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# The accuracy of mid-Pliocene $\delta^{18}\text{O}$ -based ice volume and sea level reconstructions

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## Abstract

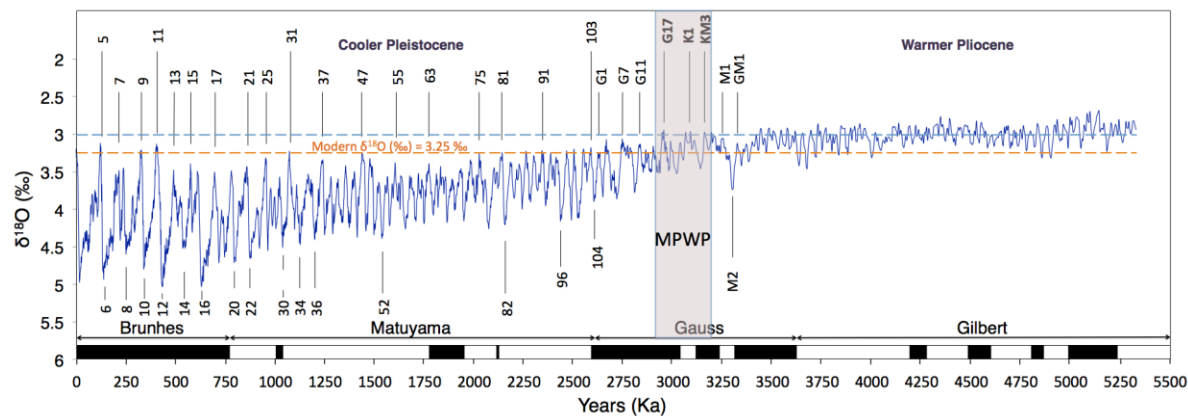
Understanding the sensitivity of the polar ice caps to a modest global warming (2–3°C above preindustrial) is of paramount importance if we are to accurately predict future sea level change, knowledge that will inform both social and economic policy in the coming years. However, decades of study of the Pliocene (2.6–5.3 Ma), an epoch in recent Earth history characterized by atmospheric  $\text{CO}_2$  levels similar to today, have so far failed to provide definitive sea level and ice volume estimates for that time. Here we review the sources of uncertainty in the paired Mg/Ca- $\delta^{18}\text{O}$  methodology used to estimate past sea level, ice volume, and ocean temperature, as well as discuss common assumptions that may bias our interpretation of ocean geochemical records including the LR04 benthic- $\delta^{18}\text{O}$  stack, a global compilation of 57 oxygen isotope records that forms the standard template of climate change history for the last 5.3 million years.

**Keywords:** sea level, ice volume, paleoceanography, paleoclimate, geochemistry

## 1. Introduction

The degree of polar ice sheet decay that occurs during periods slightly warmer than today has been the subject of much scrutiny within the paleoclimate and sea level research community in recent years [Kopp *et al.*, 2009; Naish *et al.*, 2009; Blanchon *et al.*, 2009; Raymo & Mitrovica, 2012; Cook *et al.*, 2013; Rohling *et al.*, 2014; Dutton *et al.*, 2015; and Kemp *et al.* 2015, among others]. In particular, many researchers have focused their attention on the Mid-Pliocene Warm Period (MPWP; ~3.2 to 2.9 m.y., Figure 1), an interval characterized by a climatic regime ~2–3°C warmer on average than preindustrial values

[e.g., Dowsett, 2007; Dowsett et al., 2010; Haywood et al., 2013] as well as estimated atmospheric CO<sub>2</sub> concentrations of ~350-450 ppm [Raymo et al., 1996; Pagani et al., 2010; Seki et al., 2010; Bartoli et al., 2011; Badger et al., 2013; Martínez-Botí et al., 2015]. For obvious reasons, the MPWP is of great interest to the climate modeling community concerned with predicting future climate changes, in particular the long-term response of polar ice sheets to rising greenhouse gases in the atmosphere (present atmospheric CO<sub>2</sub> levels hover just above 400 ppm and are climbing steadily; <http://scrippsco2.ucsd.edu/>). If we can have confidence in the interpretation of our paleo-data, then we can better evaluate the performance and predictions of climate and ice sheet models forced by a similar increase in CO<sub>2</sub>.



principles of geomorphology and morphostratigraphic succession combined with relative and absolute geochronological dating of paleo-shoreline features and intertidal to subtidal facies [Dowsett & Cronin, 1990; Krantz, 1991; Wardlow & Quinn, 1991; James *et al.*, 2006; Naish & Wilson, 2009; Miller *et al.*, 2005; 2012; Rovere *et al.*, 2014; Dutton *et al.*, 2015; Kemp *et al.*, 2015; Rovere *et al.*, 2016].

The early field studies of the MPWP were sometimes corrected for local tectonic effects (typically by reference to well-dated late Pleistocene shorelines) and sometimes for subsidence caused by sedimentary loading [Krantz, 1991]. However, we now recognize that Pliocene paleo-sea level horizons also need to be evaluated within the context of on-going glacial isostatic adjustments (GIA; Raymo *et al.* [2011]), as well as mantle-driven dynamic topography (DT) effects which become significant on time scales longer than a million years [Moucha *et al.*, 2009; Rowley *et al.*, 2013; Rovere *et al.*, 2014, 2015; Austermann *et al.*, 2015]. Gravitational changes in the geoid also likely occur over millions of years and need to be quantified, although these corrections are probably significantly less than those due to GIA and DT across low to mid-latitudes. Given that the post-depositional changes to shoreline elevations (or shallow subtidal facies) due to these global effects have been shown to be on the order of tens of meters, *and* are very poorly constrained (see above references), published estimates of maximum eustatic sea level for the Pliocene based solely on field observations therefore carry the same degree of uncertainty. Certainly these studies cannot distinguish whether sea level was 10 m or 25 m higher in the Pliocene (in other words, whether or not there was a significant contribution to sea level rise from the melting of the EAIS).

The second widely applied approach to estimating MPWP sea level is by using the ocean geochemical record, in particular oxygen isotope ratios recorded by calcium carbonate-secreting organisms recovered from deep-sea sediment cores. Temporal variation in the oxygen isotope composition of seawater recorded by foraminifera shells has served as the primary climate proxy used by marine geologists and paleoceanographers for over half a century. Early pioneering studies by Epstein *et al.* [1953], Emiliani [1955], Shackleton [1967] and others demonstrated how the isotopic ratio of O-18 to O-16 in seawater ( $\delta^{18}\text{O}_{\text{sw}}$ ) and in calcite precipitated from seawater ( $\delta^{18}\text{O}_{\text{carb}}$ ) reflects changing global ice volume as well as ocean temperature and salinity changes through time (and many excellent reviews of the use and calibration of oxygen isotopes in marine settings have been written in the years since, including Mix & Ruddiman, 1984; Bemis *et al.*, 1998; Adkins *et al.*, 2002; Waelbroeck *et al.*, 2002; Schmidt & Mulitza, 2002; and Marchitto *et al.*, 2014).

Shackleton [1967] recognized that if one measured  $\delta^{18}\text{O}_{\text{carb}}$  in bottom-dwelling benthic foraminifera, rather than in planktic surface dwellers, the  $\delta^{18}\text{O}_{\text{carb}}$  variability associated with the large temperature and salinity fluctuations in surface seawater would be minimized, leaving a record dominated by the global ice volume (and therefore sea level) signal. However, a bottom water temperature (BWT) variation of even a degree or two would be enough to confound an estimate of Pliocene ice volume as will be discussed below. To independently constrain the BWT signal, investigators have thus measured the

Mg/Ca ratio of foraminiferal calcite, which is primarily controlled by seawater temperature at the time of precipitation [Nürnberg *et al.*, 1996; Rosenthal *et al.*, 1997; Lear *et al.*, 2000, 2002; Anand *et al.*, 2003; Elderfield *et al.*, 2006]. In this paper, we review recent efforts to constrain the maximum sea level rise and polar ice volume during the warm extremes of the MPWP using this paired  $\delta^{18}\text{O}$ -Mg/Ca technique. While we focus on the LR04 stack [Lisiecki & Raymo, 2005] and query some of the standard interpretations of the stack's features, particularly with respect to inferred sea level, our results are relevant to any Pliocene  $\delta^{18}\text{O}$  record.

Three recently published papers provide additional, and valuable supplements, to this review, and we discuss them briefly below—Winnick & Caves [2015] challenge common assumptions about polar ice sheet  $\delta^{18}\text{O}$  values in the Pliocene and explore the influence of these assumptions on geochemical estimates of MPWP sea level. Marchitto *et al.* [2014] compile an extensive calibration data set for benthic foraminiferal  $\delta^{18}\text{O}$  and provide a more accurate equation relating bottom water temperature to benthic  $\delta^{18}\text{O}$ . And Lawrence & Woodard [2017] explore uncertainties in various methods used to estimate sea surface temperature, some of which are also used to examine bottom water temperatures. Here, we will focus primarily on carbonate diagenesis as well as the chemical evolution of seawater and explore how uncertainties in these processes might also influence sea level/ice volume interpretations. Lastly, we should add that the combination sill depth- $\delta^{18}\text{O}$  sea level reconstruction method of Rohling *et al.* [2014] combines both the methodologies described above and hence would carry all the uncertainties of both methods.

## 2. The benthic $\delta^{18}\text{O}$ record and Pliocene sea level

Due to the rapid mixing time of the ocean and the temporal resolution of deep-sea sediments ( $\sim 1000$  years) relative to the time it takes to grow and melt polar ice sheets (thousands to tens of thousands of years), changes in  $\delta^{18}\text{O}_{\text{sw}}$  are nearly synchronous everywhere in the deep ocean. Thus, despite potential differences of several kyr [Skinner & Shackleton, 2005; Waelbroeck *et al.*, 2011; Lisiecki & Raymo, 2009; Stern & Lisiecki, 2014],  $\delta^{18}\text{O}$  remains the premier correlation tool for intervals beyond the limits of radiocarbon dating, used to match sediment core records separated by thousands of kilometers and across different oceans and hemispheres [e.g., Pisias *et al.*, 1984; Imbrie *et al.*, 1984; Prell *et al.*, 1986; Imbrie *et al.*, 1992; Lisiecki & Raymo, 2005; Channell *et al.*, 2009]. However, individual downcore  $\delta^{18}\text{O}_{\text{carb}}$  records can also reflect unique variability due to local influences of bioturbation, sedimentation rate, and/or regional temperature and salinity changes. To minimize these local hydrographic effects and isolate the global signal recorded by  $\delta^{18}\text{O}_{\text{carb}}$ , Imbrie *et al.* [1984] pioneered the strategy of creating graphically correlated and averaged  $\delta^{18}\text{O}_{\text{carb}}$  “stacks”, composed of numerous individual records and considered to be the idealized representation of a mean global  $\delta^{18}\text{O}_{\text{carb}}$  signal that could be used to more accurately read Earth's ice volume and climate history.

From 1984 to 2004, stacks improved in length and in the quantity and quality of the  $\delta^{18}\text{O}_{\text{carb}}$  data, culminating in the *Lisiecki & Raymo* [2005] LR04 stack and timescale (Figure 1). This stack includes 57 benthic records, many derived from cores recovered by the Ocean Drilling Program. Development of this stack also used newly developed graphical correlation software to process the data [*Lisiecki & Lisiecki*, 2002], and included only data from the benthic foraminiferal genera *Cibicidoides* and *Uvigerina*. Because this stack was constructed by graphic correlation, its stratigraphic features were essentially independent of any timescale and the LR04 stack can be easily adapted for use with other timescales.

More than a decade later, the now canonical view of how Earth's climate has changed over the last five million years can be read in the ups and downs and wiggles of the LR04 stack. The traditional interpretation of the sea level and ice volume history of the Plio-Pleistocene begins with the two million year interval between  $\sim 5.32$  and  $3.32$  Myr. This interval, spanning the Gilbert Chron, is characterized by dozens of low-amplitude  $\delta^{18}\text{O}$  cycles with a mean value of  $3.00\text{‰}$  (Figure 1, dashed blue line), which is  $\sim 0.25\text{‰}$  more negative than the Holocene value (mean of last 5 kyr, dashed red line). These low amplitude cycles exhibit "interglacial" or warm values  $\sim 0.35\text{‰}$  more negative than the Holocene on average with minimum  $\delta^{18}\text{O}_{\text{carb}}$  values as low as  $2.65\text{‰}$ , or  $0.6\text{‰}$  more negative than at present. The maximum (colder, more ice)  $\delta^{18}\text{O}_{\text{carb}}$  values are rarely more positive than the Holocene value and, taken at face value, imply that high-latitude climate was almost always warmer and/or had less continental ice than the late Holocene. Between  $3.2$  to  $2.9$  Myr—the MPWP—the negative  $\delta^{18}\text{O}_{\text{carb}}$  excursions represented by marine isotope stages (MIS) G17, K1, and KM3 reflect the last warm intervals of the pre-glacial Pliocene, after which a long-term trend of increasing mean  $\delta^{18}\text{O}_{\text{carb}}$  values reflects the cooling temperatures and expanding polar cryosphere that culminated in widespread glaciation of the Northern Hemisphere by  $2.5$  Ma [*Shackleton & Hall*, 1984; *Raymo et al.*, 1989].

Based on empirical studies and observations from the last glacial cycle it has been estimated that a  $10$  m eustatic change in sea level due to a change in ice volume would alter the mean ocean  $\delta^{18}\text{O}$  by  $0.08$ - $0.11\text{‰}$  [*Fairbanks and Matthews*, 1978; *Fairbanks*, 1989; *Schrag et al.*, 1996; *Adkins et al.*, 2002; *Elderfield et al.*, 2012; *Rohling et al.*, 2014]. Here we use the commonly cited value of  $0.11\text{‰}/10$  m SL change. It was also empirically determined that a  $1^\circ\text{C}$  decrease in water temperature would increase the  $\delta^{18}\text{O}_{\text{carb}}$  of precipitated calcite by  $+0.2$  to  $0.25\text{‰}$  [*Epstein et al.*, 1951, 1953; *Urey et al.*, 1951; *O'Neal et al.*, 1969; *Kim & O'Neal*, 1997; *Bemis et al.*, 1998; *Marchitto et al.*, 2014]. Note that these conversions were derived using observations from the laboratory and the recent past, but have been applied to the interpretation of  $\delta^{18}\text{O}_{\text{carb}}$  records throughout the Plio-Pleistocene (and indeed over the entire Cenozoic). Three notable exceptions are the studies of *Bailey et al.* [2010], *Winnick & Caves* [2015], and *Gasson et al.* [2016] who questioned whether the mean  $\delta^{18}\text{O}$  of polar ice remains constant over millions of years.

Since only about  $7$  m of sea level equivalent (SLE) of ice is sequestered on Greenland at present [*Shepherd & Wingham*, 2007], less than  $0.1\text{‰}$  of the more negative  $\delta^{18}\text{O}_{\text{carb}}$  values observed prior to  $2.9$  Ma can be assumed to be due to the melting of ice in

the Northern Hemisphere (given the current volume and isotopic composition of ice on Greenland). Therefore, the main contributors to the more depleted  $\delta^{18}\text{O}_{\text{carb}}$  values are typically assumed to be some combination of deep-ocean warming and/or an ice volume decrease in Antarctica. However, despite decades of study, the maximum sea level rise (minimum ice volume) during this interval still remains highly uncertain [e.g., *Raymo*, 1994; *Mudelsee & Raymo*, 2005; *Sosdian & Rosenthal*, 2009; *Raymo et al.*, 2011; *Miller et al.*, 2012; *Woodard et al.*, 2014].

Consider—if the entire amplitude of the negative  $\delta^{18}\text{O}$  excursion in the MPWP relative to the mean Holocene value of the LR04 stack,  $3.25 - 2.92 = 0.33\text{‰}$ , was attributed to an ice volume decrease relative to present, then the traditional rule of thumb given above would imply that an equivalent of  $\sim 23$  m SLE of ice was lost from Antarctica during the warm extremes of the MPWP ( $0.33\text{‰}/0.11\text{‰} \times 10\text{m} = 30\text{ m} - 7\text{m} = 23\text{ m}$  after removing 7 m for Greenland Ice Sheet (GIS) which we assume melts completely). This would require mass loss of  $>30\%$  of the present-day East Antarctic Ice Sheet, which is estimated to have a total volume of  $\sim 56$  m SLE (*Shepherd & Wingham* [2007]) after accounting for  $\sim 5$  m SLE came from the ice currently frozen in the West Antarctic Ice Sheet. On the other hand, if the minimum  $\delta^{18}\text{O}$  values in the benthic isotope records are attributed solely to warming of the deep ocean (and thus, presumably, also the polar surface regions where bottom water forms), then it would imply a bottom water warming of only  $>1.6^\circ\text{C}$  ( $(0.33\text{‰}/0.2\text{‰}) \times 1^\circ\text{C}$ ).

The problem with these scenarios is that it is hard to imagine, in the first case, how one could lose such a significant fraction of the Antarctic ice sheet without any concurrent warming of bottom-waters, especially as much of these waters originate in the surface regions surrounding Antarctica. Equally perplexing, in the second case, it seems unlikely that a  $1.6^\circ\text{C}$  warming of surface and bottom waters in polar regions could occur with no concomitant loss of ice. State-of-the-art climate model results reinforce these intuitions (for instance, *Pollard et al.*, 2015), leaving most investigators to assume the truth lies in some combination of these two effects [e.g., *Kennett & Hodell*, 1993; *Miller et al.*, 2012]. But herein lies a conundrum. If the climate of the Pliocene was significantly warmer (as the data suggests, e.g. *Dowsett et al.* [2010]), how does one “fit” both a polar latitude warming as well as a decrease in the size of the cryosphere into the meager  $\sim 0.3\text{‰}$   $\delta^{18}\text{O}_{\text{carb}}$  decrease that characterizes the warm extremes of the MPWP? And is the widely cited view that  $\sim 2/3$  of the  $\delta^{18}\text{O}_{\text{carb}}$  signal is due to ice ( $\sim 22$  m SLE including loss of GIS) and  $1/3$  to BWT change ( $\sim 1^\circ\text{C}$ ), as observed for the last glacial cycle, a robust assumption (e.g., *Miller et al.* [2012] and *Winnick & Caves* [2015])?

### 3. Geochemical proxy derivation of Pliocene sea level

With only the  $\delta^{18}\text{O}_{\text{carb}}$  value of foraminifera, neither the  $\delta^{18}\text{O}_{\text{sw}}$  nor the seawater temperature can be reliably determined without independent quantification of one or the other. While *Miller et al.* [2012] assume the ratio of ice effect to temperature effect in the MPWP  $\delta^{18}\text{O}_{\text{carb}}$  signal was the same as determined for the last glacial maximum  $\sim 20,000$

years ago (67%/33%, respectively, *Schrag et al.* [1996]), other investigators have used Mg/Ca ratios to independently isolate the temperature component of the  $\delta^{18}\text{O}$  signal [e.g., *Sosdian & Rosenthal*, 2009; *Elderfield et al.*, 2012; *Woodard et al.*, 2014; or *Dwyer & Chandler*, 2009 working with benthic ostracods]. To do this, researchers pair benthic  $\delta^{18}\text{O}_{\text{carb}}$  with bottom water temperatures (BWT) estimated from Mg/Ca ratios measured in foraminiferal (or ostracod) shells from the same sample depth. This approach allows for a continuous, independent assessment of  $\delta^{18}\text{O}_{\text{sw}}$  and thus inferred continental ice volume and sea level, all else being equal to modern.

However, using paired benthic  $\delta^{18}\text{O}_{\text{carb}}$  and Mg/Ca ratios to reconstruct past changes in sea level is complicated by uncertainties in fossil species- and proxy-specific calibrations [e.g., *Lear et al.*, 2004]. Factors other than temperature might alter the Mg/Ca ratios of foraminifera. These include dissolution [*Regenberg et al.*, 2014; *Rosenthal et al.*, 2000], diagenetic recrystallization/overgrowths [*Brown & Elderfield*, 1996; *Sexton et al.*, 2006; *Kozdon et al.*, 2013; *Regenberg et al.*, 2007], or changes in salinity [*Dissard et al.*, 2010; *Ferguson et al.*, 2008] and/or carbonate ion saturation [*Elderfield et al.*, 2006; *Rosenthal et al.*, 2006]. Similar uncertainties may exist for the preservation of the Mg/Ca signal in ostracods [*Elmore et al.*, 2012; *Farmer et al.*, 2012]. Furthermore, the evolution of seawater Mg/Ca is not known in detail but evidence from fluid inclusions, carbonate veins found in mid-ocean ridges, dolomite abundance with time, and echinoderm spines suggest that Mg/Ca ratios may have been increasing from the middle Cenozoic to the present [*Wilkenson & Algeo*, 1989; *Dickson*, 2001; *Horita et al.*, 2002; *Lowenstein et al.*, 2001; *Coggon et al.*, 2010]. While several studies have focused on understanding whether changing seawater Mg/Ca exerts a linear or nonlinear control on shell chemistry [*Delaney et al.*, 1985; *Evans & Müller*, 2012; *Evans et al.*, 2016], important when accounting for these secular changes in seawater Mg/Ca, others chose to leave foraminiferal Mg/Ca ratios uncorrected [*Lear et al.*, 2004, 2015]. Finally,  $\delta^{18}\text{O}_{\text{carb}}$  and Mg/Ca measurements would ideally also be derived from the same shell, but analytical approaches facilitating  $\delta^{18}\text{O}$  and Mg/Ca measurements within the same microfossil have not been available until recently and still have relatively large errors [*Kozdon et al.*, 2011; *Kozdon et al.*, 2013]. And even as the errors are being brought down, the domains analyzed are so small that they might not be representative of the entire shell. Thus, in addition to the aforementioned uncertainties, an additional source of error may be introduced by analyzing  $\delta^{18}\text{O}$  and Mg/Ca in different shells or pooled populations of homogenized shells that are assumed to be age-equivalent.

Using benthic foraminifera at DSDP Site 607, and correcting for the carbonate ion effect and Mg/Ca temperature calibration errors, *Sosdian & Rosenthal* [2009] were the first to estimate BWT for the MPWP using the paired  $\delta^{18}\text{O}_{\text{carb}}$ -Mg/Ca technique. After applying a three-point running mean to their data, they calculated that maximum eustatic sea level exceeded 35 m above present. However, they also emphasized that Mg/Ca BWT and  $\delta^{18}\text{O}_{\text{carb}}$  uncertainties contribute an error of  $\pm 21$  m for the mean trend of sea level and a propagated uncertainty of  $\pm 31$  m for the glacial–interglacial amplitude. While these errors are large, additional sources of error also become relevant when foraminifera are millions of years old. Next, we address analytical and geologic uncertainties not considered in the



Pliocene sea level studies discussed above, including the possible influence of carbonate diagenesis on long-term trends, as well as changes in the Mg/Ca ratio of the ocean. We evaluate the potential influence of these factors on the interpretation of Plio-Pleistocene ice volume history (and the LR04 stack) as well as estimates of Pliocene sea level.

#### 4. What do we know about post-burial diagenesis?

Could any long-term bias exist in benthic  $\delta^{18}\text{O}$  records, including the LR04 stack, caused by post-depositional diagenetic processes? There is a growing recognition that calcite precipitation in pore waters has the potential to chemically alter foraminiferal tests as they are buried within the sediment column [McKenzie *et al.*, 1978; Pearson *et al.*, 2001; Sexton *et al.*, 2006; Pearson *et al.*, 2007; Curry & Marchitto, 2008; Kozdon *et al.*, 2013]. For surface-dwelling warm-water planktic foraminifera in particular, which settle post-mortem into the cold abyss, any diagenetic overgrowths deposited at or below the seafloor would be isotopically heavy and therefore have the potential to significantly alter the test's mean  $\delta^{18}\text{O}$  value, especially over tens of millions of years (e.g., this mechanism has been invoked to explain the “cool tropics paradox”; Wilson & Opdyke, 1996; D'Hondt & Arthur, 1996; Norris & Wilson, 1998; Wilson & Norris, 2001; Pearson *et al.*, 2001; Wilson *et al.*, 2002; but see also Zeebe, 2001). But what of much younger, benthic foraminifera that have only been buried for a few million years in an environment somewhat similar to that in which they lived? Could diagenetic alteration be significant enough to impact the interpretations of sea level studies such as those discussed above (where a 0.1‰ change in  $\delta^{18}\text{O}$  is equivalent to a 10 m error in estimated sea level)?

For decades it has been assumed that foraminifera tests showing no visible signs of dissolution or diagenetic overprinting under the optical microscope were well preserved and that their original stable isotope and elemental composition had not changed over time. However, this approach to assessing preservation has been questioned on the grounds that foraminiferal tests can have the superficial appearance of being unaltered even as diagenetic calcite has replaced delicate test structures with little or no visible change [e.g., Sexton *et al.*, 2006; Evans *et al.*, 2015b]. Indeed, over the last 15 years, the diagenetic alteration of planktic foraminiferal tests has received considerable attention [e.g., Pearson *et al.*, 2001; Pearson *et al.*, 2007; Pena *et al.*, 2005; Curry & Marchitto, 2008; Kozdon *et al.*, 2013] and it is now demonstrated that recrystallization or the post-depositional addition of secondary calcite can significantly alter the mean  $\delta^{18}\text{O}$  of planktic foraminiferal tests [Pearson *et al.*, 2001; Sexton *et al.*, 2006; Kozdon *et al.*, 2011; 2013].

Fewer studies have assessed the preservational state of benthic foraminifera tests with notable exceptions being Collen & Burgess [1979], Corliss & Honjo [1981], Showers *et al.* [1987], Widmark & Malmgren [1988], Carmen & Keigwin [2004], Sexton & Wilson [2009], and Edgar *et al.* [2013]. In an examination of Pliocene benthic foraminifera, Collen & Burgess [1979] found well-developed overgrowths and evidence for recrystallization, although the samples were taken from a shelly sandstone outcrop. Both Sexton & Wilson [2009] and Edgar *et al.* [2013] show that significant recrystallization of benthic foraminifera occurs in the early stages of burial (the first few million years) with both studies cautioning

that a large change in bottom water temperature or  $\delta^{18}\text{O}_{\text{sw}}$  (such as that which occurred from the mid Pliocene to the late Pleistocene for instance, Figure 1) could result in large isotopic offsets between original shell  $\delta^{18}\text{O}$  and the diagenetic material later added to fossil benthic shells in the upper sediment column.

While additional investigations of (a) the progression of diagenesis over time and (b) the average contribution of diagenetic calcite to the mass of a benthic foraminifera test are needed, it is clear that assuming negligible diagenetic bias in benthic tests may be incorrect. While alteration and recrystallization likely begins immediately upon death (in pore waters close in temperature and isotopic composition to the waters in which the tests were originally secreted [e.g., Walker & Goldstein, 1999; Fontanier *et al.*, 2005]), this would not be the case if large changes in climate were altering bottom water characteristics on the same temporal scale. Indeed, with respect to the timing of foraminiferal diagenesis, numerical models (as well as the aforementioned studies) all suggest that carbonate recrystallization in deep-sea sediments begins at deposition [Adkins & Schrag, 2001; Rudnicki *et al.*, 2001]. Therefore, the degree of exchange between sediments and pore fluids during the early post-burial phase surely holds the key to determining the isotopic and elemental composition of the diagenetic calcite [Delaney, 1989; Schrag *et al.*, 1995; Schrag, 1999; Rudnicki *et al.*, 2001; Fantle & DePaolo, 2006; Fantle *et al.*, 2010; Higgins & Schrag, 2012]. In the next section we explore the possibility that Plio-Pleistocene benthic  $\delta^{18}\text{O}$  records could be influenced by diagenesis to the degree that it might impact paleoclimate interpretations, for instance, maximum sea level in the Pliocene.

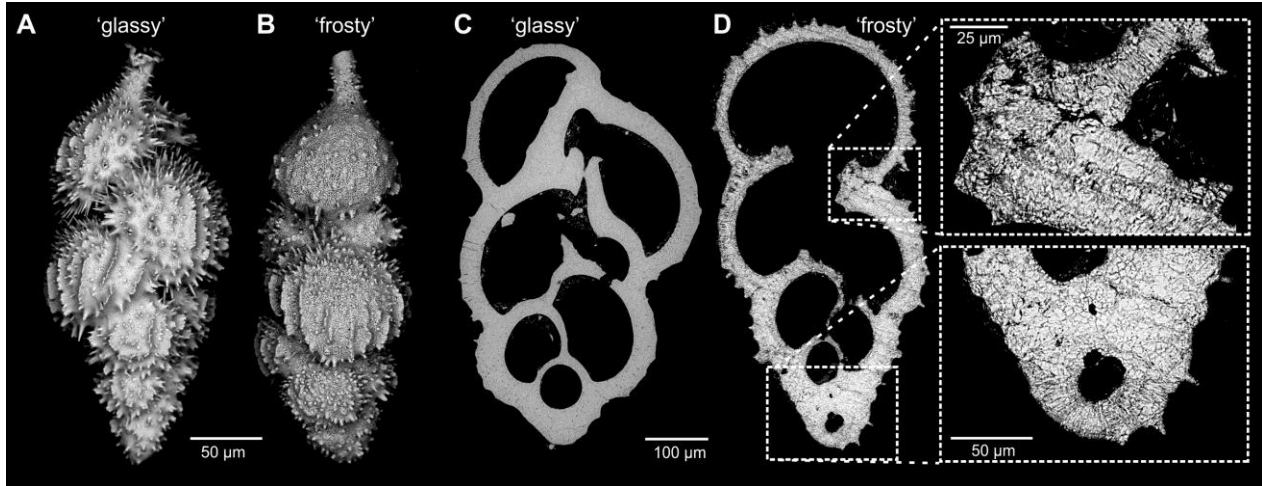
#### 4.1. A secular bias in the LR04 stack caused by diagenesis?

The LR04 stack is a compilation of  $\delta^{18}\text{O}$  data from the benthic foraminiferal genera *Uvigerina* and *Cibicidoides* with standard corrections made for the species-specific vital effects in  $\delta^{18}\text{O}$  (after Shackleton & Hall [1984]). The correction factor for *Cibicidoides wuellerstorfi* is +0.64‰, which is the largest correction factor for  $\delta^{18}\text{O}$  among the benthic foraminifera commonly used for paleo-reconstructions. In other words, *Cibicidoides wuellerstorfi* is believed to precipitate its test with  $\delta^{18}\text{O}$  values that are, on average, 0.64‰ lower (more negative) than those expected from calcite precipitated in equilibrium with temperature and ambient seawater  $\delta^{18}\text{O}$  [Shackleton & Hall, 1984]. Consequently, any early diagenetic calcite deposited by abiotic precipitation on *Cibicidoides* tests could have a significantly higher/more positive  $\delta^{18}\text{O}$  than the original, biologically-precipitated calcite – this would immediately elevate the mean  $\delta^{18}\text{O}$  of the tests.

For instance, if a benthic specimen living at 3 Ma originally had a  $\delta^{18}\text{O}_{\text{carb}}$  value of 2.3‰ (prior to the vital effect correction), and subsequent dissolution and reprecipitation from pore waters added, for example, 15 wt.% diagenetic calcite, then the whole test  $\delta^{18}\text{O}_{\text{carb}}$  value would shift by +0.1‰, just due to the difference in biological and abiotic isotope fractionation (e.g.,  $0.85 \times (2.3\text{‰}) + 0.15 \times (2.94\text{‰}) = 2.4\text{‰}$  where 2.94‰ is the value for abiotic calcite precipitated in equilibrium with temperature and ambient water  $\delta^{18}\text{O}$ ). If correct, this would result in a systematic bias in *Cibicidoides* records that would be

equivalent to an overestimation of the amount of polar ice at that time by 10 m SLE; in other words, a larger inferred ice loss/sea level rise could possibly be masked by a seemingly subtle addition of diagenetic calcite).

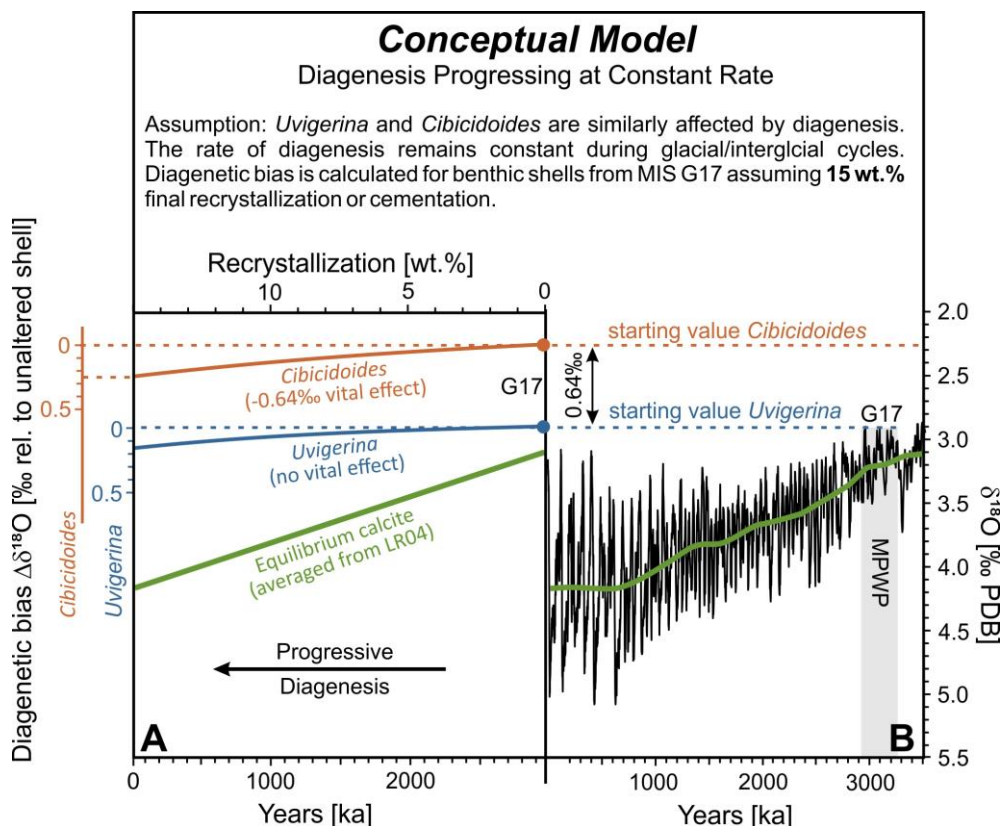
Is there evidence for significant diagenetic calcite in benthic foraminifera of



**Figure 2.** A) SEM image of a *Uvigerina* shell from ODP Site 1208A, ~950 ka, translucent (glassy) under optical microscope. The surface largely retains the original microgranular texture, with ornaments and pores preserved. B). *Uvigerina* shell from ODP Site 1208A, ~965 ka, with frosty appearance under optical microscope. The diagenetic process of ‘frosting’ replaced the original microgranular texture with larger crystals. SEM images of (C) a glassy and (D) frosty *Uvigerina* shell from ODP Site 1208A, picked from ~3017 and ~2437 ka old sediments, respectively, show that the chamber walls of the glassy shell are still largely composed of microgranular crystals, indicating minimal alteration. In contrast, the chamber walls of the younger frosty shell contain large ‘blocky’ crystals, many of them >5 µm in size, indicating a significant degree of recrystallization and/or replacement of the original material.

Pliocene age? First, we note that a study of diagenesis in Paleogene planktonic foraminifera estimates that diagenetic calcite can contribute 15-50 wt.% to the mass of the shell [Kozdon *et al.*, 2011], a value consistent with the ~30 wt.% recrystallization estimates of Schrag *et al.* [1995], Schrag [1999], and Tripathi *et al.* [2003]. Furthermore, our SEM examination of late Pliocene and early Pleistocene benthic foraminifera show clear evidence of the presence of both glassy microgranular (well-preserved) specimens as well as frosty “coarse crystalline” (significantly altered) specimens (Figure 2), and the early Pleistocene benthic specimen shown in Figure 2D suggests that 15-30% diagenetic recrystallization could be a conservative estimate. With respect to the above calculation, we also note that the widely-used correction factor of +0.64‰ for *Cibicidoides* has been questioned by calibration studies suggesting calcification is actually occurring closer to equilibrium with temperature and ambient  $\delta^{18}\text{O}_{\text{sw}}$  [Bemis *et al.*, 1998; Marchitto *et al.*, 2014]. Furthermore, these authors suggest that it may be *Uvigerina* that is characterized by a positive vital effect. Whichever is the case, diagenetic mass balance arguments, such as that given above, would need to be applied to any benthic foraminifera featuring a vital effect. Indeed, it seems almost certain that at least one of these two commonly used benthic foraminiferal is forming its tests offset from ‘equilibrium’ calcite and, as shown above, this uncertainty would likely propagate through to paleoclimate interpretations of past sea level.

In addition to the fixed offset from bottom water  $\delta^{18}\text{O}$  due to biologic vital effects, one must also consider the implications of the transition to cooler temperatures and greater global ice volume that began immediately after the MPWP, a trend that culminated



**Figure 3:** Model calculation for the effect of diagenesis on  $\delta^{18}\text{O}$  of *Cibicidoides* and *Uvigerina* shells. We assume *Cibicidoides* has a vital effect of -0.64‰ [Shackleton & Hall, 1984]. Therefore, any diagenesis elevates whole-shell  $\delta^{18}\text{O}$ , even if occurring at similar temperatures and  $\delta^{18}\text{O}_{\text{sw}}$  as foraminiferal shell growth. Assuming 15% recrystallization, as shown in the figure, the  $\delta^{18}\text{O}$  of the *Cibicidoides* shell is elevated by 0.25‰ while *Uvigerina* changes by a lesser amount (~0.15‰, because it does not have a vital effect for  $\delta^{18}\text{O}$ ), thus theoretically reducing the offset in  $\delta^{18}\text{O}$  between these two species ( $\Delta\delta^{18}\text{O}_{\text{Uvig-cib}}$ ) as diagenesis progresses (A). Benthic  $\delta^{18}\text{O}$  values from the LR04 stack (B).

in widespread glaciation of the Northern Hemisphere 2.5 Ma ago (Figure 1). A benthic foraminifer that existed at 3 Ma would, over its first ~15 meters of burial (lasting ~500 kyr using a typical deep sea sedimentation rate of 3 cm/kyr), be exposed to pore waters that were exchanging with bottom waters that were increasing in  $\delta^{18}\text{O}$  (due to ice growth between 2.9 and 2.4 Ma), as well as becoming progressively colder (due to climate cooling over that same interval; Figure 3). Assuming that a benthic test formed its calcite in equilibrium with seawater (forgetting for a moment the diagenetic vital-effect issue described in the previous paragraph), the  $\delta^{18}\text{O}$  value of any diagenetic calcite added to a benthic test over the first 15 m of burial would be higher/more positive than that of the original test. If the benthic foraminifera also had a negative (lower than equilibrium  $\delta^{18}\text{O}$ ) biologic vital effect, then the downcore “climate trend” diagenetic offset described above would be additive to the vital-effect effect. Keep in mind that the rate and depth to which

diagenesis proceeds, and possibly tapers off [e.g., *Pearson & Burgess, 2008; Sexton & Wilson, 2009; Edgar et al., 2013*], downcore, remains a major uncertainty with one comprehensive study suggesting carbonate recrystallization is virtually over by ~10 Ma post-burial [*Rudnicki et al., 2001*].

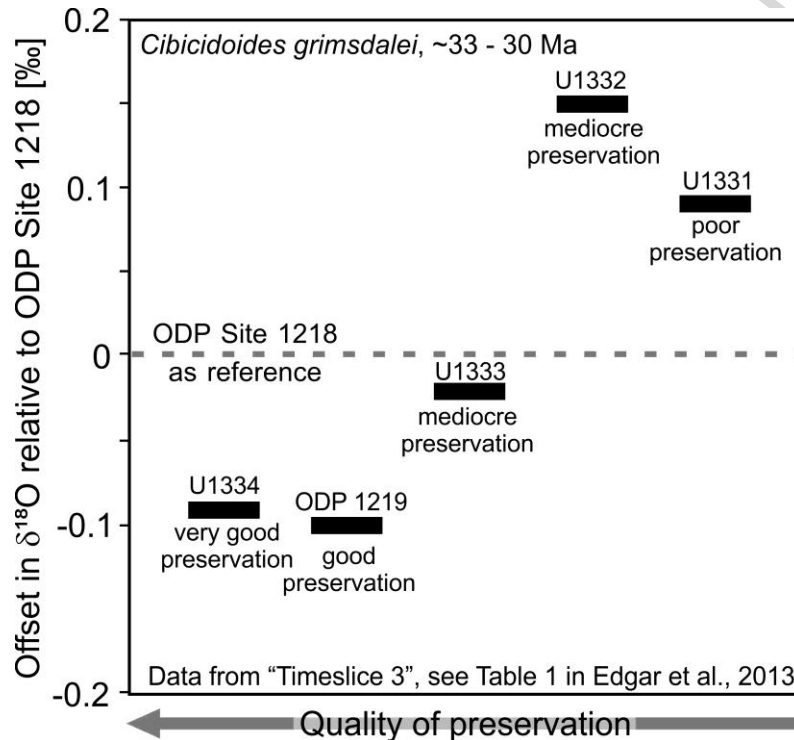
To illustrate the potential for even subtle changes in shell diagenesis to impact interpretations of past temperatures, sea level and ice volume, Figure 3 shows the cumulative impact of 15% diagenetic calcite added to *Uvigerina* and *Cibicidoides* specimens from the MPWP. Here we assume that diagenesis continues at a constant rate throughout the subsequent 3 Myr of burial (over a depth range of 100 m instead of only during the first 15 meters or so of burial considered above, although note that one would also have to consider the competing effects of the geothermal gradient increasing with depth as well as the impact of sediment compaction on pore water circulation). In this example, the additive impact of changing bottom water characteristics and the vital effect-offset on *Cibicidoides* is 0.25‰, a change that would lead to the MPWP  $\delta^{18}\text{O}$  values of that species being shifted to more positive values by ~0.25‰. As this would be equivalent to the addition of >20 m SLE of additional ice at the poles, the potential for significant systematic errors in ice volume estimates becomes apparent—both in individual  $\delta^{18}\text{O}$  records and in the LR04 stack which is dominated by *Cibicidoides* measurements during the MPWP. In addition, if the accepted vital effects attributed to various species were to be changed [e.g., *Marchitto et al., 2014*], then one would also have to alter estimates of the potential biases inherent in individual species.

In summary, if the mean  $\delta^{18}\text{O}$  of a hypothetical MPWP *Cibicidoides* test is shifted by even +0.1‰ by the precipitation of diagenetic calcite under conditions where pore waters are both cooling and increasing in  $\delta^{18}\text{O}_{\text{sw}}$ , the additional amount of inferred polar ice during the MPWP could easily exceed 20m SLE (>10m from this effect + 10 m due to vital-effect offset, assuming the canonical value for the *Cibicidoides* vital effect). We suggest that interpreting the Pliocene benthic foraminiferal  $\delta^{18}\text{O}$  record at face value, relative to today, to derive Pliocene ice volume/sea level, might lead one to seriously underestimate the magnitude of deglaciation or warming at that time, to a degree that exceeds the stated errors in recent compilations [e.g., *Miller et al., 2012; Rohling et al., 2014*]. On the other hand, such a bias could solve the conundrum of how one “fits” both a polar surface/bottom water warming as well as a decrease in the size of the cryosphere into the <0.4‰  $\delta^{18}\text{O}_{\text{carb}}$  decrease that characterizes the warm extremes of the MPWP (Figure 1).

How plausible is our hypothesis that the measured  $\delta^{18}\text{O}$  of Plio-Pleistocene benthic foraminiferal shells is biased by diagenesis? One indicator of a diagenetic process would be temporal changes in the  $\delta^{18}\text{O}_{\text{carb}}$  offsets between benthic foraminifera with differing vital effects (e.g., Figure 3). For decades, it was assumed that the species-specific vital effects in benthic foraminiferal  $\delta^{18}\text{O}$  were constant in time and space [e.g., *Mix et al., 1995*]. It was not until recently that *Hoogakker et al. [2010]* reported downcore variations in  $\delta^{18}\text{O}$  offsets between contemporaneous benthic foraminiferal species that were not related to short-term random variability. The authors evaluated a variety of potential causes for these temporal changes in benthic  $\delta^{18}\text{O}$  offsets including bioturbation,

dissolution, metabolic activity, a change in carbonate ion concentration ( $[\text{CO}_3^{2-}]$ ), and productivity, and concluded that the mechanisms for these differences remained elusive. It may be that diagenetic cementation or recrystallization leads to downcore variations in  $\delta^{18}\text{O}$  offsets between benthic species such as *Uvigerina* and *Cibicidoides*, a process that could be particularly pronounced on glacial-interglacial transitions that are associated with rapid changes in BWT and  $\delta^{18}\text{O}_{\text{sw}}$ .

Our model would also predict that more diagenetically altered samples would be more positive in  $\delta^{18}\text{O}$  relative to less altered specimens of an equivalent age. Data suggestive of this effect can be found in the data tables of *Edgar et al.* [2013]. In this study,



**Figure 4.** Relation between foraminifera preservation and  $\delta^{18}\text{O}$  in early Oligocene *Cibicidoides* shells from five ODP and IODP Sites from the eastern equatorial Pacific, shown as the offset in  $\delta^{18}\text{O}$  relative to the ‘reference’ Site ODP 1218 for the time interval ~33 – 30 Ma. The selected sites have been correlated to each other by the original authors, allowing for a direct comparison of the  $\delta^{18}\text{O}$  of groups of age-equivalent foraminifera shells (see *Edgar et al.*, 2013 for details). The site-specific offsets in  $\delta^{18}\text{O}$  relative to the ‘reference’ Site 1218, as shown in the figure, are based on dozens of measurements for each site (*Edgar et al.*, 2013). Shell preservation was assessed by optical microscope, supported by SEM imaging of selected shells (*Edgar et al.*, 2013).

age-equivalent intervals (33-30 Ma) of mean  $\delta^{18}\text{O}_{\text{carb}}$  values from *Cibicidoides* were compared to a reference site across six total core locations in the equatorial Pacific. In addition, average shell preservation was assessed at each site, by the authors, using both optical microscopic and SEM methods. When we plot the mean site-to-site  $\delta^{18}\text{O}_{\text{carb}}$  offset against preservation state (Fig. 4), we observe a strong correlation with the  $\delta^{18}\text{O}_{\text{carb}}$  of the *Cibicidoides* shells generally increasing with degrading preservation. The total offset between sites featuring the best- and poorest preserved shells is ~0.20‰, consistent with

predictions in Figure 3 of how an increasing diagenetic effect would bias shell  $\delta^{18}\text{O}$ . It is notable that much of the Pacific Ocean today is bathed in a homogenous deep-water mass [Palike *et al.*, 2006] and it seems unlikely that differences in water mass properties, within the much smaller region of the eastern equatorial Pacific, can account for the offsets observed in the Oligocene sediments.

Additional research is needed to establish whether a significant volumetric percentage of diagenetic calcite may have been added to mid Pliocene benthic foraminifera, and whether this diagenetic calcite differs isotopically from the original biogenic record. Preliminary investigation using *in situ* analytical approaches such as secondary ion mass spectrometry (SIMS) and electron probe microanalyzers (EPMA) suggest this is a possibility for Pleistocene planktic foraminifera [Wycech *et al.*, 2016] but more such studies are needed to shed light on the potential magnitude of diagenesis in late Cenozoic benthic foraminifera. Following this line of argument, we cannot exclude the possibility that some of the climate interpretations from the LR04 stack, or indeed any long benthic  $\delta^{18}\text{O}$  record, may be systematically biased by diagenetic processes that unfold after burial within the sediment column, processes which start the moment a foraminifera dies.

#### 4.2 Could diagenesis influence Mg/Ca ratios of calcite?

Much less is known about the impact of calcite diagenesis on trace metal ratios, in particular Mg/Ca in foraminifera tests. A number of studies have shown that dissolution of planktic foraminifera settling through the water column and/or deposited on the sea floor can alter shell Mg/Ca ratios through the preferential removal of Mg-rich calcite [Hastings *et al.*, 1998; Rosenthal & Boyle, 1993; Rosenthal *et al.*, 2000; Lea *et al.*, 2000; Brown & Elderfield, 1996; Regenberg *et al.*, 2007, 2014; Hertzberg & Schmidt, 2013]. Dekens *et al.* [2002] developed core top calibrations for different planktic foraminifera that would account for this effect by taking the depth (or  $\text{CO}_3^{2-}$  concentration) for the core site into consideration; however, Hönisch *et al.* [2013] demonstrated that such a correction systematically biased SST data from cores shallower than 4.4 km implying that dissolution may be minimal in core top samples from well above the lysocline, which was subsequently confirmed by the global analysis of Regenberg *et al.* [2014].

But what of calcite dissolution and reprecipitation that occurs in contact with pore waters after burial? Precipitation experiments [Mucci, 1987] demonstrate that the Mg/Ca ratios of inorganically precipitated calcite are about an order of magnitude higher than those reported from foraminiferal tests, suggesting that biological processes play a significant role in controlling the low Mg-content of tests formed during calcification [e.g., Barker *et al.*, 2005; Erez, 2003; Lea, 2003]. Indeed, Mg/Ca ratios measured by EPMA in planktic shells associated with the extreme climate event at the Paleocene-Eocene Thermal Maximum exhibit a significant increase across the transition from original to diagenetic calcite, from ~3 mmol/mol to over 12 mmol/mol in the study of Kozdon *et al.* [2013]—however, this is still much less of a change than predicted from inorganic precipitation experiments. The authors speculate that the Mg/Ca ratio of the diagenetic calcite is lower than inferred from precipitation studies because it may be comprised of re-precipitates

from older low-Mg biogenic carbonates. Although Mg-loss during dissolution and Mg-gain during diagenesis/precipitation could be counterbalancing each other, a recent study of planktic foraminifera suggests that diagenetic calcite can significantly alter both the Mg/Ca and radiocarbon ages of Pleistocene planktic foraminifera [Wycech *et al.*, 2016].

But what of benthic foraminifera? If Mg/Ca ratios in benthic foraminifera were overprinted diagenetically, the presence of even a small volume of diagenetic calcite with a higher Mg/Ca ratio could raise mean foraminiferal test Mg/Ca ratios and lead one to overestimate the amount of  $\delta^{18}\text{O}$  change due to warming and, therefore, underestimate the amount of ice volume change (and equally, the amount of sea level rise). This systematic error would be in the *same* direction as, and additive to, errors caused by addition of diagenetic  $\delta^{18}\text{O}$  as discussed in the previous section. However, Mg/Ca records from *Uvigerina*, *O. umbonatus*, and *Cibicidoides* spanning 1.5 to 0.5 Myr at DSDP Site 607 show no obvious indication of any inter-species trends or offsets that could be attributed to diagenesis [Ford *et al.*, 2016], although even a 0.1 mmol/mol bias, challenging to identify by any analytical technique, could impact sea level reconstructions by ~10 m (see below).

Ultimately, trace element measurements of diagenetic precipitates or recrystallized domains are sparse and existing data indicate that the processes that control the Mg/Ca of diagenetic calcite formed in the sediment column are still not well understood. Critical issues that await robust inquiry include: (1) SEM imaging combined with cathodoluminescence (CL) and electron backscatter diffraction (EBSD) characterization of Plio-Pleistocene benthic foraminiferal tests from multiple sites and multiple ages (whole shells, open chambers, and polished cross-sections) to evaluate their preservational state in more detail; (2) minor/trace element mapping by laser-ablation, EPMA and NanoSIMS to understand compositional heterogeneity and identify diagenetic phases; and (3) intrashell  $\delta^{18}\text{O}$  measurements by SIMS to evaluate the intrashell  $\delta^{18}\text{O}$ -range and correlate measured  $\delta^{18}\text{O}$  with domains that are classified as well-preserved or altered based on SEM, EBSD, and CL images. Lastly, all of these data need to be calibrated by comparison to modern shells cultured under controlled conditions [e.g., Hintz *et al.*, 2006; Barras *et al.*, 2010; Hönisch *et al.*, 2013; Evans *et al.*, 2016].

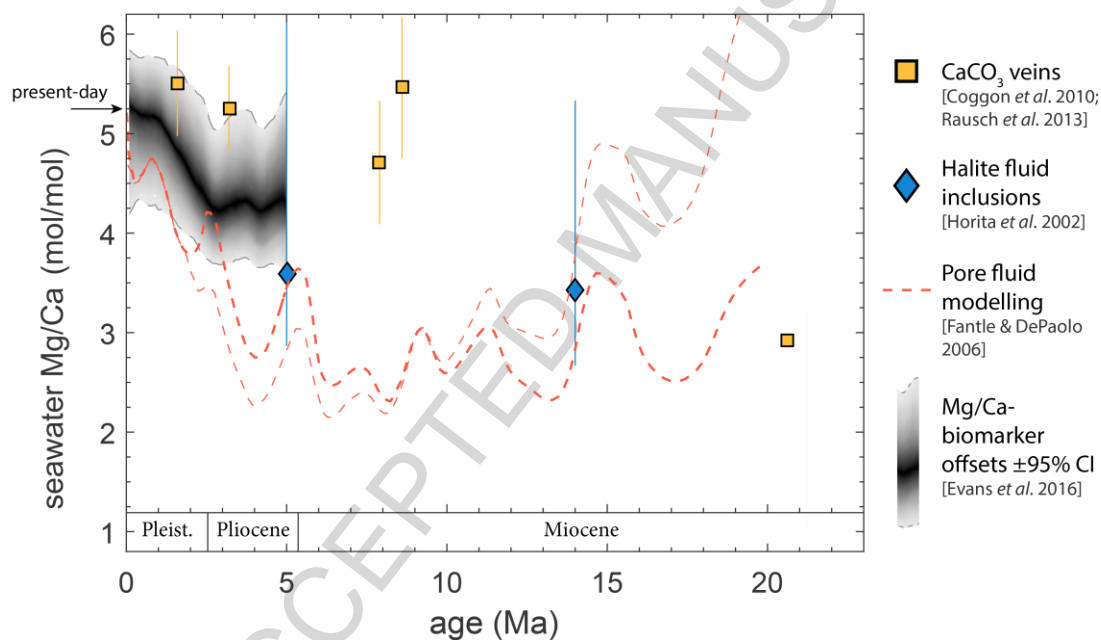
## 5. Could changing Mg/Ca seawater ratios affect Pliocene sea level estimates?

A vibrant debate surrounds Pliocene SST reconstructions from the tropical Pacific derived from different proxies [e.g., Zhang *et al.*, 2014; O'Brien *et al.*, 2014; Ravelo *et al.*, 2014; Ford *et al.*, 2015]. These proxies include those based on biomarkers (e.g., TEX<sub>86</sub> [Zhang *et al.*, 2014] and alkenone U<sup>K</sup><sub>37</sub> [Dekens *et al.*, 2008; Herbert *et al.*, 2010]) and those derived from foraminiferal carbonate (Mg/Ca ratios; e.g., Wara *et al.* [2005]). In particular, this debate has focused attention on the possibility that the Mg/Ca temperature proxy could be biased by long-term secular changes in the Mg/Ca composition of seawater [Medina-Elizalde *et al.*, 2008]. Indeed, O'Brien *et al.* [2014] argued that the observed difference between Mg/Ca and TEX<sub>86</sub> temperature reconstructions for ODP Site 1143 (in the South China Sea) could be entirely explained by a secular change in seawater chemistry



over the last few million years, although opposing viewpoints are given by *Ford et al.* [2015] and *Brierley et al.* [2015].

Both culturing experiments and fossil data suggest that the  $Mg/Ca_{carb}$  is nonlinearly dependent on the  $Mg/Ca$  ratio of seawater [*Evans & Müller, 2012; Evans et al., 2015a*] and thus a calibration based on modern core top studies would not be applicable if the seawater  $Mg/Ca$  ratio changed over millions of years. Given the residence times of Ca and Mg are  $\sim 1$  Myr and  $\sim 13$  Myr respectively [*Li, 1982*], it is possible that the seawater  $Mg/Ca$  ratio ( $Mg/Ca_{sw}$ ) has changed over the 3 Myr since the mid-Pliocene. The most extreme view suggests that  $Mg/Ca_{sw}$  could have increased by as much as 25% just since the early Pliocene (halite fluid inclusion data of *Horita et al.* [2002] in Fig. 5). Pore fluid modeling by *Fantle & DePaolo* [2006] and comparison of biomarker and foraminifera  $Mg/Ca$  data in light of laboratory calibrations on the effect of changing  $Mg/Ca_{sw}$  [*Evans et al., 2016*] suggest a roughly similar magnitude of change while data from ridge flank carbonate veins suggests only a minor, if any, change since the early Pliocene [*Rausch et al., 2013; Coggon et al., 2010*] (Figure 5).



**Figure 5.** Proxy reconstructions of the molar ratio of Mg to Ca in seawater over the Neogene, broadly indicating an increase since the Pliocene. The pore fluid-derived reconstruction is sensitive to the assumptions made regarding potential changes in the calcium isotopic composition of seawater over time. The bold orange dashed line assumes no change whereas the thin orange line is a potential scenario wherein the Ca isotopic composition of seawater has changed.

Studies using the  $Mg/Ca$  proxy to determine SST or BWT in the past usually assume that  $Mg/Ca_{sw}$  has remained constant [e.g. *Wara et al., 2005; Sosdian & Rosenthal, 2009; Miller et al., 2012; Friedrich et al., 2013; Rohling et al., 2014*], with notable exceptions being *Medina-Elizalde et al.* [2008] and those utilizing  $Mg/Ca$  measurements from earlier in the Cenozoic [e.g. *Lear et al., 2000*]. However, if we take the data from *Horita et al.* [2002] and *Fantle & DePaolo* [2006] at face value (Figure 5),  $Mg/Ca_{sw}$  rose from 3-4 mol/mol at 3-

5 Ma to 5.2 mol/mol at present. The implication of these results is that benthic foraminiferal Mg/Ca data, if uncorrected for this change, would underestimate Pliocene BWT by  $\sim 0.9$ - $1.4^\circ\text{C}$  [Evans *et al.*, 2016]. Using the paired Mg/Ca- $\delta^{18}\text{O}_{\text{carb}}$  method to get at ice volume, this would lead one to overestimate the change in Pliocene polar ice volume/sea level by 18-28 meters. This is opposite to, and comparable in magnitude to, the direction of the diagenetic effects discussed in the previous sections.

While several (though not all) lines of proxy Mg/Ca<sub>sw</sub> evidence for the last 5 Ma are in agreement with regards to the direction of change since the Pliocene, precise knowledge of the magnitude of this shift is one more prerequisite for deriving an accurate ice volume reconstruction from biogenic calcite. For example, an uncertainty in MPWP Mg/Ca<sub>sw</sub> of  $\pm 0.5$  mol/mol (Figure 5) would translate to a sea level error of  $\pm 14$  m for a measured Mg/Ca ratio in benthic foraminifera of 1.5 mmol/mol. In addition, while progress has been made in calibrating the response of shell chemistry to Mg/Ca<sub>sw</sub> in planktonic and shallow benthic foraminifera [Segev & Erez, 2006; Evans *et al.*, 2016], the shape of this relationship has only been indirectly calculated for benthic foraminifera [Evans & Müller, 2012; Evans *et al.*, 2016]. Due to the difficulty of maintaining the commonly used benthic species in culture, these calculations assume that the relationship between calcite and seawater Mg/Ca is best described by a power function, as has been shown to be the case for most other marine calcifiers [Hasiuk & Lohmann, 2010]. Tighter constraints are needed on the sensitivity of Mg incorporation in benthic foraminifera to Mg/Ca<sub>sw</sub>.

## 6. Additional influences on paired Mg/Ca - $\delta^{18}\text{O}$ estimates of MPWP sea level

Other secondary factors that may impact Mg/Ca ratios in foraminifera and thus bias Plio-Pleistocene sea level estimates are salinity, and the carbonate ion concentration of ambient seawater. Similar to the effects discussed above, these variables could also lead to systematic errors in past sea level/ice volume reconstructions, rather than randomly distributed uncertainty. Here, we briefly discuss and quantify the potential bias of these secondary factors on benthic foraminiferal Mg/Ca ratios but recognize that these particular variables are topics of more widespread discussion and ongoing research.

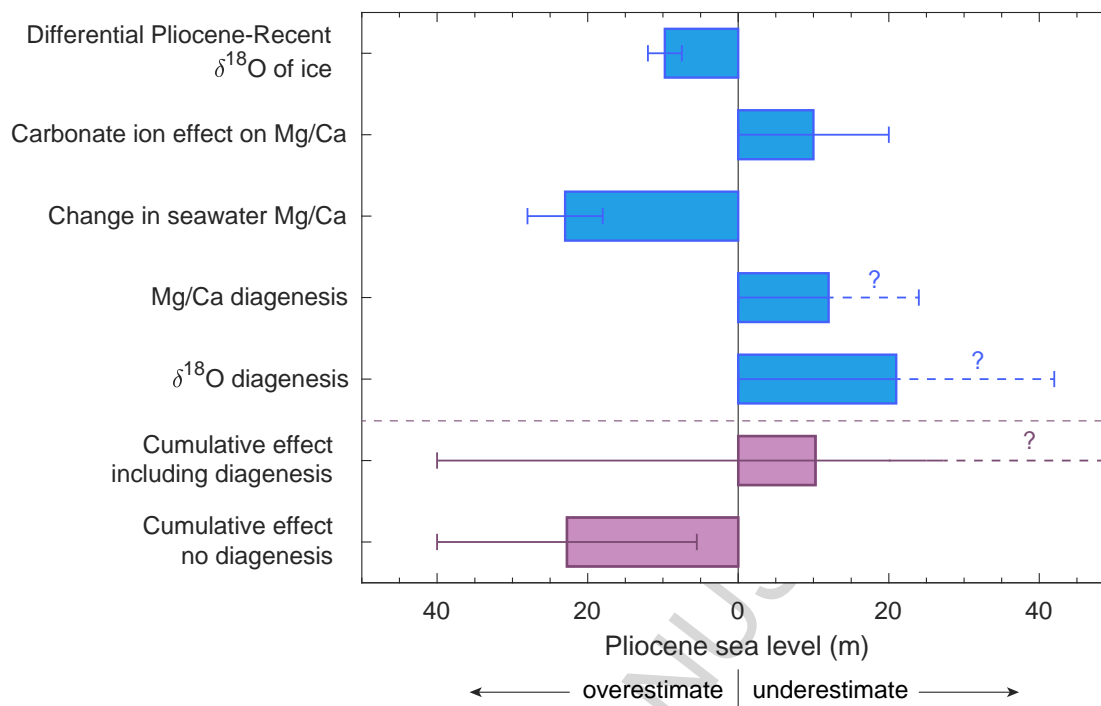
As an example, a decrease in ice volume equivalent to +10 m SLE would decrease the salinity of the ocean by about a tenth of a salinity unit [Adkins *et al.*, 2002]. In both planktic and benthic foraminiferal culturing studies, a 4-8% increase in Mg/Ca per salinity unit is observed [Nürnberg *et al.*, 1996; Kısakürek *et al.*, 2008; Dissard *et al.*, 2010; Hönisch *et al.*, 2013]. Thus, with a Mg/Ca-temperature sensitivity of about 0.12 mmol/mol per  $^\circ\text{C}$  reported for *Cibicidoides* [Marchitto *et al.*, 2007], the effect of ice volume-induced salinity changes in benthic Mg/Ca temperatures is likely negligible.

Likewise, long-term secular changes in the pH and carbonate ion content of the ocean are being evaluated with respect to their influence on the Mg/Ca proxy [e.g., Lea *et al.*, 1999; Zeebe, 2001; Hönisch & Hemming, 2005; Yu & Elderfield, 2008; Bartoli *et al.*, 2011]. For pH, estimates of mid-Pliocene values appear to fall squarely within the range observed in the late Pleistocene [Bartoli *et al.*, 2011]. For carbonate ion effects, we can

consider if there is any evidence for long-term secular changes in the depth of the sedimentary lysocline and calcite compensation depth (CCD) over the last 3 Myr. *Elderfield et al.* [2006] suggest that carbonate ion effects can become significant in cold bottom waters near the CCD. In the deep Atlantic at least, the lysocline may have shoaled *after* the MPWP (*Ruddiman et al.* [1987], although see also *Lang et al.* [2014] who suggest that dilution of pelagic sediment by terrigenous material may be responsible for the carbonate trends observed). If the lysocline shoaled in the Atlantic this would likely lead to a secular decrease in the carbonate ion concentration at a location near the lysocline; this in turn might have caused a decline in the Mg/Ca ratio of calcite from the MPWP to today (by  $\sim 1\%$  per  $\mu\text{mol kg}^{-1}$  and perhaps influencing some species more than others; see for instance, *Elderfield et al.* [2006], *Yu & Elderfield* [2008] and *Elderfield et al.* [2010]). Thus, in places where the bottom water carbonate ion concentration was higher during the MPWP, the correspondingly higher Mg/Ca ratio would lead one to overestimate the actual BWT change and therefore ascribe too little of the  $\delta^{18}\text{O}_{\text{carb}}$  change to a decrease in global ice volume during the MPWP warm extremes.

What is the potential magnitude of this effect? *Sosdian & Rosenthal* [2009] estimate that a decline in  $[\text{CO}_3^{2-}]$  ion of  $10 \mu\text{mol kg}^{-1}$  (with a temperature sensitivity of  $\sim 0.15 \text{ mmol mol}^{-1}/^\circ\text{C}$  after *Yu & Elderfield* [2008]) implies a BWT error of  $0.6^\circ\text{C}$ ; this would equate to  $0.12\text{‰}$  in  $\delta^{18}\text{O}_{\text{carb}}$  that should actually be attributed to a decrease in MPWP ice volume relative to today, a decrease equivalent to  $\sim 10 \text{ m SLE}$ . On the other hand, the *Ford et al.* [2016] inter-comparison of Pleistocene Mg/Ca records from three benthic species at DSDP Site 607 concludes that the lack of coherence between observed Mg/Ca variability and the variability observed in proxies of deep water carbon chemistry, between 1.5 and 0.5 Ma, suggests that temperature is the main influence of Mg/Ca values—they conclude no strong evidence for a carbonate ion effect is observed.

Lastly, as mentioned earlier, *Bailey et al.* [2010] and later *Winnick & Caves* [2015] considered how changing one's assumptions of the average  $\delta^{18}\text{O}$  of polar ice during the warm Pliocene could bias sea level estimates. Using Pliocene Antarctic surface temperature reconstructions and observed  $\delta^{18}\text{O}$ -temperature relationships in polar ice *Winnick & Caves* [2015] argue that  $\delta^{18}\text{O}_{\text{ice}}$  was  $1\text{‰}$  to  $4\text{‰}$  more positive than at present. Conserving  $^{18}\text{O}/^{16}\text{O}$  in the ocean-ice system would imply less sea level change for a given  $\delta^{18}\text{O}_{\text{carb}}$  change in the Pliocene. They go on to conclude that ice mass loss during the MPWP has likely been overestimated and that the  $0.3\text{‰}$  benthic  $\delta^{18}\text{O}_{\text{carb}}$  change in the LR04 stack is consistent with a Pliocene sea level of only 9-13.5 m above modern (compared to +21 m estimated obtained by *Miller et al.* [2012] when not accounting for the possibly more positive isotopic value of Pliocene ice sheets).



**Figure 6.** Summary of likely bias (in meters) to an estimate of MPWP sea level, derived from paired Mg/Ca -  $\delta^{18}\text{O}_{\text{carb}}$  measurements, caused by various effects discussed in text. The Mg/Ca diagenesis bar shows the resulting bias from an arbitrary 0.1 mmol/mol increase in shell Mg/Ca. No uncertainty is shown for the cumulative effect including diagenesis as this is sensitive to the magnitude of site-specific diagenetic bias on both Mg/Ca and  $\delta^{18}\text{O}_{\text{carb}}$ .

## 7. Conclusions

In the sections above we considered factors that pose a challenge to the canonical interpretation of benthic  $\delta^{18}\text{O}$  records and derived sea level histories for the past three million years. In particular, we discuss sources of error in paired  $\delta^{18}\text{O}$ -Mg/Ca sea level estimates, especially diagenesis and long-term changes in seawater chemistry, effects that are poorly constrained and potentially large. These and other variables are often ignored or assumed to remain at modern values, strategies that can no longer be justified, especially as the likely response of polar regions to a modest increase in global temperature carries great relevance to our future climate [e.g., Hansen *et al.*, 2008; 2015].

Rather than allude to a consensus on Pliocene sea level that doesn't exist, or cite mean values with error ranges that do not reflect the full spectrum of uncertainty (Fig. 6), we need to dig deeper into these issues. Diagenesis has the potential to impart a systematic bias in our data that would lead one to underestimate the ice volume decrease of the Pliocene. A long-term change in the Mg/Ca of seawater could potentially offset this systematic error and, thus, is also an important area of investigation given the range of  $\text{Mg}/\text{Ca}_{\text{sw}}$  suggested by existing studies (e.g. Figure 5). We need to carry out targeted investigations, using new analytical tools and approaches, aimed at increasing our understanding of two of the most important paleoclimate proxies we have,  $\delta^{18}\text{O}$  and

Mg/Ca (Lawrence & Woodard [2017] arrived at a similar conclusion about SST proxies). Many researchers are doing this now but our rate of progress is slow, especially in the face of the inexorable rise in greenhouse gases and the profound threat to coastal communities posed by ongoing and accelerating sea level rise.

Ultimately, robust estimates of sea level during past warm climates, such as the mid-Pliocene warm period, can provide a direct measure of the Earth system sensitivity to modest increases in atmospheric CO<sub>2</sub> [e.g., Hansen *et al.*, 2008, Foster & Rohling, 2013; Palaeosens Project Members, 2013; DeConto & Pollard, 2016]. For the Pliocene, geochemical sea level proxies currently carry uncertainties too large to allow any meaningful estimate of equilibrium polar ice volume in a world with >350 ppm CO<sub>2</sub>. Likewise, uncertainty in the pattern and temporal history of surface elevation changes driven by dynamic topography preclude robust Pliocene sea level estimates being derived from coastal geomorphic and sedimentary features, silled basins such as the Red Sea, atolls, or passive margins (see recent reviews by Dutton *et al.*, 2015 and Kemp *et al.*, 2015). Improvements in sea level estimates derived from field evidence must await advances in our understanding of mantle viscosity and structure as well as the mantle convection models dependent on these parameters.

For the geochemical proxies, increasing awareness of potential diagenetic alteration is already leading to more careful selection of sample material for geochemical analysis. In addition, recent methodological improvements in *in situ* analytical techniques such as EPMA, laser ablation ICPMS, and SIMS now permit investigation of microscopic domains within shells which, when combined with advances in foraminiferal culturing, are leading to a richer understanding of the mechanisms by which foraminifera record – and archive – information about their environment. In particular, the assumption that diagenesis takes millions to tens of millions of years to alter foraminiferal calcite is no longer viable—we need to consider the possibility that Plio-Pleistocene carbonate geochemical records such as  $\delta^{18}\text{O}$  or Mg/Ca, even those from benthic foraminifera, may be biased by post-depositional dissolution and recrystallization. Ultimately, these studies will lead to a deeper understanding of ice sheet stability in a warmer world, knowledge that could guide social, economic, and political actions aimed at minimizing human-caused disruption of the global climate system.

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