

c0011 Carbon Isotope Stratigraphy

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s0010 11.1. PRINCIPLES OF CARBON ISOTOPE STRATIGRAPHY

p0015 The potential of marine carbonate $\delta^{13}\text{C}$ values to date and correlate rocks relies on the fact that their $^{13}\text{C}/^{12}\text{C}$ values have varied over time, mainly as the result of partitioning of carbon between organic carbon and carbonate carbon reservoirs in the lithosphere (e.g., Shackleton and Hall, 1984; Berner, 1990; Kump and Arthur, 1999; Falkowski, 2003; Sundquist and Visser, 2004). Precipitation of carbonates involves little carbon isotopic fractionation relative to dissolved inorganic carbon (DIC), and the $\delta^{13}\text{C}$ of carbonate is relatively insensitive to changes in temperature (about 0.035‰ per °C; Lynch-Stieglitz, 2003). Therefore the $\delta^{13}\text{C}$ of inorganically and biologically precipitated carbonate in the oceans is very close to that of the DIC in the oceans (Maslin and Swann, 2005), the largest reservoir in the recent ocean-atmosphere system (Figure 11.1). To explain changes in this isotopic signature we need to consider the global carbon cycle on different time scales (Falkowski, 2003; Sundquist and Visser, 2004).

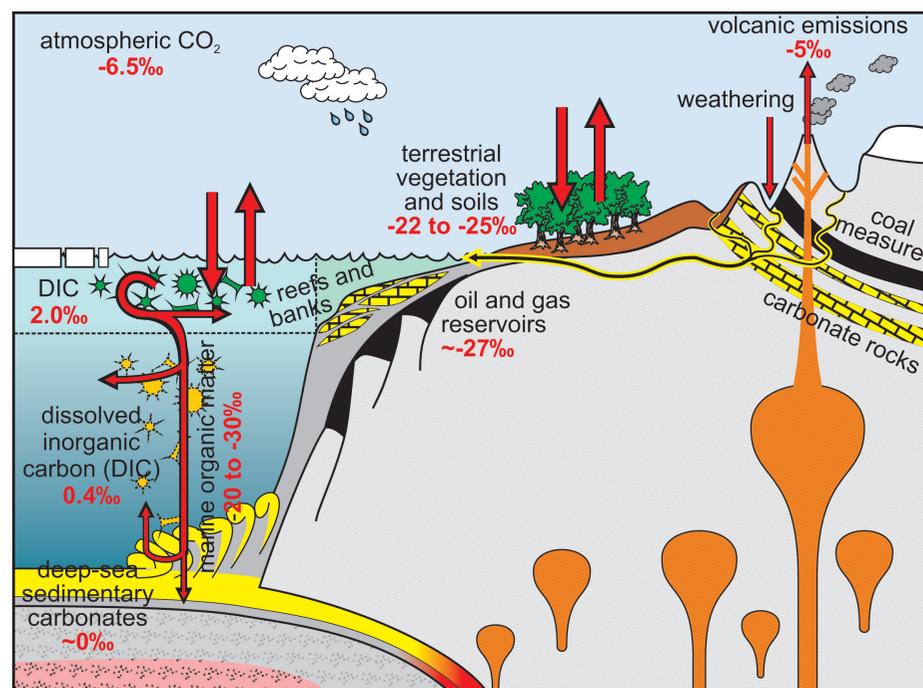
p0020 Carbon cycling between the ocean and the atmosphere occurs on time scales of <1000 years. At the present pH conditions of sea water (7.5–8.3), >90% of the carbon in the deep ocean is present as bicarbonate (HCO_3^-). The deep oceanic DIC reservoir is about 50 to 60 times as large as the atmospheric reservoir was in pre-industrial times (e.g., Ravizza and Zachos, 2003; Sundquist and Visser, 2004; Sarmiento and Gruber, 2006; Houghton, 2007). Carbon in the atmosphere is present as carbon dioxide (CO_2), whereas the lithosphere, which exchanges carbon

with the ocean-atmosphere system on longer time scales (10^5 – 10^6 years), contains carbon in both organic matter and carbonate rock (limestones and dolomites) (Berner, 1990).

The carbon isotopic composition of CO_2 in the atmosphere was about -6.4 ‰ prior to anthropogenic fossil fuel burning, close to the mantle value of about -6 ‰ (Sundquist and Visser, 2004) (Figure 11.1). The photosynthetic fixation of carbon using atmospheric CO_2 involves a large negative fractionation, so that all organic carbon compounds are strongly depleted in ^{13}C relative to atmospheric CO_2 (e.g., Maslin and Thomas, 2003). Most Recent land plants use the C3 photosynthetic pathway, and have $\delta^{13}\text{C}$ values between -23 and -33 ‰ (mean value ~ -26 ‰). Plants in dry regions (tropical grasses, salt water grasses) use a different photosynthetic pathway (C4), and have $\delta^{13}\text{C}$ values ranging from -9 to -16 ‰ (mean value ~ -13 ‰) (Maslin and Thomas, 2003). The photosynthetic reaction pathways of marine phytoplankton are less well-known; $\delta^{13}\text{C}$ values in marine phytoplankton range between -10 and -32 ‰ (most lie between -17 and -22 ‰) depending upon temperature, with values in the tropics ranging up to -13 ‰, and at high latitudes as low as -32 ‰ (Sarmiento and Gruber, 2006).

The $\delta^{13}\text{C}$ value of whole-ocean DIC has not been constant over geologic time. Variations in $\delta^{13}\text{C}$ in DIC in the oceans over time scales of tens of thousands of years or less, as for instance seen in the Quaternary glacial/interglacial cycles, can be understood in terms of redistribution of carbon among the Earth's surface carbon reservoirs, i.e., atmosphere, oceans, biosphere and superficial sediments (see

f0010 **FIGURE 11.1** The carbon reservoirs of the present (pre-industrial) carbon cycle with their carbon isotopic composition. The numbers showing the size of reservoirs are expressed in the units presently most commonly used in the literature: petagrams carbon (Pg C, 10^{15} g carbon). Figure after Dunkley-Jones et al., 2010.



e.g., Sundquist and Visser, 2004). Over timescales of hundreds of thousands to millions of years, variations in $\delta^{13}\text{C}$ of DIC are mainly the results of changes in the size and rate of the exchange fluxes between the Earth's surface carbon reservoirs and the lithosphere (e.g., Berner, 1990; Kump and Arthur, 1999; Sundquist and Visser, 2004; Maslin and Swann, 2005), specifically storage in the lithosphere of varying amounts of carbon as organic carbon relative to the amount stored in carbonates. The lithospheric organic carbon reservoir includes coal measures, oil and gas reserves, but is dominated by dispersed organic matter (Figure 11.1). Presently the carbon out-flux from the oceans into calcium carbonate is about 4 times as large as the out-flux of carbon into organic matter (Shackleton and Hall, 1984; Shackleton, 1987). If relatively more/less carbon is removed from the oceans in organic matter (relative to carbonate), the $\delta^{13}\text{C}$ value of DIC in the whole ocean increases/decreases (Shackleton, 1987; Berner, 1990; Kump and Arthur, 1999; Hayes et al., 1999; Derry et al., 1992; Des Marais et al., 1992; Zachos and Ravizza, 2003; Sundquist and Visser, 2004; Maslin and Swann, 2005). When there is net deposition of organic matter globally, the $\delta^{13}\text{C}$ value of DIC in the whole ocean increases; when there is net oxidation of organic matter globally, the $\delta^{13}\text{C}$ value of DIC in the whole ocean decreases.

[AU1]

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The carbon isotopic composition of DIC in the oceans is not only linked to the $\delta^{13}\text{C}$ of CO_2 in the atmosphere through exchange between the atmosphere and surface ocean, but also through circulation between surface and deep waters in the oceans: the "atmosphere is the slave of the ocean" because of its

much smaller size (Sundquist and Visser, 2004; Maslin and Swann, 2005). A change in carbon isotope composition of the large oceanic DIC reservoir is thus reflected in the isotopic composition of other components of the carbon cycle, within times on the order of circulation of the deep-sea (~1000 years) (Figure 11.1): organic matter in marine and terrestrial sediments (Hayes et al., 1999), plant material (e.g., Robinson and Hesselbo, 2004), carbonate nodules in soils (Ekart et al., 1999), and carbonate in herbivore teeth (e.g., Koch et al., 1992).

This coupling between carbon isotope values in DIC and organic matter may not have been in existence in the Proterozoic, when the reservoir of dissolved and particulate organic carbon may have been much larger than that of DIC (Rothman et al., 2003, Fike et al., 2006; McFadden et al., 2008; Swanson-Hysell et al., 2010), although there are potentially diagenetic explanations for this lack of coupling (e.g., Derry et al., 2010). [AU2] Until the early 1990s, changes in the sizes of the global reservoirs were thought to have occurred on time-scales of 10^5 to 10^6 years and more (the oceanic residence time of carbon being about 10^5 years), because oceanic deposition and erosion and weathering on land cannot be re-organized quickly (e.g., Shackleton, 1987; Magaritz et al., 1992; Thomas and Shackleton, 1996). More recently, negative carbon isotope excursions (NCIEs) have been documented with a duration of several ten thousands to hundred thousands of years, with transition into the NCIE possibly over $\ll 10^4$ years, although this is still under discussion (Zachos et al., 2007, Cui et al., 2011). Such NCIEs include the one during the Paleocene-Eocene Thermal Maximum (PETM; ~ 55.5 Ma; p0040

e.g., Kennett and Stott, 1991; Sluijs et al., 2007), smaller NCIEs during other late Paleocene and early Eocene hyperthermal events (Cramer et al., 2003; Lourens et al., 2005), and possibly earlier events, for example the Early Cretaceous and Early Jurassic ~183 Ma Oceanic Anoxic Events (Jenkyns, 1985, 2010; Gröcke, 2002; Gröcke et al., 2003; Cohen et al., 2007; but see also McArthur et al., 2008) and the Permo-Triassic extinction event (e.g., Magaritz et al., 1992; Erwin, 1993; Bowring et al., 1998; Berner, 2002; Retallack and Jahren, 2008). The origin of these rapid, global, negative CIEs is under debate, but they require a fast input of large amounts of isotopically light carbon into the ocean-atmosphere from a lithospheric source, e.g., methane from dissociation of clathrates, as proposed independently for the Permo-Triassic by Erwin (1993) and for the Paleocene-Eocene by Dickens et al. (1995) and Matsumoto (1995), or organic matter heated by volcanic intrusions (Svensen et al., 2004), or various combinations of oxidation of organic matter and hydrates (reviews by Zeebe et al., 2009; Dickens 2011). Such NCIEs have been compared to the effects of anthropogenic fossil fuel burning, which has occurred over a few centuries, resulting in a decrease in $\delta^{13}\text{C}$ of atmospheric CO_2 from about -6.4 to -7.9‰ (Francey et al., 1999), and propagating into the oceans (e.g., Quay et al., 1992; Cao et al., 2009).

s0015 11.2. SPATIAL HETEROGENEITY OF $\delta^{13}\text{C}$ OF DISSOLVED INORGANIC CARBON

p0045 Carbon isotope values in marine carbonates do not simply reflect the average global $\delta^{13}\text{C}$ values of DIC in the oceans, but are influenced by local primary and export productivity, the regional and global pattern of ocean circulation, and local to regional effects such as addition of light HCO_3^- in coastal regions. The equilibrium fractionation between dissolved $\text{CO}_{2(\text{aq})}$ (thus atmospheric CO_2) and bicarbonate (thus dissolved inorganic carbon, DIC or ΣCO_2) changes by about 0.1‰ per $^\circ\text{C}$ change in temperature. It follows that the $\delta^{13}\text{C}$ value in DIC in surface waters at high latitudes (colder) is higher with respect to the atmosphere than in the warmer, low latitude ocean surface waters by $\sim 2\text{‰}$ (Lynch Stieglitz et al., 1995; Lynch-Stieglitz, 2003). This equilibrium is not achieved anywhere because surface waters are replaced too quickly, but colder waters generally have higher $\delta^{13}\text{C}$ values in DIC than warmer waters. Colder surface waters invariably ventilate the deep ocean, so this effect (called “the solubility pump”) would result in a surface-to-bottom gradient in which the DIC in surface waters is isotopically lighter than that in deep waters (Raven and Falkowski, 1999).

p0050 In most places in the present oceans we observe the reverse, and the DIC of surface waters has $\delta^{13}\text{C}$ values that are heavier by about $+2$ to $+3\text{‰}$ than deep-water values, with the average whole ocean $\delta^{13}\text{C}$ value of total DIC within about 1‰ of the average deepwater value of $\sim 0\text{‰}$ (Figure 11.1)

(e.g., Kroopnick, 1985; Gruber et al., 1999; Sarmiento and Gruber, 2006). This vertical gradient is due to biological activity (the “biological pump”, Raven and Falkowski, 1999). Photosynthesis in the oceans is limited to the photic zone, causing depletion in ^{12}C in DIC in the surface waters. The $\delta^{13}\text{C}$ values of DIC in waters below the photic zone, down to the ocean floor, are lower than those in surface waters, because organic matter sinks, and isotopically light carbon dioxide from its remineralization is added to these waters. The magnitude of this vertical gradient depends upon the primary productivity of the surface waters and the export productivity of organic matter to deeper waters: higher export productivity leads to a steeper gradient, with the largest gradient in the present oceans found to be around 3‰ (Raven and Falkowski, 1999; Sarmiento and Gruber, 2006).

Remineralization of organic matter adds nutrients (nitrate, p0055 phosphate) as well as DIC to the deeper waters in the oceans. The concentration of nutrients and isotopically light carbon derived from remineralization of organic matter increases with increasing water-mass residence times (or “aging”) in the deep ocean (e.g., Kroopnick, 1985; Lynch-Stieglitz, 2003; Sarmiento and Gruber, 2006).

As a result of the aging process we see a generally good p0060 correlation between $\delta^{13}\text{C}$ values in DIC and nutrient levels (phosphate) in open ocean. This relationship can be determined using the equation from Broecker and Maier-Reimer (1992):

$$\delta^{13}\text{C} - \delta^{13}\text{C}^{\text{MO}} = \frac{\Delta_{\text{photo}} / \Sigma\text{CO}_2^{\text{MO}}}{C/P_{\text{org}}} \frac{(\text{PO}_4 - \text{PO}_4^{\text{MO}})}{\text{C/P}_{\text{org}}} \quad (1)$$

where MO stands for mean ocean, Δ_{photo} is the photosynthetic p0065 fractionation factor and C/P_{org} is the carbon to phosphorus ratio in marine organic matter. For the modern ocean ($\Delta_{\text{photo}} = -19\text{‰}$, $\delta^{13}\text{C}^{\text{MO}} = +0.5\text{‰}$, $\Sigma\text{CO}_2^{\text{MO}} = 2200 \mu\text{mol/kg}$, $\text{PO}_4^{\text{MO}} = 2.2 \mu\text{mol/kg}$, and $C/P_{\text{org}} = 128$) so that equation 1 becomes:

$$\delta^{13}\text{C} = 2.9 - 1.1 \text{PO}_4 \quad (2)$$

The $\delta^{13}\text{C}$ of modern tropical and temperate surface waters p0070 that average $0.2 \mu\text{mol/kg}$ of PO_4 is about 1.5‰ higher than surface waters of the Antarctic, which contain the highest PO_4 values ($1.6 \mu\text{mol/kg}$) of the surface oceans. The highest PO_4 values in the modern ocean are found in the deep Pacific (up to $3 \mu\text{mol/kg}$), and these waters have a $\delta^{13}\text{C}$ of about -0.3‰ , which differs modestly from mean ocean carbon at $+0.5\text{‰}$ with a $\text{PO}_4^{\text{MO}} = 2.2 \mu\text{mol/kg}$ (Broecker and Maier-Reimer, 1992). In the present oceans we thus see a difference in isotopic composition of DIC in the deep Atlantic (younger waters) and the deep Pacific (older waters), with the north Pacific about 1‰ lighter than the Atlantic, and reflecting the net aging of waters in the global deep-sea circulation pattern from North Atlantic to North Pacific (Lynch-Stieglitz, 2003; Ravizza and Zachos, 2003; Sarmiento and Gruber, 2006).

p0075 In semi-restricted water masses above modern carbonate platforms, we see a fairly severe version of “aging”, i.e., an increase in time during which the water has not been in contact with the atmosphere (Patterson and Walter, 1994; Immenhauser et al., 2002). In addition, lighter $\delta^{13}\text{C}$ values occur in DIC in coastal waters, especially close to major river inflows. The major sources of carbon contributing to DIC in natural waters are CO_2 derived from the decay of organic matter in continental soils and from the dissolution of carbonate, while in general the contribution of atmospheric CO_2 is negligibly small (Mook and Tan, 1991). The large amounts of dissolved organic carbon (DOC) in rivers contribute to light DIC in coastal waters upon their oxidation, in addition to the DIC derived from oxidation of organic matter due to plankton blooms in eutrophied coastal regions where water column stratification develops seasonally (Thomas et al., 2000; Fry, 2002; Diz et al., 2009).

p0080 Local to regional negative carbon isotope excursions in restricted basins with a stratified water column have been explained by advection of the isotopically light, organic matter-derived DIC formed within anoxic bottom waters below a pycnocline, e.g. for the Toarcian and Kimmeridgian events (Kuespert, 1982; Jenkyns and Clayton, 1986, 1997; Saelen et al., 1998; Schouten et al., 2000). A similar process on an ocean-wide scale has been proposed for the Permo-Triassic, at which there was widespread anoxia in the global ocean (Pantallasa), so that isotopically light carbon as well as toxic H_2S could have advected from below the pycnocline (e.g., Erwin, 1993, 2006; Kump et al., 2005). Ventilation of carbon from the ocean interior (i.e., redistribution of carbon within the ocean-atmosphere system) even in the absence of anoxia has also been proposed as cause of some of the smaller Eocene hyperthermals, but not for the PETM (Sexton et al., 2011).

p0085 In conclusion, one can be confident that an observed $\delta^{13}\text{C}_{\text{carb}}$ trend represents global primary seawater DIC values only if it is reproducible globally, and in a wide range of depositional settings that have undergone differing degrees of diagenetic alteration.

s0020 11.3. MATERIALS AND METHODS

p0090 In Figures 11.2 through 11.7, $\delta^{13}\text{C}_{\text{carb}}$ is plotted according to the time scale presented in this volume. Correlation among stratigraphic sections by comparison of the $\delta^{13}\text{C}$ curves is a common practice, but curves covering any time interval show considerable spatial and temporal variability. In order to be applied successfully for dating and correlating, $\delta^{13}\text{C}_{\text{carb}}$ excursions must therefore be recognized in sections from different parts of the world, and $\delta^{13}\text{C}_{\text{carb}}$ chemostratigraphy must be carefully scrutinized and integrated into a bio-, magneto- and sequence stratigraphic framework. We can use the carbon isotope pattern to correlate and date more precisely, as was done for example, for the Paleocene-Eocene Thermal Maximum or the Late Cambrian Paibian Stage, only

when we identify a CIE in coeval records from different environments, dated independently (e.g., Zachos et al., 2005; Saltzman et al., 2000).

Carbon isotope records based on organic matter ($\delta^{13}\text{C}_{\text{org}}$) p0095 and in terrestrial carbonate nodules may also be used for correlation (e.g., Koch et al., 1992), but long-term trends through most of Earth history are in general less well known and not covered here in detail. Furthermore, $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{org}}$ measured in the same rocks may show significant differences in the magnitude and/or timing of carbon isotope excursions (e.g., in the Cambrian, Ordovician, Cretaceous and Paleocene/Eocene – see Section 11.4) that may relate to temporal changes in photosynthetic fractionation, or poor carbonate preservation (e.g. Hayes et al., 1999; McCarren et al., 2008; Jenkyns, 2010).

Materials analyzed for $\delta^{13}\text{C}_{\text{carb}}$ differ between authors, p0100 a fact that should be kept in mind when comparing $\delta^{13}\text{C}$ curves. Which carbonate materials are analyzed depends on availability and preservation of sediment, depositional environments, and the presence of calcifying organisms which evolved through geological time. In addition, choice of materials is governed by the spatial and temporal scale of the problem to be addressed.

11.3.1. Depositional Setting: Deep (Pelagic) s0025 Versus Shallow

Pelagic calcifiers predominantly consist of calcareous p0105 nannoplankton, which evolved in the late Triassic (Norian, ~ 215 Ma, Bown et al., 2004) and planktonic foraminifera, which evolved in the early Jurassic (Toarcian, ~ 183 Ma, Hart et al., 2006). Both groups were originally restricted to epicontinental seas, and then colonized the open ocean in the Early Cretaceous (Roth, 1986). Subduction has destroyed most pre-Jurassic oceanic crust, so deep-sea carbonates of pre-Jurassic age rarely preserved (Martin, 1995; Ridgwell 2005). This evolution of planktonic calcifiers, commonly seen as part of the Mid-Mesozoic Revolution of life on Earth (Vermeij, 1977), caused a major reorganization of the global carbon cycle by shifting the locus of carbonate deposition from the continental shelves to the deep open ocean, so that biologically driven carbonate deposition could provide significant buffering of ocean chemistry and of atmospheric CO_2 from that time on (Zeebe and Westbroek, 2003; Ridgwell, 2005).

Jurassic through Cenozoic C-isotope records have been p0110 derived mostly from pelagic carbonates (e.g., Scholle and Arthur, 1980; Vincent and Berger, 1985; Shackleton, 1987; Zachos et al., 2001, 2008; Cramer et al., 2009; Jenkyns, 2010), either obtained by deep sea drilling in the oceans, where crust younger than about middle Jurassic is present (Jenkyns et al., 2002; Katz et al., 2005), or from land sections, many of which are located in the Mediterranean region of Europe

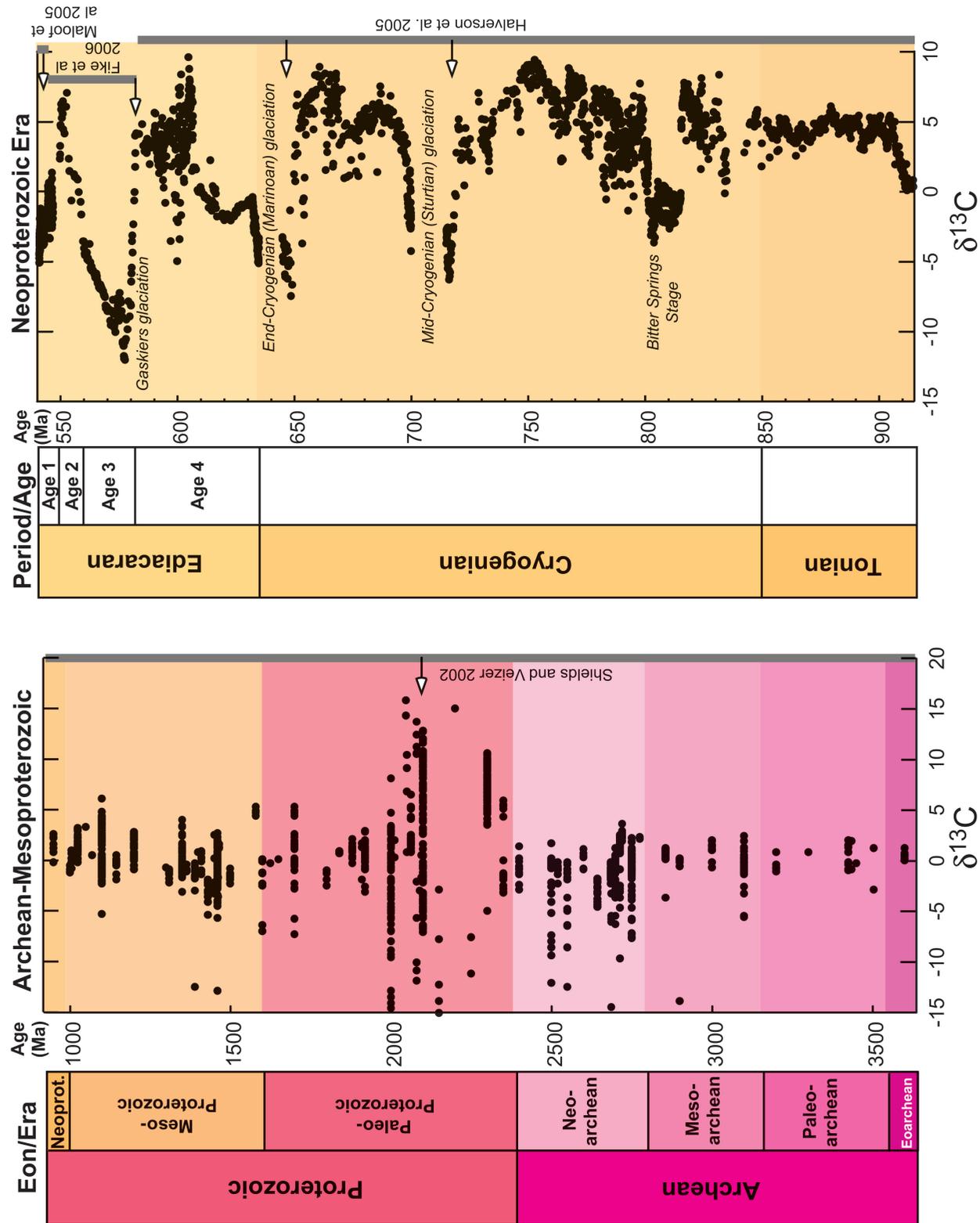


FIGURE 11.2 Variation of $\delta^{13}\text{C}_{\text{carb}}$ from the Archean to Neoproterozoic. Data sources are indicated by vertical bars to right of data. Arrows mark well-studied excursions.

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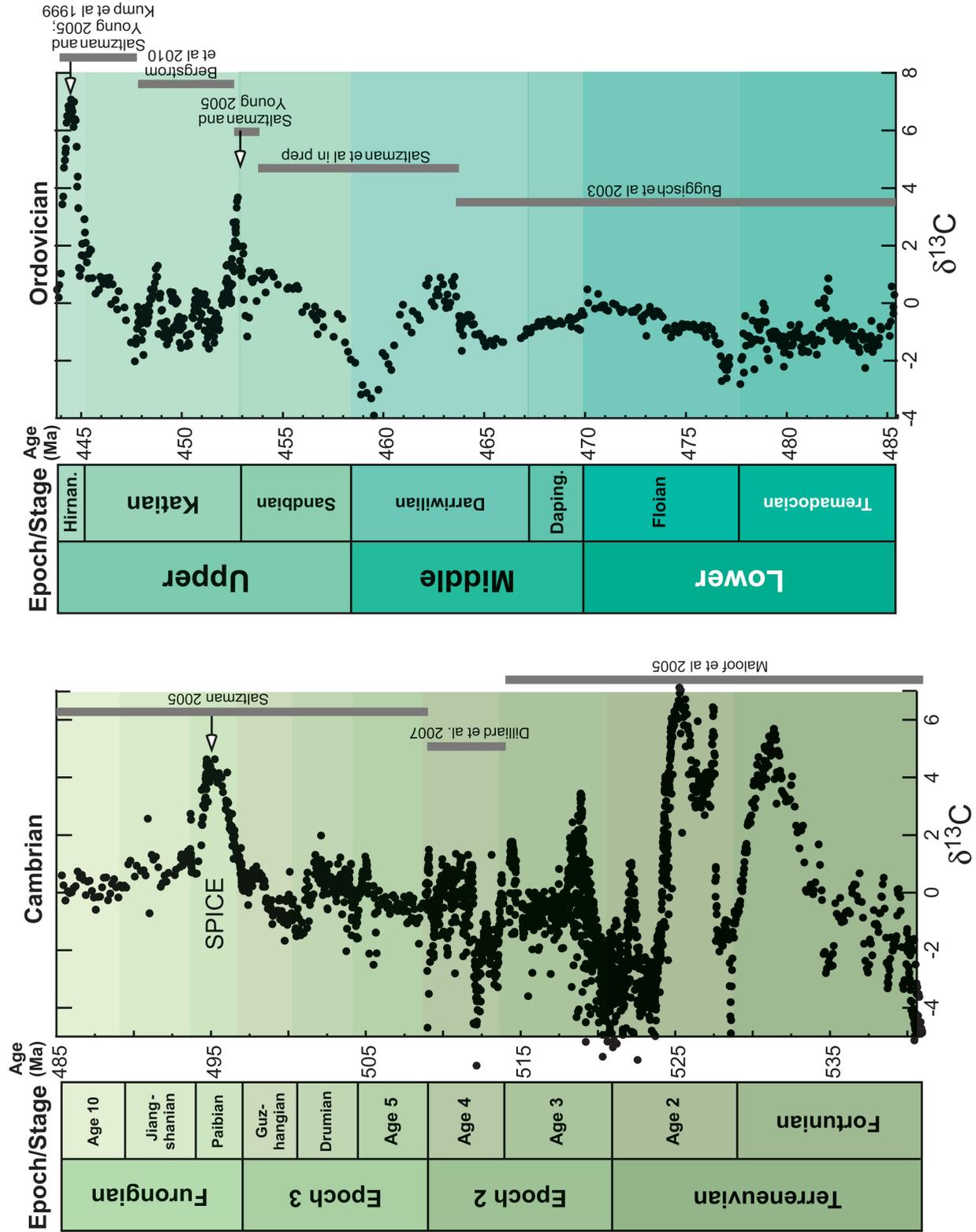


FIGURE 11.3 Variation of $\delta^{13}C_{carb}$ through the Cambrian and Ordovician. Data sources are indicated by vertical bars to right of data. Arrows mark well-studied excursions.

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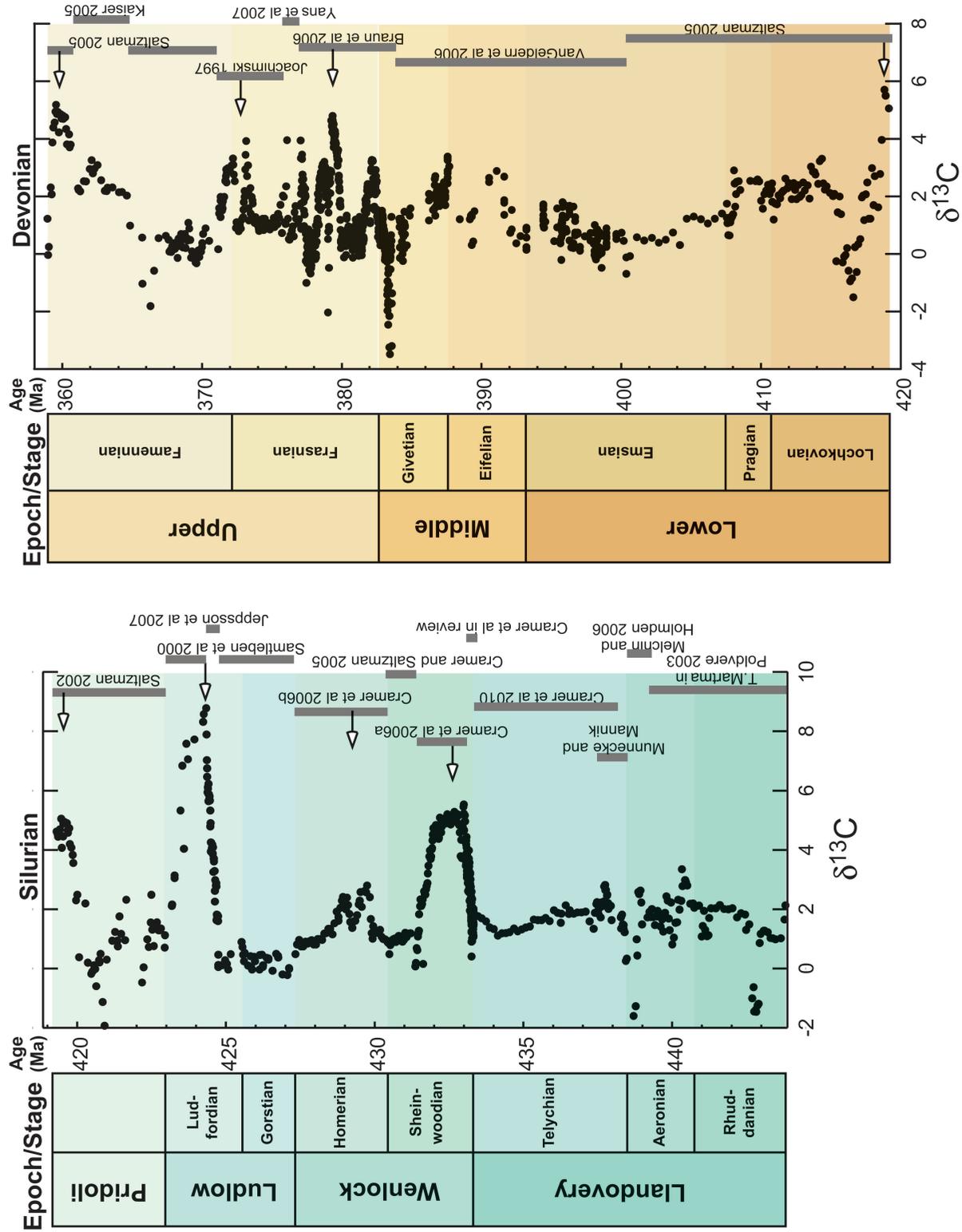
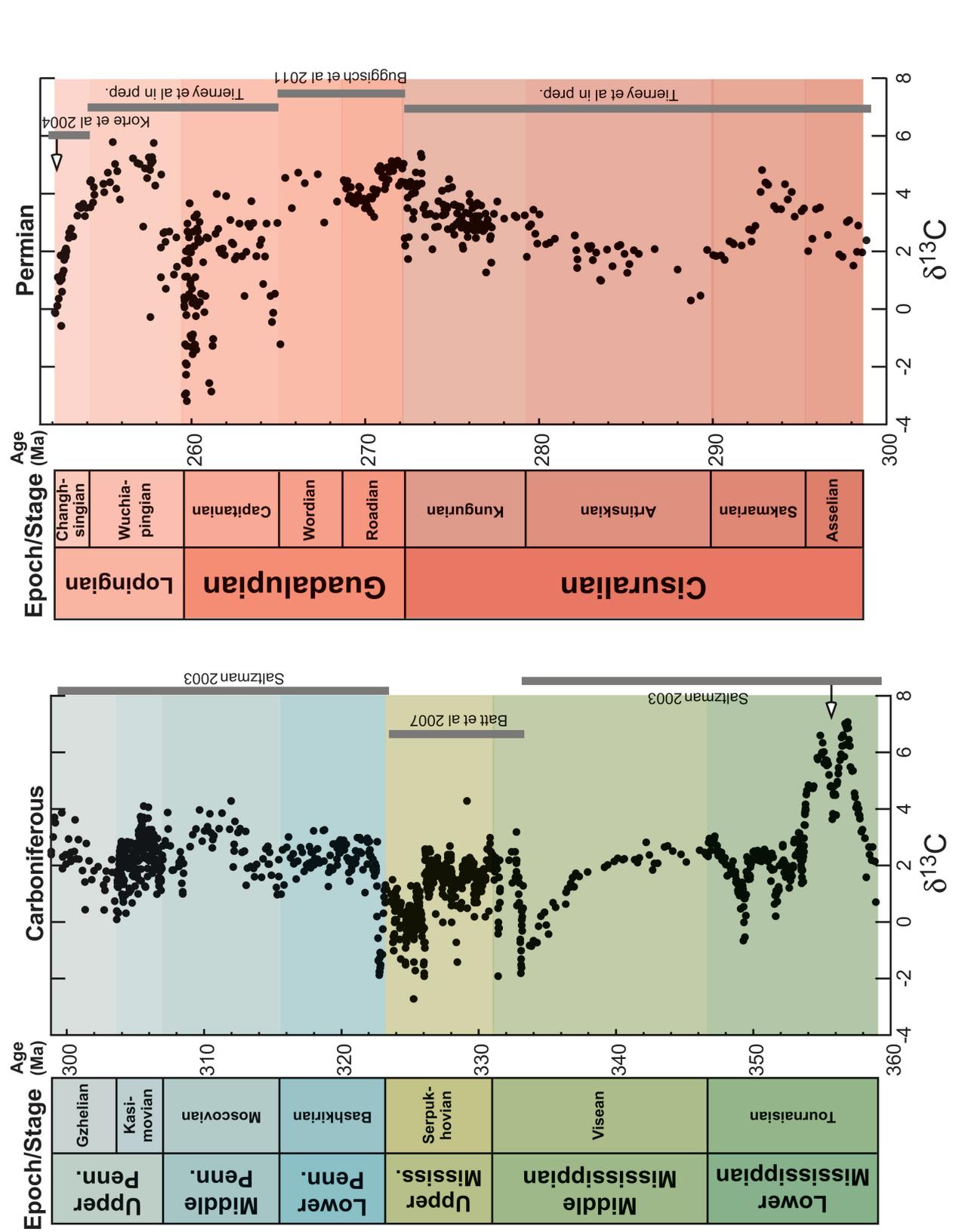


FIGURE 11.4 Variation of $\delta^{13}C_{carb}$ through the Silurian and Devonian. Data sources are indicated by vertical bars to right of data. Arrows mark well-studied excursions.

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f0030 **FIGURE 11.5** Variation of $\delta^{13}\text{C}_{\text{carb}}$ through the Carboniferous (Mississippian and Pennsylvanian) and Permian. Data sources are indicated by vertical bars to right of data. Arrows mark well-studied excursions.

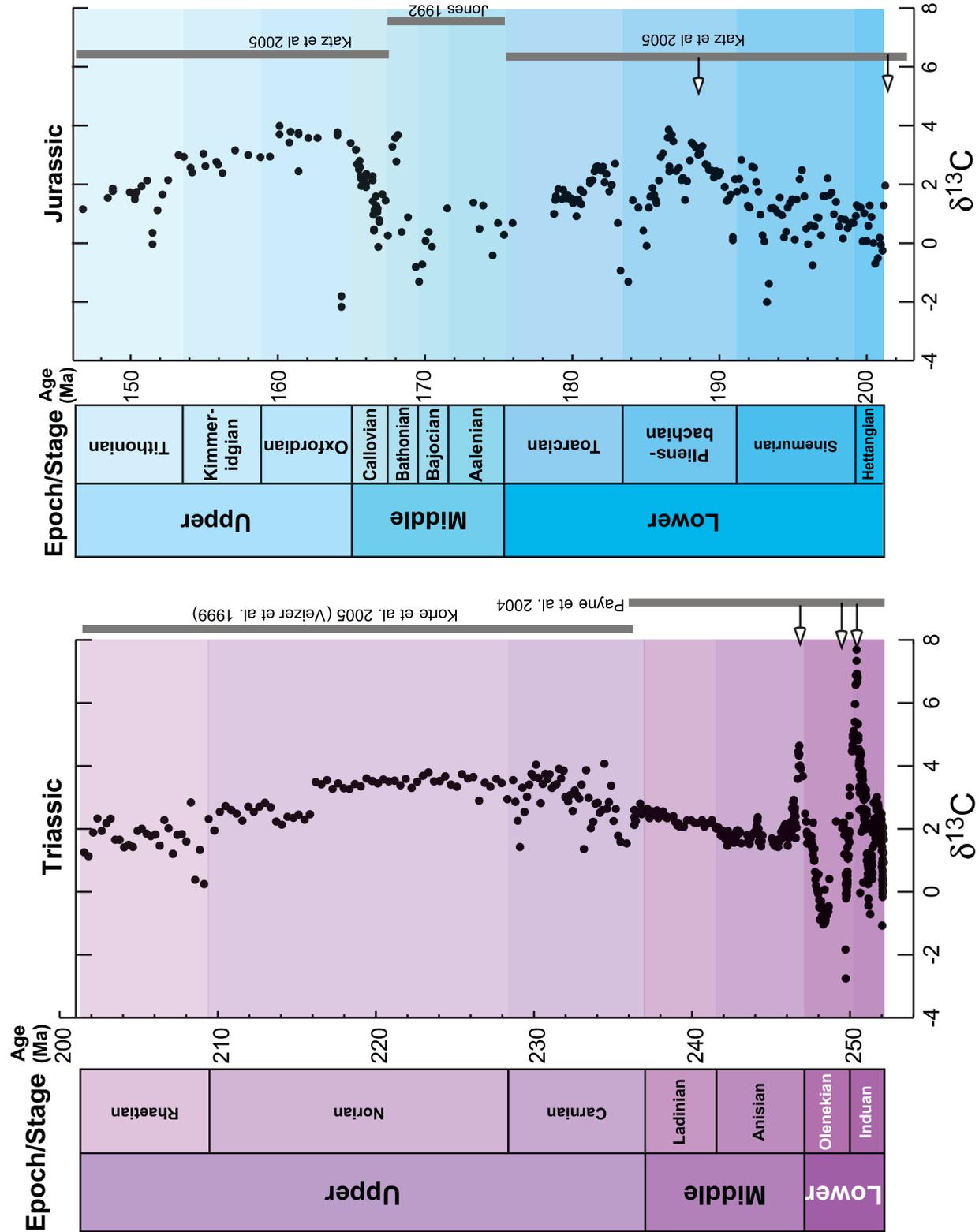


FIGURE 11.6 Variation of $\delta^{13}C_{carb}$ through the Triassic and Jurassic. Data sources are indicated by vertical bars to right of data. Arrows mark well-studied excursions.

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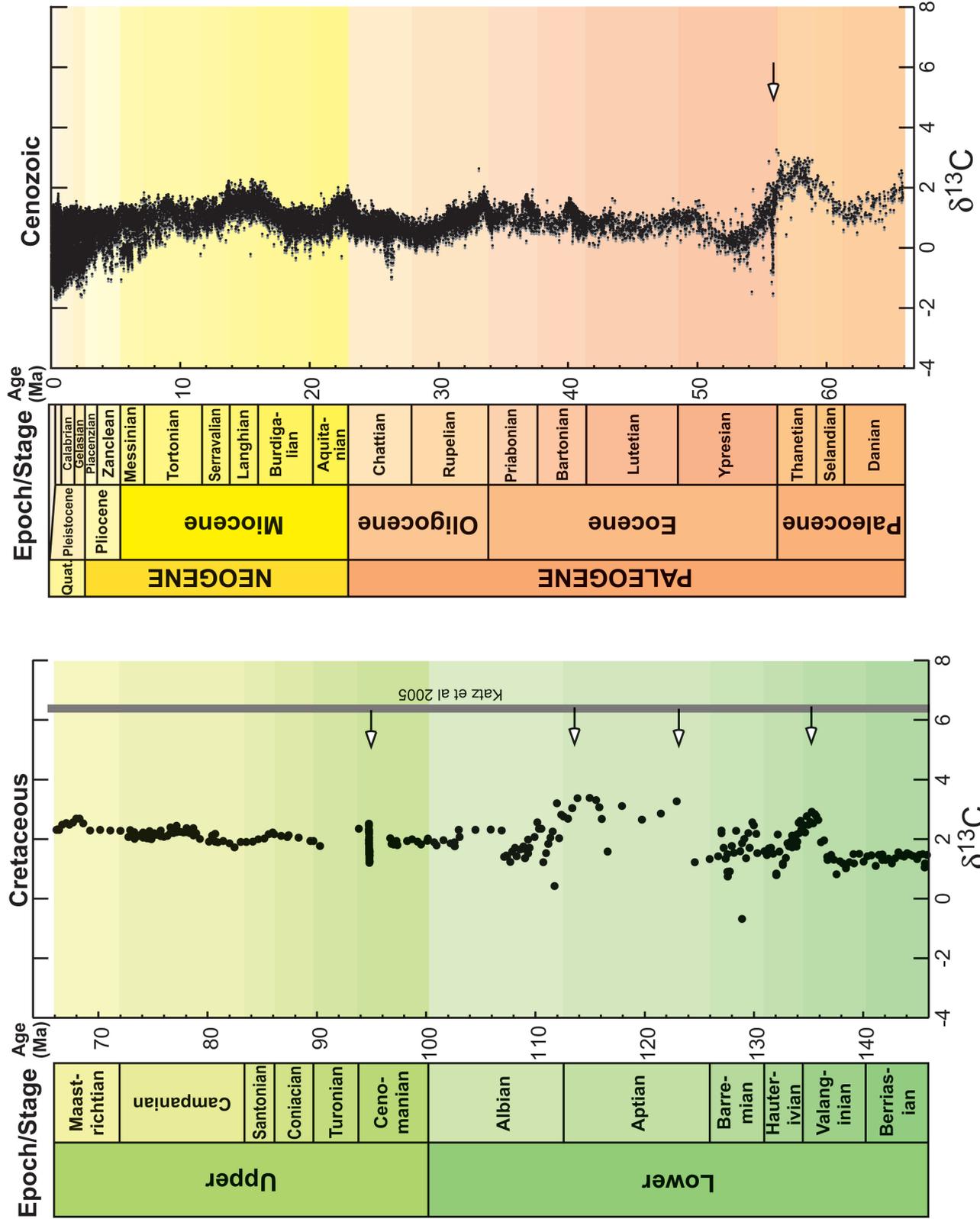


FIGURE 11.7 Variation of $\delta^{13}\text{C}_{\text{carb}}$ through the Cretaceous and Cenozoic. Data sources are indicated by vertical bars to right of data. Arrows mark well-studied excursions.

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(e.g., Jenkyns, 2010). Such pelagic carbonates are dominantly made up of carbonate secreted by planktonic organisms, calcareous nannoplankton and planktonic foraminifera, with a negligible contribution from benthic organisms (e.g., Milliman, 1993, Sarmiento and Gruber, 2006). For high-resolution work, or analysis of indurated material from which single fossils cannot be liberated, or to approximate the average marine average $\delta^{13}\text{C}$ of the total carbonate produced and preserved in the marine system, many researchers have been using the bulk isotope record, which takes much less time to produce (e.g., Shackleton and Hall, 1984; Shackleton, 1987; Katz et al., 2005). The bulk record in pelagic carbonates is dominated by carbonate secreted by the photosynthesizing calcareous nannoplankton. Their carbonate gives an isotopic value not typical for the waters in the surface mixed layer, which outside the polar regions is limited to less than 100m, but for the deeper thermocline (e.g., Bown et al., 2004).

p0115 From times prior to the Middle Jurassic, only shallow-water (platform), near-shore carbonate is preserved (Martin, 1995; Ridgwell, 2005). For Middle Jurassic sediments and younger, platform and pelagic carbon isotope records can both be used for correlation, and commonly show very similar records (Ferreri et al., 1997; Amodio et al., 2008). However, in ancient carbonate rocks it may be difficult to discern the original depositional environment and water mass sampled by individual materials, either because diagenesis of the sediment has masked the origins, or because the ecological niche of a particular fossil is not known. The multiple, complex origins of fine-grained (micritic) carbonate can also frustrate such efforts (e.g., Minoletti et al., 2005).

s0030 11.3.2. Bulk Versus Component

p0120 For pelagic sections, researchers have measured the carbon isotope signatures of pelagic calcifiers living at different depths in the surface waters, as well as benthic organisms, so that insight can be obtained regarding the structure of the thermocline, as well as oceanic productivity and circulation (e.g., Vincent and Berger, 1985; Lynch-Stieglitz, 2003; Ravizza and Zachos, 2003; Maslin and Swann, 2005). The deep-sea benthic signal is closest to that of whole ocean DIC (though potentially complicated by ocean circulation patterns, Section 10.2), but benthic foraminifera are generally very rare, so producing benthic records is time-consuming (Zachos et al., 2001, 2008; Cramer et al., 2009). In the production of all records from individual or groups of fossils, researchers must take into account the details of biocalcification, with different species calcifying carbonate with different offsets from isotopic equilibrium, so that taxonomic knowledge is required (e.g., Rohling and Cooke, 1999; Katz et al., 2003). In addition, infaunal species reflect pore water $\delta^{13}\text{C}$ in DIC in pore waters, hence should be excluded from analysis (Zachos et al., 2001, 2008; Cramer et al., 2009).

Preservation of foraminifera in some Paleogene through p0125 Middle Cretaceous sediments is excellent and allows analyses of separate species (Wilson and Norris, 2001), but more commonly Paleogene and older sediments are too lithified for separation of single species, and bulk samples of pelagic carbonate must be analyzed (Scholle et al., 1980; Jenkyns, [AU3] 2010). Some studies, for example of the Jurassic, have analyzed isolated macroscopic skeletal components such as belemnites, but large skeletal materials commonly give scattered data, even when screened for diagenetic alteration (Podlaha et al., 1998; Jenkyns et al., 2002). Detailed morphological analysis of shells (e.g., Cretaceous ammonites) is needed to reliably detect diagenesis, which may affect isotopic values even in specimens with good visual preservation (Cochran et al., 2010).

In Paleozoic platform carbonates, the skeletal components p0130 most commonly isolated for analysis are brachiopods, composed of low-Mg (magnesium) calcite (e.g., Popp et al., 1986; Grossman et al., 1991, 1993, 2008; Brand, 1982, 2004; Wenzel and Joachimski, 1996; Veizer et al., 1999; Mii et al., 1999). Brachiopod workers differ in their approaches to sampling, reflecting the complex multi-layered nature of the shell, taxonomic differences, and taphonomic differences, i.e., the variable preservation states encountered (e.g., Carpenter and Lohmann, 1995; Veizer et al., 1999; Grossman et al., 2008). Taxonomic influences (“vital effects”) on brachiopod $\delta^{13}\text{C}$ have been recognized when systematic paleontology is combined with isotope analysis (e.g., Mii et al., 1999; Batt et al., 2007). For instance, the Carboniferous brachiopod *Composita* has a consistently heavier carbon isotope composition than associated species (Mii et al., 1999).

Others have analyzed bulk carbonate from Paleozoic p0135 shallow-water platform settings, either because preserved macrofossils were absent, or to maximize stratigraphic resolution (e.g., Ripperdan et al., 1992; Joachimski and Buggisch, 1993; Saltzman et al., 1998; 2000; Payne et al., 2004; Maloof et al., 2005). Precambrian carbonates lack macroscopic skeletal components, so only analysis of bulk materials is possible (e.g., Knoll et al., 1986; Derry et al., 1992; Hoffman et al., 1998; Halverson et al., 2006; Fike et al., 2006; Li et al., 2009). Bulk sampling, which typically targets fine-grained (micritic) carbonate, can be carried out by microdrilling in order to isolate small amounts of material (i.e., 0.5–10 mg) and avoid obvious secondary veins, while at the same time providing enough material to be confident of a homogeneous sample. Disc or ball mills are less selective but generate large amounts of powder (~ 10–100 g) so that $\delta^{13}\text{C}_{\text{carb}}$ can be measured, as well as other proxies (e.g., strontium, sulfur, organic carbon).

11.3.3. Diagenesis

The potential of diagenesis to alter primary $\delta^{13}\text{C}$ values must p0140 be evaluated on a case by case basis (Marshall, 1992; Cochran et al., 2010). In samples collected from outcrops (in contrast

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to samples recovered by ocean or continental drilling), isotopically light carbon (^{12}C) may be introduced in meteoric waters containing DIC from oxidized organic matter. Meteoric diagenesis can alter carbonate towards more negative $\delta^{13}\text{C}$, with varying magnitude of the effect. In general, meteoric water diagenesis results in lowered $\delta^{18}\text{O}$ as well as $\delta^{13}\text{C}$ values, and correlation between the two is thus commonly observed in samples affected by diagenesis [AU4] (Knauth and Kennedy, 2009; Cochran et al., 2011). Some workers report preservation of original trends even below major exposure surfaces (e.g., Halverson et al., 2006), whereas others indicate alteration to more negative $\delta^{13}\text{C}$ beneath exposure surfaces (e.g., Allan and Matthews, 1983; Lohmann, 1988; Algeo et al., 1992). Negative $\delta^{13}\text{C}$ shifts have been combined with other geochemical parameters to identify exposure surfaces in cases when the geologic evidence is subtle or cryptic (Railsback et al., 2003).

p0145 The incorporation of ^{12}C derived from oxidized organic matter must be ruled out before an observed negative $\delta^{13}\text{C}$ excursion can be considered a primary signal. Such incorporation is most common in sediments with a low CaCO_3 content (e.g., Bralower et al., 1997; Zachos et al., 2005). Reliable results for pelagic carbonate $\delta^{13}\text{C}$ trends were obtained when the ratio of carbonate carbon to organic carbon in the sediments was high, suggesting that a ratio of approximately $> 7:1$ may be a useful cutoff point (Scholle and Arthur, 1980).

s0040 11.3.4. Global Versus Local Water Mass Signals

p0150 Carbonates from epicontinental seas record DIC values from water masses that did not have unrestricted circulation with the open ocean (Section 11.2; e.g., Patterson and Walter, 1994; Holmden et al., 1998; Immenhauser et al., 2002). This restriction allows larger amplitude and/or higher frequency in $\delta^{13}\text{C}$ variability than the global ocean reservoir, which might at least in part explain the observation that Cretaceous and Cenozoic curves (Figures 11.6 and 11.7) generated from pelagic carbonates record less variability than curves generated from epicontinental sea carbonates (Figure 5 in Falkowski 2003; Figures 11.2–11.6). Comparison of Jurassic and younger platform carbonate records with those of pelagic carbonates, however, indicates that the larger variability in older records cannot be completely explained in this way, because curves from platform carbonates strongly resemble coeval pelagic curves (Ferreri et al., 1997; Mutti et al., 2006; Amodio et al., 2008).

p0155 Furthermore, epicontinental sea carbonates may contain low-Mg, high-Mg calcite, and aragonite, which fractionate carbon differently (Romanek et al., 1992), and potentially superimpose low amplitude ($\sim 1\text{‰}$) trends through time, as observed in recent, mineralogically complex, platform carbonates (Gischler et al., 2009). However, even for time

periods when epicontinental seas were particularly widespread and local water mass $\delta^{13}\text{C}$ differences well documented (e.g., the Ordovician period), distinct $\delta^{13}\text{C}$ trends and large excursions are still recognizable and can be correlated globally (e.g., Patzkowsky et al., 1997; Ainsaar et al., 1999; Young et al., 2005; Panchuk et al., 2005).

The above considerations pose significant challenges to p0160 the use of $\delta^{13}\text{C}$ records as a global correlation tool, particularly for periods when the amplitude of variation is low (Figures 11.2–11.7). For $\delta^{13}\text{C}$ excursions larger than 1–2 per mille, broad-scale correlations may be confidently applied if independent age control is available. However, if variations in absolute magnitudes of excursions are observed locally, it may be difficult to distinguish unconformities (i.e., parts of the record not represented in the sediments) from the effects of local epicontinental carbon cycling (e.g., Hirnantian; Brenchley et al., 2003; Melchin and Holmden, 2006a). Even for relatively young sediments (Paleocene/Eocene), minor unconformities may make detailed correlations difficult (e.g., McCarren et al., 2008).

In summary, $\delta^{13}\text{C}_{\text{carb}}$ integrates the combined influence of p0165 diagenesis, mineralogical variability, vital effects depending upon the calcifying organisms, and vertical and/or horizontal water mass differences depending upon productivity and ocean circulation, so that one must be cautious in identifying “global” trends or excursions based on a limited number of $\delta^{13}\text{C}$ data points. For bulk epicontinental carbonate analyses, a margin of uncertainty of $\sim 1\text{‰}$ may be assumed (e.g., Halverson et al., 2006), for species-specific Cenozoic curves $\sim 0.5\text{‰}$ (Zachos et al., 2001, 2008; Cramer et al., 2009).

11.4. CORRELATION POTENTIAL AND EXCURSIONS

s0045

The following discussion briefly summarizes the major p0170 features and sources of data for the $\delta^{13}\text{C}$ curves in Figures 11.2–11.7. We do not discuss the use of $\delta^{13}\text{C}_{\text{carb}}$ stratigraphy on timescales of a few tens of thousands of years (orbital timescales) as routinely used in studies of the Plio-Pleistocene ice ages (Maslin and Swann, 2005), but increasingly for detailed stratigraphy of older time periods.

Archean through Mesoproterozoic: A Precambrian p0175 marine carbonate isotope database was published by Shields and Veizer (2002), and its Archean to Mesoproterozoic portion is plotted in Figure 11.2. More detailed curves for parts of this time period have become available more recently, but the difficulties of compiling these records are many. There is a growing consensus regarding the pattern of changes, beginning with the positive Lomagundi carbon isotope excursion at $\sim 2.22\text{--}2.058\text{ Ga}$ (Bekker et al., 2006; Melzchnik et al., 2007). Following this period of anomalously high $\delta^{13}\text{C}$, values for the Paleoproterozoic are mostly between $\sim 0\text{‰}$ to -3‰ , and then $\sim 0\text{‰}$ to $+2\text{‰}$ in the late

Paleoproterozoic (Wilson et al., 2010). Relatively stable $\delta^{13}\text{C}$ at $\sim 0 \pm 2\%$ characterizes much of the Mesoproterozoic (Buick et al., 1995; Knoll et al., 1995; Frank et al., 2003; Xiao et al., 1997; Kah et al., 2001; Brasier and Lindsay, 2000; Bartley and Kah, 2004; Chu et al., 2007). Chu et al. (2007) correlated a rise in $\delta^{13}\text{C}$ at $\sim 1250\text{--}1300$ Ma between China and sections in Russia and Canada (Bartley et al., 2001; Frank et al., 2003; Bartley and Kah, 2004). Kah et al. (1999) suggested that the moderately positive values between ~ -1.0 and $+4.0\%$, characteristic of the interval between 1300 and 800 Ma, could be useful for broad time correlation, when compared with earlier Mesoproterozoic (values near 0%) and younger Neoproterozoic sections with values $>+5\%$.

Neoproterozoic: A Neoproterozoic $\delta^{13}\text{C}_{\text{carb}}$ composite was published by Halverson et al. (2006), and updated in Halverson et al. (2007) (Figure 11.2). In addition to the data of Halverson et al. (2006), data from Fike et al. (2006) and Maloof et al. (2005) were included to complete the Neoproterozoic up to the base of the Cambrian. The carbon isotopic record of the Neoproterozoic is extremely volatile, with the lightest $\delta^{13}\text{C}$ values and largest net shifts of the entire geologic timescale. This time is considered a period of very large climatic swings, with fluctuations between “Snowball Earth” with glaciation extending to low latitudes and “Super Greenhouse” episodes, linked to variability in the carbon cycle and atmospheric CO_2 levels (Allen and L’Etienne, 2008).

The precise number of excursions remains the subject of debate, reflecting in part the lack of independent biostratigraphic constraints. As mentioned above, we can feel confident about carbon isotopic stratigraphy only after evaluation of independent stratigraphic evidence. In the compilation of Halverson et al. (2007), a large negative excursion prior to 800 Ma (Bitter Springs Stage) is followed by a period of heavy values between $+5$ and $+10\%$ that lasts for ~ 75 million years. Values fall spanning the Sturtian glaciation (~ 711.5 Ma; Macdonald et al., 2010) before rising again to levels observed prior to the glaciation. The negative shift across the Marinoan glaciation (~ 635.2 Ma; Macdonald et al., 2010) is similar to that in the Sturtian, but the return to heavy values is slower, and the subsequent positive mid-Ediacaran $\delta^{13}\text{C}$ excursion is more transient. Values drop for the fourth time across the Gaskiers glacial interval (Shuram anomaly; e.g., Fike et al., 2006; Grotzinger et al., 2011), and then rise to around $+5\%$ before falling again across the Precambrian-Cambrian boundary (Grotzinger et al., 1995; Condon et al., 2005).

Cambrian: The Cambrian curve (Figure 11.4) is compiled from Maloof et al. (2005), Dilliard et al. (2007), and Saltzman (2005). The Lower Cambrian is characterized by considerable volatility throughout. At least two large positive shifts between ~ 535 and 525 Ma are known from sections in Morocco (Maloof et al., 2005) and Siberia (Kouchinsky et al., 2007), and younger excursions have a lower amplitude

(Brasier and Sukhov, 1998). A significant negative excursion is apparent near the Epoch 2–3 boundary (Stage 4–5 boundary) (Montanez et al., 2000; Zhu et al., 2006; Dilliard et al., 2007) and there may be a younger event in the Drumian (Howley and Jiang, 2010). The Steptoean Positive carbon Isotope excursion (SPICE) at about ~ 495 Ma of the Paibian Stage (Furongian Epoch) is one of the best known $\delta^{13}\text{C}$ excursions on a global scale, and has been documented in sections in North America, China, Australia, Siberia and Kazakhstan (Saltzman et al., 1998; Glumac and Walker, 1998; Saltzman et al., 2000; Saltzman et al., 2004; Kouchinsky et al., 2008), and in the $\delta^{13}\text{C}$ of organic matter in Baltica (Ahlberg et al., 2009) and Avalonia (Woods et al., 2011). The $\delta^{13}\text{C}_{\text{org}}$ shows a smaller excursion that peaks earlier than the shift in $\delta^{13}\text{C}_{\text{carb}}$ (Saltzman et al., 2011). The final stage of the Furongian is characterized by relatively low variability associated with trilobite extinction events (e.g., Ripperdan et al., 1992; Saltzman et al., 1995).

Ordovician: The Ordovician compilation is from five different sources, including published and some unpublished data (Saltzman et al., in prep) (Figure 11.3). Relatively steady values with small excursions are recognized during the Tremadocian (Buggisch et al., 2003; Saltzman, 2005) and low amplitude and low frequency shifts are observed for the Floian, Dapingian and Darriwilian in Argentina (Buggisch et al., 2003), North America (Saltzman, 2005; unpublished) and China (Munnecke et al., 2011). Most of this Early to Middle Ordovician time period is characterized by unusually light values (below 0%). Positive shifts to values above 0% occur near the base of the Dapingian and in the mid-Darriwilian (Buggisch et al., 2003; Ainsaar et al., 2010; Saltzman et al., in prep). Two positive excursions occur in global records in the lower Katian and Hirnantian (Brenchley et al., 1994; Ainsaar et al., 1999, 2010; Patzkowsky et al., 1997; Kump et al., 1999; Finney et al., 1999; Kaljo et al., 2001; Saltzman and Young, 2005; Bergström et al., 2006, 2009, 2010; LaPorte et al., 2009; Young et al., 2010; many others). The Hirnantian $\delta^{13}\text{C}_{\text{carb}}$ positive excursion, occurring during a period of global cooling and glaciation, reaches peaks near $+7\%$ globally (e.g., Nevada and Estonia; Kump et al., 1999; Finney et al., 1999; LaPorte et al., 2009; Young et al., 2010). Both the Katian and Hirnantian $\delta^{13}\text{C}_{\text{carb}}$ excursions are recorded in $\delta^{13}\text{C}_{\text{org}}$ (Patzkowsky et al., 1997; LaPorte et al., 2009), but their timing and magnitudes may differ (Young et al., 2008, 2010; Delabroye and Vecoli, 2009). The basic shape of the $\delta^{13}\text{C}$ curves from brachiopod and bulk rock studies agree well in records from the Upper Ordovician (e.g., Brenchley et al., 1994; Marshall et al., 1997; Finney et al., 1999; Kump et al., 1999),

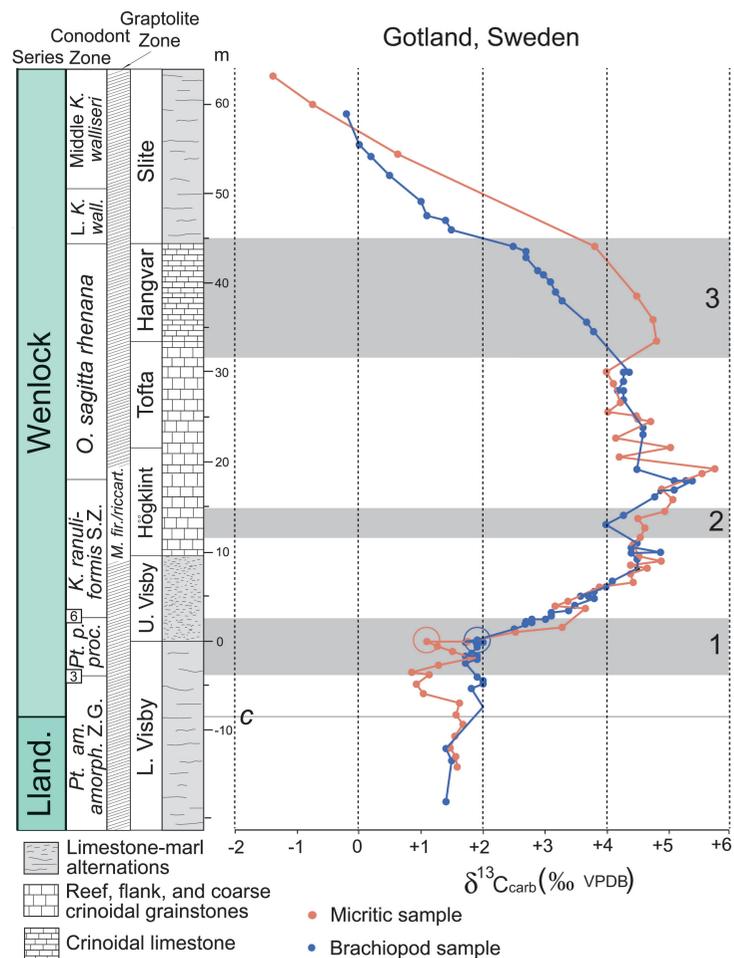
Silurian: The Silurian compilation (Figure 11.4) is from ten different sources. The Llandovery Series is characterized by low-amplitude variability with several small positive $\delta^{13}\text{C}_{\text{carb}}$ excursions in the early Aeronian, late Aeronian, and

early Telychian as well as a significant negative shift near the Aeronian-Telychian boundary (Pöldvere, 2003; Melchin and Holmden, 2006; Munnecke and Männik, 2009; Gouldey et al., submitted). Considerable data exist from the island of Gotland for the Sheinwoodian through Ludfordian stages (Wenlock and Ludlow) (Samtleben et al., 1996, 2000; Bickert et al., 1997; Wenzel and Joachimski, 1996; Azmy et al., 1998; Wigforss-Lange, 1999; Kaljo et al., 2003; Munnecke et al., 2003; Jeppsson et al., 2007) and three prominent positive excursions are recognized (the Ireviken, Mulde and Lau events). The Ireviken event is associated with extinctions, and has been recognized in brachiopods and micrite (bulk rock) from coeval horizons from the Silurian of Gotland (Sweden) (Cramer et al., 2010; Figure 11.8). Data from North America and Arctic Canada confirm the shifts in the early Sheinwoodian (Ireviken), Homerian and middle Ludfordian (Saltzman, 2001; Cramer and Saltzman, 2005). The Pridoli appears to be a relatively stable period in the curve (Kaljo et al., 1997; Azmy et al., 1998) until a positive excursion just before the boundary with the Devonian (Hladikova et al., 1997; Saltzman, 2002b). The basic shape of the $\delta^{13}\text{C}_{\text{carb}}$ curves from brachiopod and bulk rock studies agrees well in records from

the Silurian (e.g., Wenzel and Joachimski, 1996; Bickert et al., 1997; Azmy et al., 1998; Saltzman, 2001).

Devonian: The Devonian compilation (Figure 11.4) is from seven different sources. Carbon isotope curves tied to conodont zones are known from Europe (Buggisch and Joachimski, 2006; van Geldern et al., 2006) and North America (Saltzman, 2005). A large positive excursion is recognized across the base of the Devonian Lochkovian Stage in North America, Europe, and Australia (Hladikova et al. 1997; Saltzman, 2002; Buggisch and Joachimski, 2006). Values fell in the mid-Lochkovian before reaching a broad peak in the Pragian. Emsian values were low, and then gradually increased before a significant negative shift in the late (not terminal) Givetian, which occurred before a series of higher amplitude positive excursions in the early to middle Frasnian, associated with the *falsiovalis*, *punctata*, *hassi*, and *jamieae* conodont zones (Yans et al., 2007; Racki et al., 2008). The excursions across the Frasnian-Famennian boundary, associated with a major extinction episode (e.g., Joachimski and Buggisch, 1993; Joachimski, 1997; Joachimski et al., 2002) were followed by a terminal Devonian positive excursion (Hangenberg) (Brand et al., 2004; Buggisch and Joachimski,

f0045 **FIGURE 11.8** Carbonate carbon ($\delta^{13}\text{C}_{\text{carb}}$) isotope data from Gotland, Sweden (Cramer et al., 2010). The italic lower-case 'c' bisected by a thin gray line represents the base of the Wenlock Series as defined by the LAD of *O. polinclinata polinclinata*. Each data point represents the average of three or more brachiopod samples. This composite figure is synthetic in its representation of unit thickness because each stratigraphic unit varies across the island and data were collected from over 50 localities with a maximum distance of over 60 km. The onset of the early Sheinwoodian (Ireviken) $\delta^{13}\text{C}_{\text{carb}}$ excursion (open circle) occurs in this composite between Datum 3 and Datum 6 of the Ireviken Event (precisely at Datum 4).



2006; Kaiser et al., 2008; Cramer et al., 2008; Myrow et al., 2010). The basic shape of the $\delta^{13}\text{C}$ curves from brachiopod and bulk rock studies agrees well in records from the Late Devonian Frasnian-Famennian boundary interval (Joachimski and Buggisch, 1993; van Geldern et al., 2006). However, some Devonian excursions are poorly known or are yet to be documented globally (e.g., Buggisch and Joachimski, 2006; van Geldern et al., 2006; Myrow et al., 2010).

p0210 **Mississippian and Pennsylvanian** (Figure 11.5): The Mississippian compilation is from Saltzman (2005), with data from Batt et al. (2007) from the upper Visean and Serpukhovian (Chesterian). The Pennsylvanian curve is from Saltzman (2003). The Tournaisian Stage contains a positive excursion (Mii et al., 1999), with the heaviest values ($\sim +7\%$) recorded in multiple sections in Nevada (Saltzman, 2002a) and a smaller peak ($\sim +5\%$) recorded in Europe (Saltzman et al., 2004). A negative shift in the Serpukhovian (Saltzman, 2003; Batt et al., 2007) occurred before the rise of values across the base of the Pennsylvanian, although thicker sequences show multiple excursions in the Chesterian (Wynn and Read, 2007). No other prominent shifts are known globally, and the curve is characterized by high frequency, low amplitude variability in the Great Basin (Saltzman, 2003). As discussed in the section on global and local water mass signals above, Panthalassian values from western North America appear to be lighter than Tethyan values (Mii et al., 1999; Veizer et al., 1999; Saltzman, 2003; Buggisch et al., 2011).

p0215 Detailed Upper Mississippian (Chesterian) bulk rock $\delta^{13}\text{C}$ curves show generally good agreement with values from the secondary shell layers of associated brachiopods (Batt et al., 2007). Other brachiopod layers (e.g., tertiary prismatic layers), however, and taxa (*Composita*) show an offset from bulk carbonate and secondary shell layers by as much as 2 to 5‰ (Batt et al., 2007). Lower Mississippian bulk carbonate and brachiopod calcite $\delta^{13}\text{C}$ curves from widely separate geographic regions reveal a large positive excursion that can be independently biostratigraphically correlated (Mii et al., 1999; Saltzman et al., 2000; Saltzman, 2002, 2003).

p0220 **Permian:** The Permian compilation (Figure 11.5) is from Tierney et al. (in prep), Buggisch et al. (2011) and Korte et al. (2004). Brachiopod data from the Ural Mountains (Grossman et al., 2008) and unpublished data from bulk rock studies in China and Nevada show significant shifts in the Asselian-Sakmarian and across the Artinskian-Kungurian boundary intervals (Buggisch et al., 2011; Tierney et al., unpublished). The Middle Permian Guadalupian Series is characterized by heavy values in China, North America (Texas) and Japan (Korte et al., 2005a; Isozaki et al., 2007; Buggisch et al., 2011), with a negative excursion in the Capitanian (Wignall et al., 2009; Bond et al., 2010). Lopingian values are generally high ($\sim +5\%$) with two very large negative shifts in the Permian-Triassic boundary interval, which have been correlated to major extinctions (Jin et al., 2000; Korte et al., 2004;

Payne et al., 2004; Yin et al., 2007; Xie et al., 2007; Riccardi et al., 2007; Algeo et al., 2007a, b; many others). The basic shape of the $\delta^{13}\text{C}$ curves from brachiopod and bulk rock studies agrees well in records from the Permian (Korte et al., 2005a; Isozaki et al., 2006).

Triassic: The Triassic compilation (Figure 11.6) is from Payne et al. (2004) (up to the Carnian), and Veizer et al. (1999) and Korte et al. (2005b). The lowermost Induan Stage (Griesbachian-Dienerian) shows values generally increasing overall, but punctuated by one or two excursions (e.g., Payne et al., 2004; Galfetti et al., 2007; Horacek et al., 2007). Curves for the Olenekian (Smithian-Spathian) show extreme variability with positive shifts approaching $+8\%$ in some regions, and intervening negative shifts near -4% (e.g., Hauser et al., 2001; Payne et al., 2004; Galfetti et al., 2007; Horacek et al., 2007). Following a positive shift in the early Anisian Stage, relatively stable values appear to characterize the rest of the Middle Triassic, with values falling towards the end of the Late Triassic (e.g., Preto et al., 2009).

Jurassic: The Jurassic compilation (Figure 11.6) is from Katz et al. (2005), except for the period from 175 to 164 Ma, which is from Jones, 1992 (compiled in Veizer, 1999). A positive $\delta^{13}\text{C}_{\text{carb}}$ excursion to values between $+5$ and $+6\%$ occurred in the earliest Jurassic (Hettangian) in Italy (Van de Schootbrugge et al., 2008), although this well-defined excursion is not resolved in the lower-resolution compilation of Katz et al. (2005) that was used for Figure 11.3. The positive Triassic-Jurassic boundary excursion is also observed in separate studies of $\delta^{13}\text{C}_{\text{org}}$ from shales (Williford et al., 2009; Whiteside and Ward, 2011) and is also present in the carbonate carbon compilation of Dera et al. (2011). A negative excursion across the Triassic-Jurassic boundary is also recognized (Pálffy et al., 2001; Hesselbo et al., 2002; Korte et al., 2009; but see also Van de Schootbrugge et al., 2008) and modeled as resulting from the Central Atlantic Magmatic Province (CAMP) eruptions and related methane release in a positive feedback loop with warming (Beerling and Berner, 2002).

Another well-studied period of $\delta^{13}\text{C}$ changes occurs in the Late Pliensbachian-Early Toarcian, where a large positive excursion (Jenkyns, 1985, 1988) is preceded (Littler et al., 2010), and punctuated by negative excursions in both marine and terrestrial sequences (Hesselbo et al., 2000, 2007; Jenkyns et al., 2002; Hermoso et al., 2009). The Early Toarcian positive excursion is associated with excess global organic carbon burial during an Oceanic Anoxic Event (Jenkyns et al., 2002, Jenkyns, 2010). A negative $\delta^{13}\text{C}$ excursion in some Lower Toarcian sections has been proposed to be a result of sampling in restricted seaways (van de Schootbrugge et al., 2005; McArthur et al., 2008), but has also been interpreted as resulting from the release of methane from gas hydrates (Hesselbo et al., 2000, 2007). The younger Jurassic Aalenian through Bajocian contains small shifts (e.g., Bartolini et al., 1999; Sandoval et al., 2008; Dera et al.,

2011), and the Oxfordian contains significant positive and negative excursions (e.g., Jenkyns et al., 2002; Gröcke et al., 2003; Weissert and Erba, 2004; Katz et al., 2005). Smaller changes are recognized throughout the Kimmeridgian-Tithonian (Bartolini et al., 1999; Schouten et al., 2000).

p0240 **Cretaceous:** The Cretaceous compilation (Figure 11.7) is from Katz et al. (2005), and shows positive excursions marking all Oceanic Anoxic Events (e.g., Jenkyns, 2010). The Berriasian stage $\delta^{13}\text{C}$ curve is relatively stable before a significant positive excursion (called the Weissert Event or Late Valanginian Oceanic Anoxic Event, Jenkyns, 2010), which occurred in the Valanginian (Weissert and Erba, 2004; Westermann et al., 2010). Values decrease across the base of the Hauterivian, but the Katz et al. (2005) compilation does not resolve the positive excursion which has been described from the uppermost Hauterivian Faraono Oceanic Anoxic Event (Jenkyns, 2010). A major positive excursion in the early Aptian (Scholle and Arthur, 1980; Weissert and Erba, 2004) is associated with Oceanic Anoxic Event 1a (Selli Event). A more complex positive excursion, possibly including several peaks, spans the late Aptian to early Albian and is associated with Oceanic Anoxic Event 1b (the Paquier Event; Jenkyns, 2010).

p0245 A well known and widely documented global positive shift in carbon isotope values occurs across the Cenomanian-Turonian boundary (named the Bonarelli Event), correlates with Oceanic Anoxic Event 2, and has been observed in carbonate and organic matter (Scholle and Arthur, 1980; Arthur et al., 1987; Sageman et al., 2006; Weissert et al., 2008; Barclay et al., 2010). This event has been documented at many locations, including the Western Interior of the US, boreal shelf seas (UK), western Tethys (Tunisia), and Tethys (Italy) (e.g., Erbacher et al., 2005). Several records are high resolution, recognizing orbital fluctuations (Lanci et al., 2010). The $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{org}}$ excursions differ somewhat in magnitude and possibly in timing, but in general the records can be well correlated (e.g. Arthur et al., 1988; Erbacher et al., 2005). In some sections, the positive carbon isotope excursion is preceded by smaller negative events (Jenkyns et al., 2010). The remainder of Upper Cretaceous is characterized by relatively minor variability (e.g., Jarvis et al., 2006).

p0250 **Cenozoic:** The Cenozoic compilation of bulk isotope $\delta^{13}\text{C}$ values is from Katz et al. (2005), the most comprehensive bulk compilation (Figure 11.7). This record shows reasonable similarity to the higher resolution benthic foraminiferal records shown in the compilation of Zachos et al., 2008 (Figure 11.7). After a large positive shift in the middle Paleocene, a major negative CIE (duration ~ 170 kyr) occurred across the Paleocene-Eocene boundary interval, associated with the extensively documented Paleocene-Eocene Thermal Maximum (PETM) (Zachos et al., 2001, 2008; Sluijs et al., 2007). This event is considered by some to represent a weak version of the Cretaceous Oceanic Anoxic

Events, with emission of isotopically light carbon from lithosphere into the atmosphere-ocean leading to rapid global warming (Jenkyns, 2010). Several smaller negative excursions associated with warming (hyperthermal events) have been recognized in the upper Paleocene-lower Eocene (Cramer et al., 2003; Lourens et al., 2005; Zachos et al., 2010), but are not resolved in the Katz et al. (2005) record. The benthic record shows that these events, lasting overall 30–40 kyr, are global, but they are not resolved in Figure 11.7, where they show as a broad region of overall low values in the lower Ypresian (e.g., Westerhold et al., 2011).

Globally recognized positive carbon isotope excursions p0255 occur in the lowermost Oligocene just above the Eocene-Oligocene boundary (Figure 11.7), across the Oligocene-Miocene boundary (Figure 11.7), and in the middle Miocene (Burdigalian), before values become progressively lighter beginning in about the middle Miocene (Katz et al., 2005). These three positive excursions are all correlated with positive excursions in oxygen isotopes in the same samples, indicative of episodes of global cooling and expansion of ice-sheets on Antarctica (Shackleton and Kennett, 1975; Savin, 1977; Berger et al., 1981; Miller et al., 1987; Zachos et al., 2001, 2008; Cramer et al., 2009). Benthic foraminiferal values for late Miocene through Recent show a broad range (-1 to $+1.5$), reflecting the differences in deep waters of the Pacific and Atlantic oceans, as the modern circulation pattern and aging pattern developed at that time (Cramer et al., 2009). A vast literature exists for Cenozoic $\delta^{13}\text{C}_{\text{carb}}$ measurements, and the reader is referred to the compilations of Zachos et al. (2001, 2008) and Cramer et al. (2009) for references and discussion of globally documented shifts and excursions.

11.5. CAUSES OF CARBON ISOTOPE EXCURSIONS s0050

Interpretation of carbon isotope excursions in terms of global p0260 climate change is a topic of great interest, because of its potential relevance for understanding direct and indirect effects of future, anthropogenic climate change (such as ocean acidification and deoxygenation) and for estimating climate sensitivity of increasing atmospheric CO_2 levels, (e.g., NRC, 2011). Several episodes of extinction and/or rapid evolutionary turnover have been speculated as having resulted from an abrupt rise in temperature, caused by a rapid influx of CO_2 into the atmosphere from volcanogenic and/or methanogenic sources, leading to an accelerated hydrological cycle, increased continental weathering, enhanced nutrient discharge to oceans and lakes, intensified upwelling and increased organic productivity, as well as widespread oceanic anoxia and acidification. These episodes range from the termination of Snowball Earth episodes in the Neoproterozoic (Kennedy et al., 2008), to the Permo-Triassic extinction (Bernier, 2002; Erwin, 2006; Retallack and Jahren, 2008;

[AU11] Kidder and Worsley, 2010), the Jurassic-Cretaceous Oceanic Anoxic Events, as well as the Paleocene-Eocene Thermal Maximum (Cohen et al., 2007; Dunkley-Jones et al., 2010; Jenkyns, 2010).

p0265 There has been considerable debate regarding how high productivity can be sustained over geologic time scales (e.g., several hundred thousand years for most OAEs) to potentially cause positive $\delta^{13}\text{C}$ excursions (e.g. Kump and Arthur, 1999). To achieve anoxia in the deeper waters, replenishment of O_2 from the surface must be slower than the rate of decomposition of organic matter, seeming to imply sluggish vertical circulation. However, export of organic matter from the photic zone required to use the available oxygen can imply high productivity in the surface waters, particularly in cooler time periods in Earth history, in which high latitude, deep water formation incorporates high initial oxygen concentrations in sinking water masses compared to warmer climate (e.g., Hotinski et al., 2001). High productivity surface waters in turn can imply vigorous circulation because the supply of nutrients from land is very small compared that from upwelling of nutrient-rich intermediate and deeper waters (e.g., Hay, 2008). A possible way to reconcile sustained high productivity with sluggish circulation has been that the carbon to phosphorus (C/P) ratio of the buried organic matter may have increased due to the spread of anoxia, which lowers rates of iron oxide formation and associated scavenging of P (e.g., Van Cappellen and Ingall, 1994; Schrag et al., 2002; Mort et al., 2007). Under such circumstances, nitrogen fixation should also increase to counterbalance loss of N to denitrification in anoxic waters (e.g., Murphy et al., 2000; Anbar and Knoll, 2002; Kuypers et al., 2004; Saltzman, 2005).

p0270 Increased preservation of organic matter under certain conditions (e.g., anoxia, high sedimentation rates) can also increase organic matter burial independent of primary production (Bralower and Thierstein, 1984; Sageman et al., 2003; Meyers et al., 2005; Cramer and Saltzman, 2005). In addition, adsorption of carbon compounds onto clay-mineral surfaces may have been an important variable in organic matter burial (Kennedy et al., 2002), although this is controversial for some time periods (e.g., Tosca et al., 2010). Finally, changes in the $\delta^{13}\text{C}$ of the globally integrated weathering (riverine) flux have been proposed as being at least as a partial cause for some $\delta^{13}\text{C}$ excursions that are not obviously linked to relatively high burial rates of organic matter (e.g., Kump et al., 1999; Melchin and Holmden, 2006a, b).

s0055 11.6. CONCLUSION

p0275 In conclusion, the carbon isotopic record is of great value, not only in stratigraphic correlation, but also has the potential to assist us in unraveling the development of Earth's climate, evolution of its biota, and carbon dioxide levels in the

atmosphere. Our present knowledge, however, is limited, because our interpretation of the global carbon isotope record depends on our understanding of the global carbon cycle, which decreases with increasing age of the records. Not only do we lack information on physicochemical parameters, such as ocean circulation (Hay, 2008), but many features of the present global carbon cycle are linked to the present state of biotic evolution. For instance, the increased abundance of C4 plants in the late Miocene may have affected the carbon isotopic composition of the oceans and atmosphere (Derry and France-Lanord, 1996; Kump and Arthur, 1999; Cerling and Ehleringer, 2000).

The evolution and proliferation of pelagic calcifiers in the p0280 Jurassic through Early Cretaceous thoroughly changed the global carbon cycle and made it possible to buffer the saturation state of the oceans (e.g., Zeebe and Westbroek, 2003; Ridgwell, 2005). Evolution of land plants in the Devonian, and the great expansion of the terrestrial biosphere in the Carboniferous, must have affected carbon storage as well as weathering of silicate minerals, which takes up CO_2 from the atmosphere (e.g., Berner, 1990; Royer et al., 2001). Evolution of multicellular calcifying invertebrates in the early Phanerozoic (e.g., Knoll and Carroll, 1999; Narbonne, 2010) led to major changes in carbon secretion in the oceans, as well as making it possible to select specific organisms for isotope analysis. Oxygenation of atmosphere and oceans as the result of the evolution of photosynthesis constitutes the largest change in the carbon cycle during Earth history, possibly occurring in steps, at 800–542Ma and 2300 Ma (Fike et al., 2006).

Considerably more research is necessary, for example, p0285 before we can confidently evaluate whether the Neoproterozoic carbon isotope record can indeed be interpreted as reflecting the functioning of an unfamiliar carbon cycle (Rothman et al., 2003, Fike et al., 2006), or reflects diagenetic processes (Knauth and Kennedy, 2009; Derry, 2010), and before we can confidently use the carbon isotope record to its full potential.

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Abstract:

Variations in the $^{13}\text{C}/^{12}\text{C}$ value of total dissolved inorganic carbon (DIC) in the world's oceans through time have been documented through stratigraphic study of marine carbonate rocks ($\delta^{13}\text{C}_{\text{carb}}$). This variation has been used to date and correlate sediments. The stratigraphic record of carbon isotopes is complex because the main process fractionating ^{12}C from ^{13}C is photosynthesis, with organic matter depleted in the heavy isotope (^{13}C). The carbon isotope record (on the geological timescales considered here) is to a large extent defined by changes in the partitioning of carbon between organic carbon and carbonate, and therefore linked directly to the biosphere and the global carbon cycle. This chapter summarizes $\delta^{13}\text{C}_{\text{carb}}$ variations through geologic time compiled from multiple literature sources. Materials analyzed for curve-construction differ between authors and between geological time periods, and one should carefully consider whether skeletal carbonate secreted by specific organisms or bulk carbonate has been used in evaluating or comparing carbon isotope stratigraphic records. Mid-Jurassic through Cenozoic curves have been mainly derived from pelagic carbonates, and exhibit low amplitude $\delta^{13}\text{C}_{\text{carb}}$ variability (from -1 to $+4\text{‰}$) relative to curves for the earlier part of the record (from -3 to $+8 \text{‰}$ for the Phanerozoic, from -15 to $+15\text{‰}$ for the Proterozoic and Archean). The Mid-Jurassic and older curves are dominantly based on data from platform carbonates, which show greater variability and more spatial heterogeneity. The different character of carbon isotope curves derived from older platform carbonates as compared to younger pelagic records may reflect primary and/or diagenetic processes, difference in paleoenvironments, difference in calcifying organisms, or inherent changes in the global carbon cycle with geologic time and biotic evolution (e.g., changes in reservoir size).

Keywords: ■■■