

# Testing the impact of diagenesis on the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ of benthic foraminiferal calcite from a sediment burial depth transect in the equatorial Pacific

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[1] Stable oxygen and carbon isotope ( $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$ ) values measured in foraminiferal calcite are one of the primary tools used in paleoceanography. Diagenetic recrystallization of foraminiferal calcite can act to reset primary isotopic values, but its effects are typically poorly quantified. Here we test the impact of early stage diagenesis on stable isotope records generated from a suite of drill sites in the equatorial Pacific Ocean recovered during Ocean Drilling Program Leg 199 and Integrated Ocean Drilling Program Expedition 320. Our selected sites form paleowater and burial depth transects, with excellent stratigraphic control allowing us to confidently correlate our records. We observe large intersite differences in the preservation state of benthic foraminiferal calcite, implying very different recrystallization histories, but negligible intersite offsets in benthic  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values. We infer that diagenetic alteration of benthic foraminiferal calcite (in sedimentary oozes) must predominantly occur at shallow burial depths (<100 m) where offsets in both the temperature and isotopic composition of waters in which the foraminifera calcified and pore waters in which diagenesis occurs are small. Our results suggest that even extensive recrystallization of benthic foraminiferal calcite results in minimal shifts from primary  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values. This finding supports the long-held suspicion that diagenetic alteration of foraminiferal calcite is less problematic in benthic than in planktic foraminifera and that in deep-sea sediments routinely employed for paleoceanographic studies benthic foraminifera are robust recorders of stable isotope values in the fossil record.

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## 1. Introduction

[2] The stable isotopic composition of foraminiferal tests is a valuable archive for the reconstruction of paleoclimatic and paleoceanographic changes, and for global stratigraphic correlation. Stable oxygen isotope ratios in foraminiferal calcite are a function of both the temperature and  $\delta^{18}\text{O}$  composition of parent seawater [e.g., Urey, 1947; Emiliani, 1954; Shackleton, 1967]. Thus, it is possible to employ  $\delta^{18}\text{O}$  values to help reconstruct past ocean temperatures, salinity, and global ice volume. The  $\delta^{13}\text{C}$  value of foraminiferal calcite

reflects the  $\delta^{13}\text{C}$  of dissolved inorganic carbon (DIC) of seawater at the point of calcification and can be used to track shifts in ocean circulation and paleoproductivity [Duplessy *et al.*, 1984; Zeebe and Wolf-Gladrow, 2001]. Utilization of foraminiferal calcite for accurate paleoceanographic reconstructions relies on knowing (1) that foraminifer precipitate their tests in isotopic equilibrium with parent ambient seawater and (2) that these primary isotope values are not altered significantly by diagenetic processes.

[3] Dissolution of biogenic calcite and reprecipitation of inorganic calcite (overgrowth and recrystallization) at the seafloor and in the sediment column can alter the primary isotopic composition of the foraminifers' test potentially biasing any resulting paleoreconstruction [D'Hondt and Arthur, 1996; Norris and Wilson, 1998; Pearson *et al.*, 2001; Wilson and Norris, 2001; Wilson *et al.*, 2002; Sexton *et al.*, 2006]. This can be problematic because there is often little discernable change in test morphology visible under light microscopy with increasing recrystallization. Specifically, wall pores and surface ornamentation are often retained, giving the impression that sample material is relatively well preserved. This is particularly true for benthic foraminifera, one of the main substrates on which many paleoceanographic reconstructions and stratigraphic correlations are based but for which the impacts of diagenesis are poorly known. The conflict between apparent

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preservation state and isotopic integrity is perhaps best illustrated by the “cool tropics paradox” [D’Hondt and Arthur, 1996; Wilson and Opdyke, 1996]. This paradox describes the cool or similar-to-modern tropical sea surface temperature (SST) estimates derived from  $\delta^{18}\text{O}$  values of recrystallized or “frosty” planktic foraminiferal test calcite [Crowley and North, 1991; Price et al., 1998; Crowley and Zachos, 2000], in conflict with other lines of evidence for very warm Cretaceous and Paleogene tropics [Kolodny and Raab, 1988; Wilson and Opdyke, 1996; Andreasson and Schmitz, 1998]. This issue was resolved by the discovery of unusually well preserved “glassy” microfossils hosted in clay-rich sediments yielding much higher tropical SSTs than their recrystallized “frosty” counterparts [e.g., Norris and Wilson, 1998; Pearson et al., 2001; Wilson and Norris, 2001; Wilson et al., 2002; Sexton et al., 2006]. Thus, it is now apparent that, during early stage diagenesis, recrystallization of planktic foraminifera occurs in bottom waters that are significantly cooler than the surface waters in which foraminifer first calcified, shifting test  $\delta^{18}\text{O}$  to higher values and leading to artificially cool SST estimates. It is now well recognized that the  $\delta^{18}\text{O}$  values of planktic foraminifera are highly susceptible to diagenetic alteration [e.g., Pearson et al., 2001; Sexton et al., 2006] but there are few studies of the effects of diagenetic alteration on benthic foraminifera. This discrepancy largely arises because stable isotopes in benthic foraminiferal calcite are widely thought to be less susceptible to diagenetic overprinting than their planktic counterparts. There are several reasons why this view may be valid. (1) Recrystallization of benthic foraminiferal calcite typically proceeds in waters with temperatures similar to those in which the foraminifera calcified [Schrag et al., 1995]. (2) Benthic foraminifera have more heavily calcified tests than planktic foraminifera, increasing the likelihood of their preservation in the fossil record and their resilience to diagenetic alteration. (3) Cenozoic stable isotope records generated in benthic foraminiferal calcite from sediments in different ocean basins, with different lithologies and burial histories, show similar values and patterns of change over multiple timescales. Certainly, in deep-sea sediments, calcareous benthic foraminifera are more resistant to dissolution than their planktic counterparts [Parker and Berger, 1971; Schlanger and Douglas, 1974; Pälke et al., 2010]. Anomalously low Eocene benthic  $\delta^{18}\text{O}$  values measured at Ocean Drilling Program (ODP) Site 647 in the North Atlantic have been attributed to selective diagenetic overprinting of benthic and not planktic calcite but scanning electron microscope (SEM) analysis reveals little or no evidence of recrystallization in benthic and planktic foraminifer tests [Arthur et al., 1989; Pearson and Burgess, 2008]. Other studies are largely limited to low-resolution assessment of downhole changes in the preservation and stable isotopes in benthic foraminifer with changing lithology at a single site [Schlanger and Douglas, 1974; Douglas and Savin, 1975], the role of selective dissolution on carbonate chemistry and taphonomy [Widmark and Malmgren, 1988; McCorkle et al., 1995], or the impact of changes in sedimentation rates on foraminifer geochemistry [Sexton and Wilson, 2009]. However, it is difficult to differentiate the relative effects of diagenesis versus paleoceanographic changes on low-resolution data sets from a single hole, and many of the sections investigated are not necessarily representative of sections targeted in modern paleoceanographic work.

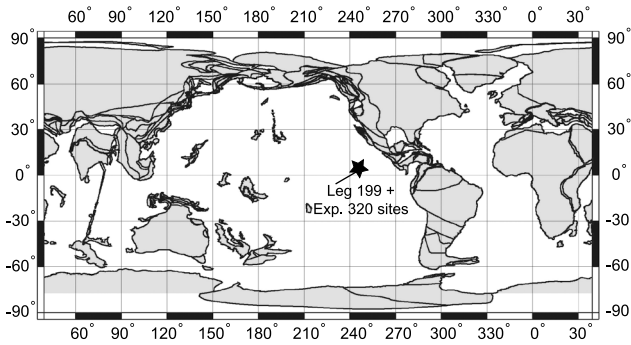
[4] Results of numerical modeling experiments imply that most calcite recrystallization occurs during the early stages of burial (in the first 10 Myr) [Richter and Liang, 1993; Rudnicki et al., 2001; Fantle et al., 2010]. However, pore fluid chemistry profiles used to constrain numerical models provide a signal of the alteration of bulk carbonate and may not be applicable to the individual foraminifera picked by paleoceanographers. Furthermore, in addition to burial depth and sediment age, lithology (including sediment porosity and permeability) and sedimentation rates also play important roles in controlling the rate of carbonate recrystallization. Clay-rich sediments often yield glassy foraminifera [Norris and Wilson, 1998; Wilson and Norris, 2001; Pearson et al., 2001; Wilson et al., 2002; Sexton et al., 2006; Pearson and Burgess, 2008; Expedition 342 Scientists, 2012]. In these studies, it has always been suggested that it is likely the low permeability of clays relative to unlithified biogenic oozes that limits postdepositional recrystallization. But further investigation is necessary to test this working hypothesis. However, sediments containing glassy foraminifera are relatively rare and are most frequently associated with sites proximal to continents, so we cannot rely on them to suit all our paleoceanographic needs. Higher sedimentation rates will result in samples being more deeply buried, and thus, recrystallization will occur at higher temperatures than found at the seafloor and diagenetic calcite will have a  $\delta^{18}\text{O}$  composition offset from biogenic calcite [Schrag et al., 1995; Sexton and Wilson, 2009].

[5] To minimize the influence of diagenesis on deep-sea sediment proxies, and to facilitate better, more continuous, sediment recovery using advanced piston coring technology, ocean drilling frequently targets shallowly buried sediments (typically ~300 m) but there are few tests of the effectiveness of this strategy. In part, this is because there are very few deep-sea sites that fulfill the necessary prerequisites for such an experiment, that is, a multimillion year time interval that can be confidently correlated across a depth transect of sites containing carbonate microfossils with different burial histories. A series of sites drilled in the equatorial Pacific during Ocean Drilling Program (ODP) Leg 199 (Sites 1218 and 1219) and recent Integrated Ocean Drilling Program (IODP) Expedition 320 (Sites U1331–U1334) provide an ideal opportunity to test the fidelity of stable isotope values recorded in fossil foraminiferal calcite from typical deep-sea biogenic oozes (Figure 1). The selected sites are stratigraphically continuous in the Oligocene and early Miocene (at least to magnetozone and biozone level), have benthic foraminifera present throughout, and most importantly, benefit from excellent stratigraphic control (uncertainty on magnetochron boundaries typically tens of centimeters).

## 2. Materials and Methods

### 2.1. Site Selection

[6] To isolate the effects of diagenesis on benthic foraminiferal stable isotope ratios, it is essential to select deep-sea sites with no (or minimal) oceanographic differences between them, so that sites are bathed by the same water mass. The Pacific Ocean is the largest in the world, and at present, much of the Pacific basin is bathed by Pacific Deep Water; a homogenous deep water mass sourced at high southern latitudes. This homogeneity is illustrated by the extensive



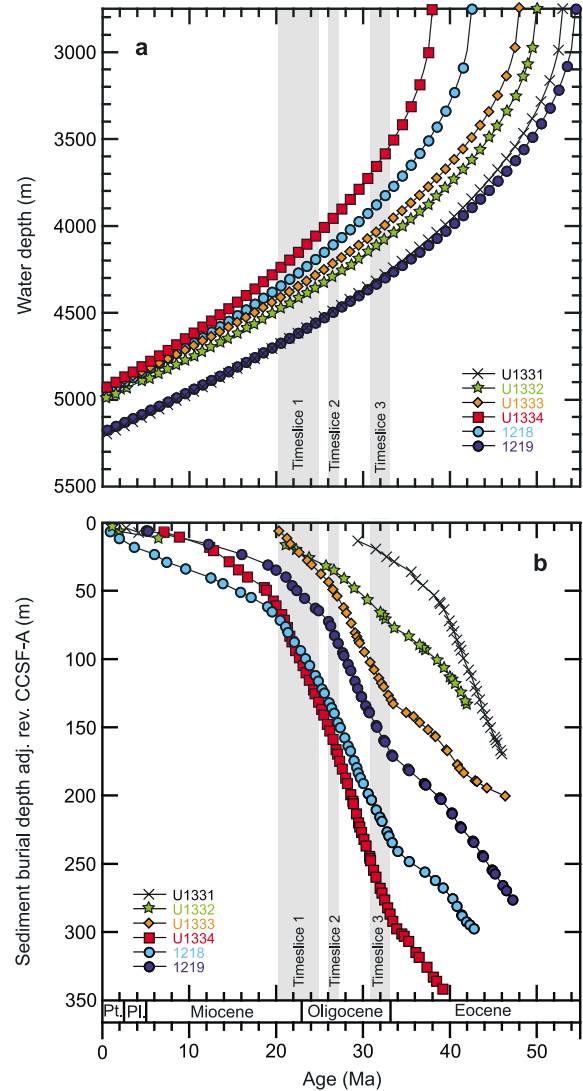
**Figure 1.** Oligocene paleogeographic reconstruction for ~32 Ma showing the paleolocation of closely spaced ODP Sites 1218 and 1219 from ODP Leg 199, and IODP Sites U1331–1334 from IODP Expedition 320 (black star). The base map was generated from <http://www.odsn.de/odsn/series/palaeomap/palaeomap.html>.

chemical and physical property water column profiles generated by the World Oceanographic Circulation Experiment [Talley, 2007] and the very similar (~1.5°C) measured bottom water temperatures at each of the selected study sites [Lyle *et al.*, 2002; Pälike *et al.*, 2010]. Ocean circulation is likely to have been differently configured in the Oligocene as a result of different continental geometries and latitudinal thermal gradients to modern; for example, numerical models suggest that the North Pacific was likely a site of deep water formation in the late Oligocene [von der Heydt and Dijkstra, 2006]. Yet a number of lines of evidence suggest that the study sites that we have selected in the Pacific were bathed by a single water mass, akin to the modern, and should not result in any intersite stable isotope offsets: (1) published Oligocene interbasin  $\delta^{13}\text{C}$  records show essentially zero gradient implying small water mass aging gradients and a relatively homogenous global deep ocean [Zachos, *et al.*, 2001; Billups *et al.*, 2004; Pälike *et al.*, 2006; Katz *et al.*, 2011], and (2) high-resolution sediment property records can be correlated, to the decimeter scale, between sites separated by many hundreds of kilometers in the equatorial Pacific [Pälike *et al.*, 2005; Westerhold *et al.*, 2012].

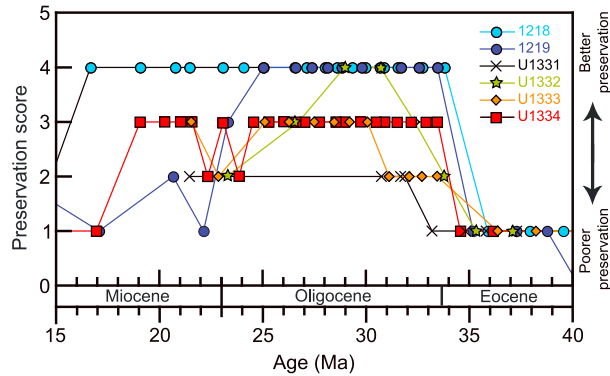
[7] ODP Leg 199 and IODP Expedition 320 drilled a suite of sites in the eastern equatorial Pacific [Lyle *et al.*, 2002; Pälike *et al.*, 2010] ideally suited to testing the impact of diagenesis on closely spaced sites with different subsidence and burial histories (Figure 2). All of these sites are situated on the same segment of the East Pacific Rise ridge crest but with different basement ages and thus are assumed to have the same original starting water depth of ~2.75 km (Figure 2a). Sites initially subside rapidly as the underlying ocean crust cools and moves away from the ridge crest until reaching their present depths. The shape of the curves in Figure 2b is similar across all sites with relatively high sedimentation rates from basement to ~75 m below the seafloor and thereafter lower sedimentation rates. The highest sedimentation rates (and steepest slopes in Figure 2b) occur as the sites move northward away from the ridge crest and pass under the narrow equatorial high productivity zone resulting in the deposition of thick biogenic-rich deposits. The break in slope at ~75 m reflects a combination of the sites moving outside of the equatorial high productivity zone

reducing sediment input and sinking below the local lysocline reducing the preservation of carbonate sediments. Thus, the Neogene and Quaternary sediment overburden above targeted Paleogene sediments is relatively thin at each of the sites and sediments are considered shallowly buried. Therefore, these sediments should yield the best possible preserved carbonate for the focal time interval at this locality.

[8] The bulk of this study focuses on Sites 1218 (8°53.378'N, 135°22.00'W) and 1219 (7°48.019'N, 142°00.940'W), where high temporal resolution climate proxy records are available. These two sites are separated laterally by >740 km, are



**Figure 2.** Burial and paleowater depth reconstructions for equatorial Pacific study sites over the past 55 Myr. (a) Subsidence curves for ODP Sites 1218 and 1219, and IODP Sites U1331–U1334. Calculated using established crustal basement ages, current basement depth, and assumed mid-ocean ridge depth of 2.75 km [Lyle *et al.*, 2002; Pälike *et al.*, 2010]. (b) Sediment burial depth curves for ODP Sites 1218 and 1219, and IODP Sites U1331–U1334. [Lyle *et al.*, 2002; Pälike *et al.*, 2010]. Ages are calculated from Pälike *et al.* [2010] and Westerhold *et al.* [2012]. Vertical shaded grey bars represent the three timeslices studied here.



**Figure 3.** Compilation of light microscope assessments of the preservation state of benthic foraminifer using data from Shipboard Scientists [Lyle et al., 2002; Pälike et al., 2010]. Preservation state recorded as very good (4), good (3), moderate (2), and poor (1) reflecting a progressive increase in the amount of overgrowth, dissolution, fragmentation, or abrasion of specimens within the assemblage.

vertically offset in water depth by between ~300 and 500 m and in burial depth by ~50 m (Figures 1 and 2). Detailed site-to-site correlation between Sites 1218 and 1219, down to the decimeter scale, permits confident sampling between sites to ensure time-equivalent samples [Pälike et al., 2005]. Additional samples were also utilized from IODP Expeditions 320/321, which were designed to recover the best preserved carbonate sequences from the paleoequatorial Pacific to develop a continuous Cenozoic record for this region. IODP Sites U1331 (12°04.088'N, 142°09.708'W), U1332 (11°54.722'N, 141°02.743'W), U1333 (10°30.996'N, 138°25.159'W), and U1334 (7°59.998'N, 131°58.408'W) were drilled during IODP Expedition 320 in 2009 (Figure 1) [Pälike et al., 2010]. Extensive shipboard and postcruise work resulted in site-to-site correlations between new IODP sites and integration of Leg 199 and Expedition 320 sites to provide a rare opportunity to correlate between Paleogene deep-sea sites [Pälike et al., 2010; Westerhold et al., 2012].

## 2.2. Strategy

[9] We generated benthic foraminiferal stable isotope data (~20 kyr sample spacing) from ODP Site 1219 for three discrete timeslices (numbered 1 to 3 in Figure 2) in the early Oligocene and Miocene, for comparison with published stable isotope records from Site 1218 [Coxall et al., 2005; Lear et al., 2004; Pälike et al., 2006; Tripathi et al., 2006; Wade and Pälike, 2004]. The three timeslices are characterized by different proportions of calcium carbonate (%CaCO<sub>3</sub> by weight) and variability in %CaCO<sub>3</sub> values and thus, inferred calcareous microfossil preservation [Pälike et al., 2010; Pälike et al., 2012]. We also generated data from timeslice three (~30–33 million years ago, Ma) for four new IODP Sites (U1331–U1334) for which carbonate is present at all sites at this time and the largest burial (and paleowater) depth range transect is available (~60–100 kyr sample spacing; Figure 2). Sediment lithologies are predominantly radiolarian or nannofossil oozes with rare chalks (at the base of Sites 1218 and U1334) within the intervals covered by this study [Lyle et al., 2002; Pälike et al., 2010]. The relatively high sediment porosity and permeability, and carbonate-rich

lithologies mean that these sediments have a relatively high “diagenetic potential” sensu [Schlanger and Douglas, 1974] relative to clay-rich sediments [Spinelli et al., 1994; Gamage et al., 2005] and provide a good test set of samples to investigate the impact of diagenesis in the type of sediments routinely employed for paleoceanographic analyses. We utilize the wealth of physical property and geochemical data generated by shipboard scientists in our later analyses [Lyle et al., 2002; Pälike et al., 2010].

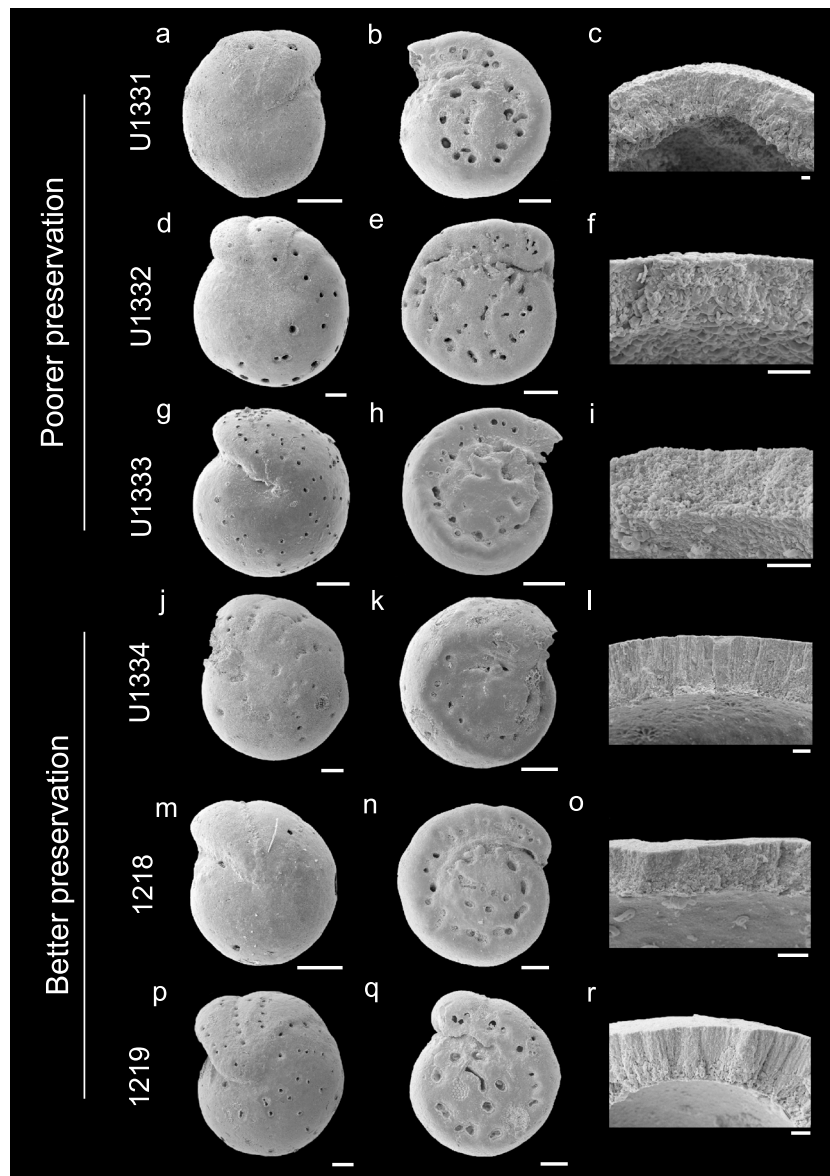
[10] Benthic foraminifera are present throughout the studied timeslices and show evidence of recrystallization, i.e., specimens are “frosty” not “glassy” [Sexton et al., 2006], as is common in deep-sea sediments with low hemipelagic clay content. Data were generated using monospecific separates of *Cibicidoides grimsdalei* from the 250 to 450 μm size fraction to minimize potential interspecies offsets. Taxonomy follows van Morkhoven et al. [1986]. All samples were cleaned in methanol and ultrasonicated prior to analysis, between one and six individuals were analyzed. Stable isotope values ( $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$ ) were determined using a Europa GEO 20–20 mass spectrometer equipped with automated carbonate preparation device at the University of Southampton. Stable isotope results are reported relative to the Vienna Pee Dee Belemnite (VPDB) standard with an external analytical precision of better than  $\pm 0.03\text{‰}$  for  $\delta^{13}\text{C}$  and  $\pm 0.07\text{‰}$  for  $\delta^{18}\text{O}$  based on replicate analysis of an in-house standard calibrated to NBS-19. Representative specimens of *C. grimsdalei* from timeslice three for all six sites were selected for scanning electron microscope (SEM) analysis. All specimens were mounted on adhesive pads on SEM stubs and gold coated prior to imaging to provide better topographic imaging and reduce charging of specimens. Scanning electron micrographs were generated using a Leo 1450VP (variable pressure) digital SEM with a tungsten filament at the University of Southampton.

## 3. Results and Discussion

### 3.1. Down-Core and Intersite Variability in Benthic Foraminiferal Taphonomy

[11] The standard view is that as carbonate sediments transition from biogenic oozes to chalks to limestones, they undergo compaction, dissolution, recrystallization, and eventually cementation [Schlanger and Douglas, 1974]. At the same time, foraminifera in the sediments undergo dissolution (particularly planktic foraminifera) and develop mineral infillings, and then develop extensive overgrowths during late stage diagenesis [Matter, 1974; Schlanger and Douglas, 1974; Pearson et al., 2001].

[12] A first-order assessment of the down-core preservation from light microscope observations, collected by shipboard scientists, is compiled and shown in Figure 3. Preservation state is determined from the estimated degree of overgrowth, dissolution, fragmentation, and abrasion of benthic foraminiferal specimens at each site [Lyle et al., 2002; Pälike et al., 2010]. The best (albeit “frosty”) preservation of benthic foraminifera at all sites occurs in the early-middle Oligocene, coincident with the highest carbonate contents and carbonate mass accumulation rates [Lyle et al., 2002; Pälike et al., 2010, 2012]. In contrast, preservation was poorest during the uppermost Eocene, latest Oligocene, and Miocene, when sites were close to or below the long-term lysocline.

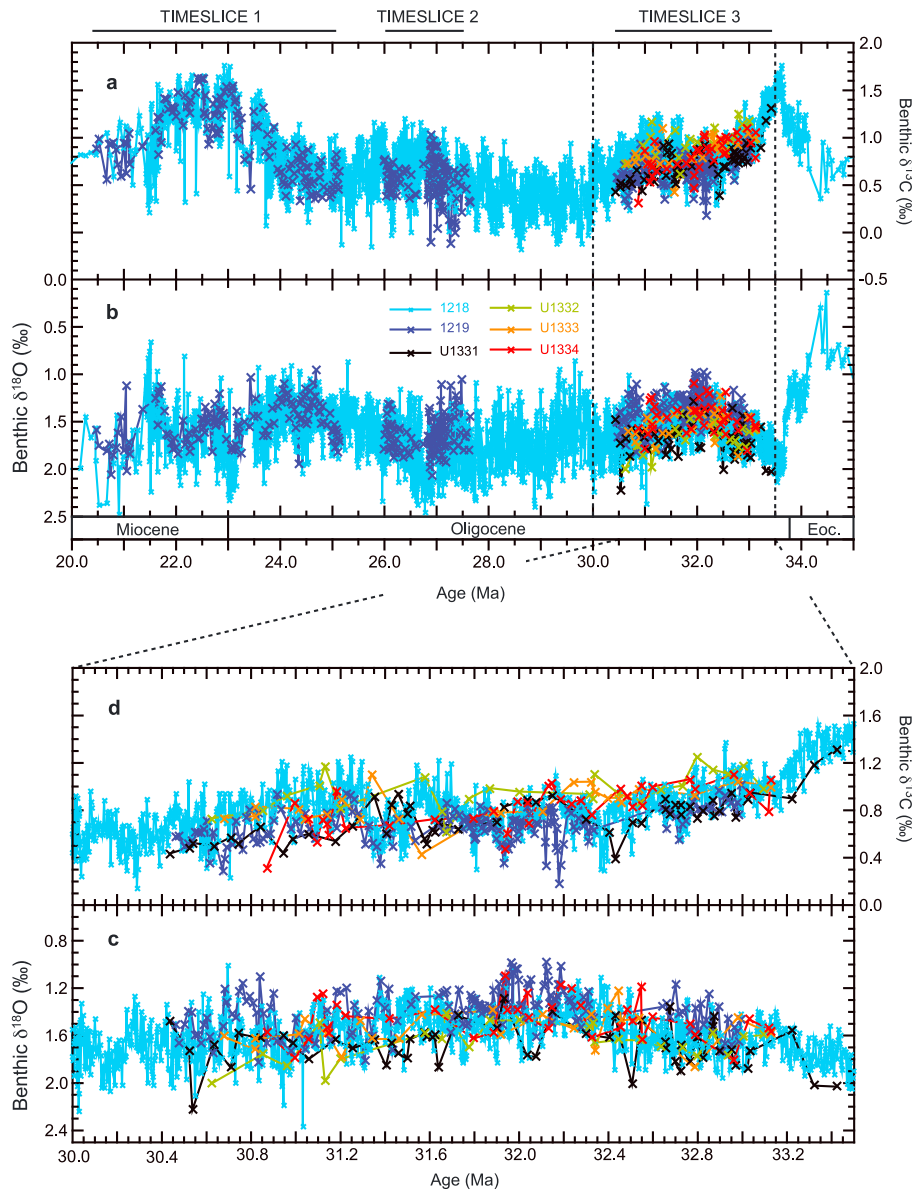


**Figure 4.** Assessment of *Cibicoides grimsdalei* test preservation using scanning electron micrographs of whole tests and external wall cross sections at each of the study sites. The scale bar for the whole tests is 100  $\mu\text{m}$  and for wall cross sections 10  $\mu\text{m}$ .

[13] To investigate micron-scale recrystallization of benthic foraminiferal calcite not detectable by light microscope, we examined specimens by scanning electron microscopy. Figure 4 shows images of representative benthic foraminifera of the species *Cibicoides grimsdalei* from timeslice three for each of the deep-sea sites investigated. Whole-specimen images are presented for each site showing that all sites have a similar “frosty” taphonomy. Higher magnification images of test wall cross sections tell a different story. Foraminiferal tests from Site U1334 with the shallowest paleowater depth in this study have the best preservation with what appears to be the original calcite crystal arrangement still visible and only minor apparent recrystallization of the original test wall structure. For instance, images show a submicron-scale microgranular wall texture, micropores on the internal wall surface, and what look like vertical pore channels running through the test wall in some places. Furthermore, internal and external wall

surfaces are relatively smooth and predominantly free of infilling and overgrowths. Sites 1218 and 1219 show evidence of minor recrystallization and limited delamination of the internal test wall but are relatively free of infilling and overgrowths. In contrast, benthic foraminifera from IODP Sites U1331–U1333 are less well preserved and more heavily recrystallized, with abundant large crystals of inorganic calcite projecting from the interior wall surface and micron-scale recrystallization of the original crystal arrangement in the test wall. Benthic foraminiferal wall textures illustrate that specimens from Site U1331 are the most poorly preserved, i.e., are extensively recrystallized, yet this is the most shallowly buried site whereas Site U1334, the most deeply buried site, has the best benthic foraminiferal preservation (Figure 4). In fact, the best benthic foraminifera test preservation is consistently observed in the most deeply buried sediments here at Sites 1218, 1219, and U1334. This finding differs from the





**Figure 5.** New and existing benthic foraminiferal stable isotope data for ODP Sites 1218 and 1219, and IODP Sites U1331–U1334. Stable isotope data from ODP Site 1219 and IODP Sites U1331–U1334 (this study) are generated from *Cibicidoides grimsdalei*. ODP Site 1218 data from Lear *et al.* [2004], Wade and Pälke [2004], Coxall *et al.* [2005], Tripathi *et al.* [2006], and Pälke *et al.* [2006] are generated from *Cibicidoides* spp.

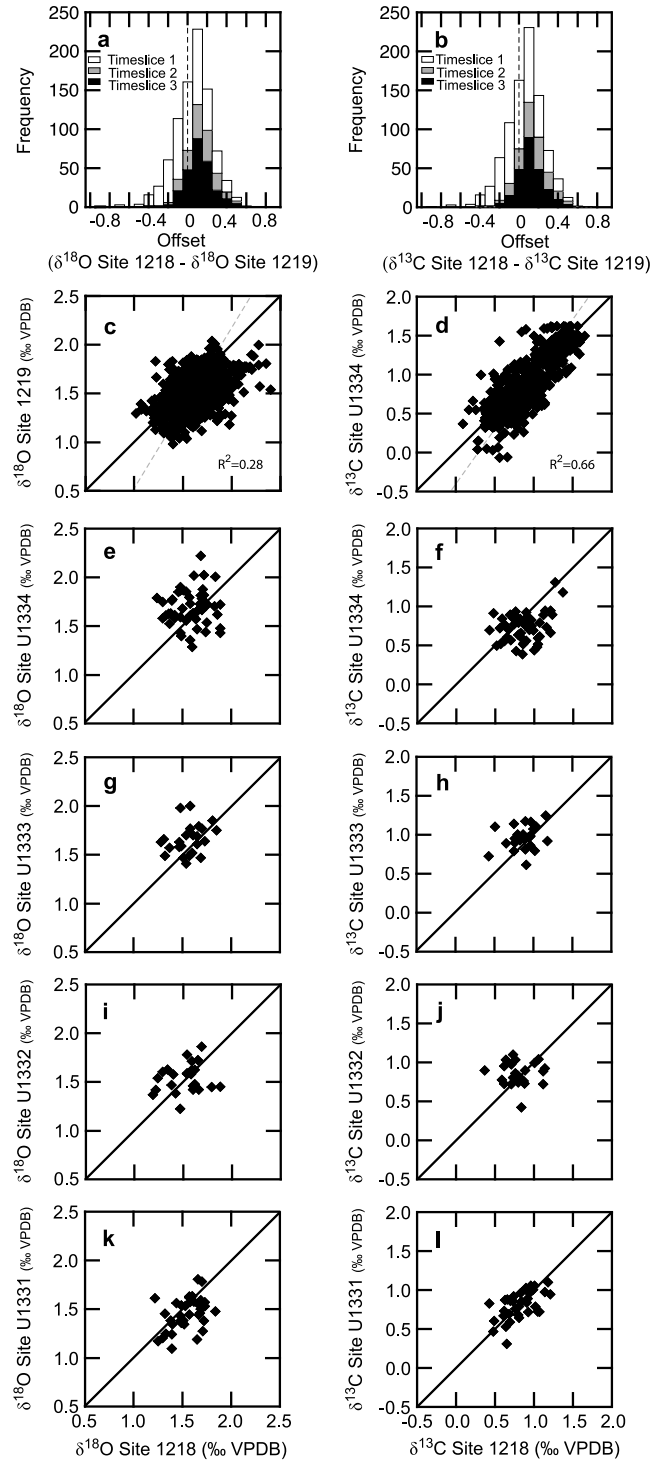
conventional view that the degree of recrystallization of foraminiferal calcite increases down-core [e.g., Schlanger and Douglas, 1974], and thus, other factors must be important. Similarly, dissolution of test walls and subsequent recrystallization is not related to paleowater depth as shown by the much better apparent preservation of specimens at Site 1219 compared to Site U1331, which is situated at a similar water depth (Figures 2a and 4).

### 3.2. Impact of Burial Depth on Benthic Foraminiferal Stable Isotope Values

[14] Diagenetic alteration of  $\delta^{18}\text{O}$  in foraminifera has received the most attention because oxygen isotope fractionation is highly temperature dependent with recrystallization typically driving  $\delta^{18}\text{O}$  toward lower values as in situ temperature

increases with sample depth in the sediment column [Matter *et al.*, 1975; Schrag *et al.*, 1995]. Consequently, the bulk of our further discussion focuses on the impact of diagenesis on  $\delta^{18}\text{O}$  rather than on  $\delta^{13}\text{C}$  values. ODP Sites 1218 and 1219 provide an ideal opportunity to test for the role of diagenesis on stable isotope values of foraminiferal calcite in siliceous nannofossil oozes that are relatively shallowly buried (<300 m). Furthermore, these two sites have a similar heat flow gradient [Lyle *et al.*, 2002] but Oligocene sediments at Site 1218 are more deeply buried than at Site 1219; thus, it is also possible to test for any stable isotope offsets between the two sites attributable to diagenetic overprinting as well as down-core.

[15] At Sites 1218 and 1219, the multimillion yearlong stable isotope records are in good agreement with one another,



**Figure 6.** Analysis of benthic foraminiferal stable isotope offsets between ODP Site 1218 and other equatorial Pacific sites. (a and b) Histograms showing the distribution of benthic stable isotopic offsets between ODP Sites 1218 and 1219. Vertical dashed lines in Figures 6a and 6b represent zero offset. (b to l) Crossplots between benthic foraminiferal stable isotopes from ODP Site 1218 and: (Figures 6c and 6d) ODP Site 1219, (Figures 6e and 6f) IODP Site U1334, (Figures 6g and 6h) IODP Site U1333, (Figures 6i and 6j) IODP Site U1332, and (Figures 6k and 6l) IODP Site U1331. Solid diagonal lines in Figures 6c through 6l represent a 1:1 relationship. Diagonal dashed lines in Figures 6c and 6d represent the calculated line of best fit using a linear regression. Prior to plotting, stable isotope records from Sites 1218 and 1219 were interpolated to 10 kyr spacing for each timeslice.

**Table 1.** Summary of Benthic Foraminiferal Stable Isotope Data and Statistical Significance From ODP Sites 1219 and 1219, and IODP Sites U1331–U1334<sup>a</sup>

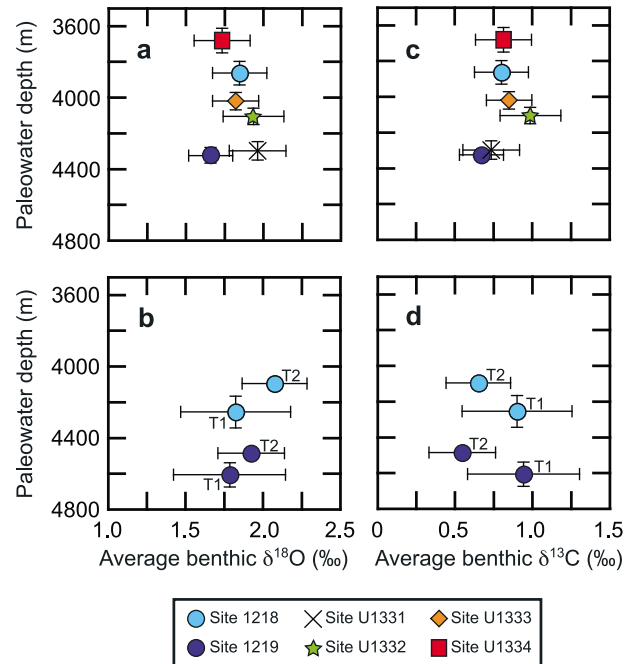
Proxy	Timeslice 1				Timeslice 2				Timeslice 3				All Timeslices			
	<i>P</i> Value	Mean 1218	Mean 1219	Offset	<i>P</i> Value	Mean 1218	Mean 1219	Offset	<i>P</i> Value	Mean 1218	Mean 1219	Offset	<i>P</i> Value	Mean 1218	Mean 1219	Offset
$\delta^{13}\text{C}$	9.20E-01	1.27	1.26	0.01	1.09E-07	0.91	0.80	0.11	1.11E-19	1.06	0.92	0.14	2.00E-03	1.14	1.10	0.04
$\delta^{18}\text{O}$	1.04E-08	1.88	1.79	0.09	4.52E-08	2.05	1.92	0.13	5.73E-23	1.85	1.70	0.15	1.76E-04	1.88	1.78	0.10
U1331 $\delta^{13}\text{C}$	-	-	-	-	-	-	-	-	0.01	0.87	0.74	0.13	-	-	-	-
U1331 $\delta^{18}\text{O}$	-	-	-	-	-	-	-	-	0.07	1.87	1.96	0.09	-	-	-	-
U1332 $\delta^{13}\text{C}$	-	-	-	-	-	-	-	-	0.04	0.88	0.99	0.11	-	-	-	-
U1332 $\delta^{18}\text{O}$	-	-	-	-	-	-	-	-	0.03	1.84	1.94	0.10	-	-	-	-
U1333 $\delta^{13}\text{C}$	-	-	-	-	-	-	-	-	0.34	0.80	0.85	0.05	-	-	-	-
U1333 $\delta^{18}\text{O}$	-	-	-	-	-	-	-	-	0.64	1.80	1.82	0.02	-	-	-	-
U1334 $\delta^{13}\text{C}$	-	-	-	-	-	-	-	-	0.84	0.82	0.82	0.00	-	-	-	-
U1334 $\delta^{18}\text{O}$	-	-	-	-	-	-	-	-	0.02	1.82	1.73	0.09	-	-	-	-

<sup>a</sup>The stable isotope record from Site 1218 was generated from epifaunal *Cibicidoides* spp [Lear et al., 2004; Wade and Pälike, 2004; Coxall et al., 2005; Tripathi et al., 2006; Pälike et al., 2006] and in this study from *C. grimsdalei* at Site 1219. Prior to statistical analysis, stable isotope records from Sites 1218 and 1219 were interpolated to 10 kyr spacing. However, widely spaced sampling at the Pacific Equatorial Age Transect (PEAT) sites prevented meaningful interpolation of data to higher resolution; thus, offsets were determined directly between PEAT samples and the most closely occurring sample from Site 1218. An unpaired Student's *t* test was conducted between Site 1218 and another study site for each timeslice and *p* values are shown here. *P* values less than 0.05 and 0.01 imply that stable isotope offsets are significant at the 95% and 99% significance levels, respectively. Note that timeslices are defined in Figure 2.

in terms of the patterns and amplitudes of isotopic change that they record (Figure 5; 1219 isotope data provided in Table S1 of the supporting information). The absolute stable isotope values are offset from one another by  $<0.15\text{‰}$  at the 99% significance level ( $n = 415$ ; Figures 6a, 6b, and Table 1) with measured values at both sites falling close to a 1:1 relationship (Figures 6c and 6d) in agreement with the similar recrystallization states of benthic foraminiferal tests observed at the two sites (Figure 4).

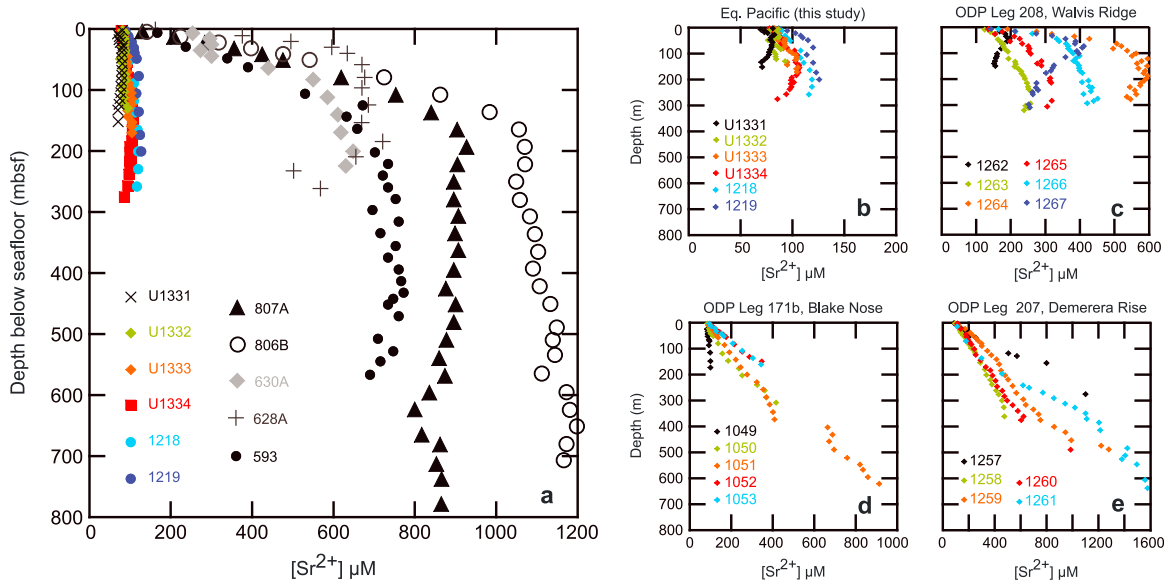
[16] The new stable isotope records generated between 30 and 33 Ma from IODP Sites U1331 to U1334 spanning burial depths of  $\sim 275$  m are generally consistent with the long-term trends that are recorded at Sites 1218 and 1219 but appear “noisier,” likely a function of the lower-resolution records at these additional sites (Figure 5). Tentative estimates of isotopic offsets between the highest resolution record available for timeslice three from Site 1218 and the lower-resolution records from Sites U1331 to U1334 reveal only very small intersite differences ( $<0.1\text{‰}$ ; Table 1 and Figures 6e–6l), which is noteworthy in light of the highly variable recrystallization states observed between the sites (Figure 4). Crucially, if there are any burial depth influences on stable isotope signals between the investigated sites, they are very small and can be considered negligible because they fall well within the uncertainties associated with standard analytical methods ( $\pm 0.07\text{‰}$ ) and the natural variability in geological samples used in paleoceanography [e.g., Stap et al., 2010; Zachos et al., 2007].

[17] Ultimately, we find no evidence for a decrease in benthic foraminifer  $\delta^{18}\text{O}$  values (or increasing recrystallization of benthic foraminifera) solely with increasing burial depth and/or sediment age within our sample set. For instance, at Sites 1218 and 1219, stable isotope values recorded in the oldest and most deeply buried timeslice three do not record the lowest  $\delta^{18}\text{O}$  values, and there is no obvious accompanying taphonomic deterioration down-core. Furthermore, samples from the most deeply buried Site U1334, which also has the “best” benthic test preservation in the transect, does not record the lowest  $\delta^{18}\text{O}$ . Together, these findings along with the negligible intersite isotope offsets observed here,



**Figure 7.** Paleowater depth estimates versus average stable isotope values for each of the timeslices at the study sites. (a and c) Stable isotope values for timeslice three (T3). (b and d) Stable isotope values for timeslices one (T1) and two (T2). Note that only values within the same timeslice should be directly compared. Site paleowater depths calculated from crustal basement ages, current basement depth, and assumed mid-ocean ridge depth of 2.75 km [Lyle et al., 2002; Pälike et al., 2010]. Stable isotope values are averaged over each timeslice, and *x* axis bars represent one standard deviation ( $1\sigma$ ). *Y* axis “error” bars are the range of paleowater depth estimates for each site during any given timeslice. The value of  $1\sigma$  is highest in timeslice 1 because of the larger amount of time, and thus, climatic variability encompassed in this timeslice compared to timeslices 2 and 3 ( $\sim 4.6$  versus 2.0 Myr, respectively).





**Figure 8.** Comparison of  $[\text{Sr}^{2+}]$  pore fluid profiles in carbonate deep-sea sediments at “classic” deeply buried and at shallowly buried DSDP, ODP, and IODP sites. (a) Data are from: shallowly buried Sites 1218 and 1219 [Lyle *et al.*, 2002], Sites U1331–U1334 [Pälike *et al.*, 2010], and “classic” Sites 806B and 807A [Kroenke *et al.*, 1991], 628A and 630A [Swart and Guzikowski, 1988], and 593 [Baker, 1986]. Shallowly buried paleoceanographic sections shown in small panels are (b) IODP Expedition 320 [Pälike *et al.*, 2010], (c) ODP Leg 208 [Zachos *et al.*, 2004], (d) ODP Leg 171b [Norris *et al.*, 1998], and (e) ODP Leg 207 [Erbacher *et al.*, 2004].

support findings from earlier work suggesting that the impact of diagenetic alteration on benthic foraminifera  $\delta^{18}\text{O}$  in shallowly buried oozes ( $<300$  m) is likely to be minimal [Schlanger and Douglas, 1974; Matter, 1974].

[18] While recrystallization can arguably lead to the largest potential stable isotope offsets in foraminiferal calcite, it is also important to briefly consider the role of dissolution. To assess any dissolution-driven biases in stable isotopes between sites, the average measured stable isotope values are plotted versus the paleowater depth for each site (Figure 7). We find no consistent relationship between  $\delta^{18}\text{O}$  or  $\delta^{13}\text{C}$  values and paleowater depth over the depth range investigated here ( $\sim 600$  m in timeslice three). This is in-keeping with the small isotopic changes ( $<0.13\text{‰}$ ) inferred from core-top studies over the depth range of this study [McCorkle *et al.*, 1995].

### 3.3. Can Pore Fluid Profiles Constrain the Early Diagenetic History of Carbonates?

[19] Traditionally, one means of assessing the early diagenetic history of bulk carbonate (calcite dissolution and precipitation) in the top  $\sim 20$  to 200 m of carbonate deep-sea sections is to use pore fluid  $\text{Sr}^{2+}$  concentrations.  $\text{Sr}^{2+}$  is released into sediment pore fluids during calcite dissolution and then subsequently excluded during calcite recrystallization [Gieskes, 1975; Baker *et al.*, 1982; Richter and Liang, 1993]. Pore fluid profiles from “classic” ODP and Deep Sea Drilling Project (DSDP) sites containing very thick sediment sequences all show prominent increases in  $[\text{Sr}^{2+}]$  from modern seawater values of  $\sim 90 \mu\text{M}$  at the sediment–water interface to  $[\text{Sr}^{2+}] > 4$  times higher at  $\sim 200$  m (black and white symbols in Figure 8a). Below  $\sim 200$  m,  $[\text{Sr}^{2+}]$  remains high and is relatively invariant at each site to basement. The inflection point in these  $[\text{Sr}^{2+}]$  profiles at 200 m is commonly

associated with the transition from an ooze to chalk lithology and is thus inferred to coincide with maximum rates of carbonate recrystallization and  $\text{Sr}^{2+}$  exchange [Baker *et al.*, 1982; Gieskes *et al.*, 1986]. Although this interpretation has been challenged by Rudnicki *et al.* [2001]. The steep  $[\text{Sr}^{2+}]$  gradient in shallow sediments is thus caused by the upward diffusion of  $\text{Sr}^{2+}$  from the level of inferred maximum recrystallization to the seafloor. Below 200 m,  $[\text{Sr}^{2+}]$  profiles reflect equilibrium between pore fluids and solids and provide little information on recrystallization rates [Gieskes, 1981; Richter and Liang, 1993; Schrag *et al.*, 1995; Fantle *et al.*, 2010]. In contrast, many of the shallowly buried Paleogene sections targeted for paleoceanographic drilling lack the “classic”  $[\text{Sr}^{2+}]$  profile (Figures 8b, 8d, and 8e). IODP Expedition 320 and ODP Leg 199 sites have overall low  $[\text{Sr}^{2+}]$ , more similar to seawater values, and show relatively much smaller changes in  $[\text{Sr}^{2+}]$  down-core ( $<100 \mu\text{M}$ ; Figures 8a and 8b). Pore fluid profiles from ODP Legs 171B and 207 show a relatively large and linear increase in  $[\text{Sr}^{2+}]$  with burial depth from seawater values at the sediment–water interface. Intersite differences can be explained by differences in site character, specifically sediment age and thickness. The rate of carbonate dissolution and reprecipitation is highest in the first million years following deposition and subsequently decreases rapidly until after  $\sim 10$  Ma there is very little or no flux of  $\text{Sr}^{2+}$  to pore fluids from carbonate phases [Richter and Liang, 1993; Fantle *et al.*, 2010]. Thus, in the “classic” and some ODP Leg 208 sites (Figures 8a and 8c, respectively), the presence of relatively young and “reactive” sediments at the top of the sediment column mean that carbonate recrystallization is still ongoing and contributing  $\text{Sr}^{2+}$  to the pore fluids. The main flux of  $\text{Sr}^{2+}$  to sediments  $>10$  Ma is from noncarbonate reactions in underlying sediments or

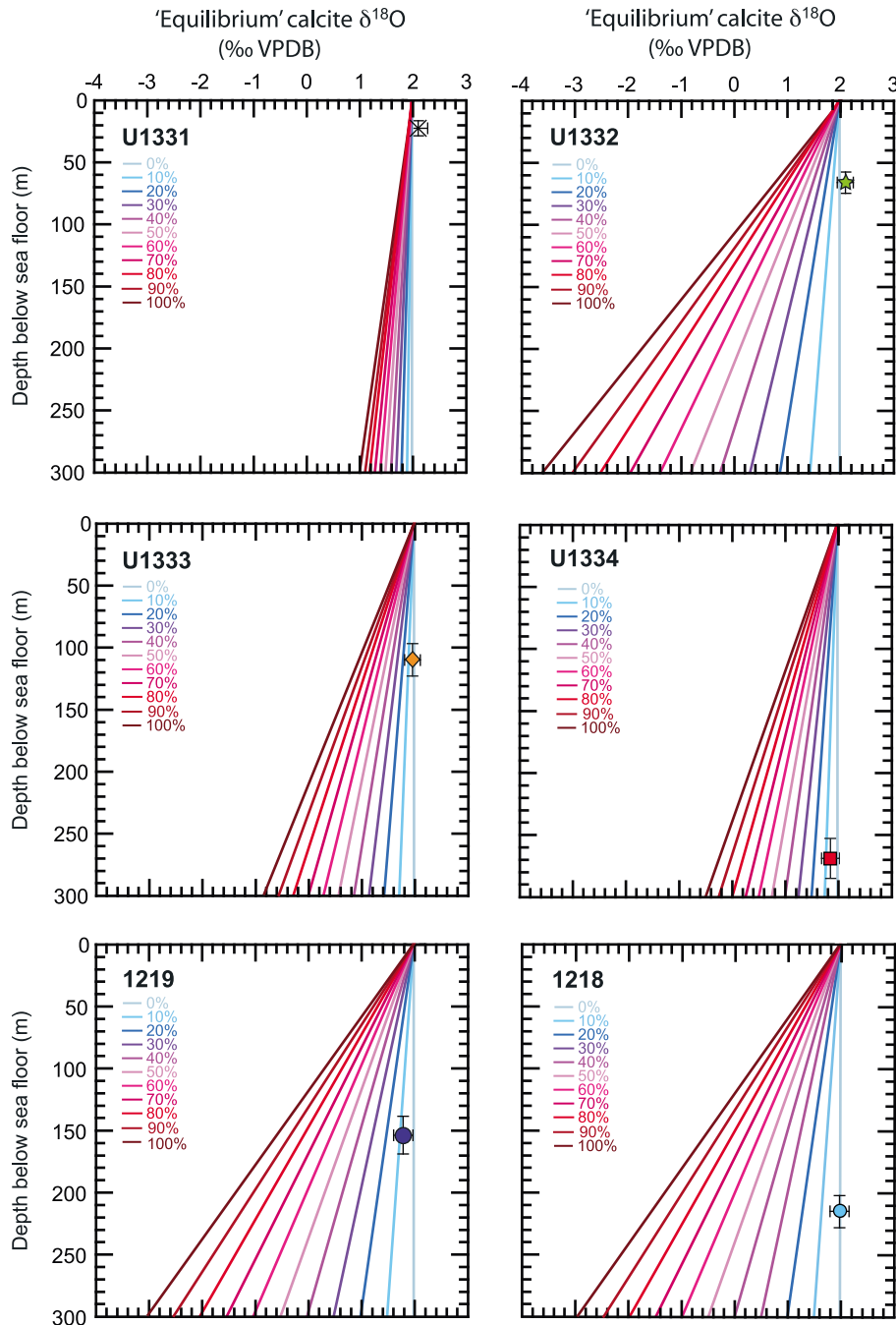


Figure 9

seawater-basalt interactions creating the pore water  $[\text{Sr}^{2+}]$  gradient recorded at Legs 171B and 207. In the equatorial Pacific, the sediments investigated here are old ( $>20$  Ma) and relatively inert; there are no overlying younger sediments to react and the total sediment thickness overlying basement rocks is relatively thin ( $<400$  m; Figure 2b) in comparison to the “classic” sites ( $>600$  m). Therefore, in the absence of ongoing carbonate recrystallization, the pore water  $[\text{Sr}^{2+}]$  gradient is quickly lost by ongoing upward diffusion of  $\text{Sr}^{2+}$  from basement. Thus, down-core  $[\text{Sr}^{2+}]$  profiles cannot be used to constrain the early history ( $<10$  Ma) of carbonate recrystallization in shallowly buried sediments ( $<250$  m) such as those investigated here.

### 3.4. Recrystallization at Shallow Burial Depths Reconciles Benthic Foraminiferal Taphonomy and Stable Isotope Values

[20] The  $\delta^{18}\text{O}$  values appear robust regardless of benthic foraminiferal taphonomic state but this discrepancy raises a question: How can a foraminifera test be extensively recrystallized without significantly altering the original stable isotope values? In section 3.2, we demonstrated that benthic foraminiferal  $\delta^{18}\text{O}$  and their preservation did not decrease with burial depth at our sites. Here we investigate the role of other site-specific factors on carbonate diagenesis, specifically the thermal gradient in the sediment column, using a

simple mass balance calculation following the approach of *Sexton and Wilson* [2009] (for further details, see Figure 9 caption). In Figure 9, we show the relationship between sample burial depth and  $\delta^{18}\text{O}$  for different degrees of in situ recrystallization. Colored diagonal lines denote the calculated  $\delta^{18}\text{O}$  value of calcite with different contributions of inorganic and primary calcite precipitated in equilibrium with pore fluids, increasing from zero recrystallization (i.e., 100% primary calcite; pale blue line) to 100% recrystallization (i.e., 0% primary calcite; dark red line) over the full range of burial depths in our transect. Colored symbols represent the average benthic foraminiferal  $\delta^{18}\text{O}$  values over timeslice three for each site and are plotted at the current burial depth of the sample with the  $y$  axis error bars indicating the full depth range over the investigated timeslice. Comparison of the offset between primary calcite values (pale blue line) and the  $\delta^{18}\text{O}$  of our foraminifers permits a first-order assessment of the extent to which the primary  $\delta^{18}\text{O}$  values have been reset. Using this method, the average measured  $\delta^{18}\text{O}$  values for each site falls to the right of the dark blue lines in Figure 9 indicating a maximum contribution of  $\sim 20\%$  inorganic calcite to our samples at their current burial depth. Critically, the small (and most importantly similar) estimated contribution of inorganic calcite to benthic foraminiferal  $\delta^{18}\text{O}$  values for all of our samples is inconsistent with the large range of preservation states observed. Thus, it is difficult to explain the observed preservation state and isotopic patterns if recrystallization of samples occurs at their present burial depths.

[21] Negligible isotopic offsets between sites encompassing a range of preservation states are best explained if recrystallization proceeds close to the top of the sediment column allowing extensive recrystallization in pore waters with temperatures and  $\delta^{18}\text{O}$  very similar to seawater values and therefore measured  $\delta^{18}\text{O}$  values very close to primary calcification values (Figure 9). Thus, even a large change in the amount of recrystallization visually observed under the microscope corresponds to only a small shift in foraminiferal oxygen isotope values (note the convergence of colored diagonal lines  $<200$  m in Figure 9). This finding is consistent with the site-specific  $[\text{Sr}^{2+}]$  profiles presented in Figure 8 and results of reactive transport models that integrate chemical reactions with the transport of fluids through marine sediments

which suggest no significant recrystallization at the current burial depths of the samples [*Richter and Liang*, 1993; *Rudnicki et al.*, 2001; *Fantle et al.*, 2010]. Ultimately, our work confirms the view that shallowly ( $<300$  m) buried unlithified sediments can be considered virtually inert at their present burial depth [*Richter and Liang*, 1993; *Rudnicki et al.*, 2001]. However, it is important to note that our findings do not apply to  $\delta^{18}\text{O}$  values in planktic foraminifera and bulk carbonate precipitated in warm waters which follow a different early diagenetic trajectory [see *Schrag et al.*, 1995].

[22] While decreasing sediment reactivity (and  $\text{Sr}^{2+}$  exchange) with sediment age provides a mechanism to reconcile apparent decoupling of isotopes and taphonomy in benthic foraminiferal calcite, it does not explain why benthic foraminifera are more poorly preserved at some sites than at others (Figure 4). Reactive transport models indicate that carbonate reaction rates can also vary as a function of sedimentation rate with sites characterized by low sedimentation rates having higher reactive rates [*Richter and Liang*, 1993]. This is presumably because the samples remain at shallow depths within the so-called “diffusive zone” and are influenced by high fluid flow for longer. If bulk carbonate investigated in these models and foraminiferal tests react in a similar manner to one another, then this may help to explain the generally poorer preservation (i.e., more heavily recrystallized nature) of benthic foraminifera in the shallowly buried sites (e.g., Sites U1331 and U1332) which also have the lowest sedimentation rates in the burial depth transect (Figure 2b).

[23] Our work suggests that recrystallization of benthic foraminiferal calcite from sedimentary oozes typically occurs rapidly (i.e., in less than 10 Ma) and at shallow burial depths, resulting in only negligible isotopic offsets from primary values. There will be marked exceptions to this rule. For example, if recrystallization proceeds at shallow depths, any breaks in sedimentation accompanied by changing bottom water parameters (e.g., temperature and  $\delta^{18}\text{O}$  values) may lead to a large isotopic offset from original biogenic calcite values [*Sexton and Wilson*, 2009]. Following empirical observations, foraminifer may undergo extensive recrystallization at their recovered burial depth as sediments are lithified (become chalks then limestones) and interstitial cement, carbonate infilling, and overgrowths develop [*Schlanger and Douglas*, 1974;

**Figure 9.** Relationship between sample burial depth and  $\delta^{18}\text{O}$  of calcite with different proportions of primary and diagenetic calcite at each of the study sites. Average measured  $\delta^{18}\text{O}$  values of benthic foraminiferal calcite between  $\sim 31$  and 33 Ma (colored symbols) relative to the calculated benthic  $\delta^{18}\text{O}$  assuming different contributions of inorganic calcite grown in equilibrium with pore waters (colored diagonal lines) at each site. Diagonal  $\delta^{18}\text{O}$  “mixing” lines calculated between carbonate end-members; primary and secondary calcite using the following mass balance equation  $\delta^{18}\text{O}_{\text{BF}} = (\delta^{18}\text{O}_0 \times f_0) + (\delta^{18}\text{O}_x \times f_x)$ . Where  $\delta^{18}\text{O}_{\text{BF}} = \delta^{18}\text{O}$  of benthic foraminiferal calcite,  $\delta^{18}\text{O}_0 = \delta^{18}\text{O}$  of “equilibrium” calcite precipitated at the seafloor,  $f_0 =$  fraction of original calcite in foraminiferal test,  $\delta^{18}\text{O}_x = \delta^{18}\text{O}$  of secondary calcite and  $f_x =$  fraction of secondary calcite added to foraminiferal test ( $f_x = 1 - f_0$ ). To calculate the  $\delta^{18}\text{O}$  of equilibrium calcite precipitated at the seafloor (“primary” calcite), we rearranged the low light (LL) paleotemperature equation of *Bemis et al.* [1998] and utilize a calculated early Oligocene bottom water temperature of  $4^\circ\text{C}$  and seawater  $\delta^{18}\text{O}$  of  $-0.6\text{‰}$  [*Lear et al.*, 2004]. The Bemis LL equation provides the best fit to *Cibicoides* core-top  $\delta^{18}\text{O}$  data below  $10^\circ\text{C}$ .  $\delta^{18}\text{O}_x$  is determined by calculating the amplitude of the  $\delta^{18}\text{O}$  shift between 0 and 300 m burial depth using site-specific geothermal gradients shown in Figure S1 [*Lyle et al.*, 2002; *Pälike et al.*, 2010] following the equilibrium fractionation relationship determined by *Kim and O’Neil* [1997]. The resulting  $\delta^{18}\text{O}$  shift is subtracted from  $\delta^{18}\text{O}_0$  to obtain  $\delta^{18}\text{O}_x$  at 300 m, one of the mixing end-members. Numbers in each panel refer to the ODP or IODP site shown. “Error” bars represent the standard deviation of  $\delta^{18}\text{O}$  values in timeslice three and the range of sediment burial depths during timeslice three on the  $x$  and  $y$  axes, respectively. *Cibicoides*  $\delta^{18}\text{O}$  values are adjusted to “equilibrium” calcite values by adding  $0.4\text{‰}$  VPDB following the offset between *Oridorsalis* and *Cibicoides* across the Eocene-Oligocene boundary from *Coxall and Wilson* [2011].

Baker et al., 1982]. Lithification is most likely to occur deep in the sediment column where sediment temperatures are higher and pore fluids are offset from isotopic equilibrium with seawater; thus, foraminifera from lithified sediments may possess a greater contribution of diagenetically precipitated calcite with an isotopic signature offset from original values than in oozes. Results of modeling experiments suggests that maximum recrystallization is not necessarily focused at the ooze-chalk transition; thus, recrystallization may be more dependent on the lithological “diagenetic potential” of the constituent sediments rather than burial depth [Rudnicki et al., 2001]. Theoretically, very high geothermal gradients, as seen in seismically active areas, could also result in large  $\delta^{18}\text{O}$  offsets at shallow burial depths but such regions are not typically drilled for paleoceanographic reconstructions.

#### 4. Conclusions

[24] Here we exploit a depth transect of drill sites in the equatorial Pacific Ocean that recovered Oligocene strata benefiting from outstanding stratigraphic control. We present new stable isotope records from Sites 1219 and U1331–U1334 and utilize them together with published records from ODP Site 1218 to test the relative effects of the addition of diagenetic calcite on stable isotope ratios in benthic foraminifera. We find negligible  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  intersite offsets through time. Benthic foraminifera at these sites have experienced very different recrystallization histories but show negligible intersite isotope offsets. These observations imply that recrystallization of calcite occurs predominantly at shallow burial depths supporting the suggestion that recrystallization rates are greatest in the first few million years after burial. The global reproducibility of benthic isotope records from sites with different water depths and burial histories lends support to our hypothesis that a primary isotope signal is typically preserved in shallowly buried benthic foraminiferal calcite. Ultimately, we conclude that benthic foraminifera from sedimentary oozes (specifically) are robust recorders of stable isotope ratios in the fossil record and support paleoceanographic drilling strategies aimed at recovering shallowly buried sediments.

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