Seawater calcium isotope ratios across the Eocene-Oligocene transition

Elizabeth M. Griffith[1,2], Adina Paytan[2], Anton Eisenhauer[3], Thomas D. Bullen[4], and Ellen Thomas[5]
[1]Department of Geology, 221 McGilvrey Hall, Kent State University, Kent, Ohio 44242, USA
[2]Institute of Marine Sciences, University of California–Santa Cruz, Santa Cruz, California 95064, USA
[3]Leibniz-Institut für Meereswissenschaften (IFM-GEOMAR), Wischhofsraße 1-3, D-24148 Kiel, Germany
[4]Branch of Regional Research, Water Resources Division, U.S. Geological Survey, MS 420, 345 Middlefield Road, Menlo Park, California 94025, USA
[5]Department of Geology & Geophysics, Yale University, P.O. Box 208109, New Haven, Connecticut 06520-8109, USA, and Department of Earth and Environmental Sciences, Wesleyan University, Middletown, Connecticut 06459, USA

ABSTRACT

During the Eocene-Oligocene transition (EOT, ca. 34 Ma), Earth's climate cooled significantly from a greenhouse to an icehouse climate, while the calcite ($CaCO_3$) compensation depth (CCD) in the Pacific Ocean increased rapidly. Fluctuations in the CCD could result from various processes that create an imbalance between calcium (Ca) sources to, and sinks from, the ocean (e.g., weathering and $CaCO_3$ deposition), with different effects on the isotopic composition of dissolved Ca in the oceans due to differences in the Ca isotopic composition of various inputs and outputs. We used Ca isotope ratios ($\delta^{44/40}Ca$) of coeval pelagic marine barite and bulk carbonate to evaluate changes in the marine Ca cycle across the EOT. We show that the permanent deepening of the CCD was not accompanied by a pronounced change in seawater $\delta^{44/40}Ca$, whereas time intervals in the Neogene with smaller carbonate depositional changes are characterized by seawater $\delta^{44/40}Ca$ shifts. This suggests that the response of seawater $\delta^{44/40}Ca$ to changes in weathering fluxes and to imbalances in the oceanic alkalinity budget depends on the chemical composition of seawater. A minor and transient fluctuation in the Ca isotope ratio of bulk carbonate may reflect a change in isotopic fractionation associated with $CaCO_3$ precipitation from seawater due to a combination of factors, including changes in temperature and/or in the assemblages of calcifying organisms.

INTRODUCTION

Calcite ($CaCO_3$) sedimentation in the ocean represents the largest sink for calcium and carbon in the combined atmosphere-biosphere-ocean system, connecting the global carbon and Ca cycles (Milliman, 1993; Ridgwell and Zeebe, 2005). Determining fluctuations in the rate and locations of $CaCO_3$ sedimentation and their association with carbon cycle perturbations over climate transitions provides important information on the behavior of the coupled Ca-C biogeochemical system (e.g., Lyle et al., 2008). However, reconstructing global changes in $CaCO_3$ sedimentation patterns during geologically rapid events is complicated, because preservation is not spatially homogeneous and the calcite compensation depth (CCD) is affected by local (as well as global) processes (van Andel, 1975; Iglesias-Rodriguez et al., 2002).

In the equatorial Pacific, the CCD (the depth where rates of $CaCO_3$ dissolution and deposition are equal, below which $CaCO_3$ is not preserved in the sediment) increased by 1200–1500 m in <300 k.y., a unique event (e.g., van Andel, 1975; Coxall et al., 2005; Lyle et al., 2005) that occurred during the Eocene-Oligocene transition (EOT), the transition from a warm greenhouse to a cold icehouse world (Katz et al., 2008; Lear et al., 2008; Liu et al., 2009).

Processes that result in deepening of the CCD (and carbonate accumulation in the deep sea) combined with changes in seawater $\delta^{44/40}Ca$ include the following. (1) An increase in $CaCO_3$ saturation (and preservation) is caused by an imbalance between Ca input to the ocean and output as $CaCO_3$ sediments (Rea and Lyle, 2005), and is accompanied by a decoupling of the Ca and carbon cycles. This requires an increase in the flux of Ca to the ocean relative to alkalinity (e.g., through increased weathering of carbonate rocks relative to silicate rocks; Heuser et al., 2005), leading to an increase in Ca concentration in seawater, with a decrease in seawater $\delta^{44/40}Ca$ (De La Rocha and DePaolo, 2000). (2) An increase in silicate weathering rates (e.g., due to glaciation), reduces atmospheric CO_2, increases alkalinity in the oceans, and deepens the CCD (Zachos et al., 1999; Ravizza and Peucker-Ehrenbrink, 2003; Zachos and Kump, 2005). If changes occurred over a time period longer than the residence time of Ca in the oceans, and there was no net change in total marine carbonate sedimentation, seawater Ca concentrations would increase, with increasing seawater $\delta^{44/40}Ca$ (Sime et al., 2007). (3) If the CCD deepening was associated with a smaller globally averaged fractionation during carbonate sedimentation resulting from a shift from aragonite to calcite precipitation for a period of time longer than the oceanic Ca residence time, seawater $\delta^{44/40}Ca$ would decrease to a new steady-state value (Sime et al., 2007; Fantle, 2010).

Alternatively, a scenario of increased weathering and alkalinity input to the ocean could cause a deepening of the CCD without a change in seawater $\delta^{44/40}Ca$, if compensation occurred over a period shorter than the oceanic Ca residence time (Opdyke and Wilkinson, 1988; Kump and Arthur, 1997; Coxall et al., 2005; Tripati et al., 2005; Merico et al., 2008).

The $\delta^{44/40}Ca$ values of bulk marine carbonates decreased by 0.6‰ close to the EOT, in agreement with scenario 1 (De La Rocha and DePaolo, 2000). If the observed change of 0.6‰ represents seawater $\delta^{44/40}Ca$, it implies a 50% increase in Ca weathering relative to sedimentation flux (De La Rocha and DePaolo, 2000), too large to reconcile with modeling results or mass balance calculations that account for increased carbonate burial associated with the observed changes in the CCD (Lyle et al., 2008; Merico et al., 2008). The 0.6‰ shift may at least in part be due to changes in species-dependent isotopic fractionation caused by changes in calcifying plankton species, and may not represent seawater (see following discussion).

The $\delta^{44/40}Ca$ of marine (pelagic) barite is a reliable recorder of seawater $\delta^{44/40}Ca$ (Griffith et al., 2008a, 2008b). Marine barite precipitates inorganically in seawater, with a constant offset (Ca isotopic fractionation) from dissolved Ca in seawater of $-2.01‰ \pm 0.15‰$ (average $2\sigma_{mean}$), unaffected by temperature (1–14 °C; Griffith et al., 2008b). Thus barite may record seawater $\delta^{44/40}Ca$ more predictably than biogenic carbonates. We reconstructed the isotope ratio of Ca in seawater (from marine barite) and of its major sink (bulk $CaCO_3$) in order to evaluate these scenarios (see the GSA Data Repository[1]), and to constrain the amount of $CaCO_3$ deposited in the oceans relative to the input of Ca to the ocean

---

[1]GSA Data Repository item 2011210, supplementary text, figures and tables, is available online at www.geosociety.org/pubs/ft2011.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

---

via weathering, making assumptions regarding the isotopic composition of Ca sources and sinks (Skulan et al., 1997; Zhu and Macdougall, 1998; De La Rocha and DePaolo, 2000).

METHODS

A relatively high resolution record of the $\delta^{44/40}Ca$ of barite (representing seawater) and coeval bulk $CaCO_3$ (Ca sink) across the EOT was constructed using sediments collected by the Deep Sea Drilling Project and Ocean Drilling Program at Sites 574 and 1218 in the equatorial Pacific Ocean. Barite was extracted using a sequential leaching process (Paytan et al., 1993) and screened for purity using scanning electron microscopy with energy dispersive X-ray spectroscopy. Barite samples were prepared for Ca isotope analysis following methods in Griffith et al. (2008b), and bulk carbonate samples were prepared following methods in Fantle and DePaolo (2005). Ca isotopic compositions were determined by thermal ionization mass spectrometry using the double-spike technique, and reported in $\delta^{44/40}Ca$ (‰) relative to modern seawater (see the Data Repository; Griffith et al., 2008b).

VARIATIONS IN CA ISOTOPE RATIOS DURING THE EOT

Between 36 and 32 Ma, the Ca isotope ratio in marine barite fluctuated by 0.14‰ or less, within the average $2\sigma_{mean}$ of the data. The Ca isotope ratio does not covary with changes in the CCD or in deep-sea benthic foraminiferal $\delta^{18}O$ (Fig. 1). The average seawater $\delta^{44/40}Ca$, calculated from measurements of all barite samples in Figure 1, is −0.16‰ ± 0.14‰ (average $2\sigma_{mean}$), relative to modern seawater (0.00‰) (inferred seawater values determined from measured barite $\delta^{44/40}Ca$ + 2.01‰ to correct for the isotopic offset from seawater; Griffith et al., 2008a, 2008b). Values from the Pacific Ocean represent global seawater $\delta^{44/40}Ca$ due to the long residence time of Ca in the ocean relative to the mixing time (Zhu and Macdougall, 1998).

Bulk carbonate Ca isotope data show a transient decrease of ~0.3‰ (more than twice the average $2\sigma_{mean}$ of 0.11‰) beginning ca. 34.7 Ma, returning to preexcursion values by ca. 33.0 Ma (Fig. 1). The timing of the decrease is well constrained and the magnitude of the decrease is smaller (0.3‰ rather than 0.6‰) and much shorter in duration than the value given in De La Rocha and DePaolo (2000). The differences between these two bulk carbonate records (Fig. 1) suggest that one or both records are controlled by local fractionation effects, thus do not reflect the global $\delta^{44/40}Ca$ value of $CaCO_3$. Alternatively, there may be some analytical offset. Diagenetic effects could also influence the measured
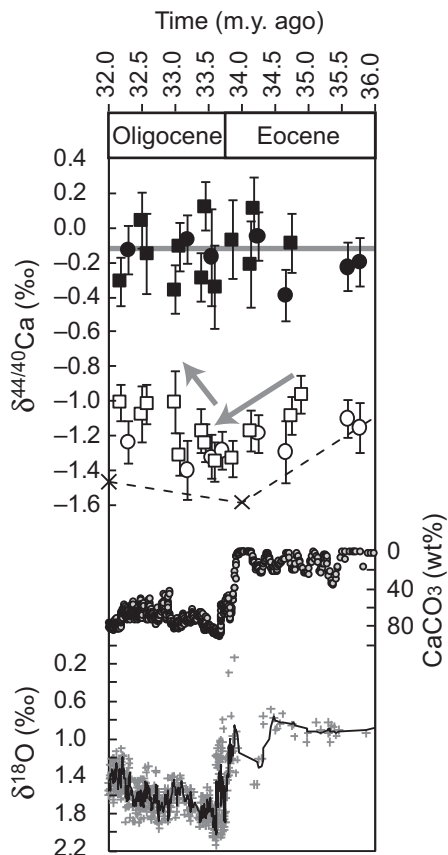
Figure 1. Seawater Ca isotope data from marine barite (calculated by adding 2.1‰ to measured values; solid symbols) and measured Ca isotope ratios of bulk carbonate (open symbols) between 36 and 32 Ma (Eocene-Oligocene transition, EOT), reported relative to modern seawater in per mil (‰). Squares—Deep Sea Drilling Project (DSDP) Site 574; circles—Ocean Drilling Program (ODP) Site 1218. Error bars are precision of value for each sample calculated as $2\sigma_{mean}$ of replicate analyses on thermal ionization mass spectrometry, or average $2\sigma_{mean}$ of samples, whichever is largest. Crosses connected by dotted line are bulk carbonate data from De La Rocha and DePaolo (2000), DSDP Site 167. Solid line indicates average inferred seawater $\delta^{44/40}Ca$ value of −0.16‰. Arrows indicate direction of transient fluctuation in $\delta^{44/40}Ca$ of bulk carbonate. $CaCO_3$ (wt%) from Site 1218 (gray circles) increased in earliest Oligocene, reflecting increase in calcite compensation depth in equatorial Pacific, from above to below the paleodepth of that site (Coxall et al., 2005). $\delta^{18}O$ (‰) of benthic foraminifera from Site 1218 (gray crosses) reported relative to Peedee belemnite (Coxall et al., 2005; Lear et al., 2008). All ages are adapted to age model of Pälike et al. (2006).

bulk carbonate $\delta^{44/40}Ca$, but this effect probably is minor (<0.15‰), due to the small difference between the $\delta^{44/40}Ca$ of $CaCO_3$ and pore waters, the equilibrium fractionation factor, and the high Ca concentration in carbonate and pore waters (Fantle and DePaolo, 2007).

DISCUSSION

In order to constrain the possible processes controlling the Ca isotopic composition of seawater and carbonate sediments, we used the barite and carbonate data in a simplified model of the marine Ca cycle, allowing us to define both the seawater $\delta^{444/40}Ca$ and the fractionation factor associated with carbonate sedimentation, $\Delta^{44/40}Ca_{sed}$. Interpretations using this model require that the system is in isotopic steady state, a reasonable assumption given that we did not observe significant changes in seawater $\delta^{44/40}Ca$ (as recorded in barite) over this time.

Bulk carbonate $\delta^{44/40}Ca$ is controlled by seawater $\delta^{44/40}Ca$ and $\Delta^{44/40}Ca_{sed}$. Since seawater Ca isotopes in our record did not change by more than 0.14‰ (average $2\sigma_{mean}$ of barite data) for periods of time longer than approximately half the oceanic Ca residence time, ~0.5 m.y., the transient fluctuation in the bulk carbonate record must indicate a transient change in $\Delta^{44/40}Ca_{sed}$ that did not result in a measurable change in the global isotopic composition of seawater (i.e., greater than our analytical resolution of ~0.14‰). Temperature, dominant mineralogy, and species composition of nannofossil and foraminiferal assemblages may all affect biogenic carbonate fractionation (Skulan et al., 1997; Zhu and Macdougall, 1998; De La Rocha and DePaolo, 2000; Gussone et al., 2005, 2007; Heuser et al., 2005; Sime et al., 2005; Kasemann et al., 2008; Fantle, 2010). Precipitation rate probably has little or no effect on biological fractionation of most marine carbonates (Gussone et al., 2007; Tang et al., 2008), although this is debated (Fantle, 2010; Kisakürek et al., 2011). Our carbonate $\delta^{44/40}Ca$ values show no strong correlation with Sr/Ca, a potential tracer for kinetic precipitation Ca isotope effects in some biogenic carbonates and in inorganic calcite precipitates (Tang et al., 2008; Kisakürek et al., 2011; for supplementary text, see the Data Repository).

Temperature at high latitudes may have decreased by as much as 5 °C during the EOT (Liu et al., 2009), but much less at equatorial Site 1218 (Coxall et al., 2005) and other low-latitude sites. A temperature change of 5 °C could result in a decrease in $\Delta^{44/40}Ca_{sed}$ of at most 0.1‰ (e.g., De La Rocha and DePaolo, 2000; Gussone et al., 2005), less than the ~0.3‰ observed. Nannofossil (Bown, 2005) and planktic foraminiferal (Berggren and Pearson, 2005) assemblages worldwide changed dramatically over this time interval, which could have affected bulk carbonate $\delta^{44/40}Ca$. Changes in dominant pelagic calcifyers (coupled with temperature changes) could explain the changes in the bulk carbonate record. The lack of changes in the global seawater $\delta^{44/40}Ca$, as evident in our barite record, indicates that the change in $\Delta^{44/40}Ca_{sed}$ (whether global or local) was small and short in duration.

A global shift from dominant aragonite sedimentation (typically represented by shelf producers) toward calcite sedimentation (typically associated with pelagic producers) during the EOT (i.e., increasing the ratio of deep to shallow carbonate deposition; Opdyke and Wilkinson, 1988; Kump and Arthur, 1997) could have resulted in a global $\Delta^{44/40}Ca_{sed}$ increase of as much as 0.6‰ due to the differences in the Ca isotopic fractionation between calcite and aragonite producers (e.g., Gussone et al., 2005). However, it would necessitate a change in seawater $\delta^{44/40}Ca$ if it were of significant duration, and would not be seen in our pelagic carbonate record unless it also affected seawater $\delta^{44/40}Ca$ (i.e., captured in the barite record).

Seawater $\delta^{44/40}Ca$ is slow to respond to small changes in Ca fluxes because of the large amount of Ca in seawater. For example, an increase in the weathering flux of shallow-marine carbonates (dominated by aragonite with low Ca isotope values) related to falling sea level requires an increase in seawater Ca concentration of >8% in 200 k.y. (if the residence time of Ca in the ocean prior to the event was 1.3 m.y.) in order to be detected in seawater $\delta^{44/40}Ca$ (i.e., more than 0.2‰ or twice our analytical resolution). This scenario would result in a permanent shift in seawater $\delta^{44/40}Ca$ if followed by a return to isotopic steady state, and such a change is not seen in our records (for modeling, see the Data Repository). A long-term increase in silicate weathering during the Oligocene is likewise not supported by our results, nor is a long-term change in the globally averaged fractionation associated with carbonate sedimentation. Our results support a scenario of increased alkalinity input (and weathering) to the oceans, most likely the result of Antarctic glaciation and falling sea levels. The alkalinity imbalance was quickly restored through shifting of shallow to deep-sea carbonate accumulation, ultimately causing the deepening of the CCD (Opdyke and Wilkinson, 1988; Kump and Arthur, 1997; Coxall et al., 2005; Tripati et al., 2005; Merico et al., 2008).

A sequence of climatic and oceanographic conditions similar to that suggested for the EOT (but of lower intensity) occurred during the Middle Miocene (ca. 14 Ma; Diester-Haass et al., 2009), but was accompanied by a shift in seawater $\delta^{44/40}Ca$ of ~0.3‰, and only minor changes in the CCD (Fig. 2; Griffith et al., 2008a). The capacity of the marine Ca-C biogeochemical system to buffer changes in weathering without dramatically altering the seawater $\delta^{44/40}Ca$ depends on the ability of biogenic carbonate formation and preservation to respond rapidly to such changes. During the EOT, the marine Ca input and outputs remained relatively balanced despite changes in the depositional environment and weathering regime. During the Middle Mio-
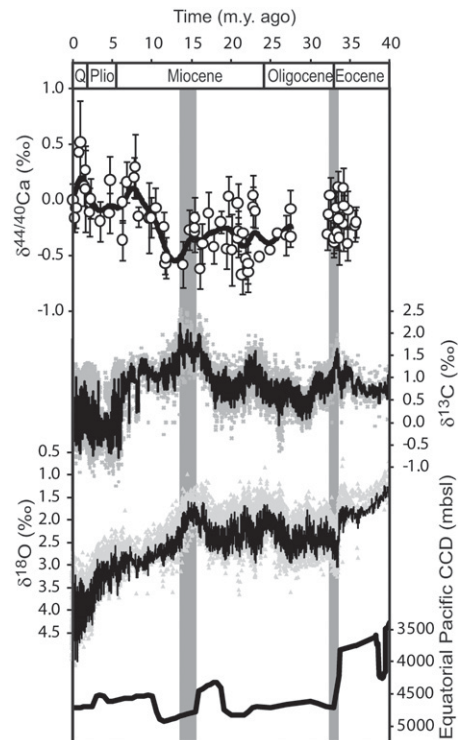
Figure 2. Seawater Ca isotope data from marine barite (calculated by adding 2.1‰ to measured values; solid symbols) over past 40 m.y., reported relative to modern seawater in per mil (‰) from this study and from Griffith et al. (2008a). Composite $\delta^{13}C$ and $\delta^{18}O$ of benthic foraminifera reported relative to Peedee belemnite (‰) (Zachos et al., 2008). Equatorial Pacific calcite compensation depth (CCD) in meters below sea level (mbsl) (Lyle, 2003; Lyle et al., 2005). Vertical gray bars indicate climate transitions at the Eocene-Oligocene transition and Middle Miocene. Q—Quaternary Period; Plio—Pliocene Epoch.

cene, in contrast, the ratio between Ca weathering and deposition fluxes changed dramatically, possibly because continental organic carbon sequestration increased, reducing the total ocean carbon pool. The carbon sequestration occurred through deposition of peat and/or lignite, as reflected by a global positive carbon isotope excursion (Diester-Haass et al., 2009). The ratio of seawater carbonate ion to Ca concentration during the Middle Miocene might have been 1:100 compared to 1:200 during the EOT (Horita et al., 2002; Tyrrell and Zeebe, 2004). Therefore the seawater Ca isotope ratio would have been more responsive to changes in weathering fluxes and imbalances in the oceanic alkalinity budget, which ultimately control the CCD.

During the EOT, however, the oceanic Ca concentration was higher and the Ca residence time longer, so that the much smaller and shorter positive C isotope excursion can be attributed to an increase in riverine dissolved carbonate from erosion of newly exposed carbonate on the

shelves (e.g., Merico et al., 2008). Under these conditions the oceanic system could respond rapidly to associated changes in the C cycle (increase in alkalinity) by deepening the CCD in the equatorial Pacific Ocean, thus balancing the reduction in shallow-marine carbonate sedimentation without much effect on the Ca cycle. The comparison of these two events indicates that differences in the coupling of the Ca and carbon cycles and their relationship to climate change during the Middle Miocene and the EOT ultimately resulted from differences in seawater composition, forcing mechanisms, and the rate of response or feedbacks by carbonate burial and/or marine productivity. Reconstructing coeval variations in seawater Ca isotopic composition (from marine barite) and bulk carbonate (the major Ca sink) thus may shed light on the biogeochemical cycling of Ca at times different from the modern day, and their relation to climatic perturbations.

REFERENCES CITED

Berggren, W.A., and Pearson, P.N., 2005, A revised tropical to subtropical Paleogene planktonic foraminiferal zonation: Journal of Foraminiferal Research, v. 35, p. 279–298, doi:10.2113/35.4.279.

Bown, P., 2005, Calcareous nannoplankton evolution; a tale of two oceans: Micropaleontology, v. 51, p. 299–308, doi:10.2113/gsmicropal.51.4.299.

Coxall, H.K., Wilson, P.A., Palike, H., Lear, C.H., and Backman, J., 2005, Rapid stepwise onset of Antarctic glaciation and deeper calcite compensation in the Pacific Ocean: Nature, v. 433, p. 53–57, doi:10.1038/nature03135.

De La Rocha, C.L., and DePaolo, D.J., 2000, Isotopic evidence for variations in the marine calcium cycle over the Cenozoic: Science, v. 289, p. 1176–1178, doi:10.1126/science.289.5482.1176.

Diester-Haass, L., Billups, K., Gröcke, D.R., Fraçois, L., Lefebvre, V., and Emeis, K.C., 2009, Mid-Miocene paleoproductivity in the Atlantic Ocean and implications for the global carbon cycle: Paleoceanography, v. 24, doi:10.1029/2008PA001605.

Fantle, M.S., 2010, Evaluating the Ca isotope proxy: American Journal of Science, v. 310, p. 194–230, doi:10.2475/03.2010.03.

Fantle, M.S., and DePaolo, D.J., 2005, Variations in the marine Ca cycle over the past 20 million years: Earth and Planetary Science Letters, v. 237, p. 102–117, doi:10.1016/j.epsl.2005.06.024.

Fantle, M.S., and DePaolo, D.J., 2007, Ca isotopes in carbonate sediment and pore fluid from ODP Site 807A: The Ca^{2+}(aq)-calcite equilibrium fractionation factor and calcite recrystallization rates in Pleistocene sediments: Geochimica et Cosmochimica Acta, v. 71, p. 2524–2546, doi:10.1016/j.gca.2007.03.006.

Griffith, E.M., Paytan, A., Caldeira, K., Bullen, T.D., and Thomas, E., 2008a, A dynamic marine calcium cycle during the past 28 million years: Science, v. 322, p. 1671–1674, doi:10.1126/science.1163614.

Griffith, E.M., Schauble, E.A., Bullen, T.D., and Paytan, A., 2008b, Characterization of calcium isotopes in natural and synthetic barite: Geochimica et Cosmochimica Acta, v. 72, p. 5641–5658, doi:10.1016/j.gca.2008.08.010.

Gussone, N., Böhm, F., Eisenhauer, A., Dietzel, M., Heuser, A., Teichert, B.M.A., Reitner, J., Wörheide, G., and Dullo, W.-C., 2005, Calcium isotope fractionation in calcite and aragonite: Geochimica et Cosmochimica Acta, v. 69, p. 4485–4494, doi:10.1016/j.gca.2005.06.003.

Gussone, N., Langer, G., Geisen, M., Steel, B.A., and Riebesell, U., 2007, Calcium isotope fractionation in coccoliths of cultured Calcidiscus leptoporus, Helicosphaera carteri, Syracosphaera pulchra and Umbilicosphaera foliosa: Earth and Planetary Science Letters, v. 260, p. 505–515, doi:10.1016/j.epsl.2007.06.001.

Heuser, A., Eisenhauer, A., Böhm, F., Wallmann, K., Gussone, N., Pearson, P.N., Nägler, T.F., and Dullo, W.-C., 2005, Calcium isotope ($\delta^{44/40}$Ca) variations of Neogene planktonic foraminifera: Paleoceanography, v. 20, doi:10.1029/2004PA001048.

Horita, J., Zimmermann, H., and Holland, H.D., 2002, Chemical evolution of seawater during the Phanerozoic: Implications from the record of marine evaporates: Geochimica et Cosmochimica Acta, v. 66, p. 3733–3756, doi:10.1016/S0016-7037(01)00884-5.

Iglesias-Rodriguez, M.D., Armstrong, R., Feely, R., Hood, R., Kleypas, J., Milliman, J.D., Sabine, C., and Sarmiento, J., 2002, Progress made in study of ocean's calcium carbonate budget: Eos (Transactions, American Geophysical Union), v. 83, no. 34, p. 365, doi:10.1029/2002EO000267.

Kasemann, S.A., Schmidt, D.N., Pearson, P.N., and Hawkesworth, C.J., 2008, Biological and ecological insights into Ca isotopes in planktic foraminifers as a palaeotemperature proxy: Earth and Planetary Science Letters, v. 271, p. 292–302, doi:10.1016/j.epsl.2008.04.007.

Katz, M.E., Miller, K.G., Wright, J.D., Wade, B.S., Browning, J.V., Cramer, B.S., and Rosenthal, Y., 2008, Stepwise transition from the Eocene greenhouse to the Oligocene icehouse: Nature Geoscience, v. 1, p. 329–334, doi:10.1038/ngeo179.

Kisakürek, B., Eisenhauer, A., Bohm, F., Harthorne, E.C., and Erez, J., 2011, Controls on calcium isotope fractionation in cultured planktic foraminifera, Globigerinoides ruber and Globigerinella siphonifera: Geochimica et Cosmochimica Acta, v. 75, p. 427–443, doi:10106/j.gca.2010.10.015.

Kump, L.R., and Arthur, M.A., 1997, Global chemical erosion during the Cenozoic: Weatherability balances the budgets, in Ruddiman, W.F., ed., Tectonic uplift and climate change: New York, Plenum Press, p. 399–425.

Lear, C.H., Bailey, T.R., Pearson, P.N., Coxall, H.K., and Rosenthal, Y., 2008, Cooling and ice growth across the Eocene-Oligocene transition: Geology, v. 36, p. 251–254, doi:10.1130/G24584A.1.

Liu, Z., Pagani, M., Zinniker, D., DeConto, R., Huber, M., Brinkhuis, H., Shah, S.R., Leckie, R.M., and Pearson, A., 2009, Global cooling during the Eocene-Oligocene climate transition: Science, v. 323, p. 1187–1190, doi:10.1126/science.1166368.

Lyle, M., 2003, Neogene carbonate burial in the Pacific Ocean: Paleoceanography, v. 18, doi:10.1029/2002PA000777.

Lyle, M., Olivarez Lyle, A., Backman, J., and Tripati, A., 2005, Biogenic sedimentation in the Eocene equatorial Pacific—The stuttering greenhouse and Eocene carbonate compensation depth, in Wilson, P.A., et al., eds., Proceedings of the Ocean Drilling Program, Scientific results, Volume 199: College Station, Texas, Ocean Drilling Program, p. 1–35, doi:10.2973/odp.proc.sr.199.219.2005.

Lyle, M., Barron, J., Bralower, T.J., Huber, M., Olivarez Lyle, A., Ravelo, A.C., Rea, D.K., and Wilson, P.A., 2008, Pacific Ocean and Cenozoic evolution of climate: Reviews of Geophysics, v. 46, RG2002, doi:10.1029/2005RG000190.

Merico, A., Tyrrell, T., and Wilson, P.A., 2008, Eocene/Oligocene ocean de-acidification linked to Antarctic glaciation by sea-level fall: Nature, v. 452, p. 979–982, doi:10.1038/nature06853.

Milliman, J.D., 1993, Production and accumulation of calcium carbonate in the ocean: Budget of a nonsteady state: Global Biogeochemical Cycles, v. 7, p. 927–957, doi:10.1029/93GB02524.

Opdyke, B.N., and Wilkinson, B.H., 1988, Surface control of shallow cratonic to deep marine carbonate accumulation: Paleoceanography, v. 3, p. 685–703.

Pälike, H., Norris, R.D., Herrle, J.O., Wilson, P.A., Coxall, H.K., Lear, C.H., Shackleton, N.J., Tripati, A.K., and Wade, B.S., 2006, The heartbeat of the Oligocene climate system: Science, v. 314, p. 1894–1898, doi:10.1126/science.1133822.

Paytan, A., Kastner, M., Martin, E.E., Macdougall, J.D., and Herbert, T., 1993, Marine barite as a monitor of seawater strontium isotope composition: Nature, v. 366, p. 445–449, doi:10.1038/366445a0.

Ravizza, G.E., and Peucker-Ehrenbrink, F., 2003, The marine [187]Os/[188]Os record of the Eocene-Oligocene transition: The interplay of weathering and glaciations: Earth and Planetary Science Letters, v. 210, p. 151–165, doi:10.1016/S0012-821X(03)00137-7.

Rea, D.K., and Lyle, M.W., 2005, Paleogene calcite compensation depth in the eastern subtropical Pacific: Answers and questions: Paleoceanography, v. 20, doi:10.1029/2004PA001064.

Ridgwell, A., and Zeebe, R.E., 2005, The role of the global carbonate cycle in the regulation and evolution of the Earth system: Earth and Planetary Science Letters, v. 234, p. 299–315, doi:10.1016/j.epsl.2005.03.006.

Sime, N.G., De La Rocha, C.L., and Galy, A., 2005, Negligible temperature dependence of calcium isotope fractionation in 12 species of planktonic foraminifera: Earth and Planetary Science Letters, v. 232, p. 51–66, doi:10.1016/j.epsl.2005.01.011.

Sime, N.G., De La Rocha, C.L., Tipper, E.T., Tripati, A., Galy, A., and Bickle, M.J., 2007, Interpreting the Ca isotope record of marine biogenic carbonate: Geochimica et Cosmochimica Acta, v. 71, p. 3979–3989, doi:10.1016/j.gca.2007.06.009.

Skulan, J., DePaolo, D.J., and Owens, T.L., 1997, Biological control of calcium isotopic abundances in the global calcium cycle: Geochimica et Cosmochimica Acta, v. 61, p. 2505–2510, doi:10.1016/S0016-7037(97)00047-1.

Tang, J., Dietzel, M., Böhm, F., Köhler, S.J., and Eisenhauer, A., 2008, Sr^{2+}/Ca^{2+} and ^{44}Ca/^{40}Ca fractionation during inorganic calcite formation: II. Ca isotopes: Geochimica et Cosmochimica Acta, v. 72, p. 3733–3745, doi:10.1016/j.gca.2008.05.033.

Tripati, A., Backman, J., Elderfield, H., and Ferretii, P., 2005, Eocene bipolar glaciations associated with global carbon cycle changes: Nature, v. 436, p. 341–346, doi:10.1038/nature0384.

Tyrrell, T., and Zeebe, R.E., 2004, History of carbonate ion concentration over the last 100 million years: Geochimica et Cosmochimica Acta, v. 68, p. 3521–3530, doi:10.1016/j.gca.2004.02.018.

van Andel, T.H., 1975, Mesozoic/Cenozoic calcite compensation depth and the global distribution of calcareous sediments: Earth and Planetary Science Letters, v. 26, p. 187–194, doi:10.1016/0012-821X(75)90086-2.

Zachos, J.C., and Kump, L.R., 2005, Carbon cycle feedbacks and the initiation of Antarctic glaciations in the earliest Oligocene: Global and Planetary Change, v. 47, p. 51–66.

Zachos, J.C., Opdyke, B.N., Quinn, T.M., Jones, C.E., and Halliday, A.N., 1999, Early Cenozoic glaciation, Antarctic weathering, and seawater [87]Sr/[86]Sr: Is there a link?: Chemical Geology, v. 161, p. 165–180, doi:10.1016/S0009-2541(99)00085-6.

Zachos, J.C., Dickens, G.R., and Zeebe, R.E., 2008, An early Cenozoic perspective on greenhouse warming and carbon-cycle dynamics: Nature, v. 451, p. 279–283, doi:10.1038/nature06588.

Zhu, P., and Macdougall, J.D., 1998, Calcium isotopes in the marine environment and the oceanic calcium cycle: Geochimica et Cosmochimica Acta, v. 62, p. 1691–1698, doi:10.1016/S0016-7037(98)00110-0.