a productivity interval. The information at an individual drill site is supported by changes along a set of drill sites occupying a latitudinal transect away from the equator since upwelling is focused at the equator. Reghellin is correct that production and dissolution are not mutually exclusive, and we agree that CaCO₃:BaSO₄ is low in the PPLC-2 interval. We will add something to the text about CaCO₃:BaSO₄ for other PPLC intervals.

CCD depth estimate from CaCO₃ MAR (section 6.1). It is not clear how MAR CCD were calculated. From reasoning in 6.1 it seems that you have calculated MAR CCD from CaCO₃ MAR using equation (1) in page 13, but in that equation there is no MAR CCD. Clarify this. I could not find the data used to calculate MAR CCD anywhere in the manuscript nor in SM. I strongly suggest to add a table listing all data used to make curves in Fig. 5 panel b. While reading section 6.1 I got the feeling that the estimation of CCD depth from CaCO₃ MAR is a weak approach. This is because you state that i) “local sediment anomalies: : : : cause significant noise to this approach” ii) “weaker signal in the Pliocene and Miocene is harder to distinguish from noise”, iii) the CCD estimate “suffers from the noise resulting from building the trend with records from only 2 sites” and iv) “minor errors in correlation: : : : are magnified in the CCD estimate”. Plus, it is not clear how you calculated CCD depth from CaCO₃ MAR.

Also, I see there are significant differences between the CCD depth record (Fig. 5 panel b) and the equatorial Pacific CCD of Pälike et al. (2012). The latter ranges between about 4200 and 4700 mbsl whereas yours mostly between 4300 and 5500 mbsl. How can you explain this difference? It seems to me that all the issues of the method are strongly affecting the CCD estimates. Isn't it enough to speculate on carbonate preservation (dissolution) over time by using the CaCO₃:BaSO₄, CaCO₃ MAR, CaCO₃ % and sedimentation rates? In my opinion the message emerging from this part of the Discussion would be much stronger without the CCD depth estimate.

We redid this section to better explain how the MAR extrapolation of the CCD is done in both the text and in the

supplementary material.

Page 17 lines 22-24. Add that evidence of early Pliocene higher SST and lower biogenic production compared to during the biogenic bloom comes also from bulk sediment stable isotopes and sedimentation rates records from Leg 138 on-equator sites and from Site 573 and U1338 (see Shackleton and Hall., 1995 and Reghellin et al., 2015) [Reghellin, D., H. K. Coxall, G. R. Dickens, and J. Backman (2015), Carbon and oxygen isotopes of bulk carbonate in sediment deposited beneath the eastern equatorial Pacific over the last 8 million years, *Paleoceanography*, 30, doi:10.1002/2015PA002825].

This will be added.

10

- Page 18 lines 5-6. Add explanation of how the “expansion of an Antarctic source: : : : and Pacific” can cause opposite changes in the $d_{13}C$ records from the Atlantic and the Pacific

The Antarctic mixes all subsurface flows to get an average $d_{13}C$. If the Atlantic outflow is displaced to a somewhat shallower depth (as happened at the LGM), Atlantic benthic $d_{13}C$ goes down, while the Pacific $d_{13}C$ may stay the same or go upward, depending on how much high $d_{13}C$ water is generated in the Atlantic. We will add better explanation to the discussion.

15

Technical corrections

Page 1 Line 12: define “XRF” Line 13: define “IODP” and “ODP” Line 23: define “DIC” *done*

20 Page 2 Line 2: add “Reghellin et al., 2013” to references. *done*

Line 25: define “DIC” *done*

Line 27: add references *added*

Line 28: define “NADW” *done*

Line 34: substitute square brackets with round brackets. *done*

25 Page 3 Lines 4-7: move this sentence to Results or Discussion Lines 13-15: add references Line 26: define “XRF” Line 31: define “IODP” *Sentence removed; XRF, IODP, ODP defined in abstract*

Line 32: define “ODP” and “GRA” *done*

Page 4 Line 2: change “3_S” to “3.0_S” Line 11: define “ccsf”. Also, “ccsf” is in the text sometimes written as lowercase and sometimes as uppercase. Modify to be consistent *defined, and consistently caps now*

30 Page 5 Line 11: add explanation of the criteria used to choose the base or master drill site, *added*

Page 6 Line 5: define “ICP-MS” Line 14: add “Reghellin et al., 2013” to references *done*

Page 7 Lines 16-17: substitute “4400 ka” with “4600 ka” Line 20: define “DSDP” *only if we change the figure. DSDP has now been defined*

Page 8 Line 3: late Miocene carbonate crash here defined from 11 to 8 Ma and on page 7 line 11 from 10 to 8 Ma. Change time periods to be consistent *Changed*

5 Line 5: in References list there are two Pälike et al., 2010b. To which one do you refer? References list *we realized that all references that we used could be directed to the Exp 320/321 summary, so eliminated the reference to the entire volume.*

Page 9 Lines 3-8: the same concept is repeated in these two sentences. Keep one and delete the other. I would also add low carbonate production as a cause for low CaCO₃ intervals. *Text has been revised*

10 Page 10 Line 26: add “(Figure 3)” after “at Site U1338” *done*

Page 11 Line 1: define “MIS” Line 14: substitute “lowest record” with “panel b” Lines

15-19: these are speculations. Move to Discussion Line 22: substitute “bottom” with “panel b” *In revision we have defined the CaCO₃/BaSO₄ ratio, so we refer to observations*

Page 12 Lines 27-30: add references *this was adequately referenced in the introduction*

15 Page 13 Line 25: is (1) a novel equation? If so state it otherwise provide reference *it is neither novel nor taken from another reference.*

Page 15 Line 5: how about PPLC-2? I see that also during this time period the CaCO₃:BaSO₄ is very low at XRF sites Line 32: specify the type of smoothing *The smoothing results from the stacking; noise cancels out because it is uncorrelated. We add a sentence about dissolution in PPLC-2*

20 Page 16 Line 10: define “AABW” *done*

Page 17 Line 5: substitute “implies” with “would imply” Line 11: define “NCW” Line 15: define “SST” *changed*

Page 18 Line 31: add “early Pliocene” after “late Miocene” Line 32: add “Reghellin et al., 2015” *early Pliocene added; did not add Reghellin reference*

Page 19 Line 34: define “CAS” *defined*

25 Page 27 There are two Pälike et al., 2010b. Fix *fixed*

Page 31 Table 1: change “length (ka) of dated record” to “length of dated record (ka)”. *That column has been removed on advice of RI*

Can you specify what is meant with “Data available”? See comment in “Specific comments” *references have been made*

30 Page 32 Specify origin of background map. In the map are present many light grey dots which (drill sites locations?) that are not labelled. Add a label or remove the dots *fixed*

Page 33 See comment “Biogenic bloom end” in Specific comments section Figure 3:subscript 3 in “CaCO₃” in panel a scales Substitute “4400 ka” with “4600 ka” in figure and figure caption In figure caption, define what is the grey vertical line *now Fig 6 see our comments about moving the line.*

Page 35 What are darker curves on panel a? is it a kind of smoothing of actual data record? Clarify in figure caption Line 4: see “biogenic bloom” comment in “Specific comments” *fixed; it is a smooth*

Page 36 Can you reverse y axis scale on panel b? With shallower depths at the top it is difficult to follow lines 5-6: see “CCD depth estimate from CaCO₃ MAR” comment *done*
in “Specific comments” line 6: specify which curve is the 50 kyr smoothing (blue line?) and which one is the 750 kyr smoothing (bold blue line?) *added to caption*

10 Page 37 Please add a sentence in figure caption about alignment of d18O glacial intervals and high opal MAR *added*

Page 39 Specify in figure caption what the dark red line on the stack isotope curve is *added*

Page 40 Specify in figure caption what are dark color lines *added*

SM Page 1 Lines 26-27: given what is written here I do not understand why in the captions of Tables SM-1 to SM-4 (ODP sites) you refer to CSF and CCSF depths and in captions of Tables SM-5 to SM-7 (IODP sites) you refer to mbsf and rncd depths. Please correct depth scales in all supplemental tables or clarify *This was clarified and was intended to reflect the change in nomenclature that is needed to*

SM Page 2 Line 16: define “IMPH” *clarified*

SM page 5 Line 24: substitute “since they have partially: : :” with “because they have partially: : :” Line 25: define “APC” Line 26: define “XCB” *done*

SM page 6 Lines 30-31: describe method used to obtain GRA estimates *expanded*

SM page 7 Lines 8-9: can you state where the “discrete CaCO₃ data” come from? And can you clarify with which data the power law estimate (5) was computed? Line 23: specify the unit of “Xe” Line 24: change “grams” to “g/cm³” *fixed. Xe is unitless (grams/grams).*

25 SM page 8 Lines 19-20: Can you provide a possible cause of this sediment accumulation/erosion feature at Site U1337? Lines 22-23: “Site U1337: : : : : significantly elevated relative to the CaCO₃ MAR” add reference to Fig. 5 *fixed*

SM page 12 On panel d there are two marks for Site 572 location. Fix SM page 14 Change “Figure SM-1” to “Figure SM-3” *Gray point is the site survey piston core RR0603-4JC*

30 SM page 15 Change “Figure SM-2” to “Figure SM-4” *fixed*

Daniele Reghellin

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- Hagelberg, T. K., Pisias, N. G., Mayer, L. A., Shackleton, N. J., and Mix, A. C.: Spatial and temporal variability of late Neogene equatorial Pacific Carbonate: Leg 138. . In: *Proceedings of the Ocean Drilling Program, Scientific Results*, 138, 321-336, 1995.
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- Lyle, M., Marcantonio, F., Moore, W. S., Murray, R. W., Huh, C.-A., Finney, B. P., Murray, D. W. and Mix, A. C.: Sediment size fractionation and sediment focusing in the equatorial Pacific: effect on ^{230}Th normalization and paleoflux measurements, *Paleoceanography*, 29, 747-763, doi:10.1002/2014PA002616, 2014.
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Late Miocene to Recent High Resolution Eastern Equatorial Pacific Carbonate Records: Stratigraphy linked by dissolution and paleoproductivity

Mitchell Lyle¹, Anna Joy Drury², Jun Tian³, Roy Wilkens⁴, and Thomas Westerhold²

5 ¹College of Earth, Ocean, and Atmospheric Science, Oregon State University, 104 CEOAS Admin Bldg, Corvallis, Oregon 97331, USA

²MARUM-Center for Marine Environmental Sciences, University of Bremen, Leobener Strasse, DE-28359 Bremen, Germany

³Laboratory of Marine Geology, Tongji University, Siping Road 1239, Shanghai 200092, PR China

10 ⁴University of Hawaii, School of Ocean and Earth Science and Technology, Honolulu Hawaii 96822, USA

Correspondence to: Mitchell Lyle (mlyle@coas.oregonstate.edu)

Abstract. Coherent variation of CaCO₃ burial is a feature of the Cenozoic eastern equatorial Pacific. Nevertheless, there has been a long-standing ambiguity whether changes in CaCO₃ dissolution or changes in equatorial primary production might cause the variability. Since productivity and dissolution leave distinctive regional signals, a regional synthesis of data using updated age models and high-resolution stratigraphic correlation is an important constraint to distinguish the two, and the new chronostratigraphy is an important foundation for future paleoceanographic studies. We report late Miocene to recent time series of X-ray Fluorescence (XRF)-derived bulk sediment composition and mass accumulation rates (MAR) from eastern equatorial Pacific Integrated Ocean Drilling Program (IODP) Sites U1335, U1337, U1338 and Ocean Drilling Program (ODP) Site 849, and also report bulk density derived CaCO₃ MAR at ODP Sites 848, 850 and 851. We use physical properties, XRF bulk chemical scans, and images along with available chronostratigraphy to inter-correlate records in depth space. We then apply a new equatorial Pacific age model to create correlated age records for the last 8 Myr with resolutions of 1-2 kyr. Large magnitude changes in CaCO₃ and bio-SiO₂ (biogenic opal) MAR occurred within that time period but clay deposition has remained relatively constant, indicating that changes in Fe deposition from dust is only a secondary feedback to equatorial productivity. Because clay deposition is relatively constant, ratios of CaCO₃ % or biogenic SiO₂ % to clay emulate changes of biogenic MAR. We define 5 major Plio-Pleistocene Low CaCO₃ % (PPLC) intervals since 5.3 Ma. Two were caused primarily by high bio-SiO₂ burial that diluted CaCO₃ (PPLC-2—1685-2135 ka, and PPLC-5—4465-4737 ka), while 3 were caused by enhanced dissolution of CaCO₃ (PPLC-1—51-402 ka, PPLC-3—2248-2684 ka, and PPLC-4—2915-4093 ka). Regional patterns of CaCO₃ % minima can distinguish between low CaCO₃ caused by high diatom bio-SiO₂ dilution versus lows caused by high CaCO₃ dissolution. CaCO₃ dissolution can be confirmed through scanning XRF measurements of Ba. High diatom production causes lowest CaCO₃ % within the equatorial high productivity zone, while higher dissolution causes lowest CaCO₃ at higher latitudes where CaCO₃ production is lower. The two diatom production intervals, PPLC-2 and PPLC-5, have different geographic footprints from each other because of regional changes in eastern

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Pacific nutrient storage after the closure of the Panama Seaway. Because of the regional variability in carbonate production and sedimentation, the carbonate compensation depth (CCD) approach is only useful to examine large changes in CaCO₃ dissolution.

1 Introduction

5 Cenozoic sediments of the eastern tropical Pacific Ocean have recorded changes to productivity and to the Pacific deep carbon reservoir (Berger, 1973; van Andel et al, 1975; Pälike et al, 2012). Distinctive CaCO₃ profiles can be correlated across thousands of km within the eastern equatorial Pacific because of coherent CaCO₃ variability within the region (Mayer et al, 1986). The large geographic response to ENSO (el Niño-Southern Oscillation; Mantua et al, 1997; Di Lorenzo et al, 2015) demonstrates that the whole surface eastern tropical Pacific changes coherently on the interannual time scale. Large scale flow of abyssal waters southward along the western flank of the East Pacific Rise (Johnson and Toole, 1993; Hautala, 2018) causes the western flank to be bathed by a common bottom water and to share a common signal of abyssal change. Both processes interact to drive these common CaCO₃ profiles across the equatorial region. Since CaCO₃ variability causes large changes of sediment bulk density in the eastern tropical Pacific (Mayer, 1979, Mayer, 1991; Reghelin et al., 2013), the extensive geographic scale of coherent CaCO₃ profiles produces a distinctive set of seismic reflection horizons (Bloomer and 15 Mayer, 1997; Tominaga et al., 2011) linked with major paleoceanographic change in the Pacific Ocean (Mayer et al, 1986).

Reconnaissance paleoceanographic descriptions of the Cenozoic equatorial Pacific (van Andel et al, 1975; Berger, 1973) often gloss over the late Miocene and early Pliocene as being periods almost like the present. The CCD variability within the last 12 million years is not nearly as dramatic as the huge changes earlier in the Cenozoic (Pälike et al, 2012). Nevertheless, as more detail has been generated from better chronology and more comprehensive regional records, significant changes can be found throughout the equatorial Pacific since the beginning of the late Miocene. Variability in the late Miocene and afterward represent profound changes in how CaCO₃ has been produced and recycled within the Pacific.

The change in the calcite compensation depth (CCD) in the world's oceans is a primary indicator of rearrangement of the 25 global carbon cycle. Well-known major changes in CCD are associated with the major climate changes of the Cenozoic (Berger, 1973; van Andel and Moore, 1974; Peterson et al., 1992; Pälike et al., 2012). Once sediments are buried, pore water concentrations quickly reach saturation with respect to CaCO₃. Buried CaCO₃ is unaffected by subsequent changes in ocean chemistry, so the variation reflects the state of the ocean at the time of burial. Fluctuations in the CCD represent changes in the balance between CaCO₃ production in surface waters and CaCO₃ dissolution of carbonate hard parts at the benthic 30 boundary layer (Milliman and Droxler, 1996; Boudreau et al., 2010). CaCO₃ particulate rain rates have a large effect upon the CCD as shown by the CCD being 1 km deeper underneath the equatorial Pacific zone of high productivity versus on its flanks (Berger et al., 1973; van Andel and Moore, 1974).

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The CCD shallows when (a) lower carbonate production results in lower CaCO_3 rain to the seafloor, (b) the $[\text{CO}_3]^{2-}$ content of bottom water decreases and becomes undersaturated with respect to calcite, or (c) rising sea levels allow significantly more CaCO_3 storage on continental shelves and shallow basins (Opdyke and Wilkinson, 1988). Because the CCD strongly responds to changes in production and regional rates of CaCO_3 burial, the global CCD has a complex response to changes in Cenozoic climate. The CCD differs between ocean basins because ocean circulation can alter where CaCO_3 -undersaturated water impinges on sediments regionally (Berger, 1970). The Holocene deep Atlantic Ocean is flushed with deep water with high $[\text{CO}_3]^{2-}$ content originating from the surface North Atlantic. Higher CaCO_3 saturation results in a much deeper CCD than that in the Pacific. The Atlantic CCD shallows in glacial intervals because of the loss of North Atlantic Deep Water (NADW) and intrusion of more undersaturated water from the Antarctic, while the Pacific CCD deepens as the intrusion of low $[\text{CO}_3]^{2-}$ water into the Atlantic basin dissolves CaCO_3 there rather than in the Pacific (Crowley, 1985). The causes for CCD change can be disentangled but require sedimentary records from the different ocean basins as well as additional bulk chemical information beyond CaCO_3 %.

The CCD has varied both on glacial-interglacial scales and over long periods of time. Since large areas of the abyssal ocean basins are subject to CaCO_3 dissolution, climate variability imposes a common regional CaCO_3 stratigraphy modulated by the change in factors that perturb rates of CaCO_3 burial. Such a common chronostratigraphic signal in the eastern equatorial Pacific has been noted through the Cenozoic (Hays et al., 1969; Mayer et al., 1986; Chuey et al., 1987; Farrell and Prell, 1989; Farrell and Prell, 1991; Hagelburg et al., 1995). The development of the typical eastern Pacific CaCO_3 burial profile is complicated by large-scale long-term variation in biogenic production (Farrell et al., 1995; Lyle and Baldauf, 2015). Such variability can change the dissolution-related CaCO_3 signal by changing not only the mass of CaCO_3 that rains to the sea floor but also the relative proportion of CaCO_3 to biogenic opal (bio- SiO_2) in the rain of biogenic hard parts. Nevertheless, knowledge of the processes that modify CaCO_3 deposition allows for common intervals to be identified.

One of the primary objectives of IODP Expeditions 320/321 (PEAT, Pacific Equatorial Age Transect; Lyle et al., 2010) was to join the equatorial portions of essentially continuous sediment records from the 8 PEAT drill sites to study the evolution of the eastern equatorial Pacific for the last 50 million years as well as to intercorrelate those records with ODP Leg 138 sediments for the late Neogene (Mayer et al., 1992). In addition, the equatorial Pacific age model was to be updated based on new chronostratigraphy data (e.g., Channell et al., 2013; Holbourn et al., 2014; Kochann et al., 2016; Drury et al., 2017, 2018).

Another important objective from the PEAT expeditions was to identify major changes and causes of carbonate storage in the eastern equatorial Pacific. Palike et al (2012) did a rapid synthesis of CaCO_3 data on a Cenozoic scale to identify changes in the CCD in the equatorial Pacific using data from the PEAT expeditions and earlier drilling. In the eastern Pacific, the CCD has been relatively deep since the middle Miocene and drill sites have not intersected the local CCD. In order to

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understand causes of eastern Pacific CaCO₃ variability we re-examine the Pliocene and Pleistocene interval, to distinguish intervals of CaCO₃ dissolution and productivity above the CCD from Palike et al (2012).

We study Pliocene and Pleistocene CaCO₃ dissolution in a time interval and region where the CCD is typically deeper than the eastern Pacific sea floor. We explore alternate methods of developing the CCD by extrapolating CaCO₃ MARs from drill sites above the CCD to the depth of zero burial (Lyle et al., 2005) and use XRF-derived CaCO₃/BaSO₄ as measure of local CaCO₃ dissolution (Lyle and Baldauf, 2015). We examine regional variation in the 7 eastern Pacific sites where we have made high-resolution depth correlations and assigned ages with a new eastern Pacific age model and new stable isotope records (Drury et al, 2016, 2017, 2018; Tian et al., 2018).

A key aim is to disentangle CaCO₃ variability caused by dissolution, versus high bio-SiO₂ paleoproductivity. Production intervals have a different CaCO₃ expression at different drill sites because of local changes in relative nannofossil production of CaCO₃ versus diatom production of bio-SiO₂. We will primarily discuss data for the interval from 5.3-0 Ma although the 7 eastern Pacific sites are depth correlated to ≥10 Ma and the age model has been applied to ~8 Ma for all sites (see Supplemental Material). We will only briefly discuss the interval between 8 and 4.5 Ma (the Late Miocene Biogenic Bloom, LMBB) because it has significantly more variability among the set of drill sites and needs further work. This depositional variability has been imposed in the eastern Pacific by the regional footprint of paleoproductivity within the LMBB interval.

2 Drill Sites Studied

We report data from 7 eastern equatorial Pacific drillsites, 4 with XRF scans along the sediment splice (IODP Sites U1335, U1337, U1338, ODP Site 849) and 4 with CaCO₃ data estimated from spliced Gamma Ray Attenuation (GRA) wet bulk density profiles (ODP Sites 848, 849, 850 and 851; see Methods for the process). Locations for the drill sites are shown in Figure 1 and in Table 1.

The seven sites span the equatorial Pacific productivity zone and their positions range from 3°S to 5.3°N (Table 1). At 5 Ma, the sites positions ranged from ~4°S to ~4°N based upon a fixed hotspot backtrack. All of the sites are west of the East Pacific Rise and contain sediments that are primarily biogenic in origin. Sites that are further from the equator and/or deeper have more clay in the sediments (Sites U1335, U1337, and 851) than those shallower and nearer the equator, primarily because of lower carbonate production and preservation but also because of higher dust deposition near the ITCZ, located north of the equator (Hovan, 1995).

The ODP Leg 138 drillsites (Sites 848-851) are positioned between 3°S to 2.8°N along 110°W (Mayer et al., 1992). They are correlated with Neogene sites from IODP Expedition 320/321 further west. All sites reside on the Pacific tectonic plate and

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have been translated to the NW over time by Pacific plate movement (Pálíke et al, 2010). The Leg 138 sites have been cored to basement, which was formed about 11 Ma along 110°W. The Exp 320/321 sites cored to progressively older basement by following a common tectonic flow line from the east Pacific Rise. Each Expedition 320/321 drill site preserves a sediment record of progressively older Pacific equatorial regions. Because they are on older ocean crust than the late Miocene basement recovered at ODP Leg 138 drill sites, the Exp 320/321 drill sites have sediments that extend back to the middle/lower Miocene boundary in the youngest drill in Site U1338, to the Oligocene/Miocene boundary in Site U1337, and to the late Oligocene at Site U1335 (Pálíke et al, 2010).

Primarily because of depth dependent carbonate dissolution, Site U1338 has a sedimentation rate only 75% of that at Site 851, which lies at the same latitude but 450 m shallower because the ocean crust that is half the age of Site U1338. From 5.3 Ma to the Holocene each site deepened by about 200 m because of crustal cooling partly mitigated by sediment deposition shallowing the sea floor. Isostatic subsidence due to sediment loading increased the depth somewhat but subsidence is only ~20% of the added sediment thickness (Lyle, 1997). While significant changes in depth have happened to the 7 drill sites because of crustal cooling and sedimentation, the sites always remained separated by a similar water depth.

3 Methods

Please see the supplemental material for more information about the assembly and calibration of data, including the age model, stratigraphic tie points, revised splices, estimated CaCO₃ profiles, and XRF bulk chemical data.

3.1 Stratigraphic Correlation of eastern Pacific drill sites

We used the Code for Ocean Drilling Data (CODD; <https://www.codd-home.net/>) analytical suite of software tools described by Wilkens et al (2017) for the stratigraphic correlation of all the drillsites. We first investigated all the offsets and splice tie points at each multi-hole drill site to check that the ties were correct. We then built a continuous sediment section for each drill site by linking the sections within the splice. The spliced sediment columns were used to make site-to-site depth correlations. Descriptions of the splicing are given in the Supplemental material and splices used are in Supplemental Tables SM-1 to SM-7. Only Site 849 had significant changes in the lower section older than 4 Ma.

Initial site-to-site correlations were made with the shipboard physical properties data from ODP or IODP collected by scans of the unopened cores prior to splitting, primarily magnetic susceptibility and GRA bulk density. If XRF and stable isotope data were available, the site-to-site correlations were refined with the additional information. During site-to-site correlation, the spliced sediment section at each drill site was stretched/squeezed to match the splice of a master drill site so that the sediment section could be expressed in the equivalent depth of the master site. Site U1338 was chosen as the master drill site, as it has the best balance between high sedimentation rates and sediment recovery across the last 8 Myr. It is also

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suitably situated in the centre of the studied sites. The CODD analytical suite allows age datum levels like magnetochrons and biostratigraphic boundaries to be displayed in the correlation space, and these were used to constrain the depth matching. [Depth ties between drill sites can be found in Supplemental Tables SM-8 to SM-13](#)

5 Correlations were achieved as equivalent depth at Site U1338. Sites U1335, U1337, 851, and 849 were tied directly to Site U1338, while Sites 848 and 850 were first tied to Site 849, and then correlated to Site U1338 through the Site 849 assigned U1338 equivalent depth. We found that there was less ambiguity to work in this fashion because of regional differences in the CaCO₃ profiles. Latitudinal differences in CaCO₃ production make nearby records easier to correlate. For this reason, Site 851 was directly correlated to Site U1338 because it was at the same latitude and its record was more similar to Site U1338 than Site 849. Site 850 has very similar profiles to Site 849 because it is only 1 degree north and has similar diatom deposition intervals. Site 848 was the only site south of the equator, but was nearest to Site 849. We checked the records by displaying them all in Site U1338 equivalent depth and searching for ambiguous correlations.

3.2 The combined Site 849-Site U1338 age model

15 The Pacific Ocean lacks an orbitally resolving age model that covers the last 8 million years. We have constructed one by joining astrochronologically tuned stable isotope data from 0-3.6 Ma from Site 849 (Mix et al. 1995) to the tuned stable isotope data from 3.5 to 8.2 Ma from Site U1338 (Drury et al. 2016, 2018). Sites 849 and U1338 are the most central sediment records to the region we correlate, and provide good stratigraphic ties between the IODP Expedition 320/321 sites and those cored by ODP Leg 138. See Supplemental Material section 3 for more details.

20 The isotope splice for Site 849 was assigned ages by correlation to the new Ceara Rise composite isotope stack in Wilkens et al (2017) to provide age control between 0-5.3 Ma. For Site U1338, we used the astrochronology developed by Drury et al. (2017) for Site U1337 between 3.5-8.0 Ma, which revised the benthic stable isotope age model in Drury et al (2016). Based on depth matching between U1337 and U1338, the better astro-magnetochronology developed at Site U1337 could be used to constrain ages at Site U1338 through the late Miocene (8.0-6.0 Ma), while the remaining 6.0-3.5 Ma interval was astronomically tuned using the benthic δ¹⁸O data (Drury et al., 2017; Drury et al., 2018).

30 The 849 and U1338 age models were grafted together at 3626 ka to make the combined Site 849-U1338 age model, with Site 849 providing the younger section and Site U1338 providing the older one. The two isotope records match well at 3.6 Ma (Figure SM-3). Using the U1338 isotope stratigraphy in the early Pliocene also eliminates missing sections in the Site 849 record found at about 3.7 Ma and 4.2 Ma. The age model was propagated to all sites through use of the site-to-site correlations derived from the depth matched physical properties and bulk composition profiles. See the supplemental material for more details and for the age model tables (Tables SM-14 to 17).

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3.3 XRF scanning at Sites 849, U1335, U1337, and U1338

Only the XRF data from Site 849 are new in this paper. XRF scanning data for Sites U1335, U1337, and U1338 result from previous work. Raw and processed (but uncalibrated) data for Sites U1335 and U1337 data are found in Shackford et al (2014). Similarly, raw and processed XRF scan data for Site U1338 are found in Lyle et al. (2012). Calibrated XRF scan data for CaCO₃ for Site U1338 are found in Lyle and Backman (2013), while calibrated Site U1335 CaCO₃ data are found in Wilson (2014). Wilson (2014) also published calibrated XRF data for major elements for Sites U1337 and U1338. Site U1335 XRF data are found in Supplemental Table SM-18, including the calibrated CaCO₃%. Calibrated XRF scan data for Site U1337 and for Site U1338 are found in Wilson (2014) and are listed in Supplemental Tables SM-19 and SM-20. XRF data for Site 849 are found in Supplemental Table SM-21. Bio-SiO₂ calibration data for Site 849 from discrete bio-SiO₂ extractions are found in Table SM-22; shipboard CaCO₃ analysis from Mayer et al (1992) was used to calibrate Site 849 CaCO₃ %.

The major elements (Al, Si, K, Ca, Fe) and significant minor elements (Ti, Mn, Ba) were measured using the Avaatech scanning XRF at the IODP Gulf Coast Repository for Sites 849, U1335, U1337, and U1338 (Lyle et al, 2012; Shackford et al., 2014; Wilson, 2014). The element data was processed using the normalized, median-scaled (NMS) method of Lyle et al (2012), and then the data for U1337 and U1338 were calibrated with Inductively Coupled Plasma Mass Spectrometer (ICP-MS) analyses of bulk sediment for the elements Al, Fe, Mn, Ti, and Ba (Wilson, 2014). NMS data were calibrated to shipboard and other discrete CaCO₃ measurements to estimate CaCO₃ in all of the XRF sites (Lyle and Backman, 2013; Wilson, 2014). In addition, bio-SiO₂ was measured on discrete samples from 3 sites (849, U1338, U1337) to calibrate an XRF bio-SiO₂ estimate. Discrete bio-SiO₂ data for Sites U1337 and U1338 are reported in Wilson (2014) and the Site 849 bio-SiO₂ data are in Table SM-22. Clay was estimated by assuming that clay has constant TiO₂ and using the calibrated XRF TiO₂ estimate. Clay is assumed to have the same composition as Taylor and McLennan (1995) upper continental crust, which has 0.3% Ti. Clay-bound Si was estimated using the Taylor and McLennan (1995) Si/Ti ratio for upper continental crust. Bio-SiO₂ was calibrated to the total Si minus the clay component (Lyle and Baldauf, 2015). See Supplemental Material Section 4.1 for more details. For Site 849, we correlated the XRF Fe₂O₃ NMS to a ²³²Th estimate of clay from the upper part of the sediment column (Winckler et al, 2008). We used the XRF Fe₂O₃ because Ti contents were often below the XRF detection limit deeper than 130 m Composite Coring Depth below Sea Floor (CCSF) and because the oxide bound Fe is minimal. We used barite data from Ma et al. (2015) to calibrate the Site 849 XRF Ba data, and used the bio-SiO₂ analyses in Table SM-22 where bio-SiO₂ was extracted using the KOH dissolution technique (Olivarez Lyle and Lyle, 2002) to calibrate the Site 849 XRF bio-SiO₂. The percentages are reported without structural water—since there is some question about the dependence of bio-SiO₂ structural water on the organisms that make the tests. See Supplemental Material Section 4.2 for more details of the Site 849 XRF data acquisition and calibration.

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The XRF scan data extend beyond 0-8.2 Ma for Sites U1335, U1337, and U1338, to basalt crust at Sites U1337 and U1338, but only to a depth of 301.2 m CCSF at Site U1335. The records for Sites U1335 and U1337 cover the entire Neogene, while Site U1338 starts just below the early/middle Miocene boundary. Because of time constraints, Site 849 was scanned only to 7.2 Ma. The XRF scanning produced continuous orbital-resolving records of estimated CaCO₃ at all 7 sites, with ages for the 0-8.2 Ma section from this study.

3.4 CaCO₃ % estimates from GRA wet bulk density, Sites 848, 849, 850, and 851

It has long been known that variations in bulk density in the eastern equatorial Pacific are correlated to changes in CaCO₃ content (Mayer, 1979; Mayer, 1991; Hagelberg et al., 1995; Reghelin et al., 2013). CaCO₃ can be calculated from wet bulk density in the equatorial Pacific because the sediments are essentially a mixture of bio-SiO₂ and biogenic CaCO₃ with less than 10% clays. CaCO₃-rich sediments have higher bulk density than porous bio-SiO₂-rich sediments (Mayer, 1991). After correcting for burial compaction that reduces porosity with depth and causes an increasing trend in bulk density, the variation in the "decompacted" bulk density can be converted to estimated CaCO₃ by correlating shipboard CaCO₃ data to the decompacted GRA bulk density. Here we provide CaCO₃ estimates from GRA bulk density for Sites 848, 850, and 851 along the revised splices we made. We also estimated CaCO₃ at Site 849 from bulk density in addition to the XRF estimate in order to compare the XRF and bulk density estimates of CaCO₃. When compared with shipboard measurements the GRA-derived CaCO₃ % estimate (sd of difference from measured ±5.86%; see Figure SM-4 in the supplemental material) was somewhat damped with respect to the discrete measurements of CaCO₃ % at Site 849. The XRF-derived CaCO₃ estimate (sd of difference from measured: ±3.86%) has a range that better matches that of the shipboard discrete measurements. Nevertheless, both estimates capture the same trends in the CaCO₃ profile. See Section 5 of the Supplemental Material for more details. Estimated CaCO₃% data are in Supplemental Tables SM-24 to SM-27.

3.5 Mass Accumulation Rate (MAR) calculation

The bulk sediment percentage data at each site were converted to MAR using the Site 849-U1338 age model, measured physical properties, and the bulk chemical data. The composition and physical properties data were interpolated to even 1-2 kyr spacing, then smoothed with a 20-point binomial filter before being resampled at 10-kyr intervals to accommodate probable errors in the age model and site-to-site correlations. MAR calculations are much more sensitive to age errors than age profiles of sediment components because they depend on the differential of depth versus time (sedimentation rate) as well as the time-depth correlation at each site. Bulk MAR was calculated by multiplying the dry bulk density by the sedimentation rate from the age-depth relationship. Individual component MARs were calculated by multiplying by the fraction of that component in the dry sample by the bulk MAR.

Bio-SiO₂, BaSO₄, and clay MAR records were created at the sites where both XRF data and independent discrete measurements for bio-SiO₂ and a clay-bound element existed. Sites U1337, U1338, and 849 had data suitable to calibrate the

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records, as discussed more in the Supplemental Material. Discrete chemical analyses have never been done for Site U1335, so only the CaCO₃ record is calibrated at this time, using shipboard CaCO₃% data from IODP Expedition 320/321. Ratios of uncalibrated Si to Ti from Site U1335 suggest that the sediments have low bio-SiO₂ contents. MAR data are found in Supplemental Tables SM-28 to SM-34

4. Eastern Equatorial Pacific Carbonate Deposition Patterns

We primarily describe the factors that have shaped CaCO₃ % and MAR profiles in the Pliocene and Pleistocene, because there are good examples of both production and dissolution dominated intervals since 5.3 Ma and because the complex nature of the LMBB interval neris additional work. We have found that the structure caused by changes in CaCO₃ production has a latitudinal component (Honjo et al, 1995), while dissolution signals are more widespread but are strongest at deep sites underneath lower production. Because the East Pacific Rise is roughly N-S in orientation, the depth effect imposes a longitudinal pattern upon the production pattern. Furthermore, a 100-kyr cyclicality of CaCO₃ content appears at about between 1.5 and 2 Ma and increases to the present, much earlier than the 100-kyr cycles of oxygen isotopes.

The CaCO₃ % and CaCO₃ MAR profiles at all seven sites exhibit long period variability and orbital cyclicality (Figures 2 and 3). We have used the CaCO₃ % profiles to define five low long-period CaCO₃ % transients (Pliocene-Pleistocene Low CaCO₃ intervals, PPLCs) in Table 2. We use CaCO₃ % rather than MAR because (1) the percentage profiles can be directly measured as the sediment sections are processed at sea and they are the basis for most CCD reconstructions, (2) the CaCO₃ % variability is chronostratigraphically synchronous across the east central Pacific, (3) the results are easily compared to earlier observations from other cores and drill sites where only CaCO₃ % data are presented (e.g., Mayer et al, 1986, Farrell et al., 1991), and (4) the large changes of CaCO₃ produce the characteristic seismic horizons found in the eastern Pacific (Mayer et al, 1986; Bloomer and Mayer, 1997). We then use MARs and other elemental data to understand the causes of each PPLC.

4.1 Low CaCO₃ % Intervals in the Pliocene and Pleistocene

Two primary factors cause low CaCO₃ intervals—excess bio-SiO₂ production and/or higher than average relative CaCO₃ dissolution. Higher dissolution can result from an increase of dissolution at the sea floor, or a reduction of CaCO₃ surface production with little change of sea-floor dissolution. The late Miocene and early Pliocene have high CaCO₃ variability in the LMBB interval largely driven by variability in relative bio-SiO₂ and CaCO₃ production. Low CaCO₃ intervals are coherent through all 7 records and have lowest CaCO₃ in deeper sites away from the highest productivity. In Table 2 and Figure 2, we have defined five PPLCs. The same low carbonate intervals can also be found in the low-resolution profiles of Deep Sea Drilling Project (DSDP) Sites 572 and 573 from Farrell and Prell (1991), although the timing of the older low CaCO₃ intervals are shifted in age because the Farrell and Prell (1991) age model contains age errors for the bio-events and

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magnetochrons that have been resolved by further study. The lowest CaCO₃ % occurs at about 4 Ma (Figure 2, PPLC-4C, 3834-4093 ka), and since that time CaCO₃% has slowly climbed to peak at about 500 ka, just before the initiation of PPLC-1.

5 The ~100 kyr CaCO₃ variation (Hays et al, 1969; Farrell et al, 1989; Murray et al, 2000) characteristic of the Pleistocene equatorial Pacific dominates the CaCO₃% records after 1.9 Ma and the CaCO₃ variation is highest after 1 Ma (Fig. 2). The large CaCO₃ swings are most prominent in Sites U1337 and U1335, which are deep and relatively far from the equatorial productivity band. Sites along the Leg 138 transect have the smallest variability because they are also the shallowest sites. Earlier studies have found that CaCO₃ % is high in Pleistocene glacial climate intervals and is low in interglacials (Chuey et al., 1987; Farrell and Prell, 1989). Development of ~100-kyr cyclicity in the carbonate record predates the development of 100-kyr periodicity in the oxygen isotope record by about 1 Myr. The 100-kyr CaCO₃ cycles are discussed further in sections 4.6 and 5.2. The older part of each record in Fig. 2 varies at a slower pace than 100 kyr.

4.2 Potential sediment focusing at U1337

15 Except for Site U1337, CaCO₃ MAR records are similar throughout the eastern equatorial Pacific, indicating that much of the variability in an individual record is caused by regional factors, not local sedimentation processes (Figure 3). Site U1337 has anomalous deposition that may be caused by local sediment focusing (Francois et al, 2004; Lyle et al, 2005a; Tominaga et al., 2011; Marcantonio et al, 2014). Variability of the bulk sediment MAR is typically caused by changes of CaCO₃ MAR that are coherent regionally. However, Site U1337 is unique because it clearly has much higher bio-SiO₂ and clay deposition unrelated to CaCO₃ burial in certain time intervals. The highest anomaly occurs between about 4.5 and 3 Ma, and a secondary anomaly occurs between 6.2 and 5.4 Ma. The two intervals may have had higher than average local deep current activity to focus the sediments to Site U1337. We propose that deposition at Site U1337 is the result of local sediment focusing adding fine sediments to the sediment column at the drill site (Marcantonio et al, 2014; Lyle et al, 2014; Lovely et al, 2017). When currents are moderate in strength, sediment focusing preferentially moves the fine fraction of sediments (Lyle et al, 2014; Lovely et al, 2017) as is observed in the Site U1337 record. Our interpretation is supported by seismic profiles and bottom bathymetry, which find active erosional channels around the northern and eastern edges of the Site U1337 survey area (Figure SM-1b, SM-5, Supplemental Material Section 7; Pálke et al., 2010).

25 Surprisingly, the sediment focusing at Site U1337 does not strongly affect the CaCO₃ % profile, but does result in anomalously high sedimentation rates, lower average CaCO₃ contents, and higher than expected CaCO₃ MAR. For example, average CaCO₃ % for Site U1337 is 39.5% versus 54.5% for U1335, despite Site U1335 being 1.5° further north and further away from equatorial production. Similarly, CaCO₃ MAR at Site U1337 averages 20% higher than the CaCO₃ MAR at Site U1338 for the last 8 Myr despite being further from the equator than Site U1338 (Fig 3). Analyses of sediment trap and surface sediment data in the equatorial Pacific found that CaCO₃ is much less affected by sediment focusing than the fine-

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grained components (Lyle et al., 2014). Observations at Site U1337 suggest that focusing over the Neogene enhances CaCO₃ MAR to some extent, but more greatly affects the MAR of finer sediment fractions.

4.3 Observed high production intervals; PPLC 5 (4465 to 4737 ka) and PPLC 2 (1685 to 2135 ka)

5 With a proper age model and with XRF scanning data it is possible to distinguish a CaCO₃ low caused by elevated bio-SiO₂ production from intervals caused by higher CaCO₃ dissolution at the sea floor. High bio-SiO₂ burial during Pliocene and Pleistocene diatom deposition intervals can be distinguished by (1) low CaCO₃ content, presumably by dilution with diatom bio-SiO₂ for sites near the equator, (2) little change in clay MAR but large change in bio-SiO₂ content and bio-SiO₂ MAR, (3) increase or little change in CaCO₃ MAR, and (4) if there is a latitudinal transect, lowest CaCO₃ % and high diatom deposition will be found at sites closest to the equatorial upwelling zone. Sites away from the equator may actually have higher CaCO₃ % and CaCO₃ MAR in the equivalent interval presumably because elevated nutrients stimulate higher calcareous nannofossil production relative to time intervals on either side. The low CaCO₃ near the equator is caused mostly by dilution of CaCO₃ by high fluxes of bio-SiO₂ to the sea floor.

15 PPLC-5 (4737-4465 ka) is the last diatom deposition interval at the end of the LMBB and exhibits all the characteristics of a high production interval. Sites 849 and 850, sites straddling the equator at 5 Ma (Table 1), exhibit a pronounced CaCO₃ % low at this time (Figure 2), but sites farther away from the equator exhibit much smaller CaCO₃ % change (Sites 848, 851, and U1338) or even slight CaCO₃ % increases (Sites U1337, U1335). All sites have relatively high or unchanged CaCO₃ MAR within PPLC 5 (Figure 3). Bio-SiO₂ data is only available for Sites 849, U1338, and U1337, and the records exhibit a large bio-SiO₂ MAR peak at Site 849 (Figure 4), a small peak at Site U1338 (Figure 6), and ambiguous change at Site 20 U1337, exacerbated by potential sediment focusing there.

PPLC-2 (2135-1685 ka) is found at the equator at Site 849, but is also found at Site U1338. The equivalent of the PPLC-2 interval has also been reported to the east of the Galapagos Islands (Sites 846 and 847, Farrell et al, 1995; Site 846, Lawrence et al., 2006; Site 1240, Povea et al., 2016). There are clear bio-SiO₂ MAR peaks at Site 849 (Figure 4) that match in time and magnitude with a similar interval from Site 1240 (Povea et al, 2016). Major bio-SiO₂ MAR highs within PPLC-2 align with glacial intervals in the oxygen isotope series between Marine Isotope Stage (MIS) 78 and MIS 60, even though the highest bio-SiO₂ MAR is in an interglacial (MIS 75). CaCO₃ % lows within PPLC-2 don't always align with high bio-SiO₂ MAR, indicating CaCO₃ dissolution has also occurred. At Site U1338, low CaCO₃ % and highest bio-SiO₂ MAR are not aligned, evidence that a dissolution overprint exists.

30 The level of dissolution can be assessed by the CaCO₃:BaSO₄ ratio (Figure 5; Supplemental Table SM-22). Lyle and Baldauf (2015) proposed that the CaCO₃:BaSO₄ ratio is a good measure of relative preservation, since CaCO₃ preservation is highly variable, but Ba preservation is relatively constant (Dymond et al, 1992; Balakrishnan Nair et al, 2005; Griffith and Paytan,

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2012). In addition, particulate Ba rain caught in sediment traps is proportional to the C_{org} rain, so normalizing to Ba largely normalizes out the production variability and leaves a signal dominated by $CaCO_3$ dissolution. Both bio-Ba and $CaCO_3$ rain are well-correlated to particulate organic carbon rain (Dymond and Collier, 1996), so changes in the $CaCO_3:BaSO_4$ ratio primarily mark changes in the relative preservation of $CaCO_3$ (Lyle and Baldauf, 2015). Highest $CaCO_3:BaSO_4$ ratios in the XRF data set are found at Site 849, which is shallower and has about twice the sedimentation rate of Site U1338 or U1337 (Table 2). As expected, the ratio indicates lower dissolution while compensating for the higher production at Site 849.

PPLC-2 has generally low $CaCO_3:BaSO_4$ ratios which indicates that the interval not only has higher bio- SiO_2 burial indicative of high surface productivity (Fig 4) but also higher dissolution (Fig 5). Production and dissolution don't have to be mutually exclusive and can be superimposed to produce a low $CaCO_3$ interval.

4.4 Early Pliocene extensive $CaCO_3$ dissolution: PPLC-4 (4093-2915 ka)

Immediately after the LMBB ends there is the PPLC-4 interval of very low $CaCO_3$ %. The minimum is found throughout the eastern and central equatorial Pacific west of the East Pacific Rise. The base of PPLC-4 constitutes the acoustic impedance contrast that causes the Pliocene 'green' seismic horizon (Mayer et al, 1986; Bloomer et al, 1997). At Site 850, Bloomer and Mayer (1997) identified a series of seismic horizons that can be linked to the $CaCO_3$ variability associated with PPLC-3, 4, and 5.

PPLC-4 is made up of 3 low $CaCO_3$ % intervals between 2915 and 4093 ka (Table 2) with lower $CaCO_3$ % and more consistently low $CaCO_3$ % at sites further away from the equator. The lowest $CaCO_3$ % in all the records is found at U1337 between 4500 and 3500 ka because apparent sediment focusing has caused extensive clay and bio- SiO_2 dilution in addition to $CaCO_3$ % dissolution (Figures 2 and 3). Nevertheless, relatively shallow sites along the Leg 138 transect also exhibit coherent $CaCO_3$ change, as exhibited by the standardized $CaCO_3$ % records (Figure 2b). The low bulk MAR and $CaCO_3$ MAR over the PPLC-4 interval indicates that dissolution was a major factor shaping the $CaCO_3$ record. The $CaCO_3:BaSO_4$ records (Fig 5) also clearly show the low $CaCO_3:BaSO_4$ ratios indicative of dissolution in the PPLC-4 intervals. They have the lowest $CaCO_3:BaSO_4$ ratios in the time series.

The PPLC-4 set of dissolution-induced $CaCO_3$ % lows occurs at an important juxtaposition of tectonic and environmental influences. Slow closure of the Central American Seaway was severing connections between the Caribbean and Pacific. However, extensive changes were also going on in global climate, so it is currently impossible to isolate the seaway closure effect from other changes in the eastern Pacific (Molnar, 2008; O'Dea et al, 2016; Molnar, 2017).

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4.5 PPLC-3 (2684-2248 ka): CaCO₃ dissolution at the initiation of Northern Hemisphere glaciation

PPLC-3 consists of two dissolution intervals separated by a distinctive triplet of high CaCO₃% peaks marked on figures 2 and 5. PPLC-3 can best be seen in the stacked and standardized CaCO₃ % profile (Figure 2, bottom). The PPLC-3 dissolution intervals surrounding a high carbonate triplet are also found at DSDP Sites 573/574 (Farrell and Prell, 1991). The consistent expression of the PPLC-3 CaCO₃ % lows merited their inclusion in this list. Deeper sites within the eastern Pacific have prominent lows around the triplet of high CaCO₃ %, while records from the shallower Leg 138 sites have weaker variability. Along the relatively shallow Leg 138 transect (~3800 m water depth) PPLC-3 lows are most pronounced south of the equator at Site 848 (3°S) and north of the equator at Site 851 (2.7°N), as expected if dissolution is superimposed upon an equatorial maximum of CaCO₃ production. The timing of PPLC-3 suggests an association with the initiation of northern hemisphere glaciation, or at least with changes in abyssal circulation at that time. Dissolution at PPLC-3 can also be determined by the CaCO₃:BaSO₄ ratio (Figure 5). The CaCO₃:BaSO₄ ratio around PPLC-3 clearly shows similar responses in all the records we have, with two low CaCO₃ intervals surrounding the CaCO₃ % high.

4.6 PPLC-1 (51-402 ka): low CaCO₃ interval among the 100-kyr Pleistocene cycles

The PPLC-1 interval is superimposed upon the classic Pleistocene Pacific 100-kyr glacial-interglacial carbonate cycles (Figure 5). Significant 100-kyr CaCO₃ cyclicity first appears at about 1900 ka in the eastern Pacific, well before appearance of 100-kyr benthic oxygen isotope cycles at ~900 ka that characterize the end of the Mid-Pleistocene Transition. If Sites U1338 and 849 are compared it is clear that dissolution is a major factor in the cycles. Site 849 has much higher CaCO₃:BaSO₄ (less dissolution) than the other sites and much weaker 100 kyr cycles, suggesting that dissolution is more important to increase the variation within the Site U1337 and Site U1338 record. Not only does dissolution increase the 100-kyr cycle amplitude but also selectively removes higher frequency changes in the CaCO₃:BaSO₄ ratio that are apparent at Site 849. Highest CaCO₃ preservation as well as highest CaCO₃ % occurs just before the beginning of PPLC-1. The time offset of the low CaCO₃:BaSO₄ ratio at Site 849 results from relatively weak dissolution in the early part of PPLC-1. These cycles largely match the Pleistocene CCD changes found by Farrell and Prell (1989) at around 140°W.

5 Discussion

Two major processes affect carbonate burial in the equatorial Pacific. High production within the surface waters of the equatorial productivity belt may increase CaCO₃ rain but dilute CaCO₃ sediment concentrations with bio-SiO₂. Dissolution by deep waters from the North Pacific rich in dissolved inorganic carbon (DIC) and low in [CO₃²⁻] may reduce CaCO₃ burial by increased CaCO₃ dissolution at the sea floor. Notably, if CaCO₃ production decreases but dissolution at the bottom stays relatively constant, increased dissolution of CaCO₃ will also occur. Thus, CaCO₃ burial is the net difference between biogenic CaCO₃ production and dissolution at the sea floor. Dissolution effects can be distinguished from those caused by productivity, in particular, dilution by high bio-SiO₂ deposition, by using burial fluxes (MAR) along with other sediment

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chemical data. BaSO_4/MAR are especially useful to distinguish between dissolution and reduced production as the primary cause of an interval of low $\text{CaCO}_3\%$.

The CCD concept is most useful at a reconnaissance scale. But, using a ratio such as $\text{CaCO}_3/\text{BaSO}_4$ to normalize for different CaCO_3 rain rates provides the best indicator of relative dissolution at any given drill site (Figure 5). We find that dissolution is most pronounced in the early Pliocene (PPLC-4) and is evidence that a major reorganization of carbon storage in the Pacific occurred then. We also found that bio- SiO_2 dilution shapes the record, especially in PPLC-5 and PPLC-2. More XRF data, especially from ODP Leg 138 and ODP Leg 202 would be very useful to better understand the Pacific carbon cycle and the regional to global biogenic sedimentation patterns that are observed.

10 5.1 Disentangling production versus dissolution: Eastern Tropical Pacific Sedimentation since the Miocene Climate Optimum (14 Ma)

Profound changes in equatorial Pacific biogenic deposition from the middle Miocene to Recent were recorded at Site U1338 (Lyle and Baldauf, 2015). Dilution of CaCO_3 by bio- SiO_2 deposition appears to be relatively common in the middle and late Miocene (Holbourn et al, 2014; Lyle and Baldauf, 2015). For the most part, CaCO_3 burial was high since the end of the Miocene Climate Optimum, except within the late Miocene carbonate crash, 11-8 Ma (Lyle et al., 1995; Roth et al., 2000; Lyle and Baldauf, 2015). Poorest CaCO_3 preservation occurred at about 9.7 Ma. Following the carbonate crash, an interval of high biogenic production, the LMBB, occurred in the equatorial region west of the East Pacific Rise from 8 to about 4.5 Ma, persisting into the early Pliocene (Farrell et al, 1995; Lyle and Baldauf, 2015). Consistently high sedimentation rates and biogenic deposition characterizes the LMBB with considerable variations in bio- SiO_2 and CaCO_3 burial. The last diatom production interval within the LMBB (PPLC-5) ended at 4465 ka, within the early Pliocene (see Section 5.2.1 for further discussion of the LMBB).

Lows in $\text{CaCO}_3\%$ caused by dissolution can be identified by using comparisons of more easily dissolved components to more dissolution resistant forms. CaCO_3 preservation at Site U1338 was derived not only using the ratio of CaCO_3 to bio- BaSO_4 (Lyle and Baldauf, 2015), but is also by benthic/planktic foraminifera ratios (Pälike et al, 2010). High bio- $\text{SiO}_2\%$ in sediments mostly reflects high bio- SiO_2 deposition, but is superimposed over elevated dissolution of CaCO_3 during the late Miocene Carbonate Crash interval. Not only are ratios and MAR variable throughout the late Miocene, but the types of diatoms and their rates of burial varied as well. In the LMBB, the most diatom-rich intervals are a mixture of mat forming and upwelling diatom species, but the upwelling species extended over much longer time ranges than the high diatom deposition intervals and are not restricted to them. Northern subtropical diatoms were abundant at the beginning of the LMBB, and were replaced by diatoms now associated with the southern hemisphere subtropics by 4.4 Ma (Lyle and Baldauf, 2015).

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Changes in biogenic deposition apparently result from variable responses under different nutrient/upwelling conditions by different plankton. At Site U1338, BaSO_4 , bio- SiO_2 , and CaCO_3 MAR reveal a major drop in burial at the end of the LMBB but also some second order cyclicity (Fig 6). PPLC-4b and -4c intervals are associated with low biogenic deposition of bio- SiO_2 and bio-Ba, so CaCO_3 dissolution within those intervals may have been enhanced by low relative production of CaCO_3 .

5 Estimated clay deposition varied much less than that of the biogenic components, especially across the LMBB. Since Ba production is linear with respect to organic carbon export production (Dymond et al, 1992), the BaSO_4 /clay ratio should be relatively constant if changes in dust-delivered Fe were the primary cause of the large-scale changes in productivity. At the end of the LMBB, the BaSO_4 /clay ratio dropped (top graph on Figure 6) but the clay remained relatively constant (bottom graph on Figure 6), indicating that changes in dust delivery of Fe was not the main cause to end the LMBB. In contrast, in

10 PPLC-2, the BaSO_4 /clay ratio was essentially constant despite relatively high BaSO_4 MAR, indicating that changes in dust-derived Fe may have been critical to the change in surface productivity.

The observed changes in apparent productivity exceed the envelope encompassed by seasonal change in the JGOFS Pacific sediment trap experiment (Honjo et al, 1995; Dymond and Collier, 1996). Further work to understand the biogeochemical

15 response to long-term climate change should be done. Not only were there long intervals of high biogenic deposition, but also the ratios of the different biogenic hard parts varied by large amounts and different species within the phytoplankton participated at different times.

5.2 Primary Productivity in the eastern equatorial Pacific (PPLC-5 & -2)

The LMBB (with PPLC-5) and PPLC-2 at 2 Ma result from major changes in primary productivity in the eastern Pacific.

20 Apparently conditions conducive to high primary production were in place for hundreds of thousands of years (Table 2) modulated by Milankovitch cycles. Here we discuss the most likely causes of these prolonged phases.

5.2.1 The Late Miocene Biogenic Bloom and PPLC-5

The LMBB has multiple intervals of high biogenic deposition after 8000 ka (Figure 3; Farrell et al, 1995; Lyle and Baldauf, 2015), ending with PPLC-5. The significant difference in biogenic sediment accumulation associated with the LMBB is

25 easily observed by the change in slope of the age-depth curves at about 4400 ka (Fig. 7). Each drill site exhibits slower sedimentation rates after -4400 ka, marking the end of the LMBB. In Figure 1, the spatial pattern of the LMBB is also shown by a ratio of the thickness of the older sediments (8-4.5 Ma) from the LMBB to that of the younger ones since the end of the LMBB (4.5-0 Ma), referred to on Figure 1 as the LMBB/Pliocene ratio. Because only two time horizons need to be identified, and because this metric uses only sediment thickness, other sites can be added easily to the map using the published site descriptions. Additional Leg 138 Sites (Sites 844, 845, 846, 847, 852, 853, and 854) plus sites from ODP Leg

30 202 (Sites 1238, 1239, and 1241) and DSDP Sites (83, 158, and 572) were used to map the regional extent of the LMBB and its strength.

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Despite the shorter total time span (3.5 versus 4.5 Myr) and additional sediment compaction suffered by the older interval, the thickness of sediment section deposited during the 8-4.5 Ma time interval from many eastern Pacific drill sites is often more than that deposited in the 4.5-0 Ma interval. During the LMBB the largest ratios mark the fastest deposition and are found in the region from roughly 88°W to 120°W, just north of the modern equator (orange shading in Figure 1). Factoring in Pacific plate motion, these sites were at the equator around 6-7 Ma. Drill sites from eastern corner of the equatorial Pacific do not have high deposition during the LMBB, although there are multiple intervals of high bio-SiO₂ deposition within that interval (Farrell et al., 1995). The difference in sedimentation has been attributed to nutrient trapping in the easternmost Pacific and increased biogenic sediment production after the Central American Seaway closed (Farrell et al., 1995).

The cause of the variability during the LMBB needs further investigation and documentation. Many regions worldwide have intervals of high production in the late Miocene and early Pliocene, which may have a common cause. Globally, high biogenic deposition in the Indian Ocean, North and Southwest Pacific, and the Benguela upwelling zone define a proposed global late Miocene production interval (Farrell et al., 1995; Filippelli, 1997; Dickens and Owen, 1999; Diester-Haass et al., 2002; Grant and Dickens, 2002).

High biogenic burial is common within the late Miocene, but the timing varies significantly between regions. Dickens and Owen (1999) propose that upwelling in the Indian Ocean was high between 9 and 3.5 Ma but most intense between 6 and 5 Ma. Dickens and Barron (1997) recognized an interval of high pennate diatom deposition between 5.9 and 5.0 Ma in the subarctic North Pacific and noted that the timing matched pennate diatom layer deposition in the equatorial Pacific (Kemp and Baldauf, 1993). Highest biogenic deposition in the Benguela current region also occurred in the period between 7 and 4.5 Ma (Diester-Haass et al., 2002). Within the Expedition 320/321 sites and the ODP Leg 138 sites along the 110°W transect, there is also high but variable biogenic MAR between ~8 Ma and the end of PPLC-5 at 4.47 Ma that indicate high primary production. The highest biogenic deposition in the eastern equatorial Pacific was between 7 and 6.5 Ma. Broadly, there is high biogenic production and burial in the late Miocene after 8 Ma.

Hypotheses to the cause of high primary productivity vary. Filippelli (1997) proposed that the uplift of the Himalayas (Molnar et al., 1993) and late Miocene intensification of the Asian Monsoon caused higher weathering and larger transport of nutrients to the oceans. Diester-Haass et al (2002) suggested that reorganization of ocean circulation is likely to have played an important role, as well as intensification of trade winds. Recent reconstructions of Himalayan uplift and changes in the monsoon have found that much of the uplift occurred prior to the late Miocene, weakening the weathering hypothesis (Tada et al. 2016).

Higher biogenic deposition within the equatorial Pacific broadly occurred within the late Miocene but also extends through the Pliocene in the easternmost equatorial Pacific (Fig 8). Million-year increments of CaCO_3 MAR and noncarbonate (mostly bio- SiO_2) MAR are shown from drill sites in the equatorial zone from near the 81°W longitude of the coast of Ecuador to almost 120°W , halfway to Hawaii. For all but the easternmost part of the equatorial transect high CaCO_3 MAR is confined within the time frame of the LMBB. However, east of about 100°W on the Nazca Plate, the bio- SiO_2 deposition is much higher in the Pliocene and Pleistocene, as shown by the increased noncarbonate (mostly bio- SiO_2) MAR post-LMBB.

A similar lack of a common pattern is found worldwide. Highest deposition in the eastern equatorial Pacific LMBB is in the region near the equator between about 88°W and 120°W (Fig 1), and the highest MAR was at the beginning of the LMBB around 7 Ma. Site 1085 within the Benguela Current has highest biogenic MAR at the end of the LMBB interval (Diester-Haass et al., 2002). Peak diatom deposition in the subarctic North Pacific occurred in the middle of the LMBB interval, between 6 and 5 Ma (Dickens and Owen, 1999; Dickens and Barron, 1997). And, in the California current region, diatom deposition decreased offshore at the beginning of the LMBB (7.5 Ma) to become more confined to the coastal region, implying decreased overall bio- SiO_2 deposition after 7.5 Ma (Barron et al., 2002).

Farrell et al (1995) described the abrupt drop in biogenic deposition along the 110°W transect at the end of the LMBB but continued high deposition to the east. They proposed that the change was related to movement of biogenic depocenters resulting from Central American Seaway (CAS) closure. Sites drilled on the Carnegie Ridge by ODP Leg 202 support a major increase in biogenic sedimentation in the east associated during the time of CAS closure (Fig 8). Both Sites 1238 and 1239, near Ecuador, are situated on crust formed in the late early Miocene. Both essentially have a hiatus until ~ 8 Ma (ODP Leg 202 Shipboard Scientists, 2003). Biogenic sedimentation at both Sites 1238 and 1239 rapidly increased after 7 Ma, peaked between 3 and 5 Ma, and continued to remain high up to the Holocene. Apparently, the easternmost Pacific became more productive because of the formation of the Isthmus of Panama. Nevertheless, high levels of paleoproductivity found after 8 Ma worldwide suggest that regional production intervals are superimposed upon a global signal. Now that high-resolution records of biogenic deposition are available from the east-central Pacific, there is a need to revisit the timing of regional changes in biogenic deposition through the late Miocene globally.

5.2.2 Unravelling the driving force of equatorial productivity

When the LMBB and PPLC-2 are examined in detail in the equatorial Pacific, it is apparent that the dynamics of nutrient delivery to the equatorial Pacific cannot be ignored. Figure 4 shows the PPLC-2 interval from Site 849, and is comparable to Site 1240 in the Panama Basin (Povea et al, 2016) and Site 846 (Lawrence et al, 2006). There is clearly an orbital periodicity at Site 849, as well as depositional events on the <1 kyr resolution of the XRF record.

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Similarly, within the LMBB at the XRF-scanned intervals of Site U1338 and Site 849 there is high bio-SiO₂ variability on the millennial scale based upon the XRF estimated bio-SiO₂:clay ratio, suggesting that long bio-SiO₂ deposition intervals are made up of large numbers of individual bio-SiO₂ deposition events. These deposition intervals correlate to the intervals where diatom mats have been found in the equatorial Pacific cores, around 4.2 Ma, 5.5 Ma, and 7.3 Ma (Figure F23, Pálike et al. 2010; Kemp and Baldauf, 1993). As mentioned previously, clay deposition within the LMBB is about the same as that through the Pliocene and Pleistocene (Fig 7), so the elevated biogenic MARs do not result from higher dust fertilization but instead apparently result from interoceanic reorganization of nutrient inventories (Ziegler et al. 2008). The BaSO₄/clay ratio (top of Fig 7) illustrates the higher relative deposition of biogenic sediments to clay within the LMBB, evidence for nutrient reorganization.

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High productivity intervals in the eastern Pacific result from a combination of factors. There appears to be elevated production globally within the LMBB, for example, indicating higher availability of nutrients in surface waters generally in the late Miocene. However, timing of intervals of high productivity depends on how the nutrients flow to different upwelling regions, and provide insight into how the sub-surface oceans have changed. The appearance of PPLC-2 and its strong expression to the east of our study (Lawrence et al. 2006; Povea et al. 2016), show that long intervals of better connection to nutrients have occurred well into the Pleistocene.

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5.3 Monitoring changes in depth dependent dissolution: eastern equatorial Pacific CCD versus CaCO₃:BaSO₄

The CCD is a common metric for variations in the carbon cycle over time. Unfortunately, changes in the CCD can be difficult to interpret because changes in CaCO₃ production affect the CCD just as strongly as variations of abyssal dissolution. Early discussions of the Pacific CCD, for example, found that the depth to complete CaCO₃ dissolution was deeper under regions of higher CaCO₃ production at the equator (Berger, 1973; van Andel and Moore, 1974). Without regional drill sites that span the CCD within the same production regime it remains difficult to define CCD changes except in low resolution or for abrupt large CCD movements like at the Eocene-Oligocene boundary (Coxall et al. 2005; Pálike et al. 2012).

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5.3.1 CaCO₃ MAR to estimate changes in CCD

Lyle et al (2005b) used the gradient in CaCO₃ MAR with depth between drill sites to define changes in the Eocene CCD. Depth is corrected for crustal cooling and sediment loading. Working backwards from CaCO₃ burial (MAR) has many ambiguities, however, and local sedimentation anomalies at the drill sites used cause significant noise. For large changes as in the Eocene, the CaCO₃ MAR gradient approach works, but the weaker signal in the Pliocene and Pleistocene is harder to distinguish from the noise.

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CaCO₃ MAR at any given location and time can be represented as a combination of the net focusing, rain, and dissolution as in equation (1):

$$\text{CaCO}_3 \text{ MAR}_T = F_T(\text{CaCO}_3 \text{ rain}_T) - D_T \quad (1)$$

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where the T subscript refers to time T, rain refers to the particulate CaCO₃ arriving at the bottom from surface CaCO₃ production, F is the sediment focusing factor, and D is the CaCO₃ dissolution at the sea floor. The variation of D responds to the chemistry of the regional water mass and depth of the sea floor; but regional variability is typically a depth function because of the large spatial scale of deep water masses. However, sediment focusing is locally variable and CaCO₃ production typically has a much smaller spatial scale than the scale of water masses that control dissolution. Production and sediment focusing are thus difficult to control to solve for the dissolution component.

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In order to isolate the dissolution component of the carbonate signal, an ideal set of sites would have similar productivity but would be at different water depths. Assuming production and focusing have remained the same at both sites over time, the depth dependent dissolution can be isolated. By dividing the change in CaCO₃ MAR between the two sites by the difference in water depth between them in the past, corrected for depth change caused by crustal cooling and sedimentation (Lyle, 1997; also see Supplemental Material Section 7) produces the drop in CaCO₃ MAR per meter of water depth. Dividing the CaCO₃ MAR at the deeper site by this gradient of CaCO₃ MAR with water depth produces the additional meters needed to reduce the CaCO₃ MAR to zero, marking the CCD. This was the approach of Lyle et al (2005) to determine changes in the Eocene CCD.

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Two of the sites in this study (Site 851 and Site U1338) are now at roughly the same latitude throughout the last 5 million years and have similar modern particulate organic carbon standing stock from satellite estimates (58 mg/m³ POC at Site 851; 57 mg/m³ POC at Site U1338, NASA Goddard Space Flight Center, 2014). Site 851 is 446 m shallower than Site U1338. Hypothetically, if relative sediment focusing at both sites remained constant, the gradient in CaCO₃ MAR from the deep site should extrapolate to zero CaCO₃ MAR at the CCD. Relative sediment focusing over long time frames in the pelagic regime appears reasonably constant (Liao and Lyle, 2014; Mitchell and Huthnance, 2013), and current-related anomalies can be discerned from the seismic profiles from site surveys. Sites chosen for drilling were chosen for the lack of anomalous seismic character in both ODP Leg 138 and IODP Exp 320/321. The CaCO₃ MAR gradient using Sites 851 and U1338 is noisy but general trends can be discerned (Fig 3). The trends are consistent with trends in CaCO₃ MAR and CaCO₃:BaSO₄ as indicators of enhanced dissolution.

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The CCD estimate using CaCO₃ MAR appears noisy over longer time frames because of a combination of relatively high frequency changes (e.g. the 100-kyr cycles in the last million years) but also suffers from the noise resulting from building

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the trend with records from only 2 sites. Minor errors in correlation plus local changes in CaCO₃ production or burial are magnified in the CCD estimate. For example, Site U1338 occasionally had higher CaCO₃ MAR than Site 851, making for a negative CCD gradient with depth. Negative trends result from either CaCO₃ production anomalies relative to modern conditions or changes in sediment focusing. These intervals were removed from the CCD estimate (e.g., the gap in the record between 2000 and 2250 ka; Table SM-35).

Figure 3 also displays the Palike et al (2012) CCD change over this period, which was reconstructed at 250 kyr intervals. The average CCD depth is similar between Palike et al (2012) and the Site 851-Site U1338 MAR CCD extrapolation, but the Palike et al (2012) version has much smaller deviation of the CCD over time. Palike et al (2012) use a graphical technique to estimate the CCD where CaCO₃ MAR is plotted versus paleodepth of each drillsite. Site U1334 constrained the change of the CCD in the youngest part of the time interval. Ideally the sites used to constrain the CCD should be within a common depositional regime. Sites U1338 and Site 851 are within the equatorial regime at the time of the LMBB, but Site U1334, without CaCO₃ at the time of LMBB deposition, was located at 6°N, and in a region of much lower CaCO₃ production in the surface waters. The low CaCO₃ production at this distance from the equator causes the CCD to be much shallower than a site nearer the high productivity (Berger, 1973). There are no drill sites in the equatorial region that pass through paleodepths of >5000 m in the late Miocene.

The unsmoothed CCD records by the MAR method are very noisy, so smoothing is necessary. Two levels of smoothing are used to make the CCD in Fig 3, 50 kyr and 750 kyr. The shorter time frame is adequate to show higher resolution changes, while the latter captures the longer trends. It is clear from these records that the late Miocene-Recent CCD has been strongly affected by changes in production. The LMBB interval has the deepest CCD since 8 Ma as well as the highest CaCO₃ MAR at both Sites U1338 and 851. The relative CaCO₃ MAR between Site 851 and Site U1338 is especially noisy in the LMBB, with frequent times when CaCO₃ MAR was higher at the deeper Site U1338. Nevertheless, it is likely that higher CaCO₃ production over Sites 851 and U1338 drove the eastern Pacific CCD deeper during this interval, although we suspect the magnitude of CCD deepening.

The CCD starts to shallow beginning at ~4800 ka, as the LMBB was fading. The shallowest CCD determinations do not precisely align with the PPLC-4 intervals although PPLC-4 is contained within a broad CCD minimum, indicating both a response to lowered CaCO₃ deposition and, as indicated by CaCO₃:BaSO₄, to increased dissolution. During PPLC-1, the low CaCO₃% is clearly averaged over broad variability in CaCO₃ dissolution. Nevertheless, low CaCO₃:BaSO₄ during the PPLC-1, 3 and 4 intervals also indicate that enhanced dissolution was an important factor in the low average CaCO₃% (Fig 5).

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5.3.2 CaCO₃:BaSO₄ ratio to define CaCO₃ dissolution

Section 4.3 discusses how the CaCO₃:BaSO₄ ratio can be used as a site specific indicator of dissolution. We found that there is a common signal to the CaCO₃:BaSO₄ variability (Fig 5). Standardizing the data using each record's standard deviation from the mean better illustrates the common signal among all the sites where Ba data are available (Fig 5b). The PPLC-3 and

5 PPLC-4 intervals clearly have lower average CaCO₃:BaSO₄ at Sites U1335, U1337, U1338, and 849. These sites span from the equator to more than 5°N and are up to 1900 km apart. The common dissolution record thus covers a significant portion of the east-central Pacific. Lowest CaCO₃:BaSO₄ ratios are found in PPLC-4c and -4a, also shown by lower CaCO₃ MAR than in other intervals (Fig 3). BaSO₄ MAR during PPLC-4c and -4a are relatively high, so dissolution must have outpaced somewhat higher CaCO₃ production relative to stratigraphic intervals on either side (See Supplemental Tables SM-17 to SM-

10 21). The difference between the CCD change and the CaCO₃:BaSO₄ probably results from the added CaCO₃ rain within PPLC-4. Similarly PPLC-2 has relatively high CaCO₃ dissolution, but not enough to make a CaCO₃ MAR minimum during the interval. The LMBB exhibits major intervals of high relative CaCO₃ deposition, although significant dissolution intervals appear at ~5810 and ~5350 ka and prior to 7500 ka (Fig 5). The high CaCO₃:BaSO₄ ratios in the LMBB broadly match the deep CCD in Figure 3.

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The dissolution anomalies cover a large regional extent as expected from the large regional extent of deep water masses. PPLC-3a and -3b are very consistent across the set of drill sites, and mark dissolution on either side of a distinctive CaCO₃:BaSO₄ maximum all occurring as the northern hemisphere glaciations began.

5.4 Early beginnings of Pleistocene 100-kyr CaCO₃ cyclicity

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Both the CaCO₃% and the CaCO₃:BaSO₄ records illustrate the development of 100-kyr dissolution cyclicity in deep Pacific dissolution (Figures 2 and 5). Surprisingly, the 100-kyr dissolution cyclicity began significantly before they strengthened towards the end of the mid-Pleistocene transition at ~900 ka, at which time 100-kyr benthic oxygen isotope cycles became prominent. The dissolution cycles isolated by CaCO₃:BaSO₄ begin at about 1900 ka (Fig 9a) and build in amplitude until MIS 16 at 655 ka. High CaCO₃ preservation is associated with periods of higher ice volume since about 1700 ka (MIS 58).

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The appearance of 100-kyr power can also be tracked via wavelet time series of the stacked CaCO₃:BaSO₄ record (Fig 9b). Strong power is found at 100 kyr from 1900 ka going forward in time and in the brief interval between PPLC-3a and -3b. Relatively strong 41-kyr power ka is also apparent associated with the 100-kyr cycles since 1900 ka, and strong 41-kyr power is found at the end of the LMBB.

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The early appearance of 100-kyr CaCO₃ dissolution cycles in the equatorial Pacific is interesting but problematic. There is a tendency even within the δ¹⁸O 41kyr world for high CaCO₃ preservation to be associated with periods of heavier than

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average oxygen isotope cycles, and presumably cooler high latitude regions. Figure 9a compares the $\text{CaCO}_3:\text{BaSO}_4$ combined stack, where a high value indicates better CaCO_3 preservation, to the combined Site 849-Site U1338 isotope record.

5 When both oxygen isotopes and $\text{CaCO}_3:\text{BaSO}_4$ have strong 100-kyr cycles (1000-0 ka), it is very clear that high CaCO_3 preservation is associated with glacial heavy isotope intervals. In the interval from 1000-1650 ka (MIS 25-59), that correlation is still strong when $\text{CaCO}_3:\text{BaSO}_4$ is compared to the smoothed oxygen isotope record. The correlation is weaker before 1600 ka, but between 2400 and 2600 ka the high CaCO_3 preservation interval between PPLC-3a and -3b is also characterized by a heavy oxygen isotope signal.

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The 100-kyr CaCO_3 cycles that appear in the Pacific could also appear in the deep Atlantic if there is cyclic weathering or NADW formation. Unfortunately, there are few CaCO_3 records for the Atlantic Ocean over the period between 1 and 2 Ma. Ruddiman et al (1989) have a CaCO_3 profile from Site 607, at a depth of 3426 mbsl. Because it is shallow relative to Antarctic Bottom Water (AABW) in the Atlantic, it is unlikely to be affected by dissolution and instead appears to be affected by changes in clay deposition over glacial-interglacial cycles (Broecker and Turekian, 1971; Bacon, 1984). The CaCO_3 % record at Site 607 changes from 41-kyr cyclicity to 100-kyr cyclicity at ~900 kyr, like the $\delta^{18}\text{O}$ record. Harris et al (1997) developed a CaCO_3 dissolution index for the Ceara Rise and found that dissolution affected the CaCO_3 records below a depth of 4356 mbsl. The index compared CaCO_3 MARs at the deep Site 929 to the shallow Site 925, and found coherence with the oxygen isotope record of ice volume for the last million years. However, 100-kyr coherence was not very strong in the 1-2 Ma period. Since the dissolution record at the Ceara Rise primarily reflects oscillations in the penetration of AABW versus NADW around Ceara Rise, changes in NADW flow do not cause the Pacific oscillation. The differences between the Atlantic and Pacific CaCO_3 records imply the development of oscillations in deep storage of DIC in the Pacific, but little communication of this oscillation between ocean basins before the 900 ka mid-Pleistocene climate transition. The lack of strong cycles at the Ceara Rise may actually be caused by relatively strong NADW formation in the Atlantic prior to 1 Ma and the development of NADW cyclicity only after the mid-Pleistocene climate transition (Kleiven et al., 2003).

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For the 2.6 million years of the Pleistocene we observe an important linkage between CaCO_3 preservation and higher ice volume. Farrell and Prell (1989) have argued for a change in carbonate ion concentration variability of about 6% to drive the glacial-interglacial cycles since 800 ka. Hodel et al. (2001) have argued that the Indo-Pacific association of high CaCO_3 burial with glacials is evidence for cycles driven by shelf-basin fractionation of carbonate burial. During high sea level stands, the additional burial of CaCO_3 on shallow tropical shelves reduces deep CaCO_3 burial, while exposure of these shelves during glacials transfers CaCO_3 burial to the deep ocean and also consumes atmospheric CO_2 through carbonate weathering. The correlation that we observe between higher $\text{CaCO}_3:\text{BaSO}_4$ and heavy oxygen isotopes is supportive of a

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primary control of deep CaCO₃ burial by shelf-basin transfer through the Pleistocene, with ocean circulation transferring the signal mostly to the Pacific.

5.5 Origins of PPLC-4 and the Pliocene temperature maximum

Pleistocene changes in dissolution are adequately explained by shelf-basin fractionation, but the Pliocene PPLC-4 dissolution series requires [additional processes](#). Most of PPLC-4 is associated with lower frequency dissolution variability prior to 2600 ka (Figs [5](#) and [9](#)) and the PPLC-4 intervals are also marked by extreme lows in CaCO₃ MAR (Fig [3](#)).

PPLC-4 occurs during the final closure of the [CAS](#) (O'Dea et al, 2016), [which might link](#) closure and the extreme dissolution. Bell et al (2015) suggest that NADW formation was strong prior to [CAS](#) closure and largely unaffected by changes in [CAS geometry](#). Furthermore, they propose that the circulation effects of closure developed prior to 4 Ma. [It does not appear that PPLC-4 dissolution is linked to flushing the Atlantic with NADW](#).

Poore et al (2006) have proposed that the deep sill at the Greenland-Scotia Ridge between 6000 and 2000 ka caused a radical increase in volume of [Northern Component deep water](#) production, as estimated by $\delta^{13}\text{C}$ gradients between the North Atlantic-Southern Ocean-Pacific. Such an increase should increase basin-basin fractionation of CaCO₃ burial between the Atlantic and Pacific. However, PPLC-4 also occurs immediately after the end of the LMBB, marking a major drop in biogenic CaCO₃ rain regionally in the Pacific, and is also a period of high estimated atmospheric CO₂ (Seki et al, 2010; Stap et al, 2016). PPLC-4 occurs during an interval of warm tropical SST after the SST minimum at 5.4 Ma (Herbert et al., 2016). In other words, [many important changes in the global biogeochemical cycles and global climate occurred at the time of PPLC-4, and it is as yet unclear how much these changes are related to CAS closure](#).

Nevertheless, it is possible to say that during the early Pliocene the Atlantic was preferentially flushed of DIC, making a strong $\delta^{13}\text{C}$ gradient from Atlantic to Pacific. Between 4 and 2.5 Ma, however, the gradient between Atlantic and Pacific gradually weakened (Fig [10](#)), indicating [penetration of low \$\delta^{13}\text{C}\$ waters from the Antarctic-controlled deep circulation into the Atlantic. The slow rise of \$\delta^{13}\text{C}\$ in the Pacific could result from a relatively high flux of Northern Component Water into the Antarctic, above that of the abyssal flow back towards the north](#). The global SST warm transient between ~5.4 to 3 Ma (Herbert et al, 2016), as well as the elevated CO₂ suggests an important perturbation of the carbon cycle. [The SST perturbation is also reflected in the bulk and planktonic foraminiferal stable isotopes at Sites U1338 and 573 \(Reghellin et al, 2015; Drury et al., 2018\)](#). At Site 1241 on the Cocos Ridge northeast of the sites in this paper, records of temperature and biogenic MAR find the interval between 5.4 and 3 Ma to be unusually warm but with relatively low biogenic production when compared to the LMBB (Seki et al., 2012).

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The movement of the equatorial Pacific locus of high biogenic deposition from the east central equatorial Pacific [further east near to South America](#) (Fig 1; Farrell et al, 1995; Lawrence et al, 2006) may have triggered PPLC-4, by removing CaCO₃ rain from the region west of the Galapagos Islands that had up until then compensated for the elevated dissolution at the sea floor. However, low CaCO₃ MAR apparently marks the PPLC-4 interval in the easternmost Pacific as well (Sites 846 and 847, Farrell et al, 1995) and gives evidence that moving the locus of production is not the primary cause for PPLC-4.

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Bell et al (2015) have given a good summary of stable isotopes in the Atlantic and far South Atlantic, which they compared to Site 849. Sites U1338 and U1337 have virtually the same $\delta^{13}\text{C}$ signature as Site 849 (Drury et al, 2016, 2017; Tian et al, 2018) so Site 849 [is representative of an east-central Pacific deep water signal](#). The [trend in the Pacific \$\delta^{13}\text{C}\$ time series rises somewhat between 5 and 3.6 Ma, but the trend toward higher \$\delta^{13}\text{C}\$ stops around then](#) (Fig J0). During the period between 4.4 and 4.2 Ma, the southernmost South Atlantic sites (Site 704) became isotopically heavier and more like the North Atlantic, and were interpreted to indicate deep expansion of the NADW tongue and somewhat stronger NADW flow during the warm Pliocene (Hodell and Venz-Curtis, 2006; Bell et al., 2015). After 4 Ma, the Atlantic profile at Ceara Rise became isotopically lighter while the Pacific profiles got somewhat heavier, evidence for expansion of an Antarctic source that penetrated more effectively into both the Atlantic and Pacific. Similarly, [Klevenz et al \(2008\) interpreted Nd isotopes and Cd/Ca on Walvis Ridge to indicate that the Antarctic end member signal reached a local minimum around 3.5-4 Ma, and concluded that NADW flow was highest then](#). We suggest that the more thorough exchange of Pacific deep water after 3.5 Ma helped to increase deep dissolution in the Atlantic and enhanced Atlantic 100-kyr cyclicity that was beginning to occur in the Pacific.

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20 In the absence of conclusive evidence, we suggest that the enhanced dissolution in PPLC-4 marks the effects of enhanced Antarctic flow within the deep Pacific and a larger reservoir of low $[\text{CO}_3]^-$ water in the deep ocean between 4.1 and 2.9 Ma. Sites U1337, U1338, and Site 849 all are sites within the mixing zone of Pacific deep water outflow with relatively weak deep flow from the Antarctic, at least compared to the western Pacific. The lack of strong change of $\delta^{13}\text{C}$ despite apparent increases in Antarctic influence worldwide, suggests continued deep DIC storage in the Pacific. Since the period between 5 and 3.5 Ma was also warm (Herbert et al, 2016), there may also be feedbacks from the carbon cycle as well as enhanced shelf storage of CaCO₃ from high sea levels reducing deep CaCO₃ burial. However, sea levels were relatively high for millions of years prior to the 4-3 Ma period of PPLC-4 (Rohling et al, 2014; Miller et al, 2005), so the sea level effect should not have been large.

6 Conclusions

30 [We have developed site-to-site correlations and a composite age model for 7 ODP and IODP drillsites from the eastern equatorial Pacific at the meter scale in order to study the evolution of eastern equatorial Pacific sedimentation. This fulfils](#)

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one of the objectives of the Pacific Equatorial Age Transect, and the high-resolution stratigraphy provides a foundation that should benefit future regional studies.

5 We identified five long-term low CaCO_3 intervals within the 7 drill sites we investigated: PPLC-5 (4737-4465 ka), PPLC-4 (3 intervals between 4093 and 2915 ka), PPLC-3 (2 intervals on either side of a CaCO_3 high, between 2684 and 2248 ka), PPLC-2 (2135-1685 ka), and PPLC-1 (402-51 ka). With bulk chemical data and the geographic range of the investigated drill sites it is possible to distinguish between dissolution and production as causes of low CaCO_3 intervals in the Pliocene-Pleistocene record. We found that PPLC-5 and PPLC-2 result from CaCO_3 dilution through diatom production, and the other 3 result from enhanced CaCO_3 dissolution.

10 The magnitude of CaCO_3 dissolution can be described by changes in the CCD. However, local and regional variability of sedimentation makes the CCD method only useful for intervals of large carbon cycle change and/or low time resolution. The ratio CaCO_3 : BaSO_4 makes it possible to study dissolution at an individual drill site. We used this ratio to show that 100-kyr dissolution cycles were regionally strong by 1600 ka, in contrast to oxygen isotopes which didn't develop 100-kyr cyclicality until ~1000 ka. We also used CaCO_3 : BaSO_4 to confirm that the highest CaCO_3 dissolution occurred in PPLC-4, between 4.1 and 2.9 Ma.

20 It is possible that PPLC-4 resulted from closure of the CAS, but there are complicating factors, like the shift of the locus of CaCO_3 burial eastward in the Pacific at the end of PPLC-5, the last high deposition interval of the LMBB. High flushing of the Atlantic basin is indicated by the Atlantic-Pacific $\delta^{13}\text{C}$ gradient, but the gradient was actually weakening in the 4-3 Ma interval suggesting more Antarctic DIC storage or more total DIC in the ocean. New work concludes that atmospheric CO_2 was declining in this interval as well (Stap et al, 2016) and is also associated with declining but still high global SST (Herbert et al, 2016). The multiple changes in climate and carbon cycle indicators show that significant reorganizations were occurring in the early Pliocene despite a relatively stable ice volume indicated by benthic oxygen isotopes. The data we have presented here suggests that regional changes are strong and will be critical to understand the transition to the beginning of Northern Hemisphere glaciation.

Acknowledgments

30 We thank all the members of IODP Expedition 320/321 and those from ODP Leg 138 (Scientists, technicians, drillers, and ships crew) who collected the basic information and sediments needed for this study. Lyle was funded by NSF grant OCE-0962184 and grant OCE-1656960. Westerhold and Drury were funded by the Deutsche Forschungsgemeinschaft (DFG) grant WE5479-1 and WE5479-3, and Drury was a postdoctoral researcher in H. Pälike's ERC Consolidator Grant

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[EARTHSEQUENCING \(grant agreement 617462\)](#), Jun Tian was funded by National Science Foundation of China (Grant No. 41525020, 41776051) and Program of Shanghai Subject Chief Scientist (A type) (16XD1403000).

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Table 1: Drill Sites investigated in this study

Site	Latitude (°N)	Longitude(°E)	Water depth (mbsf)	5 Ma Latitude(°N)	5 Ma longitude (°E)	Data Available
ODP 848	-2.994	-110.480	3854	-3.77	-106.09	GRA-CaCO ₃ , this paper scanning XRF, GRA-CaCO ₃ ,
ODP 849	0.183	-110.520	3838	-0.60	-106.25	this paper
ODP 850	1.297	-110.521	3786	0.51	-106.30	GRA-CaCO ₃ , this paper
ODP 851	2.770	-110.572	3760	1.98	-106.41	GRA-CaCO ₃ , this paper scanning XRF, Lyle et al (2012); Lyle and Backman (2013); Wilson (2014)
IODP U1338	2.508	-117.970	4206	1.43	-113.79	scanning XRF, Wilson (2014)
IODP U1337	3.834	-123.206	4468	2.55	-119.07	scanning XRF, Wilson (2014)
IODP U1335	5.312	-126.284	4333	3.92	-122.19	scanning XRF, Wilson (2014)

Table 2. Plio-Pleistocene Low Carbonate Intervals (PLCI)

Low Carbonate Interval	Age Interval(kal)	Interval length kyr	Marine Isotope Stage	Magnetic Chron	Depth Site U1318 (m CSF)	Depth Site B05 (m CSF)	Depth Site B48 (m CSF)	Depth Site B55 (m CSF)	Depth Site B51 (m CSF)	Depth Site U1217 (m CSF)	Depth Site U1215 (m CSF)	Notes
PLCI-01	51-602	551	4-11	C1a	1,065.14	1,711.271	0,815.53	1,376.52	0,794.07	0,795.87	0,552.68	Most prominent at Site B05 coldest/warm cycles appear to be weak.
PLCI-02	1695-2135	450	59-81	lower C5c-2 to lower C5c-1r	22,20-24.77	48,77-61.38	25.02-27.70	36,98-42.71	31.53-39.64	25.21-31.73	10.13-12.10	See also Porewé et al. 2016 for U258 and U240; matches B05
PLCI-03a	2340-2383	103		87-83	29.23-31.56	62.61-67.23	38.35-29.68	43.81-47.91	39.52-42.11	32.27-34.81	12.27-13.32	Two peaks 02 gets larger away from equator, 06 gets larger toward it.
PLCI-03b	2332-2668	336		83-61	33.50-51.71	71.10-74.94	30.88-31.63	51.13-51.70	45.37-47.34	30.50-39.00	14.12-16.88	Prominent CC high in between the two
PLCI-03c	2915-3372	457		G10-MG8	39.19-41.84	81.14-93.32	33.20-35.37	60.44-69.81	52.91-61.06	43.07-51.79	16.33-18.39	This gets stronger away from equator
PLCI-03d	3038-3711	673		MQ12-G11	49.24-50.85	97.68-102.36	35.83-37.12	73.45-77.31	64.46-66.95	54.34-57.93	19.04-19.68	This gets stronger away from equator. 04 is a triplet starting with low at interval. The events get larger away from the equator. PLC-04B and 04c. Weakly seen in U1215 but not distinct in U1215, U086
PLCI-04a	3834-4000	216		G11-G12-14	52.42-54.05	105.09-112.51	37.54-38.68	80.02-85.25	68.90-72.75	60.45-67.45	20.08-21.18	Very prominent at equator, missing away from it
PLCI-05	4465-4737	272		N2-N5-6	62.69-69.33	123.81-143.00	40.35-44.27	94.10-107.72	80.42-87.55	missing	missing	Very prominent at equator, missing away from it

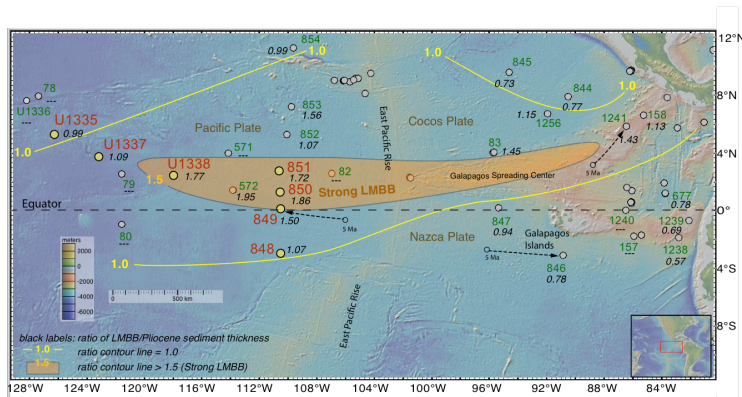


Figure 1: Overview of East Pacific drill sites from GeoMapApp (<http://www.geomapapp.org/>). Gray dots indicate positions of DSDP/ODP drill sites. Red site labels: ODP and IODP drill sites from the eastern equatorial Pacific used in this paper with other DSDP/ODP/IODP Sites labeled in green. All sites are at their modern locations. Example backtracked positions at 5 Ma are shown for Site 849 on the Pacific Plate (representative for U1335, U1337, U1338, and Sites 848-854), Site 846 on the Nazca Plate (representative for Sites 847, 1238, and 1239), and Site 1241 on the Cocos Plate (representative for Sites 844, 845, and 1256), assuming a hotspot reference frame. Thickness of the 8.5-4.5 Ma sediment divided by the 4.5-0 Ma sediment thickness (LMBB/Pliocene ratio) are indicated by the italic black labels at each drill site. Sites on crust younger than 8 Ma, or where the section was incompletely drilled, or with a hiatus in the interval are marked with "....". Yellow lines mark where the LMBB/Pliocene ratio is 1, while shaded orange region is where the ratio is >1.5, marking the major LMBB locus of deposition. Thickest LMBB sequences are found on sites with crust older than 8 Ma on the Pacific and Cocos Plates just north of the equator. Sites south of the equator in the easternmost Pacific have thicker sediments in the 4.5-0 Ma time range, indicating high young sedimentation rates.

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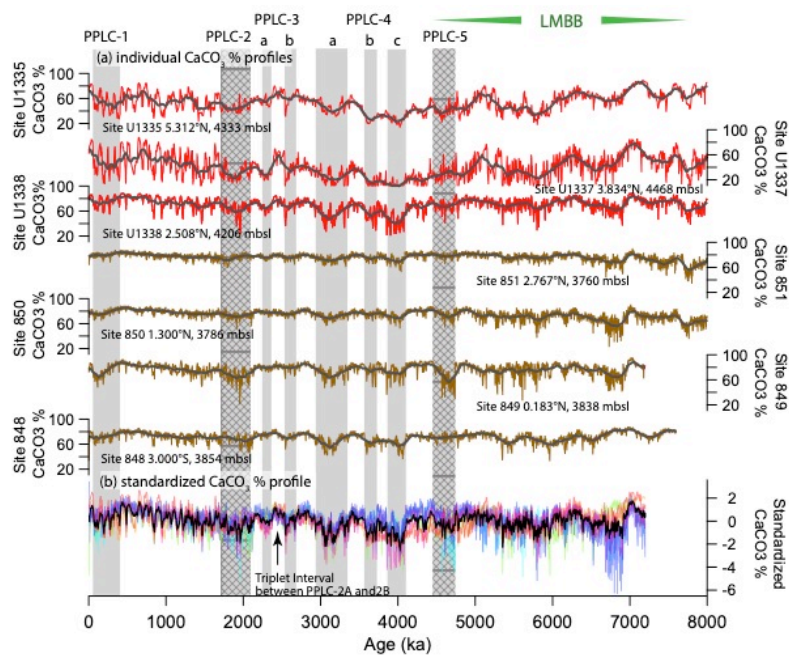
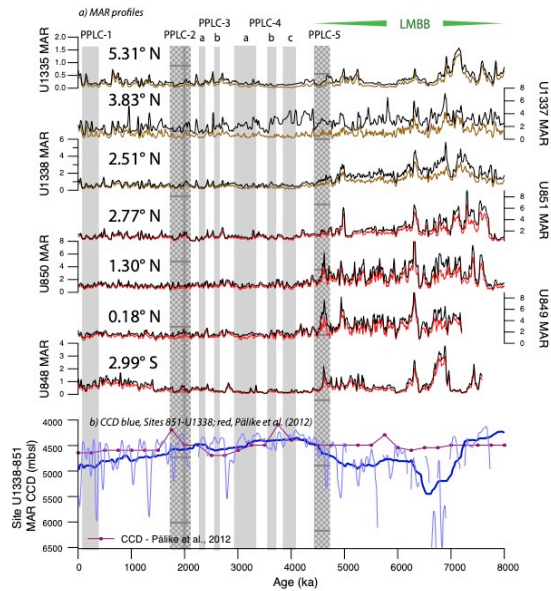


Figure 2: (a) CaCO₃ wt % profiles from the 7 drill sites in this paper. Red profiles are from sites drilled by IODP Exp 320/321 while the brown profiles are sites drilled on ODP Leg 138. Black lines are the smoothed profiles. The gray shading marks PPLC intervals determined in this paper (See Table 2), while the hatched intervals are productivity controlled. LMBB is the Late Miocene Biogenic Bloom and includes PPLC-5, actually early Pliocene in age. (b) Stacked and standardized CaCO₃ wt % profiles. Each profile is expressed in standard deviations from the mean and the data from each drill site has a different color. The black profile is the stack of all the CaCO₃ wt % curves. The PPLCs were determined by common low CaCO₃ wt % in the profiles.



5 **Figure 3:** (a) Mass Accumulation Rates (MARs) for eastern equatorial Pacific drill sites. Bulk MAR (black) and CaCO₃ MAR (brown—U1338; red—Exp 320/121) profiles from drill sites studied for this paper. Shaded intervals are PPLCs, and shaded hatched intervals are productivity controlled. MAR data are at 10 kyr intervals. Sites are arranged from south to north, at their modern position. Only Site U1337 has bulk MAR time series that diverge significantly from the CaCO₃ MAR profiles, indicative of sediment focusing at Site U1337. (b) Eastern Pacific CCD change from Pálike et al (2012; red line) and using the gradient of deposition from Site 851 (3760 m) to Site U1338 (4206 m) with two levels of smoothing, 50 kyr (light blue line) and 750 kyr (heavy blue line). Breaks in the light blue line profile are intervals where the CaCO₃ MAR at the deeper Site U1338 exceeded that at Site 851. The 50-kyr smooth finds transient CCD changes up to 1.5 km, but probably contains significant noise from local sediment variability. The 750-kyr smooth displays how the CCD was shallowest between 4200 and 3100 ka, during the time of PPLC-4.

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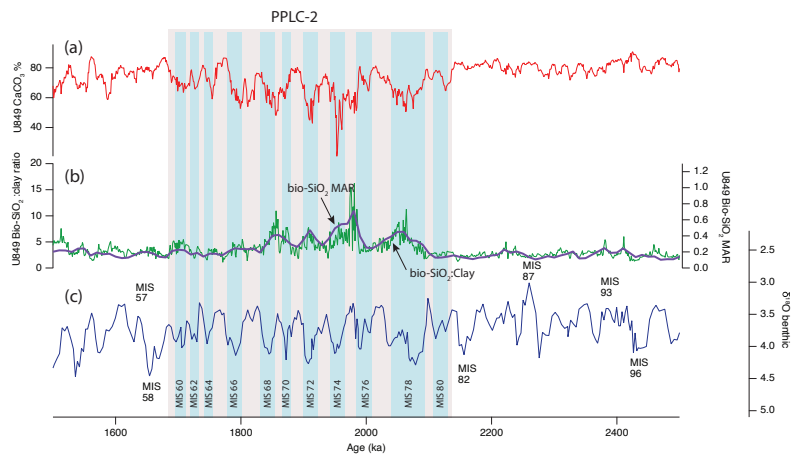


Figure 4: Site 849 profiles over low carbonate interval PPLC-2 (2135-1685 ka) showing bio-SiO₂ dilution as a primary cause of the low CaCO₃%. High bio-SiO₂ MARs are in glacial intervals. (a) Scanning XRF CaCO₃%; (b) Thick line is bio-SiO₂ MAR, and thin line is bio-SiO₂:clay ratio, showing the high bio-SiO₂ MAR associated with each sub-interval in PPLC-2. (c) Benthic oxygen isotope stratigraphy constructed with data from Mix et al. (1995) using the updated splice from this paper. Stages are numbered following Lisiecki and Raymo (2005). Glacial intervals are labelled.

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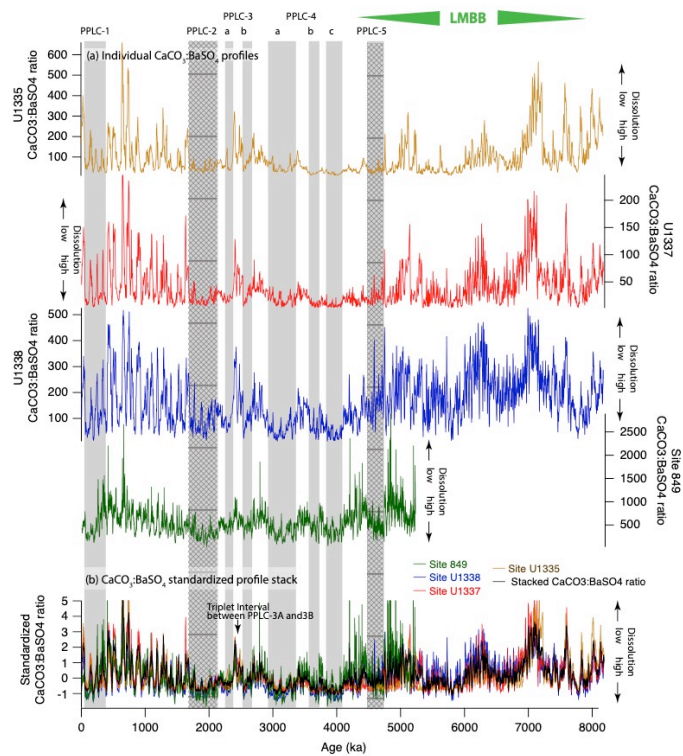


Figure 5: XRF $\text{CaCO}_3:\text{BaSO}_4$ profiles to investigate CaCO_3 dissolution at drill sites with scanning XRF profiles. Shaded intervals are PPLCs and shaded hatched intervals are productivity driven. Low $\text{CaCO}_3:\text{BaSO}_4$ indicates high dissolution of CaCO_3 . (a) Individual profiles of $\text{CaCO}_3:\text{BaSO}_4$ at Sites U1335, U1337, U1338 and Site 849. Note how ratios are higher at Site 849, the shallowest site nearest to the equator. (b) Changes in dissolution in the eastern Pacific shown by stacked $\text{CaCO}_3:\text{BaSO}_4$ records expressed as standard deviations from the average. Low $\text{CaCO}_3:\text{BaSO}_4$ coincides with PPLC's, indicating that the dissolution signal has an important impact on the record, even within high productivity intervals.

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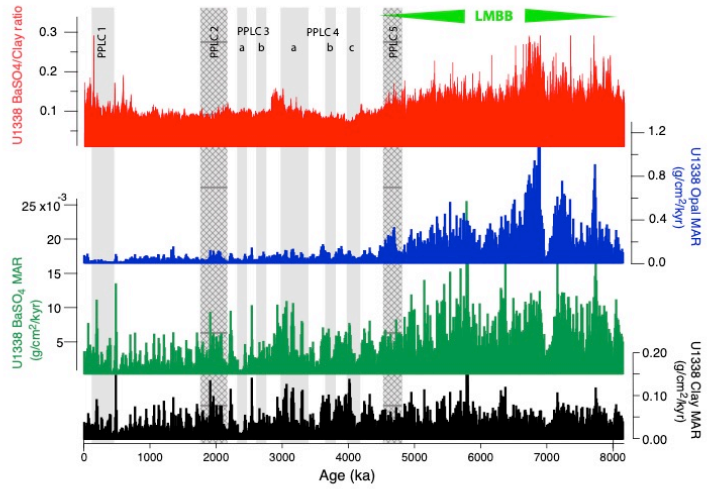


Figure 4: Site U1338 BaSO₄/clay ratio and Mass Accumulation Rates (MAR) of biogenic sediment components and clay. Gray bands mark PPLCs (Pliocene-Pleistocene Low CaCO₃ intervals) and hatched gray bands are productivity controlled. High bio-SiO₂ and BaSO₄ MAR prior to 4465 ka represents the LMBB interval at Site U1338. Clay MAR is relatively constant over the 8 million years and is shown by the drop in BaSO₄/clay ratio at that time.

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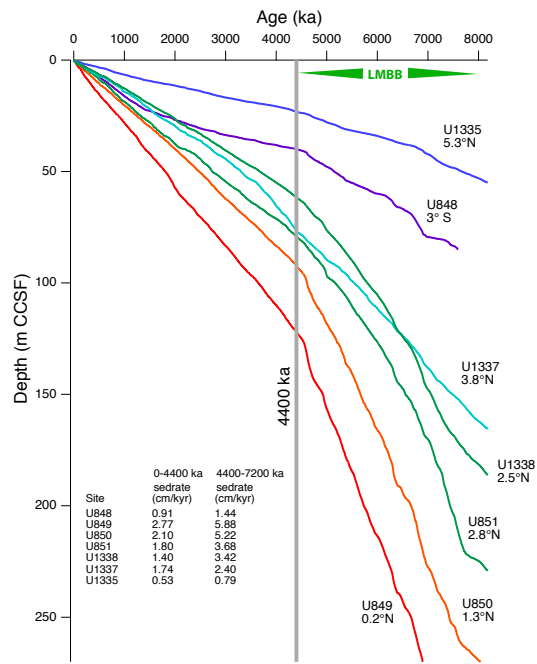
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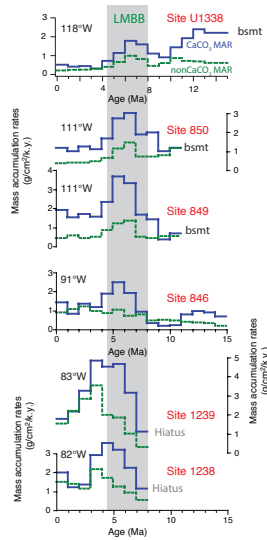
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5 **Figure 7: Age-depth curves for ODP Leg 138 Sites 848, 849, 850, and 851 with IODP Expedition 320/321 Sites U1335, U1337, and U1338, based on age model in this paper. Steeper slopes represent faster sedimentation rates. Steepest slopes are found at sites that are nearest to the high productivity equatorial upwelling zone. Average sedimentation rates for the section younger than 4400 ka and for rates between 7200 ka (base of XRF section scanned in Site 849) and 4400 ka are tabulated. The break in sedimentation at the gray line at 4400 ka marks the end of the LMBB. CCSF (Composite Coring depth below Sea Floor) is the depth within the continuous spliced sediment section**



5 **Figure 8:** 1 Myr increments of CaCO₃ MAR (blue lines) and non-CaCO₃ MAR (Green dashed lines) on a longitudinal equatorial transect from 118°W to 82°W, near Ecuador. **Non-CaCO₃ deposition is mostly biogenic silica at these drillsites.** Basement is marked by "bsmt". Data for U1338 is from this paper, while the other data are from ODP Leg 202 Shipboard Scientific Party (2003). The 8-4.5 Ma LMBB window is shaded. The end of peak CaCO₃ deposition is roughly 2 million years younger near South America than in the west. Eastern Pacific drill sites (Sites 846, 1238, and 1239) have increased biogenic deposition post-LMBB, presumably because of nutrient concentration after the Central American Seaway closed.

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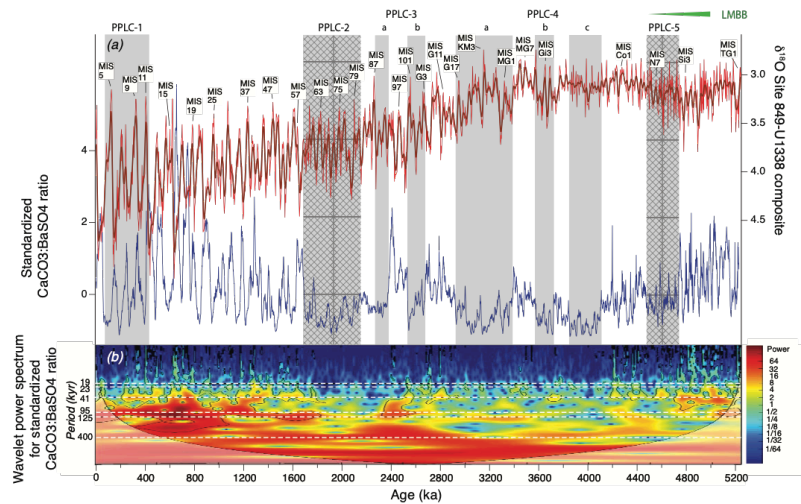
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5 **Figure 3:** (a) A comparison of the stacked $\text{CaCO}_3:\text{BaSO}_4$ record of dissolution cycles (blue line) to the combined U1338-849 isotope record (red and brown lines). The thick line on the oxygen isotope record is a 7 point binomial smooth of the data. A strong 100-kyr periodicity to the dissolution cycle begins roughly at MIS 58, with low dissolution associated with periods of high benthic $\delta^{18}\text{O}$ (high ice volume). Before MIS 58, the association is less clear. (b) Wavelet analysis of the $\text{CaCO}_3:\text{BaSO}_4$ stack, showing 400 kyr power throughout the $\text{CaCO}_3:\text{BaSO}_4$ record and development of 100 kyr power in the interval beginning about 1800 ka and continues to the Holocene.

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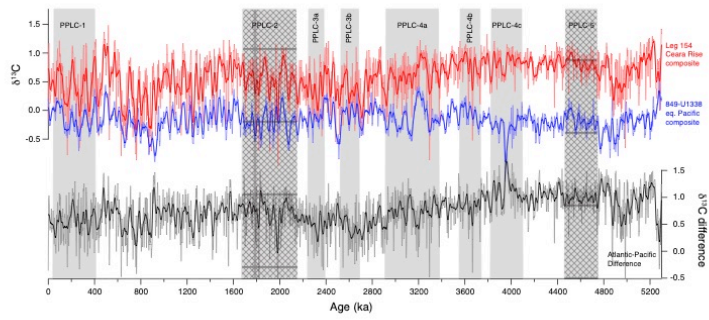


Figure 10: $\delta^{13}\text{C}$ records from Ceara Rise (Atlantic, red) and the Site 849-U1338 composite (Pacific, blue), and the Atlantic-Pacific $\delta^{13}\text{C}$ difference (black). The PPLC-4 dissolution interval falls on the period of decline of the Atlantic Pacific difference caused by a decrease in Atlantic $\delta^{13}\text{C}$ of about 0.7‰ between 4000 ka and 2500 ka, and an increase in Pacific $\delta^{13}\text{C}$ of about 0.4‰ over the same interval.

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