6.20 Records of Cenozoic Ocean Chemistry

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6.20.1 INTRODUCTION
Numerous lines of evidence show that there have been dramatic changes in the marine realm during the last 65 Myr. These changes occur over varying timescales. Some are relatively abrupt, occurring on timescales of thousands to tens of thousands of years. Others occur more gradually, over million-year timescales. Many of the most valuable monitors of past changes in ocean
chemistry, such as the $\delta^{13}$C and $\delta^{18}$O of foraminiferal calcite are subject to high-frequency variations that must be smoothed out if long-term, secular, trends are to be recognized clearly. Conversely, other records of past seawater chemistry, such as the marine strontium isotope record, respond only slowly to high-frequency external forcing and are incapable of recording it with fidelity. Nevertheless, it is likely that high-frequency forcing related to glacial erosion and shifts in the hydrologic cycle play an important role in shaping the marine strontium isotope record. Therefore, even though the focus of this review is on records of Cenozoic ocean chemistry that emphasize long-term changes, the different timescales on which Cenozoic ocean chemistry changes are not fully separable.

In this review emphasis is placed on isotopic records of ocean chemistry. In general terms, a conscious decision was made to emphasize those records that document long-term changes in the chemical and physical properties of the global ocean over the course of the Cenozoic. For example, while reconstructions of burial fluxes of barium or phosphorus may place valuable constraints on paleo-productivity in a specific setting, making extrapolations to infer globally integrated trends from these data sets is very difficult because of sparse data coverage in space and time. Similarly, we have also chosen to exclude discussion of short-residence-time tracers like lead and neodymium isotopes that can yield important information about changing patterns of ocean circulation and regional shifts in oceanic inputs. A recent discussion of these tracer systems is available elsewhere (Frank, 2002). The geological records that are emphasized include those of the stable carbon and oxygen isotopes preserved in benthic foraminiferal calcite, and marine strontium and osmium isotopes. These four records clearly manifest significant changes in global ocean chemistry. At any given time, the stable carbon and oxygen isotope records include an important component of spatial variability; however, these are not so large as to obscure the pattern of temporal variation preserved in the sediment record.

Boron isotopes as a paleo-pH proxy and Mg/Ca as a paleo-temperature proxy are also discussed, because information provided by these relatively new proxies has important implications for the better-established records mentioned in the preceding paragraph. The application of boron isotopes to reconstructing surface water pH provides a means of estimating past atmospheric CO$_2$ levels. Much of the discussion of the marine strontium isotope record in the past has been linked to implicit assumptions about Cenozoic variations in atmospheric CO$_2$ levels. New boron isotope results indicate that previous assumptions about Cenozoic atmospheric CO$_2$ levels need to be reconsidered. Mg/Ca ratio variations in benthic foraminiferal calcite are discussed because of the promise that combined Mg/Ca and $\delta^{34}$S studies hold for resolving the dual influence of ice volume and deep-water temperature on benthic foraminiferal $\delta^{18}$O records.

There are several other topics that would be equally appropriate to consider in a review of this type. Some of these, such as the $\delta^{34}$S record of seawater and the history of the calcium carbonate compensation depth (CCD), are mentioned briefly as they relate to records that are discussed in greater detail. Other topics have been omitted. We hope readers will recognize that the topics covered here are determined not only by the scientific interests of the authors, but also by the practical limits of what can be covered in a single review.

6.20.2 CENOZOIC DEEP-SEA STABLE ISOTOME RECORD

Much of what is currently understood about the Cenozoic history, of deep-sea temperature, carbon chemistry, and global ice volume, has been gleaned from the stable isotope ratios of benthic foraminifera. Benthic foraminifera extract carbonate and other ions from seawater to construct their tests. In many species, this is achieved near carbon and oxygen isotopic equilibrium. Kinetic fractionation effects tend to be small and constant (Grossman, 1984, 1987). As a result, shell $\delta^{13}$C and $\delta^{18}$O strongly covary with the isotopic composition of seawater and dissolved inorganic carbon (DIC). For both carbon and oxygen isotopes, there is also a temperature-dependent fractionation effect. For oxygen isotopes, the effect is relatively large, 0.25‰ ($^\circ$C)$^{-1}$, about an order of magnitude larger than that for carbon isotopes. As such, in addition to monitoring changes in seawater isotope ratios, the oxygen isotopes can be used to evaluate temperature. Moreover, the tests of benthic foraminifera are relatively resistant to dissolution and other diageneric processes, making them ideal archives of ocean history.

The latest "global" deep-sea stable isotope record for the Cenozoic, presented in Figure 1, is based on benthic foraminifera oxygen and carbon isotope records compiled from over 40 pelagic sediment cores (Zachos et al., 2001). The raw data were smoothed using a five-point running mean, and curve-fitted with a weighted (2%) running mean. For the carbon isotope record, the curve fit was terminated at the middle–late Miocene boundary because of a marked increase in basin-to-basin carbon isotope fractionation at that time (Wright et al., 1991). This record provides a fairly
Figure 1. The global deep-sea isotope record based on data compiled from 40 DSDP and ODP sites. These data were derived from pelagic deep-sea cores (e.g., from depths greater than 1,000 m) with lithologies that are predominantly fine-grained, carbonate-rich (>50%) oozes or chalks. Most of the data are derived from analyses of two common and long-lived benthic taxa, *Cibicidoides* and *Nuttallides*. The absolute ages are relative to the standard Geomagnetic Polarity Timescale (GPTS) for the Cenozoic (Berggren et al., 1995). To minimize biases related to inconsistencies in sampling density in space and time, the raw data were smoothed using a five-point running mean, and curve-fitted with a locally weighted mean. The smoothing results in a loss of detail that is undetectable from the long-timescale perspective. For the carbon isotope record, the global curve fit was terminated just before the Late Miocene and replaced with separate Atlantic and Pacific curves because of a marked increase in basin-to-basin carbon isotope fractionation (Wright and Miller, 1993). The temperature scale represents mean deep-sea temperature for the period of time preceding the onset of large-scale glaciation on Antarctica (~35 Ma). After this time, much of the variability in the δ¹⁸O record reflects on changes in global ice volume on Antarctica and in the N. Hemisphere. The vertical bars provide a semiquantitative representation of ice volume in each hemisphere relative to the LGM with the dashed bar representing periods of minimal ice coverage (~<50%), and the full bar representing close to maximum ice-coverage (>50% of present). In the more recent portion of the carbon isotope record, separate curve fits were derived for the Atlantic and Pacific to illustrate the increase in basin-to-basin fractionation which exceeds ~1‰ in some intervals. Prior to 15 Ma, interbasin gradients are on the order of a few tenths of a per mil or less (source Zachos et al., 2001).
coarse perspective on the long-term variations in Cenozoic climate and ocean chemistry. For the finer-scale variations that tend to be masked in this long-term perspective, individual high-resolution records are preferable. Several high-resolution records spanning “critical” intervals are plotted in Figure 2.

6.20.2.1 Oxygen Isotopes and Climate

The conservative physical and chemical characteristics of bottom waters are fixed at the site of deep-water formation, which for much of the Cenozoic appears to have been the high-latitude polar seas. As a consequence, the long-term oxygen isotope variations recorded by benthic foraminifera reflect largely on changes in high-latitude sea surface temperature (Shackleton et al., 1985). In general, a $\delta^{18}O$ increase of 1.0‰ is equivalent to roughly 4 °C of cooling. Foraminifera oxygen isotope records also record change in seawater $\delta^{18}O$, which, on the million-year timescale, is controlled primarily by changes in the volume of continental ice sheets which are isotopically depleted ($\sim$0‰ to $\sim$4‰) relative to seawater. For example, melting the present-day ice sheets would decrease mean ocean $\delta^{18}O$ by more than 1.0‰ while raising sea level by 100 m ($\sim$0.01‰ m$^{-1}$). It is assumed that the exchange of $\delta^{18}O$ occurs at a rate that is too slow to significantly affect the $\delta^{18}O$ record on the timescale of the Cenozoic.

Separating the relative contributions of these two variables to the deep-sea oxygen isotope record is a challenging exercise. Consideration of additional factors including the lower boundaries of seawater temperature (e.g., freezing) can place some limits on the temperature effect (Miller et al., 1987, 1991b; Zachos et al., 1993, 1994). However, with independent measures of temperature that are unaffected by salinity, one can effectively isolate the component related to ice volume. To this end, the degree of saturation of alkenones of autotrophs or Mg/Ca of benthic foraminifera (Lear et al., 2000; Billups and Schrag, 2002) can be used to constrain temperature.

Over the long term, the Cenozoic deep-sea oxygen isotope record is dominated by two important features that relate to major shifts in mean climatic state. The first is a rise in values from 53 to 35. This trend, which is mostly gradual but punctuated by several steps, is an expression of the Eocene transition from greenhouse to icehouse conditions. In the Early Eocene ($\sim$53 Ma) the deep sea was relatively warm, $\sim$7 °C warmer than present, and there were no ice sheets. Over the next 20 Myr, the ocean cools, and the first large ice sheets appear on Antarctica. The latter event is reflected by the relatively sharp 1.2‰ increase in $\delta^{18}O$ at 33.4 Ma. This pattern reverses slightly toward the end of the Oligocene, but by middle Miocene, ice sheets begin to expand slowly, eventually covering most of Antarctica as reflected in $\delta^{18}O$. The second significant step in the Cenozoic is associated with the gradual buildup of northern hemisphere ice sheets between 3.5 Ma and 2.5 Ma.

On short timescales, the $\delta^{18}O$ record reveals considerable variability. Most of this is concentrated in the Milankovitch bands, and therefore reflects on orbitally modulated changes in ice volume and/or deep-sea temperatures. The largest amplitude oscillations occur in the Quaternary when ice sheets are present on North America. Prior to the Quaternary, the signal amplitude in $\delta^{18}O$ is about one-third to one-half, mostly reflecting variations in the volume of Antarctic ice sheets (Figure 2(a)). These lower-amplitude oscillations persist through much of the Neogene and the Oligocene with most of the variance concentrated in the obliquity bands (Tiedemann et al., 1994; Shackleton and Crowhurst, 1997; Flower et al., 1997; Zachos et al., 2001).

A small component of the short-term variability falls under the category of anomalies or transients. This includes a short-lived but abrupt negative excursion 55 Myr ago (Figure 2(b)). The magnitude of the $\delta^{18}O$ change implies a $\sim$4–5 °C transient warming of the deep sea. This event, referred to as the Paleocene–Eocene thermal maximum, is by far the most extreme of the rapid climatic changes inferred from the oxygen isotope records. Other isotope anomalies representing brief climatic excursions have been documented in the earliest Oligocene ($\sim$33.4 Ma), at the O/M boundary (23.0 Ma), and in the middle Miocene ($\sim$14 Ma) (Miller et al., 1991a; Zachos et al., 1996).

Despite efforts to produce a globally averaged record, gradients in deep-sea temperature combined with the uneven distribution of deep-sea cores can introduce subtle biases into the global $\delta^{18}O$ record. To start, deep-sea temperature is not uniform: the upper ocean is several degrees warmer than the deep ocean. Gradients also exist spatially, especially at intermediate depths with proximity to the polar and tropical oceans. As a result, global compilations utilizing data from sites located at different water depths and basins can be somewhat misleading. For example, the older, Early Paleogene, portions of cores tend to be biased toward the upper ocean because of long-term subsidence and seafloor subduction (Zachos et al., 2001). Moreover, because no single record spans the entire Cenozoic, shifts in $\delta^{18}O$ can be artificially produced through splicing. One example is the negative shift in $\delta^{18}O$ observed in the Late Oligocene ($\sim$27 Ma), which in the compilation is larger than recorded in any individual record. A number of deep-sea records
Figure 2  (a) High-resolution 4 Myr long $\delta^{18}$O time series representing four intervals of the Cenozoic (Zachos et al., 2001). The data are from sites 659, eastern equatorial Atlantic (Tiedemann et al., 1994); 588, Southwest Pacific (Flower and Kennett, 1993); 929, western equatorial Atlantic (Paul et al., 2000); 522, South Atlantic (Zachos et al., 1996) and 689 Southern Ocean (Diester-Haass, 1996). Sampling intervals range from 3 kyr, to 10 kyr. Note that the $\delta^{18}$O axes on all plots are set to the same scale (3.0‰) although different ranges to accommodate the change in mean ocean temperature/ice volume with time. The upper curves in each panel represent Gaussian band-pass filters designed to isolate variance associated with the 400 kyr and 100 kyr eccentricity cycles. The 400 kyr filter has a central frequency ($cf$) = 0.0025 and a bandwidth ($bw$) = 0.0002; the 100 kyr $cf$ = 0.01 and $bw$ = 0.002. (b) Multiple benthic isotope records characterizing the Late Paleocene thermal maximum event at 55 Ma (Thomas and Shackleton, 1996; Bralower et al., 1995). The timing of the beginning of the event is placed at 54.95 Ma (Röhl et al., 2000). Data are plotted on the timescale of these two papers combined with the cyclostratigraphy for site 690 (Cramer, in press); data from other sites are correlated to the 690 record. The apparent late initiation of the events at 690 is the result of the lack of specimens of *N. truempyi* during the first part of the event at that site; note low-isotope values of *Bulimina ovula* in the gap in the *N. truempyi* data. The oxygen isotope data indicate an abrupt 4–6 °C warming of the deep ocean in a period of ~10 kyr, by far the most rapid rate of warming of the last 65 Myr. The negative carbon isotope excursion is thought to represent the influx of methane from dissociation of gas hydrates.
either terminate or begin at this point. The few that span this interval show a shift, but with a magnitude about half (~0.5‰) that represented in the global compilation.

6.20.2.2 Carbon Isotopes and Ocean Carbon Chemistry

The distribution of carbon isotopes within the ocean is dependent on two processes, ocean circulation and export production. The δ\(^{13}\)C\(_{\text{DIC}}\) of deep-water masses are initially set at the site of sinking (via equilibrium exchange with the atmosphere), but tend to progressively change as they slowly migrate through the basins. The respiration of organic matter delivered by export production releases isotopically depleted CO\(_2\) (\(a_{\text{TCO}_2-\text{CH}_2\text{O}} = 1.021\)) to the DIC pool. Thus, as deep waters “age” and their DIC and nutrient contents increase, δ\(^{13}\)C decreases. Initial offsets in deep-water chemical characteristics, however, are retained to the extent that δ\(^{13}\)C can be used to distinguish water masses deriving from different sources. Moreover, the relationship between dissolved nutrients, primarily PO\(_4\), and δ\(^{13}\)C\(_{\text{DIC}}\) is nearly linear such that the latter has served as a proxy for estimating the distribution of the former, at least for short timescales.

The mean value of ocean δ\(^{13}\)C\(_{\text{DIC}}\) is not stationary. It changes in response to variations in the fluxes of carbon between the ocean, and the major sources and sinks of carbon (Kump and Arthur, 1999). The major sources are volcanic and metamorphic outgassing of CO\(_2\), and rock (organic and inorganic) weathering. The major sinks are organic and inorganic carbon burial as represented by the following equation from Kump and Arthur (1999):

\[
\frac{d}{dt}(M_o \delta_{\text{carb}}) = F_w \delta_w + F_{\text{volc}} \delta_{\text{volc}} - F_{\text{b,carb}} \delta_{\text{carb}} - F_{\text{borg}} (\delta_{\text{carb}} + \Delta_B)
\]

(1)

where \(M_o\) is the total dissolved carbon in the ocean, \(F_w\) and \(F_b\) are the fluxes for weathering and burial, and \(\delta_{\text{carb}}, \delta_{\text{volc}},\) and \(\delta_w\) are the average carbon isotopic compositions of marine carbonates, volcanic CO\(_2\) (crustal + mantle), and weathered or riverine carbon, respectively. \(\delta_{\text{carb}}\) is effectively equal to the mean ocean δ\(^{13}\)C\(_{\text{DIC}}\) + 1.0‰. For \(F_{\text{borg}}\), \(\delta\) is based on a fractionation factor \(\Delta_B\) which is relatively large, on the order of ~20‰. Because of the large range in isotope values for these sources and sinks, on timescales of \(>10^3\) yr even small changes in the fluxes to or from these reservoirs can impart noticeable changes in mean ocean δ\(^{13}\)C\(_{\text{DIC}}\).
Two aspects of the Cenozoic marine δ¹³C record merit discussion. The first is the spatial distribution of δ¹³C between ocean basins, which is relatively insignificant from 65 Ma to 8 Ma (Figure 1). The lack of gradients between basins is generally viewed as evidence of a single dominant deep-water source during the Cenozoic, Antarctica (Wright and Miller, 1993). Deep waters from other regions (e.g., evaporitic, marginal seas), while important locally, are effectively negligible on a global scale. Over the last 8 Myr, the flux of North Atlantic deep water has been large enough to dominate the Atlantic, at least on a periodic basis (i.e., northern hemisphere interglacial). This, coupled with increased isolation of the deep Atlanticas the Tethys and Panamanian gateways close, allows for the development of the large carbon isotope gradient with the Pacific (i.e., basin-to-basin fractionation). This illustrates how the distribution of carbon isotopes is influenced by circulation patterns.

The second observation concerns the long- and short-term trends. Much has been said about the long-term patterns. In particular, the gradual increases in δ¹³C over the Late Paleocene and middle Miocene have been attributed to increased rates of organic carbon burial, possibly brought about by tectonic factors that created or destroyed basins, or to changes in mantle outgassing rates (Berner et al., 1983; Shackleton, 1985). The Late Neogene decline in δ¹³C is similarly viewed as a signal of changes in the size of the organic carbon reservoir and/or burial rates (Shackleton, 1985; Raymo, 1997). The ability to isolate the processes responsible for these long-term trends (i.e., >10³ yr), however, is limited by the ability to constrain other aspects of the global carbon and related geochemical cycles. For example, the burial of reduced sulfur is tightly coupled to organic carbon cycling as represented by Equation (2):

\[
2\text{CH}_2\text{O} + \text{SO}_4^{2-} + \text{H}^+ \rightleftharpoons 2\text{CO}_2 + \text{HS}^- + \text{H}_2\text{O}
\]  

(2)

This microbe mediated reaction is accompanied by significant isotopic fractionation of the sulfur (α_{SO_4-HS} = 1.025) such that large increases in the rate of sulfate reduction can significantly increase the δ³⁴S of the remaining sulfate reservoir (residence time of sulfur in the ocean would require timescales of 10⁵ yr and greater). As a result, a sustained shift in the rate of marine organic carbon production and/or burial as proposed for the Late Paleocene or Neogene should be accompanied by gradual changes in seawater δ³⁴S. Only recently, however, has a record of seawater δ³⁴S became available (Paytan et al., 1998) to test these hypotheses. This record shows relatively constant values over much of the Cenozoic with two notable exceptions, the Late Paleocene to Early Eocene and the Pleistocene.

The short-term trends, particularly the excursions, merit special consideration. The most prominent occurs at 55 Ma, approximately the Paleocene–Eocene (P–E) boundary. It is characterized by an abrupt 3.0‰ decrease in benthic foraminiferal δ¹³C as well as a 4–5 °C global warming, the P–E thermal maximum (Figure 2(b)). Such a rapid and large decrease in mean ocean δ¹³C can only be achieved with the addition of a large quantity of ¹³C enriched carbon. The mean δ¹³C of carbon derived from volcanic outgassing is −7‰, whereas the mean for methane ranges from −40‰ to −60‰, the latter dependent upon whether it is thermogenically or bacterially produced. The rate of change associated with the P–E excursion is more readily achieved through the addition of methane (Dickens et al., 1997). The largest reservoir of methane near the Earth’s surface is the marine hydrate reservoir. Computations show that dissociation and oxidation of 2,000 Gt of hydrate methane would be sufficient to produce an excursion of this magnitude. It is likely that other smaller shifts in ocean δ¹³C might have similar origins (Dickens, 2001).

The benthic δ¹³C record is marked by other excursions in the Cenozoic at the Eocene–Oligocene and Oligocene–Miocene boundaries. These anomalies, however, are positive and more gradual. The direction of change indicates perturbations in one or more fluxes of the global carbon cycle, possibly the burial rates of reduced carbon, which are inferred to increase during each of these events.

### 6.20.3 THE MARINE STRONTIUM AND OSMIUM ISOTOPE RECORDS

The marine strontium isotope record is the proxy record most commonly used to constrain the geologic history of chemical weathering. However, in recent years it has been widely criticized as a proxy indicator of past silicate weathering rates. The osmium isotope record is analogous to the strontium record in many respects, and can help to constrain interpretations of the marine strontium isotope record. In this section the geochemical factors that influence the osmium and strontium isotope compositions of seawater are reviewed, and the structure of these two records of Cenozoic ocean chemistry is discussed.

#### 6.20.3.1 Globally Integrated Records of Inputs to the Ocean

There are two critically important similarities between osmium and strontium isotopes as
paleoceanographic tracers. The first is the sense of parent–daughter fractionation during mantle melting. In the Rb–Sr and Re–Os systems, the radioactive parents, rubidium and rhenium, are partitioned into the melt preferentially to the daughter elements strontium and osmium. Continental crust, a product of mantle differentiation, is characterized by higher Rb/Sr and Re/Os ratios relative to the deep in the Earth. Given the significant mean age of average upper continental crust, ~2 Gyr, in situ decay of $^{87}\text{Sr}$ and $^{187}\text{Re}$ has produced significant amounts of $^{87}\text{Sr}$ and $^{187}\text{Os}$. Thus, in both systems, more radiogenic isotope signatures (higher $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{187}\text{Os}/^{188}\text{Os}$) characterize old-crustal rocks relative to recent mantle-derived rocks.

The second, and equally important, similarity is the relative isotopic homogeneity of both dissolved strontium and osmium in seawater. This was only recently confirmed for osmium by direct analyses of seawater (Sharma et al., 1997; Levasseur et al., 1998; Woodhouse et al., 1999). The fact that both osmium and strontium are isotopically well mixed in the modern ocean suggests that temporal variations in both isotope records can provide a globally integrated history of oceanic inputs. These two attributes provide a basis for using the marine strontium and osmium isotope records to constrain changes in the riverine solute flux through time.

Mixing of multiple sources of isotopically distinct inputs provides a useful framework for interpreting temporal variations in seawater $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{187}\text{Os}/^{188}\text{Os}$. Early efforts to understand the marine strontium isotope record recognized changing proportions of strontium derived from weathering of three end-members: old felsic crust, young basalts, and marine carbonates as the primary influence on the strontium isotopic composition of seawater (Brass, 1976). Although our understanding of the marine strontium cycle has advanced significantly, these rock reservoirs remain fundamentally important. Hydrothermal alteration of basalt at mid-ocean ridges provides a continuous supply of relatively unradiogenic strontium to the ocean that is assumed to be proportional to oceanic crustal production rate. The supply of strontium from weathering of rocks exposed on land is titrated against this unradiogenic strontium input from oceanic crust. Marine carbonates have strontium concentrations that range from several hundred to more than 1,000 ppm, and represent a third important source of strontium to the oceans. The low Rb/Sr of most marine carbonates render production of $^{87}\text{Sr}$ by in situ decay in these rocks unimportant. Consequently, strontium derived from weathering of marine carbonates is generally assumed to be similar in isotopic composition to seawater. This is strictly true of strontium released to pore waters during early diagenetic recrystallization of biogenic carbonate (Gieskes et al., 1986). In the context of these three mixing end-members, the marine strontium isotope record can be interpreted as the result of changes in the relative proportions of strontium delivered to the oceans from weathering of old continental crust and young basalts, as buffered by rapid recycling of strontium associated with marine carbonates. This simplified description of the marine strontium cycle can be represented by the equation

$$\frac{dR_{SW}}{dt} = t^{-1}(f_R(R_R - R_{SW}) + f_{HT}(R_{HT} - R_{SW}) + f_D(R_D - R_{SW}))$$

(3)

where $R_i$ is $^{87}\text{Sr}/^{86}\text{Sr}$ and $f_i$ is the ratio of the strontium flux from source $i$ to the ocean to the total flux of strontium to the ocean, and $t$ is the marine residence time of strontium (~2 Myr). The subscripts SW, R, HT, and D correspond to seawater, rivers, hydrothermal, and diagenetic terms, and $dR_{SW}/dt$ is the slope of the seawater strontium curve. A summary of representative values for the present-day marine strontium budget is given in Table 1.

An analogous expression can be written for the seawater osmium isotope system but the diagenetic term representing recrystallization of biogenic carbonate would be eliminated. Although the marine osmium cycle is less well documented than the strontium cycle, first-order estimates for most key parameters are available (Table 1). The short marine-residence time of osmium (~10–40 ky: see Peucker-Ehrenbrink and Ravizza, 2001) and the low sample density in Cenozoic osmium isotope record precludes time-dependent modeling at this time. In addition, it is uncertain if the HT term for osmium can strictly be linked to oceanic crustal production. Instead, it is perhaps better represented by a generic unradiogenic flux that includes both hydrothermal and cosmic inputs (see below for additional discussion). Available data (Table 1) suggest that similar proportions of osmium and strontium are derived from the radiogenic “continental” end-member. This provides some support for a simple “two-component” approach to the marine strontium and osmium isotope records. To the extent that globally averaged riverine input is the product of chemical weathering of average upper crust, the isotopic compositions of strontium and osmium are expected to be relatively invariant. If so, then the gross structure of the marine osmium isotope record should mimic that of the strontium record and changes in the strontium and osmium isotope composition of seawater should be representative of changing solute flux to the global ocean.
6.20.3.2 Osmium–Strontium Decoupling

A more careful examination of the geochemistry of the Rb–Sr and Re–Os systems reveals significant differences between these two isotope systems—differences that have the potential to decouple the marine strontium and osmium isotope records from one another. As monovalent and divalent cations, rubidium and strontium partition readily into major rock-forming minerals in both high- and low-temperature environments. As noted above the affinity of Sr$^{+2}$ for carbonate minerals is a particularly important aspect of the surficial strontium cycle. In contrast, rhenium and osmium, both third-series transition metals, are redox active and strongly siderophile and chalcophile. As a result, rhenium and osmium tend to be associated with trace phases like sulfides and metal oxides. These very different geochemical affinities suggest that the fluxes and isotopic composition of dissolved strontium and osmium carried by individual rivers need not be well correlated in the modern Earth system. It is also possible, though less likely, that the globally averaged fluxes and isotopic composition of dissolved strontium and osmium carried by individual rivers need not be well correlated in the modern Earth system. It is also possible, though less likely, that the globally averaged fluxes and isotopic composition of dissolved strontium and osmium carried by individual rivers need not be well correlated in the modern Earth system. If this is the case, then the Cenozoic marine strontium and osmium isotope records are not expected to resemble one another. Below we outline several specific aspects of the geochemical cycles of the Rb–Sr and Re–Os systems that have the potential to decouple oceanic inputs of osmium and strontium.

Table 1 Summary of the present-day marine Sr and Os budgets.

<table>
<thead>
<tr>
<th>Isotope ratios</th>
<th>$^{87}$Sr/$^{86}$Sr</th>
<th>$^{187}$Os/$^{188}$Os</th>
</tr>
</thead>
<tbody>
<tr>
<td>Seawater</td>
<td>0.70916</td>
<td>1.06</td>
</tr>
<tr>
<td>Average upper crust</td>
<td>1.26–1.40</td>
<td>0.716</td>
</tr>
<tr>
<td>Average riverine input</td>
<td>0.7119</td>
<td>1.4</td>
</tr>
<tr>
<td>Diagenetic flux</td>
<td>0.7084</td>
<td>Unknown</td>
</tr>
<tr>
<td>Fractional contribution from riverine flux</td>
<td>0.67</td>
<td>0.73</td>
</tr>
<tr>
<td>Elemental fluxes</td>
<td>Sr (mol yr$^{-1}$)</td>
<td>Os (mol yr$^{-1}$)</td>
</tr>
<tr>
<td>Riverine flux</td>
<td>$3.3 \times 10^{10}$</td>
<td>1,850</td>
</tr>
<tr>
<td>Diagenetic flux</td>
<td>$0.34 \times 10^{10}$</td>
<td>Unknown</td>
</tr>
<tr>
<td>Calculated hydrothermal/unradiogenic flux</td>
<td>$1.6 \times 10^{10}$</td>
<td>680</td>
</tr>
<tr>
<td>Seawater concentration</td>
<td>590 µM</td>
<td>50 fm</td>
</tr>
<tr>
<td>Seawater inventory</td>
<td>$1.3 \times 10^{17}$ mol</td>
<td>$7.4 \times 10^{7}$ mol</td>
</tr>
<tr>
<td>Calculated residence time</td>
<td>$2.4 \times 10^{6}$ yr</td>
<td>30,000 yr</td>
</tr>
</tbody>
</table>

Data sources: Sr budget as compiled by Elderfield and Schultz (1996); Os budget as compiled by Peucker-Ehrenbrink and Ravizza (2000); Average upper crust: Peucker-Ehrenbrink and Jahn (2001); Goldstein and Jacobsen (1988).

Notes: Fractional riverine contribution calculated from isotope mass balance. Calculated hydrothermal/unradiogenic flux terms are calculated assuming the present-day ocean is at steady state with respect to Sr and Os isotope mass balance.

6.20.3.2 Osmium–Strontium Decoupling

A more careful examination of the geochemistry of the Rb–Sr and Re–Os systems reveals significant differences between these two isotope systems—differences that have the potential to decouple the marine strontium and osmium isotope records from one another. As monovalent and divalent cations, rubidium and strontium partition readily into major rock-forming minerals in both high- and low-temperature environments. As noted above the affinity of Sr$^{+2}$ for carbonate minerals is a particularly important aspect of the surficial strontium cycle. In contrast, rhenium and osmium, both third-series transition metals, are redox active and strongly siderophile and chalcophile. As a result, rhenium and osmium tend to be associated with trace phases like sulfides and metal oxides. These very different geochemical affinities suggest that the fluxes and isotopic composition of dissolved strontium and osmium carried by individual rivers need not be well correlated in the modern Earth system. It is also possible, though less likely, that the globally averaged fluxes and isotopic composition of dissolved strontium and osmium carried by individual rivers need not be well correlated in the modern Earth system. If this is the case, then the Cenozoic marine strontium and osmium isotope records are not expected to resemble one another. Below we outline several specific aspects of the geochemical cycles of the Rb–Sr and Re–Os systems that have the potential to decouple oceanic inputs of osmium and strontium.

6.20.3.2.1 Decoupled riverine fluxes of strontium and osmium?

The association of strontium with carbonates, and rhenium and osmium with sedimentary organic matter may effectively decouple the riverine fluxes of strontium and osmium. It is well known that calcium carbonate weathers much more rapidly than silicate minerals and that estimates of silicate weathering fluxes based on strontium isotope data are complicated by this phenomenon (Palmer and Edmond, 1992; see also Jacobson et al. (2002a) for a discussion). In general, though not always (see below), terrestrial weathering of carbonates increases strontium flux and lowers $^{87}$Sr/$^{86}$Sr relative to an equivalent carbonate-free catchment. The lower $^{87}$Sr/$^{86}$Sr of average river flux (0.712) relative to eroding upper crust (0.716) is the global manifestation of the buffering influence that carbonate dissolution exerts on riverine strontium isotope composition.

In contrast to Rb–Sr system, there is no analogue to the buffering influence of carbonate weathering on seawater osmium isotope variations. Instead, it has been suggested that chemical weathering of old organic-rich sediments may actually cause large amplitude changes in the seawater $^{187}$Os/$^{188}$Os, because they are enriched in both rhenium and osmium and have unusually large Re/Os ratios (Ravizza, 1993). Recent studies demonstrate that rhenium and osmium are efficiently mobilized during black shale weathering (Peucker-Ehrenbrink and Hannigan, 2000; Jaffe et al., 2002; Pierson-Wickmann et al., 2002). If the Os/Corg ratios of recent Black Sea sediments (Ravizza et al., 1991) are characteristic of the sedimentary organic carbon reservoir, in general, as much as 5–10% of the continental crustal inventory of osmium may be associated with sedimentary organic matter. This is comparable to the fraction of continental crustal strontium associated with marine carbonates. While the potential importance of weathering old organic-rich shales for causing increases in the seawater...
\(^{187}\text{Os}/^{188}\text{Os}\) has been recognized in many studies (Pegram et al., 1992; Ravizza, 1993; Peucker-Ehrenbrink et al., 1995; Singh et al., 1999; Pierson-Wickmann et al., 2000), the potential buffering influence of rapid recycling of osmium rich, reducing marine sediments on continental margins has received little attention. Although the connection between erosion of sedimentary organic matter and the marine osmium isotope record is not well understood, it does provide a clear example of the contrasting aqueous geochemistry of the \(^{87}\text{Re}/^{86}\text{Sr}\) and \(^{187}\text{Os}/^{188}\text{Os}\) systems. These differences can make the marine strontium and osmium isotope records respond to different aspects of continental weathering.

6.20.3.2.2 Decoupled unradiogenic fluxes?

Dissimilarities between osmium and strontium also exist for the unradiogenic inputs to the ocean, providing additional ways in which these two paleoceanographic records could be decoupled. While it is well established that hydrothermal alteration of mid-ocean ridge basalts (MORBs) is the primary source of unradiogenic strontium to the ocean, it is unlikely that this process can balance the osmium isotope budget. Initial investigation of osmium in high-temperature vent fluids suggests that additional source(s) of unradiogenic osmium to the ocean must exist (Sharma et al., 2000). Again, the geochemistry of osmium suggests other likely unradiogenic sources to the ocean. Core formation and the compatible behavior of osmium during mantle melting are responsible for producing the \(10^4\)-fold depletion in typical crustal rocks relative to undifferentiated extraterrestrial material. Although it is unlikely that changes in cosmic dust flux through time are responsible for structure in the Cenozoic osmium isotope record (Peucker-Ehrenbrink, 1996), the flux of unradiogenic osmium contributed to the modern ocean by cosmic dust dissolution remains uncertain (see Peucker-Ehrenbrink and Ravizza, 2000) and some workers argue that it may be significant (Sharma et al., 2000). The compatible behavior of osmium during partial melting of the mantle yields concentrations in MORBs that are \(\sim\)100 times lower than in ultramafic rocks. Consequently, submarine alteration of ultramafic rocks exposed on the seafloor is commonly invoked as a potentially important source of unradiogenic osmium to the oceans (Palmer and Turekian, 1986; Martin, 1991; Snow and Reisberg, 1995; Peucker-Ehrenbrink, 1996; Levasseur et al., 1999). The recent discovery of ultramafic hosted hydrothermal systems (Douville et al., 2002; Kelly et al., 2001) has intensified interest in this potential source of osmium to seawater. Low-temperature hydrothermal activity (Ravizza et al., 1996; Sharma et al., 2000) has also been suggested as a significant source of unradiogenic osmium to seawater. This source is conceptually appealing because the low sulfide concentration of these fluids may allow osmium concentration to reach substantially higher than that in high-temperature, sulfide-rich fluids. A single analysis of a low-temperature fluid lends some support to this notion (Sharma et al., 2000), but additional data are required to document the influence of low-temperature hydrothermal activity on the marine osmium isotope balance.

Ultramafic hydrothermal alteration is the most interesting of the potential mechanisms for decoupling unradiogenic inputs of osmium and strontium to the ocean. If this proves to be the major source of unradiogenic osmium to seawater, then unradiogenic osmium flux could be anticorrelated with oceanic crustal production rates because ultramafic rocks are preferentially exposed on slow spreading ridges. Alternatively, if low-temperature hydrothermal osmium flux proves to be important, it is unclear that this would undermine the assumption that unradiogenic osmium flux is proportional to oceanic crustal production rate. While major impact events, like the K–T boundary, can clearly decouple the strontium and osmium isotope records, the short-lived nature of this perturbation makes it relatively unimportant for the Cenozoic evolution of ocean chemistry.

6.20.3.3 Reconstructing Seawater Isotope Composition from Sediments

Reconstructing the isotopic composition of ancient seawater is more problematic for osmium than for strontium. Analyses of well-preserved microfossils, typically cleaned foraminifera, yield a fairly robust record of the \(^{87}\text{Sr}/^{86}\text{Sr}\) of ancient seawater because \(^{87}\text{Sr}/^{86}\text{Sr}\) is lattice bound in biogenic carbonates. Moreover, strontium isotopic analyses of bulk carbonate and associated pore waters provide the basis for quantitative models of strontium diagenesis in carbonates demonstrating that diagenetic artifacts, even in bulk carbonate analyses, are relatively modest in nearly pure carbonate sequences (Richter and DePaolo, 1988; Richter and Liang, 1993). By comparison with strontium, osmium burial in marine sediments is both more complicated and less-well understood. Osmium burial is more complicated because authigenic osmium enrichment occurs in a variety of depositional settings. These include manganese nodules (Lluck and Turekian, 1983; Burton et al., 1999), slowly accumulating pelagic clays (Esser and Turekian, 1988), organic-rich marine sediments (Ravizza and Turekian, 1989, 1992), and metalliferous sediments accumulating near mid-ocean ridges (Ravizza and McMurtry, 1993; Ravizza et al., 1996). This pattern of
enrichment demonstrates that osmium is effectively removed from seawater to the solid phase under both oxidizing and reducing conditions. By analogy with better-studied trace metals such as vanadium and molybdenum, it is likely that sedimentary organic matter and iron and manganese oxides play important roles in sequestering osmium from seawater under reducing and oxidizing conditions, respectively. The finely dispersed nature of these phases in the sediment complicates reconstructing the marine osmium isotope record, because there is no simple means of physically isolating material that contains exclusively seawater-derived osmium.

Two different strategies are employed to reconstruct the $^{187}\text{Os}/^{188}\text{Os}$ of ancient seawater from the sediment record. Analyses of bulk sediments are used in organic-rich (Ravizza, 1998; Cohen et al., 1999) and metalliferous sediments (Ravizza, 1993) where hydrogenous osmium dominates the total sediment osmium budget. In slowly accumulating pelagic clays where osmium associated with cosmic dust and detrital material accounts for more than 50% of the total osmium inventory, leaching methods must be used to selectively liberate hydrogenous (seawater-derived osmium) from pelagic clays (Pegram et al., 1992; Pegram and Turekian, 1999). Although modern calibration studies have vindicated both approaches, neither is completely convincing because both rely on the assumptions about either the selectivity of chemical leaching methods (see Peucker-Ehrenbrink et al. (1995) and Pegram and Turekian (1999) for discussions of potential artifacts), or the osmium concentration of local detrital material. As a result of the lack of compelling geochemical arguments, demonstrating the integrity of the marine osmium isotope record, a stratigraphic approach is used in which coeval sediment records from differing locations and depositional setting are compared to one another. Similar records of temporal variations $^{187}\text{Os}/^{188}\text{Os}$ preserved in widely separated sediment sequences provide empirical evidence suggesting that both records are accurately recording seawater $^{187}\text{Os}/^{188}\text{Os}$.

6.20.3.4 Cenozoic Strontium and Osmium Isotope Records

6.20.3.4.1 Overview of the Cenozoic marine strontium isotope record

As the result of several decades of investigation the Cenozoic history of seawater $^{87}\text{Sr}/^{86}\text{Sr}$ variation has become a well-established record of changing ocean chemistry. Peterman et al. (1970) presented the first Phanerozoic record of changes in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of seawater derived from analyses of biogenic carbonate. The development of high-precision strontium isotope stratigraphy established the marine strontium isotope record as a valuable stratigraphic tool, and laid the foundation for developing a detailed composite record of Cenozoic seawater strontium isotope variations (DePaolo and Ingram, 1985). Although this record continues to be refined, its major features are well established (Figure 3). A recent compilation of marine strontium isotope record, based on a subset of all published data, can be found in McArthur et al. (2001).

The most striking aspect of the Cenozoic strontium record is the nearly monotonic, and relatively rapid rise in seawater $^{87}\text{Sr}/^{86}\text{Sr}$ ratio during the last 40 Myr, as compared to the small

![Figure 3](https://example.com/figure3.png)

**Figure 3** Composite marine strontium isotope record (sources Miller et al., 1991a; Oslick et al., 1994; Hodell and Woodruff, 1994; Mead and Hodell, 1995; Farrell et al., 1995; Martin et al., 1999; Reilly et al., 2002). For the Early Cenozoic where data coverage is sparse the best fit of McArthur et al. (2001) is plotted.
amplitude variations that characterize the Early Cenozoic record (65–40 Ma). This difference between the Early and Late Cenozoic portions of strontium record is accompanied by a dramatic contrast in data density. The latter part of the Cenozoic marine strontium isotope record is heavily sampled for two reasons. First the steep slope of the $^{87}\text{Sr} / ^{86}\text{Sr}$ versus age curve allows absolute age dating of marine carbonates with a precision that can be better than $\pm$1 Ma. Second, the hypothesis that the rapid increase in seawater $^{87}\text{Sr} / ^{86}\text{Sr}$ reflects a significant and systematic increase in alkalinity flux to the ocean associated with accelerated rates of chemical weathering driven by Himalayan uplift (Raymo and Ruddiman, 1992) provided additional impetus to refine the Late Cenozoic strontium isotope record. As a result of these efforts, the fine structure of the last 40 Ma of the Cenozoic strontium isotope record is well documented. Samples are commonly analyzed at 100 kyr intervals in multiple records and independent age control is based on magnetostratigraphy, biostratigraphy, and, more recently, orbital tuning (Farrell et al., 1995; Martin et al., 1999). By comparison the details of seawater $^{87}\text{Sr} / ^{86}\text{Sr}$ ratio variations during the first 25 Ma of the Cenozoic are only poorly constrained.

6.20.3.4.2 Overview of the Cenozoic marine osmium isotope record

The history of Cenozoic variations in the osmium isotopic composition of seawater is also preserved in the marine sediment record. This record is only poorly documented compared to the strontium record. In large part, this reflects the fact that the osmium isotope system is a fairly new paleoceanographic tracer. The first report of temporal changes in the osmium isotope composition of seawater was made only in 1992 (Pegram et al., 1992). Initially, changes in osmium isotope composition produced by decay of $^{187}\text{Re}$ (half-life $\sim$42 Gyr) to $^{187}\text{Os}$ were reported as $^{187}\text{Os} / ^{186}\text{Os}$ ratio variations. Subsequently, the convention of reporting $^{187}\text{Os} / ^{188}\text{Os}$ ratios was adopted because the decay of $^{190}\text{Pt}$ can produce small but measurable amounts of $^{186}\text{Os}$ (Walker et al., 1997). In this review all data initially reported as $^{187}\text{Os} / ^{186}\text{Os}$ ratios have been converted to $^{187}\text{Os} / ^{188}\text{Os}$. Both the present-day marine osmium budget and the marine osmium isotope record are the subject of a recent review (Peucker-Ehrenbrink and Ravizza, 2000).

The Cenozoic marine osmium isotope record is characterized by a shift from generally unradiogenic values in the Early Cenozoic to more radiogenic values in the Neogene. This trend culminates with higher present-day seawater $^{187}\text{Os} / ^{188}\text{Os}$ ratios than at any other time during the Cenozoic (Figure 4). It is clear that the marine strontium and osmium curves do not closely resemble one another. Based on a comparison of these two isotope records, the Cenozoic can be subdivided into three different intervals. (i) From the present to the mid-Miocene (0–15 Ma) the marine strontium and osmium isotope records are broadly correlated and are found to be rising toward more radiogenic isotope ratios. (ii) From

![Figure 4](source.png)

**Figure 4** Composite record of seawater $^{187}\text{Os} / ^{188}\text{Os}$ variations during the Cenozoic (sources Pegram et al., 1992; Ravizza, 1993, 1998; Peucker-Ehrenbrink et al., 1995; Reusch et al., 1998; Oxburgh, 1998; Pegram and Turekian, 1999; Ravizza et al., 2001; Ravizza and Peucker-Ehrenbrink, 2003).
the mid-Miocene to the Eocene–Oligocene transition (15–35 Ma) seawater $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is found to be rising fairly rapidly. In contrast, $^{187}\text{Os}/^{188}\text{Os}$ ratio remains relatively constant for the majority of this time interval, with the notable exception of the Eocene–Oligocene transition itself. During the Paleocene and Eocene (35–65 Ma), it appears that the osmium record exhibits considerably more variability than does the strontium record. Neither record shows clear evidence of systematic change to more or less radiogenic isotope compositions during this early part of the Cenozoic.

Recently, a substantial body of data constraining the isotope composition and flux of dissolved osmium carried by rivers has been reported (Sharma et al., 1999; Levasseur et al., 1999; Martin et al., 2001). These new data show that while the strontium and osmium isotope compositions of present-day seawater conform with a two-component mixing model fairly well (Table 1), the strontium and osmium isotope compositions of Paleogene seawater do not (Figure 5). This requires either decoupling of strontium and osmium of a magnitude that is not observed in the Neogene marine isotope balances, or a substantial shift in the strontium and osmium isotope composition of riverine influx. By assuming that the mole fractions of osmium and strontium contributing to seawater from riverine input have remained the same as in the modern, a model-based isotopic composition of Paleogene riverine input can be calculated (Figure 5). While the calculated $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is well within the range measured for modern rivers, the calculated $^{187}\text{Os}/^{188}\text{Os}$ ratio is not, being lower than average modern riverine input by a factor of $\sim 3$. A coupled Sr–C isotope model was designed to partition all seawater strontium isotope variation into changing isotope composition of river flux and the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the silicate portion of riverine flux (Kump and Arthur, 1997). These results indicate a large increase in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio and the silicate portion of riverine strontium flux from Paleogene ratio of 0.7095 to a present-day ratio of 0.716. Thus, the marine osmium isotope record may reveal substantial changes in the composition of weathered silicate rock that are partially obscured in the marine strontium isotope record by the buffering effect of carbonate weathering.

### 6.20.3.4.3 Significance of uplift and weathering of the Himalayan–Tibetan Plateau (HTP)

Among the many recent papers that discuss the marine strontium isotope record, the influence of uplift and weathering of the HTP is pre-eminent as a potential cause of the increasingly radiogenic, or “continental,” character during the Cenozoic. Several workers argue that HTP weathering is

![Figure 5](image-url)
the primary cause of the post-40 Ma rise in seawater $^{87}$Sr/$^{86}$Sr ratio (Richter et al., 1992; Edmond, 1992; Raymo and Ruddiman, 1992). Several lines of evidence have been used to support this argument. The $^{87}$Sr/$^{86}$Sr of Ganges–Brahmaputra (G–B) river waters are unusually high compared to that of global average river flux (Krishnaswami et al., 1992; Palmer and Edmond, 1992). The most rapid increase in the seawater strontium curve coincides with rapid HTP uplift (Richter et al., 1992; Hodell and Woodruff, 1994; see also Figure 6). Calculations of the influence of modern HTP rivers on the present-day seawater $^{87}$Sr/$^{86}$Sr ratio have also been used to argue for the importance of HTP weathering (Hodell et al., 1990).

The importance of HTP orogenesis as a cause of the Cenozoic rise in seawater $^{87}$Sr/$^{86}$Sr has likely been overstated by many workers. Krishnaswami et al. (1992) estimated that G–B flow could account for only one-third of the post-40 Ma rise in seawater $^{87}$Sr/$^{86}$Sr ratio. The most recent data indicate that the G–B river system contributes 2% of the global riverine strontium flux with $^{87}$Sr/$^{86}$Sr ratio of 0.73 (Galy et al., 1999). Using Equation (3) and the modern marine strontium budget to calculate hypothetical steady-state $^{87}$Sr/$^{86}$Sr seawater ratio in the absence of G–B inflow yields a value between 0.7090 and 0.7089, depending on the $^{87}$Sr/$^{86}$Sr assumed for the diagenetic strontium flux. This corresponds to ~20% of the post-40 Ma rise in seawater $^{87}$Sr/$^{86}$Sr ratio. Some argue that all rivers draining the HTP should be considered, increasing the strontium contribution to ~25% of the global strontium flux (Richter et al., 1992). However, among these rivers only the G–B has $^{87}$Sr/$^{86}$Sr ratio substantially larger than average global river input (Palmer and Edmond, 1989, 1992). This implies that strontium supplied by other HTP rivers would contribute to rising

![Figure 6](image-url)
seawater $^{87}\text{Sr}/^{86}\text{Sr}$ ratio only if their flow represented a net increase in river water flux to the ocean, and not simply a redistribution from another part of the globe. Although it is not possible to preclude a causal relationship between rising seawater $^{87}\text{Sr}/^{86}\text{Sr}$ ratio and HTP uplift, the detailed changes of the strontium isotope record are difficult to reconcile with the uplift history of the HTP (Figure 6). This is particularly true of the early phases of orogenesis because they remain poorly dated (see Najman et al., 2001).

Early interpretations of the marine osmium isotope record also emphasized a Himalayan influence (Pegram et al., 1992), particularly during the last 15 Ma when both $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{187}\text{Os}/^{188}\text{Os}$ rise in concert (Peucker-Ehrenbrink et al., 1995). The modern river data do not preclude this possibility. Recent analyses of dissolved osmium in the G–B water (Sharma et al., 1999; Levasseur et al., 1999) indicate that this river system contributes very roughly 2% of the total riverine osmium flux, similar to that estimated for strontium. The $^{187}\text{Os}/^{188}\text{Os}$ ratio associated with these analyses are highly variable ranging from 2.9 in the Ganges, twice that of global average river input, to 1.07 in the Brahmaputra. Additional osmium data from the G–B river system are needed to determine if the few available data are representative of seasonally averaged fluxes.

Weathering of Cambrian to Precambrian black shales from the Lesser Himalaya (LH) may be important in causing the rapid rise in seawater $^{187}\text{Os}/^{188}\text{Os}$ ratio during the last 15 Myr. These rocks appear to be the primary source of rhenium, and unusually radiogenic osmium to the modern G–B river system (Singh et al., 1999; Pierson-Wickmann et al., 2000; Dalai et al., 2002). Analyses of paleosols constrain the $^{187}\text{Os}/^{188}\text{Os}$ ratio of the Ganges (1.6–2.6) during the last 18 Myr, with the highest ratio in the youngest (3 Ma) sample (Chesley, 2000; see Figure 5). This range is similar to the more radiogenic measurements of modern Ganges river water (Levasseur et al., 1999) and Ganges bed load (Pierson-Wickmann et al., 2000). Mass-balance considerations suggest that total amount of $^{187}\text{Os}$ available from the LH black shales is sufficient to influence the osmium isotope composition of the global ocean (Singh et al., 1999).

Given that some workers argue that the LH carbonates are also the source of the unusually radiogenic strontium in the modern G–B system (English et al., 2000), it is tempting to link the rising strontium and osmium isotopic composition of global seawater from 15 Ma to the present to weathering of the lesser Himalaya. However, not all workers agree on the importance of LH carbonates in the G–B strontium budget (see Galy et al., 1999; Singh et al., 1998, and references therein). In addition, the onset of coupled increase of seawater strontium and osmium isotope ratios predates the estimated time of LH exposure to erosion at 11 Ma (Chesley et al., 2000). If input from the G–B is responsible for driving seawater strontium and osmium to more radiogenic isotope composition, the strontium and osmium fluxes provided by these rivers must have been substantially higher in the past (Singh et al., 1999; Chesley et al., 2000).

### 6.20.3.4.4 Glaciation and the marine strontium and osmium isotope records

Glaciation as a means of enhancing the flux of radiogenic strontium to the ocean is a second recurring theme in interpretations of the Cenozoic seawater strontium isotope record (Armstrong, 1971; Miller et al., 1988; Hodell et al., 1990; Capo and DePaolo, 1990). By comparison to the constraints on the timing of uplift and erosion in the HTP, the timings of major glacial events during the Cenozoic are very well established. Direct comparison of changes in slope of the marine strontium isotope record to oxygen isotope records that constrain changes in climate illustrates this clearly (Figure 6). For example, it has recently been argued that the initial rise in the Cenozoic $^{87}\text{Sr}/^{86}\text{Sr}$ record may be causally linked to the growth and decay of ice sheets in the Late Eocene and Early Oligocene (Zachos et al., 1999). Although changes in the slope of the $^{87}\text{Sr}/^{86}\text{Sr}$ record do occur close to the time of many other major glacial events, there is no systematic lead–lag relationship between the two records. For example, a local maximum in the slope of the $^{87}\text{Sr}/^{86}\text{Sr}$ record is nearly coincident with the first major glaciation of the Oligocene (Oi-1), but a similar local maximum clearly predates the Mi-1 glaciation (Figure 6). Nevertheless mass-balance calculations (Hodell et al., 1990; Blum, 1997) suggest that glacial enhancement of $^{87}\text{Sr}$ flux to seawater indicates that this is a plausible mechanism for driving at least part of the increasing seawater $^{87}\text{Sr}/^{86}\text{Sr}$ during the last several million years. Coupled studies of base cation flux and strontium isotopes demonstrate that silicate weathering rates are substantially increased, perhaps threefold compared to old saprolitic soils (Blum, 1997), and that the youngest moraines preferentially release $^{87}\text{Sr}$ (Blum and Erel, 1995). However, in glaciated regions with trace carbonate phases distributed throughout bedrock, rapid carbonate weathering can mute the $^{87}\text{Sr}/^{86}\text{Sr}$ signal of increased weathering rate (Jacobson et al., 2003). Thus, while glacially enhanced silicate weathering may be an effective agent of CO$_2$ drawdown, quantitatively estimating this effect based on the marine strontium isotope record is not a promising endeavor. Any such effort is further complicated by the fact that the seawater
strontium isotope record cannot capture high-frequency glacial forcing because of its long marine-residence time (Richter and Turekian, 1993; Henderson et al., 1994).

The short marine-residence time of osmium allows the isotope composition of seawater to change on glacial–interglacial timescales. Records spanning recent glacial events indicate substantial shifts, ~10%, toward lower-seawater $^{187}$Os/$^{188}$Os ratio during peak glacial conditions that are interpreted as diminished river flux to the ocean (Oxburgh, 1998). However, investigation of osmium release from glacial soil sequences shows that $^{187}$Os release is enhanced in a manner similar to that documented for $^{87}$Sr (Peucker-Ehrenbrink and Blum, 1998), suggesting that the net effect of glaciations should be to drive seawater $^{187}$Os/$^{188}$Os to higher values. This conclusion is supported by a recent investigation of the Eocene–Oligocene transition that demonstrates that the abrupt and permanent increase in seawater $^{187}$Os/$^{188}$Os ratio is contemporaneous with major Antarctic glaciation (Ravizza and Peucker-Ehrenbrink, 2003; see also Figure 7). Together, these studies provide evidence that the marine osmium isotope record is influenced by glacial cycles. This in turn suggests that the large amplitude, high-frequency glacial cycles play an important role in causing seawater osmium and strontium isotope compositions to shift to more radiogenic values in the latter part of the Cenozoic.

### 6.20.3.5 Variations in the Strontium and Osmium Isotope Composition of Riverine Input

The most widely recognized ambiguity associated with interpreting the marine strontium and osmium isotope records is the inability to distinguish between temporal changes in the isotopic composition of riverine input and temporal changes in the total flux of strontium and osmium to the ocean. Relatively early models recognized the significance of this uncertainty (Richter et al., 1992; Berner and Rye, 1992). Subsequent analyses of strontium isotope in paleosol carbonates (Quade et al., 1997) and pedogenic minerals in deep-sea clays (Derry and France-Lanord, 1996) yielded compelling evidence for $^{87}$Sr/$^{86}$Sr ratio of river input as high as 0.755 from the G–B river system 7.5 Myr ago. Prior to this time, riverine $^{87}$Sr/$^{86}$Sr ratio was 0.712, similar to global average riverine flux. Complementary analyses of osmium isotopes (Chesley et al., 2000) demonstrated coupled strontium and osmium isotope variations in rivers draining the Himalaya during the last 18 Myr (Figure 5). The studies are critically important because they demonstrate that significant temporal variations in riverine strontium and osmium isotope compositions can occur in a large river system. Given that the G–B river system is unusually radiogenic among modern rivers and yet still delivers only ~2% of

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**Figure 7** The marine osmium isotope record of the Eocene–Oligocene transition (Ravizza and Peucker-Ehrenbrink, 2003). The benthic foraminiferal oxygen isotope record from site 522 (Zachos et al., 1996) and a fit to the marine strontium isotope record are shown for comparison. Note that the rise of “ice house” conditions in the Early Oligocene is closely associated with an abrupt and permanent increase in seawater $^{187}$Os/$^{188}$Os. This provides evidence supporting the hypothesis that glaciation contributes to rising seawater $^{187}$Os/$^{188}$Os and $^{87}$Sr/$^{86}$Sr ratios ((-----)95% C. L. from McArthur et al., 2001).
the global riverine strontium flux, it is much less likely that such large and rapid changes in the strontium and osmium isotope composition of global average river flux can occur.

The combined osmium and strontium records are consistent with a shift to more radiogenic riverine isotope compositions during the Cenozoic (Figure 5). This suggests that erosion and weathering of unradiogenic lithologies were more important in the past. Several studies suggest that plateaus in the $^{87}\text{Sr} / ^{86}\text{Sr}$ record are caused by erosion of volcanic deposits characterized by low $^{87}\text{Sr} / ^{86}\text{Sr}$ values, either flood basalt provinces (Taylor and Lasaga, 1999; Dessert et al., 2001; McArthur et al., 2001) or island arc volcanics (Reusch and Maasch, 1998). The rapid decline in the slope of the $^{87}\text{Sr} / ^{86}\text{Sr}$ curve between 17 Ma and 14 Ma to near zero provides a specific Cenozoic example (Figure 6). This feature has been attributed to weathering of the Columbia River flood basalts (Hodell et al., 1990; Taylor and Lasaga, 1999), and also to island arc weathering accelerated by the collision of New Guinea with the Australian continent (Reusch and Maasch, 1998). However, emplacement of Ethiopian Traps in the Early Oligocene coincides with a much less pronounced decrease in slope of the $^{87}\text{Sr} / ^{86}\text{Sr}$ curve (Figure 6), even though it is estimated to be more than 3 times larger than the CRFB Province (Wignall, 2001). Thus, it seems unlikely that the plateau in the marine strontium isotope record between 17 Ma and 14 Ma can be attributed entirely to flood basalt weathering.

The influence of island arc and flood basalt weathering on the marine osmium isotope record is even less well understood. Analyses of modern rivers draining Papua New Guinea indicate that arc weathering represents an important source of unradiogenic osmium to seawater (Martin et al., 2000, 2001). Though detailed investigations of modern flood basalt weathering have not been made, the marine osmium isotope record across the Triassic–Jurassic boundary is consistent with the hypothesis that emplacement of the Central Atlantic magmatic province is responsible for a shift to lower $^{187}\text{Os} / ^{188}\text{Os}$ ratios (Cohen and Coe, 2002). However, available Cenozoic data do not yield evidence of a significant influence of either CRFB volcanism or arc-continent collision on the marine osmium isotope record between 14 Ma and 17 Ma (Reusch et al., 1998). The fact that the marine osmium isotope record continues to rise during the plateau in the strontium record supports the ideas outlined above that the unradiogenic sources of osmium and strontium are not tightly coupled. The pronounced excursion to un-radiogenic $^{187}\text{Os} / ^{188}\text{Os}$ values in the Late Eocene and at the K–T boundary provides additional evidence of Sr–Os decoupling (Figure 4). For the case of the K–T boundary extraterrestrial osmium associated with the K–T impact event is clearly an important factor; in the Late Eocene the influence of extraterrestrial osmium input is possible though less certain (Ravizza and Peucker-Ehrenbrink, 2003).

6.20.3.6 Osmium and Strontium Isotopes as Chemical Weathering Proxies

The need to constrain the geologic history of chemical weathering motivated the detailed reconstruction of past changes in the strontium and osmium isotope composition of seawater. While these combined records remain the best available indicators of changes in patterns of Cenozoic weathering, neither can be used to quantitatively reconstruct CO₂ consumption rates associated with chemical weathering. Silicate weathering rate is only one of the many factors that influences the flux of $^{87}\text{Sr}$ to the ocean. Detailed comparisons of strontium isotope data and river solute chemistry in modern rivers demonstrate that other factors, particularly the influence of strontium released by rapidly weathering carbonates, can obscure the contribution from silicate weathering (Palmer and Edmond, 1989; Jacobson et al., 2002a,b, 2003). Similarly for osmium, silicate-weathering contributions to the $^{187}\text{Os}$ flux are likely convoluted with those from weathering of organic-rich sediments. The former process represents a CO₂ sink in the weathering cycle, while the latter represents a CO₂ source. In addition, the $^{187}\text{Os} / ^{188}\text{Os}$ of osmium contributed by weathering of sedimentary organic matter is strongly influenced by the age of the sediment. This further complicates separating the various sources contributing to riverine osmium flux. Thus, for osmium, like strontium, there is no simple connection between seawater isotope composition and silicate weathering rates.

The marine strontium and osmium isotope records remain important records of ocean chemistry, because they do reflect the changing influence of continental inputs through time. In this regard the marine osmium isotope record has considerable unexplored potential because of its ability to respond to high-frequency external forcing, allowing detailed correlation with carbon and oxygen isotope records. For example, the excursion to more radiogenic seawater $^{187}\text{Os} / ^{188}\text{Os}$ ratio during the unusual warmth of the Paleocene–Eocene thermal maximum (PETM) provides the best available evidence supporting the operation of feedback between global climate and chemical weathering rates (Figure 8). The combined marine strontium (Figure 6) and osmium (Figure 7) isotope records are consistent with the hypothesis that the first major Oligocene glaciation (Oi-1) enhanced silicate weathering rates, providing a positive feedback for additional
cooling. Contemporaneous changes in the carbon isotopic composition of deep water (Figure 1) and a substantial deepening of the calcium carbonate compensation depth suggest that changes in the ocean–atmosphere carbon cycle were intimately associated with this climatic event. Considered in isolation, the marine strontium and osmium isotope records are ambiguous in that there is not a single unique interpretation of the underlying causes of these documented changes in global ocean chemistry. However, these records can place important constraints on the models of changing ocean chemistry when they are carefully integrated with other records of global climate and ocean chemistry.

6.20.4 Mg/Ca RECORDS FROM BENTHIC FORAMINIFERA

Over the past several years, Mg/Ca variations preserved in benthic foraminifera have received attention as a record of deep-ocean paleo-temperatures (Lear et al., 2000; Billups and Schrag, 2002). This work is part of a large and vigorous effort to exploit the potential of Mg/Ca ratio as a paleo-temperature proxy in both benthic and planktonic foraminifera on a variety of timescales. From a historical perspective, it is noteworthy that a positive correlation between the Mg/Ca ratio of biogenic calcite and precipitation temperature was recognized long ago (Chave, 1954). Other factors such as taxa, growth rate, and saturation state are also known to influence the Mg/Ca ratio of biogenic calcite (see Mackenzie et al. (1983) for a summary of this early work). These complicating factors detracted from early notions that Mg/Ca ratio of biogenic carbonates might be useful for reconstructing paleo-temperatures. Renewed interest in Mg/Ca ratio as a paleo-temperature proxy differs from these early efforts in many respects. For the purpose of this review some of the more important differences include improved analytical precision and accuracy, the emphasis on microfossils, and the abundance of complementary oxygen isotope data (see also Chapter 6.14).

6.20.4.1 Coupling Benthic Foraminiferal Mg/Ca and Oxygen Isotope Records

The Mg/Ca and δ18O of benthic foraminifers are both influenced by the temperature of calcification. This link is the reason that a discussion of Mg/Ca is included in this review. As outlined above, the oxygen isotope composition of biogenic calcite is a function of the temperature and the oxygen isotope composition of the water in which the organism calcified. For benthic foraminiferal records it is widely assumed that mainly the ice volume changes drive the temporal variations in the δ18O of seawater. Thus, benthic foraminiferal δ18O records have the dual influence of changing ice volume and deep-water temperatures embedded in them. Mg/Ca paleo-thermometry applied to benthic foraminifera offers the possibility of determining absolute deep-water temperatures. These temperature estimates can be used with the measured δ18O of the same benthic foraminifera to calculate temporal changes in δ18O of seawater. Reconstructions of the δ18O of seawater are of interest because variance in this parameter is strongly influenced by the growth and decay of ice sheets. Note however, that even with benefit of a well-constrained δ18O of
seawater record, quantitative estimates of Cenozoic ice volume still require assumptions about the average $\delta^{18}O$ of the global ice reservoir. Still the possibility of accurately determining deep-sea paleo-temperatures and simultaneously better constraining changing ice volume throughout the Cenozoic has motivated a great deal of recent interest in Mg/Ca variations in benthic foraminifera. Lear et al. (2000) first applied this approach to a composite record spanning much of the Cenozoic. More recently, this initial effort was supplemented by additional data from a Southern Ocean site spanning roughly the last 28 Myr (Billups and Schrag, 2002).

### 6.20.4.2 Calibration of the Mg/Ca Thermometer

Before discussing Cenozoic benthic foraminiferal Mg/Ca records, we present an overview of how Mg/Ca ratios measured in benthic foraminifera are used to calculate paleo-temperatures. The most recent calibration efforts postdate the most recent work on the Cenozoic Mg/Ca ratio. Revisions to the calibration equation and other aspects of core-top data sets have important implications for how Cenozoic benthic Mg–Ca records are interpreted. The influence of temperature on Mg/Ca ratio of mixed Cibicidoides reported by Lear et al. (2002; Figure 9(a)) is: 

$$(\text{Mg/Ca})_{\text{foram}} = 0.867e^{0.1097T},$$

where $T$ represents bottom-water temperature. Also, because these data are largely from core-top calibration studies, this formulation implicitly assumes that calcification occurs from modern seawater with a Mg/Ca ratio of approximately 5.2 mol mol$^{-1}$. Explicitly including the possibility of variable seawater Mg/Ca ratio results in a modified equation: 

$$(\text{Mg/Ca})_{\text{foram}} = R(0.867e^{0.1097}),$$

where $R$ is the Mg/Ca ratio of seawater at some time in the past divided by the present-day seawater Mg/Ca ratio. Other terms are the same as in the previous equation. The problems this possibility poses for Mg/Ca paleo-thermometry are conceptually similar to those presented by $\delta^{18}O$ of seawater variations in oxygen isotope paleo-thermometry, because shell composition depends both on the temperature and the composition of seawater. Variation in seawater Mg/Ca ratio is likely to be less directly coupled to climate change than $\delta^{18}O$ of seawater because changing ice volume should not directly influence seawater Mg/Ca ratio. Presumably seawater Mg/Ca ratio is less variable on short timescales, because the marine residence times of magnesium and calcium are relatively long. Current estimates of the oceanic residence times of calcium in seawater are ~1 Myr while estimates of magnesium residence times are substantially longer. Possible secular trends in seawater Mg/Ca ratio are discussed below.

Examination of core-top calibration data at low temperature (<5 °C), particularly those reported by Martin et al. (2002), reveals a distinctly stronger temperature dependence, and a more nearly linear relationship, than is indicated by the full data set (Figure 9(b)). If magnesium incorporation into biogenic calcite behaves as a true solid solution, equilibrium thermodynamics predicts that Mg/Ca ratio should depend exponentially on temperature. The deviation of the low-temperature data from the exponential best fit can be interpreted as evidence that factors other than temperature exert an increasingly important influence on the Mg/Ca ratio of foraminiferal calcite at these low temperatures (Lear et al., 2002). This calibration uncertainty is less important than the potential influence of factors other than temperature on Early Cenozoic benthic foraminiferal Mg/Ca records, because warm deep-water temperatures amplify the temperature component of Mg/Ca variation. Lear et al. (2002) include vital effects, dissolution artifacts, growth rate effects, and carbonate saturation state in a list of factors that may exert a secondary control on the Mg/Ca ratios of benthic foraminifera. Some of these same parameters have been recognized as important influences on the Mg/Ca ratio of larger calcifying organisms. For example, Mg/Ca ratios in coralline algae and pelecypods are influenced by growth rate, which is likely to be influenced by temperature (Moberly, 1968). A similar scheme of “nested” influences on Mg/Ca records of benthic foraminifera could be invoked to explain the unusually strong apparent influence of temperature on Mg/Ca ratio in the study by Martin et al. (2002) (see Figure 9(b)).

### 6.20.4.3 Cenozoic Benthic Foraminiferal Mg/Ca Records

Although recent studies of benthic foraminiferal Mg/Ca ratio variations do not span the entire Cenozoic, one study (Lear et al., 2000) does extend back to approximately 50 Ma capturing the unusual warmth of the Eocene climatic optimum. A second study (Billups and Schrag, 2002) reports additional data spanning the last 28 Myr. Results from these two studies are grossly similar in that both show generally decreasing Mg/Ca ratios in benthic foraminifera with time (Figure 10). This is consistent with cooling deep-water temperatures. However, direct comparison of the two data sets is made complicated by several factors. Lear et al. (2000) compiled a composite record that includes several different species of benthic foraminifera. Differences between measured Mg/Ca ratios of coexisting species were interpreted as evidence of vital effects, and data were adjusted by empirical correction factors to yield a record that is effectively normalized to O. umbonatus.
In addition, this record was smoothed in order to facilitate comparison to composite benthic foraminiferal δ18O records. In contrast, the Billups and Schrag (2002) record is based predominately on a single species, C. mundulus, with some additional data from C. wuellerstorfi. Smoothing is not required for calculating δ18O of seawater in this record because paired Mg/Ca and δ18O data are available for the majority of the samples. This approach is desirable because it provides a framework for examining higher-frequency variations in deep-water temperature and δ18O of seawater. Comparison of these two data sets, in the context of the recent calibration efforts discussed above, indicates that application of the Mg/Ca paleo-temperature proxy to benthic foraminifera is more complicated than initially assumed.

Potential analytical bias, vital effects, and calibration issues all complicate interpretation of the records shown in Figure 10. Measured benthic foraminiferal Mg/Ca ratios in site 747 (Billups and Schrag, 2002) are in general higher than in coeval samples from the composite record of...
Lear et al. (2000) implying warmer temperatures. The sense of this offset is unexpected given the high latitude of site 747. A systematic analytical bias between the two data sets is possible because different methods were used to make Mg/Ca measurements. Note that applying corrections used by Lear et al. (2000) to normalize C. mundulus (+0.15) and C. wuellerstorfi (+0.45) to normalize Mg/Ca data to O. umbonatus tend to amplify this difference. It is noteworthy that core-top analyses discussed above (Lear et al., 2002) did not substantiate a systematic offset between O. umbonatus and C. wuellerstorfi, highlighting the fact that the general question of vital effects remains open. Although the best available calibration (Figure 9(a)) is based on a mixed assemblage of Cibicidoides, C. mundulus is not included. Note that not all extant Cibicidoides species conform to the calibration shown in Figure 9(a) (Lear et al., 2002). Thus, even the nearly monospecific data set of Billups and Schrag (2002) does not entirely avoid potential problems associated with vital effects. Uncertainty in the functionality of the appropriate Mg/Ca calibration also deserves mention. Billups and Schrag (2002) used a linear calibration curve linking Mg/Ca to temperature rather than an exponential fit. The slope of the calibration line is essentially identical to that shown by the Martin et al. (2002) data (Figure 9(b)), but as noted above there is an offset in absolute Mg/Ca ratio. Applying the more recent exponential calibration (Lear et al., 2002) to the Billups and Schrag (2002) data set amplifies the amplitude of calculated temperature variations and increases the average temperature by approximately 3 °C (Figure 11). These differences propagate directly into calculated records of δ18O of seawater. Given that modern calibration studies can yield linear Mg/Ca versus temperature responses at low temperature (Figure 9(b)),

Figure 10 Comparison of Mg/Ca ratios measured in benthic foraminifera from a smoothed, composite record (thick solid curve: Lear et al., 2000), and from site 747 (filled circles: Billups and Schrag, 2002). Both records display an overall trend of declining Mg/Ca ratio with decreasing age. This trend is indicative of cooling deep-water temperatures during the Cenozoic.

Figure 11 Comparison of deep-water temperatures calculated from the Mg/Ca data of Billups and Schrag (2002) using the linear calibration originally used in this publication and the more recent exponential calibration reported by Lear et al. (2002).
careful consideration of the appropriate calibration approach is warranted. This is particularly true in the Late Cenozoic where deep-water temperature estimates tend to be lower.

6.20.4.4 Changing Seawater Mg/Ca Ratio

Possible variations in the Mg/Ca ratio of seawater during the Cenozoic also contribute uncertainty to temperature estimates based on Mg/Ca ratios measured in benthic foraminifera (see Billups and Schrag 2002 for a discussion of model based estimates of the Cenozoic evolution of seawater Mg/Ca ratios; see also Chapter 6.21). Analyses of fluid inclusions in evaporites (Zimmermann, 2000) are consistent with declining seawater Mg/Ca ratio during the Cenozoic. Taken at face value these data suggest a 12% seawater magnesium depletion 5 Myr ago, and further declining to 30–40% of modern value by the Late Eocene (37 Myr ago). However, Zimmermann (2000) notes that dolomitization of calcium carbonate during evaporite formation could create the false impression of lower-seawater magnesium concentrations in the fluid inclusion data. On Phanerozoic timescales, seawater Mg/Ca estimates based on fluid inclusions (Lowenstein et al., 2001) and fossil echinoderms (Dickson, 2002) yield similar records. This lends some credibility to estimates of Cenozoic seawater Mg/Ca ratio based on fluid inclusions. Based on benthic δ18O data, the assumption of ice-free conditions, and the revised Mg/Ca temperature calibration, Lear et al. (2002) calculated that the maximum likely depletion in seawater Mg/Ca ratio was approximately 35%. Even though the magnitude of this estimate is similar to fluid inclusion-based estimates, the timing of these changes remains ill-constrained. While substantial uncertainty remains in converting foraminiferal Mg/Ca data to absolute temperature, it is clear that this proxy has great potential. Likely the most immediate progress will be made in studies that emphasize high temporal resolution and couple Mg/Ca and stable oxygen isotope data to deconvolve the dual influence of changing deep-water temperatures and ice volume during events of rapid growth and decay of ice sheets. On these short timescales abrupt changes in seawater Mg/Ca proportions are unexpected.

6.20.5 BORON ISOTOPEs, PALEO-pH, AND ATMOSPHERIC CO2

The boron isotopic composition of calcite precipitated by foraminifera has been used to reconstruct the pH of the ancient seawater. In appropriate oceanographic settings, pH estimates derived from boron isotope analyses of planktonic foraminifera, in conjunction with additional assumptions about the dissolved inorganic carbon inventory in the surface ocean, can be used to calculate atmospheric CO2 concentrations. Declining levels of atmospheric CO2 have been invoked commonly (Raymo and Ruddiman, 1992) as a potentially important causative factor in long-term cooling and the expansion of polar ice that is indicated by the Cenozoic benthic δ18O record (Figure 1). In this context, the use of boron isotopes as a paleo-pH proxy represents an important new record of changing ocean chemistry during the Cenozoic.

6.20.5.1 The pH Dependence of Boron Isotope Fractionation

There are two stable isotopes of boron, 10B and 11B. 10B is the more abundant of the two, accounting for ~80% of all boron atoms. Variations in boron isotope abundance are reported relative to an NIST boric acid standard as δ11B. In seawater there are two different species of boron. The relative proportion of the two species is a function of pH as indicated by the reaction

\[ \text{B(OH)}_3 + H_2O = \text{B(OH)}_4^- + H^+ \]

The pKa of boric acid is ~8.7 so that in the pH range relevant to seawater, 7.2–8.2, these two forms of boron coexist. Isotope exchange equilibrium with respect to boron isotopes occurs rapidly such that 10B is preferentially partitioned into the tetrahedral B(OH)4 species relative to trigonal boric acid species. At isotopic equilibrium the difference between the δ11B of these two species is close to 20 per mil. This isotope fractionation factor appears to be largely insensitive to other factors such as temperature and pressure. Given the constant contrast in δ11B between B(OH)3 and B(OH)4, mass-balance considerations require that the δ11B of the two species vary systematically with pH. The δ11B of each species can be calculated explicitly once the δ11B of seawater, the pKa of boric acid, and the isotope fractionation are specified (Figure 12). It is important to note that because the pKa of boric acid is temperature dependent, calcification temperature can also exert an important influence on the δ11B of the B(OH)4 species (Palmer et al., 1998). It is also noteworthy that at the low end of the seawater pH range boron isotopes lose sensitivity as a pH proxy, because the slope of the δ11B versus pH curve (Figure 12) becomes nearly flat for both the boron species. This reflects the fact that boron occurs dominantly as boric acid at these lower pH values with only roughly 2% of B(OH)4.
6.20.5.2 Boron Partitioning into Calcite

Both inorganic precipitation experiments (Sanyal et al., 2000) and culture experiments (Sanyal et al., 1996, 2001) have shown that the isotopic composition of boron incorporated into calcite is a function of pH (Figure 13). The measured $\delta^{11}$B of calcite precipitated over a range of pH are similar to that predicted for $\text{B(OH)}_4^-$ indicating that the anionic species of boron is selectively partitioned into calcite as suggested in earlier studies (Vengosh et al., 1991; Hemming and Hanson, 1992). The selective partitioning of a single boron species into calcite effectively records the pH of the water from which the calcite precipitated. Culture studies exhibit a systematic offset in the $\delta^{11}$B measured in different species of foraminifera indicating that vital effects can influence the absolute $\delta^{11}$B of foraminiferal calcite. Detailed comparison to theoretical predictions of boron isotope fractionation is hampered by uncertainties in both the isotope fractionation factor and the pK$_a$ of boric acid. Both vital effects in the biogenic material and kinetic factors in the inorganic system may contribute to the variable offset between the $\delta^{11}$B of biogenic and inorganic calcite (Figure 13). In the case of planktonic foraminifera that host photosymbionts, daytime drawdown of CO$_2$ within a microenvironment may contribute to the documented vital effect (Sanyal et al., 2001). Correlated variations in $\delta^{11}$B and $\delta^{13}$C in modern coral support such an interpretation (Hemming et al., 1998a). Investigations of both core-top and cultured specimens of *G. sacculifer* and *O. universa* show a similar $\delta^{11}$B offset relative to one another providing strong evidence that species-dependent vital effects do influence the $\delta^{11}$B of planktonic foraminiferal calcite (Sanyal et al., 2001; Figure 13).

The few analyses of boron concentration variations in calcite as a function of precipitation pH that have been done in culture (Sanyal et al., 1996) and inorganic precipitation (Sanyal et al., 2000) experiments indicate that boron concentrations increase with increasing precipitation pH. This observation is grossly consistent with

![Figure 12](image-url) Schematic illustration of isotopic contrast between coexisting boron species as a function of pH. The range of pH shown encompasses all pH values relevant to seawater. Note that at low-pH boric acid dominates the boron inventory and $\delta^{11}$B becomes relatively insensitive to small pH changes. These curves were calculated using a pK$_a$ of 8.7 for boric acid, a constant isotopic fractionation of 20 per mil between the two boron species, and $\delta^{11}$B of 39.6 per mil for the total seawater boron reservoir.
the increasing concentration of B(OH)$_4^-$ with increasing pH and a simple proportionality between the B(OH)$_4^-$ concentration in seawater and the boron concentration in calcite. Although there is some scatter in the available data, these results suggest that boron concentration analyses may be complementary to $\delta^{11}$B analyses in paleo-pH reconstructions. However, it is important to note that subtle surface structural effects can give rise to sixfold variations in boron concentration on small spatial scales within a single crystal (Hemming et al., 1998b). Thus, it could be argued that $\delta^{11}$B could accurately record precipitation pH, even though boron concentrations do not exhibit the systematic variation expected based on simple models of element partitioning. While much remains to be learned about the details of boron incorporation into inorganic and biogenic calcite, available data yield strong evidence that calcite $\delta^{11}$B can record the pH of the solution from which it precipitated.

6.20.5.3 Paleo-pH and Atmospheric CO$_2$

Reconstruction

Several efforts to reconstruct the pH of ancient seawater have been made, starting with the work of Spiavack et al. (1993). Efforts to quantify changes in surface and deep-water pH during recent glacial–interglacial cycles followed Sanyal et al., 1995, 1996, 2000, 2001). The shape of the dashed curves is that predicted by the pH control on the $\delta^{11}$B of B(OH)$_4^-$ . The position of these curves was adjusted to fit the O. universa and G. sacculifer data, highlighting the nearly constant boron isotopic offset between these two species of planktonic foraminifera. The upper curve closely approximates the calculated $\delta^{11}$B of B(OH)$_4^-$ (see Figure 12). Note that the O. universa and G. sacculifer data plotted include both cultured foraminifera and core-top samples.

Records of Cenozoic Ocean Chemistry

![Figure 13](image_url) Summary of efforts to calibrate $\delta^{11}$B variations in calcite as a function of the pH of precipitation. Results are replotted from Sanyal et al. (1995, 1996, 2000, 2001). The shape of the dashed curves is that predicted by the pH control on the $\delta^{11}$B of B(OH)$_4^-$ . The position of these curves was adjusted to fit the O. universa and G. sacculifer data, highlighting the nearly constant boron isotopic offset between these two species of planktonic foraminifera. The upper curve closely approximates the calculated $\delta^{11}$B of B(OH)$_4^-$ (see Figure 12). Note that the O. universa and G. sacculifer data plotted include both cultured foraminifera and core-top samples.

Ocean over Cenozoic timescales as a means of constraining atmospheric CO$_2$ variations. In the modern ocean pH exhibits substantial spatial variability unrelated to atmospheric CO$_2$ levels. For example, in highly productive regions pH can vary by as much as 0.7 pH units in the upper 1,000 m to values below 7.5. This variability is driven largely by the production of CO$_2$ during oxidation of sinking organic matter. By concentrating their efforts on a region of the ocean that is likely to have remained thermally stratified, and exhibited only modest productivity variations, Palmer et al. (1998) argued that surface-dwelling foraminifera are likely to have grown in waters close to exchange equilibrium with respect to atmospheric CO$_2$. Analyses of multiple species of foraminifera believed to calcify over distinct depth ranges exhibit trends of $\delta^{11}$B that become less positive with increasing depth in the water column (Palmer et al., 1998). This is consistent with the expected trend of decreasing pH with increasing depth, resulting from organic matter oxidation in the water column. By applying a similar approach to an assemblage of Eocene foraminifera, Pearson and Palmer (1999) estimated the $\delta^{11}$B of Eocene seawater to fall between 38 per mil and 41 per mil, with a most likely value of 40.5 per mil. Values greater than 41 per mil imply a very steep vertical pH gradient and absolute pH values so low as to interfere with calcification. Seawater $\delta^{11}$B lighter than 38‰ imply only small pH changes with depth, and these authors argued that the low productivity implied by such a shallow pH gradient was unlikely. Only gradual changes in $\delta^{11}$B of seawater are likely, because the marine residence
time of boron is on the order of 10 Myr. Detailed paleo-pH profiles at a few time intervals distributed throughout the Cenozoic (Palmer et al., 1998; Pearson and Palmer, 1999) provide a framework constraining seawater $\delta^{11}$B during the Cenozoic. In a follow-on study Pearson and Palmer (2000) combined data from analyses of planktonic foraminifera that calcified in the mixed layer with their model-based constraints on seawater $\delta^{11}$B to make 35 individual surface water pH estimates distributed over the past 60 Myr (Figure 14). To estimate atmospheric CO$_2$ from this surface ocean pH requires additional assumptions. As noted above the surface waters at this site are assumed to remain close to equilibrium with respect to atmospheric CO$_2$ throughout the Cenozoic. Second, an independent estimate of either total alkalinity or total DIC is required to calculate the partial pressure of CO$_2$ from pH. To make this estimate, Pearson and Palmer (2000) used reconstructions of CCD, and assumed the depth of calcite saturation relative to the CCD remained invariant with time. They further assumed that the vertical gradient in alkalinity remained constant with time and that the calcium concentration of seawater varied in concert with alkalinity.

Although the atmospheric CO$_2$ record resulting from the Pearson and Palmer (2000) study is subject to substantial uncertainty, several features of the record are of interest. Although Figure 14 does indicate that CO$_2$ levels were roughly 10 times higher than present-day levels during the Early Eocene, the record as a whole does not, however, suggest a gradual decline in CO$_2$ levels throughout the Cenozoic. This is best illustrated by the variability in the middle Eocene CO$_2$ estimates ranging over nearly an order of magnitude on relatively short timescales. Note that this time is characterized by relatively light benthic $\delta^{18}$O values indicative of warm deep-water temperatures and little or no polar ice (Figure 1). The last 25 Myr of the CO$_2$ reconstruction show smaller amplitude variations with the majority of data suggesting values between 200 ppm and 400 ppm. Reconstructions of CO$_2$ between 16 Ma and 4 Ma based on carbon isotope variations in alkenones yield similar values ranging between 180 ppm and 320 ppm (Pagani et al., 1999). As these two methods are largely independent of one another, the similarity of the two data during the time interval where they overlap lends credibility to the combined data sets. Both records suggest a component of high-frequency variation in atmospheric CO$_2$ levels, but detailed comparison of the two records is hampered by the low-temporal resolution of the two records. For example, the boron isotope record suggests that high atmospheric CO$_2$ levels may have been associated with emplacement of the Columbia River flood basalts at $\sim$17 Ma, while the expansion of the East Antarctic ice sheet at 15 Ma may be associated with a local minimum in CO$_2$ (Pearson and Palmer, 2000). In contrast, alkenone-based CO$_2$ estimates do not indicate a pronounced CO$_2$ decrease during expansion of the east Antarctic ice sheet (Pagani et al., 1999). Based on available data it is unclear if these two records contradict one another or if aliasing of high-frequency variation simply creates this impression.

![Figure 14](image)

**Figure 14**  Estimates of mixed-layer pH and atmospheric CO$_2$ derived from boron isotope analyses of planktonic foraminifera recovered from drill cores taken in the western equatorial Pacific. Results are replotted from Pearson and Palmer (2000). Note that uncertainty associated with both pH and CO$_2$ estimates amplifies in the Early Cenozoic. This reflects the intrinsic insensitivity of the boron isotope pH proxy at low pH (see Figure 12). Atmospheric CO$_2$ estimates require additional assumptions about the size of the DIC pool in surface waters.
6.20.5.4 Outstanding Questions about Paleo-pH Reconstructions

Several important questions related to the use of boron isotopes as a paleo-pH proxy remain unanswered. While progress has been made documenting the presence of vital effects on the δ11B of biogenic calcite (Sanyal et al., 2001; Hemming et al., 1998a), further work on this issue is required. Reconstruction of Early Cenozoic pH requires working with planktonic foraminifera that are no longer extant and thus vital effects cannot be well constrained without a substantial additional effort to work on multiple species with overlapping age ranges. Dissolution effects and diagenetic alteration are known to adversely affect the application of other paleoceanographic proxies, and the influence of this phenomenon on δ11B is yet to be investigated. Given that tropical planktonic foraminifera are particularly vulnerable to diagenetic alteration on the seafloor (Pearson et al., 2001), the influence of this process on δ11B of foraminiferal calcite is important to evaluate. Recent efforts to estimate glacial–interglacial pH changes in deep waters that are based on preservation of carbonate microfossils (Anderson and Archer, 2002) have yielded results that are at odds with boron-isotope-based estimates (Sanyal et al., 1995), also highlighting the need for additional work. The potential for temporal variations in the δ11B of seawater also warrants additional investigation. Model calculations based on a refined version of the present-day marine boron cycle, and assumptions about oceanic crustal production and weathering rates (Lemarchand et al., 2000) suggest that temporal changes in the δ11B of seawater may be substantially larger than estimated by Pearson and Palmer (2000) using the pH profile approach. The model calculations of Lemarchand et al. (2000) suggest that seawater δ11B could have been as low as 36 per mil. If true, this would imply that the high CO2 levels estimated in the Early Cenozoic (Figure 14) are incorrect and that levels similar to modern values are more likely. Thus, independent data constraining the δ11B of seawater would also represent an important contribution to advancing the use of boron isotopes as a paleo-pH proxy. Both continuing refinements to application of boron isotopes to paleo-pH reconstructions and coupled application of independent means of estimating paleo-pCO2 levels are important areas for future work.

6.20.6 CLOSING SYNTHESIS: DOES OROGENESIS LEAD TO COOLING?

Recently much debate has focused on the hypothesis that increased silicate weathering rates, associated with Himalayan uplift, played a causative role in long-term Cenozoic cooling by reducing atmospheric carbon dioxide levels (Raymo et al., 1988; Raymo and Ruddiman, 1992). Indeed, it seems appropriate to revisit this idea at the close of this review because the idea fueled much of the effort to refine and integrate the paleoceanographic records discussed above. What is the current status of this idea? Two key problems with the “orogenesis leads to cooling” hypothesis as initially articulated by Raymo and co-workers have been raised. First, simple mass-balance considerations preclude the possibility of accelerated rates of CO2 drawdown by chemical weathering throughout the Cenozoic without a comparable increase in the flux of CO2 to the atmosphere from volcanic and metamorphic sources (Caldeira et al., 1993; Volk et al., 1993; Berner and Caldeira, 1997; Broecker and Sanyal, 1998). Second, recent efforts to determine the history of atmospheric CO2 levels suggest that cooling and ice growth during the Neogene are not associated with systematic decreases in atmospheric CO2 (Pagani et al., 1999; Pearson and Palmer, 2000), also undermine this hypothesis.

In spite of the critiques outlined in the preceding paragraph, it is inappropriate to discount entirely the role of orogenesis in Cenozoic cooling entirely. The mass-balance problems outlined above can be addressed. Kump and Arthur (1997) presented a conceptual framework in which steady-state levels of atmospheric CO2 could be reduced without changes in global weathering flux by increasing “weatherability.” In essence they argued that tectonic and climatic factors could act to allow weathering fluxes to remain high enough to balance CO2 input in spite of significantly cooler global climate. This concept provides a defensible framework for a causative link between Himalayan uplift and global cooling, because physical weathering can be reasonably argued to enhance “weatherability” (Kump et al., 2000). It also provides a basis for arguing that a limited decoupling of average global temperatures and silicate weathering rates played an important role in Cenozoic cooling. Both of these are key components of the “orogenesis leads to cooling” hypothesis.

The available data constraining the Cenozoic history of atmospheric CO2 suggest nearly 10-fold higher concentration during the Paleocene and Early Eocene, relative to the Neogene (Pearson and Palmer, 2000). Thus, the gross contrast between the unusual warmth of the Early Paleogene and the “ice house” conditions of the Neogene can still be interpreted as the result of tectonically driven changes in weathering, even though the many features of Neogene climate change cannot. It is likely that factors other than orogenesis contributed to enhanced weatherability.
during the Cenozoic. For example, accelerated physical erosion due to glaciation may greatly increase the area of fresh mineral surfaces available to chemical weathering (Blum, 1997; Zachos et al., 1999). Many factors, in addition to atmospheric CO$_2$ concentration, may influence Earth’s climate over the course of the Cenozoic. Thus while the “orogenesis leads to cooling” hypothesis is not dead, it does not provide a single unified explanation of the established record of Cenozoic climatic variation.

The mass-balance argument that CO$_2$ consumption by silicate weathering cannot outpace CO$_2$ production by volcanic and metamorphic degassing also has important implications for interpretation of heavy isotope records. If, to first approximation, the average long-term rate of silicate weathering has remained constant during the Cenozoic, and this can be extended to the total flux of strontium and osmium, then the variations in the marine $^{87}$Sr/$^{86}$Sr and $^{187}$Os/$^{188}$Os records are better interpreted as the result of changing isotopic composition of riverine flux (Kump and Arthur, 1997). Under this interpretation, the Cenozoic strontium and osmium isotope record imply a secular change in the age and/or composition of weathered material. Both records suggest that the Cenozoic is characterized by an increasing contribution from older material with a cratonic affinity and radiogenic strontium and osmium characteristics relative to recently mantle-derived material (Figure 5). Such a shift in the nature of weathered material might influence “weatherability,” or if it would at all, has not been considered in detail.

The efforts of many researchers have contributed to a greatly improved history of Cenozoic ocean chemistry and climate history. These efforts have revealed a great deal of fine structure in these records that is global in nature, ranging from episodes of unusual warmth such as the PETM to episodes of rapid glacial expansion in the Early Oligocene and Early Miocene. It is possible that short-term fluctuations in atmospheric CO$_2$ played an important causative role in some of these events, even though available data argue against a simple causal link between atmospheric CO$_2$ and long-term Cenozoic cooling. A refined vision of a global thermostat originally proposed by Walker et al. (1981) that includes secular changes in global “weatherability” (Kump and Arthur, 1997) can be invoked to explain how a negative feedback between global temperature and silicate weathering rate can stabilize Earth’s climate system in the wake of large perturbations.

The causes of events that perturb Earth’s climate system are less well understood and more varied in nature. Understanding these phenomena likely requires studies that focus on specific climatic events rather than long-term climate evolution. Careful integration of the various paleo-proxies discussed in this review offers the potential for the first time to establish the lead–lag relationships between ice growth, deep-water temperature change, continental weathering, and atmospheric CO$_2$ during important climate transitions and on timescales similar to the residence of inorganic carbon in the ocean-atmosphere system. These types of studies will represent a major step forward in our ability to test fundamental hypotheses about the underlying causes of the many climate changes documented during the Cenozoic. This integrated multiproxy approach may also lay a foundation for exploring the possibility that these short-term climate events can influence Earth’s long-term climate evolution.

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