Authigenic Carbonate and the History of the Global Carbon Cycle

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We present a framework for interpreting the carbon isotopic composition of sedimentary rocks, which in turn requires a fundamental reinterpretation of the carbon cycle and redox budgets over Earth's history. We propose that authigenic carbonate, produced in sediment pore fluids during early diagenesis, has played a major role in the carbon cycle in the past. This sink constitutes a minor component of the carbon isotope mass balance under the modern, high levels of atmospheric oxygen but was much larger in times of low atmospheric O_2 or widespread marine anoxia. Waxing and waning of a global authigenic carbonate sink helps to explain extreme carbon isotope variations in the Proterozoic, Paleozoic, and Triassic.

Since the observation of isotopic fractionation of carbon during photosynthesis more than 60 years ago (1), the contrast in the isotopic composition of organic carbon and calcium carbonate has been used to reconstruct the history of the global carbon cycle and its connection to the oxidation state of the planet, including the rise of atmospheric oxygen (2). The input of carbon to Earth's surface reservoirs ($\delta^{13}C_{in}$) (3) is balanced by the burial of carbon either as organic carbon ($\delta^{13}C_{org}$), which is depleted in ^{13}C relative to dissolved inorganic carbon in seawater (DIC), or as calcium carbonate ($\delta^{13}C_{carb}$), which has a similar isotopic composition to DIC. Changes in the isotopic composition of marine carbonate in the geologic record have thus been interpreted as changes in the fractional burial of organic carbon relative to carbonate carbon (f_{org}), as described by the simple equation (4)

$$\delta^{13}C_{in} = \delta^{13}C_{org}f_{org} + \delta^{13}C_{carb}(1 - f_{org}) \quad (1)$$

For much of Earth history, $\delta^{13}C_{carb}$ has fluctuated around a value of 0 per mil (‰), with $\delta^{13}C_{org}$ and $\delta^{13}C_{in}$ values at roughly –25 and –5‰ respectively, implying that 20% of total carbon burial has been as organic matter (5).

The isotopic mass balance requires a fundamental linkage between the carbon cycle and the oxidation state of Earth's surface as manifest by the amount of oxygen in the atmosphere. An increase in $\delta^{13}C_{carb}$ implies the burial of a higher fraction of organic carbon, or alternatively a decrease in the oxidation of organic matter relative to the weathering of carbonate rocks. In either case, this would increase the amount of oxygen in the atmosphere unless other redox-sensitive elements such as sulfur or iron serve as alternative electron donors.

This basic framework has been used to interpret $\delta^{13}C_{carb}$ variations throughout Earth history. For example, observations of $\delta^{13}C_{carb}$ above +5‰ for more than 10 million years during the Neoproterozoic have been explained in terms of sustained periods of high fractional organic carbon burial (5). Similarly, high $\delta^{13}C_{carb}$ values in the late Paleozoic have been attributed to high organic carbon burial after the proliferation of land plants (2). These interpretations directly inform models of atmospheric oxygen levels over the Phanerozoic (6), leading to suggestions of pulses of oxygen production and consumption throughout the geologic record (7, 8). Thus, a correct reading of carbon isotope mass balance is critical to our understanding of the accumulation of oxidizing capacity (atmospheric O_2 and seawater sulfate) at the Earth's surface through geologic time.

Certain aspects of the $\delta^{13}C_{carb}$ record are challenging to explain in the simple framework described above. First, sustained high $\delta^{13}C_{carb}$ values (>+5‰), such as what is observed throughout the Neoproterozoic (9, 10) and in the early Paleoproterozoic (7), imply very high rates of organic burial and hence accumulation of atmospheric oxygen to levels tens to hundreds times that of the present (4, 7). This is inconsistent with geological evidence for lower oxygen levels during these times (11). Second, large negative isotopic excursions of –10 to –15‰ in the Neoproterozoic are very difficult to explain either by oxidation of large amounts of organic matter (7, 12) or methane (13, 14) because both require a very large change in atmospheric oxygen as well as a very large increase in atmospheric carbon dioxide, neither of which is supported by independent geological evidence. Surveying the $\delta^{13}C_{carb}$ record in its entirety, one is forced to conclude that our basic framework is lacking some fundamental process and that it provides a misleading basis for understanding Earth history. We suggest that authigenic carbonate, produced in sediments during early diagenetic reactions primarily associated with sulfate and iron reduction, has played a major role in the carbon isotope mass balance over Earth

history, although it represents a minor component of the modern isotope mass balance because of high levels of atmospheric oxygen in the modern world. If correct, this requires a reinterpretation of the $\delta^{13}C_{carb}$ record.

Authigenic carbonate refers to any carbonate mineral precipitated inorganically in situ, whether at the sediment-water interface or within sediment pore waters. In the modern ocean, most authigenic carbonate is formed in sediments when alkalinity is produced from diagenetic reactions—usually those that reduce sulfate or ferric iron—resulting in supersaturation of carbonate minerals, including calcite, dolomite, or siderite. Precipitation of pyrite can also be an important source of alkalinity that enhances the precipitation of authigenic carbonate phases. Because most reduction of iron and sulfate occurs through oxidation of methane (anaerobic methane oxidation) or organic carbon, the DIC from which authigenic carbonate forms is generally depleted in ^{13}C, although enrichment is possible if carbonate precipitation occurs deeper in the sediment column, where methanogenesis drives the $\delta^{13}C$ of DIC to higher values. Authigenic carbonates composed of calcite, aragonite, and dolomite occur in continental margin sediments in North and South America and Eurasia; they are characterized by $\delta^{13}C_{carb}$ values ranging from –60 to +26‰, with most values <<0‰ (15). Authigenic carbonates ($\delta^{13}C_{carb}$ = –18 to –55‰) are found over the entire depth range of the Gulf of Mexico slope (16); in Peru Margin sediments, the $\delta^{13}C$ of dolomite varies between –36.1 and +11.5‰, although the majority of measurements lie between –9 and –12‰ (17). This carbonate sink is also common in sediments in anoxic basins and fjords (18, 19), as well as deltaic environments. In the mobile mudbelts of the Amazon shelf, for example, authigenic carbonate forms primarily as siderite and mixed Ca-, Mg-, Fe-, and Mn-carbonates associated with iron reduction and pyrite burial, rather than with sulfate reduction through anaerobic methane oxidation, with mass-weighted $\delta^{13}C_{carb}$ between –15 and –19‰ (20). Approximately 30% of the total carbon burial in the Amazon fan occurs as authigenic carbonate (21). This phenomenon is not limited to modern examples; similar $\delta^{13}C_{carb}$ values have been observed in Cenozoic sediments from the Arctic Ocean and the Norwegian-Greenland Sea (22).

Despite its widespread occurrence, authigenic carbonate does not appear to represent a substantial component (by mass) in the modern global carbon cycle. One reason is that the formation of authigenic carbonate is inhibited by the amount of O_2 in seawater because both oxic respiration and oxidation of reduced compounds [such as Fe(II) and H_2S] lowers the saturation of carbonate phases. A recent study explored a model for the global alkalinity and carbonate cycles, proposing that changes in organic carbon cycling, electron acceptor [Fe(III), SO_4^{2-}, and O_2] concentrations, and the concentration of DIC would

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lead to a greater importance of authigenic carbonates in marine sediments during times of low O_2, such as the Proterozoic or times of widespread anoxia in the Phanerozoic (23). More generally, environmental conditions that minimize aerobic respiration in the water column and in sediments (because this essentially acidifies the pore fluid) and maximize the production of alkalinity per unit of organic carbon respired will favor a large sink of carbon as authigenic carbonate (23).

Is there evidence for high burial rates of isotopically depleted authigenic carbonate in the geologic past? A challenge is that $\delta^{13}C_{carb}$ records before the Jurassic are heavily biased toward shallow-water carbonate platforms because slope and deep-basin sections are typically consumed or highly deformed during subduction. One expects authigenic carbonate to be dominant in slope settings with more anaerobic respiration, rather than in shallow water carbonate platforms with low organic burial and greater oxygen availability. In addition, many studies of $\delta^{13}C_{carb}$ have been motivated by stratigraphy by using the isotope variations to correlate across regions and even continents (10); it is possible that sections with authigenic carbonate may have been excluded from records of $\delta^{13}C_{carb}$ variations if they were considered artifacts of postdepositional processes (7). For stratigraphic studies, such exclusions may be appropriate because the $\delta^{13}C$ of authigenic carbonate does not necessarily capture a global change in the $\delta^{13}C$ of DIC. From the perspective of the global carbon cycle, however, such carbonate deposition cannot be ignored because it may represent a substantial carbon sink.

A series of studies of $\delta^{13}C_{carb}$ focused on global geochemical surveys rather than stratigraphy provides some support for the widespread occurrence of authigenic carbonates in the past

(24). Bulk carbonates from Proterozoic and Early Paleozoic continental margins from around the world record $\delta^{13}C_{carb}$ values that range from +18 to –20‰ (Fig. 1) (24). The lowest values (<–5‰)—and perhaps some of the highest values—are most easily explained with an authigenic component, formed during early diagenesis rather than in the water column. Additional support comes from more detailed studies of Ediacaran (late Neoproterozoic) stratigraphy in China, where deeper water sections have $\delta^{13}C_{carb}$ values as low as –16‰, compared with –2‰ for the shallowest onshore sections (25, 26). These data were originally interpreted as representing a very large $\delta^{13}C$ gradient in DIC over hundreds of meters in the water column, which is difficult to reconcile with rates of ocean mixing; we suggest instead that these micritic carbonates in slope settings with low $\delta^{13}C_{carb}$ values are largely composed of authigenic carbonate, formed in a similar fashion to imperfect modern analogs in the Amazon Fan, the Santa Barbara basin, or the Peru margin (17, 18, 21). Overall, observations of authigenic carbon in modern and ancient settings, as well as theoretical arguments (27), suggest a major role for authigenic carbonate in the global carbon cycle, particularly at times of lower atmospheric O_2.

If authigenic carbonate is a substantial sink for carbon burial at times in the geologic past, the isotopic mass balance described in Eq. 1 must be broadened to make explicit the fraction of carbonate burial that is authigenic (f_{ac}), as well as the different isotopic fractionation factors for organic carbon, authigenic carbonate, and normal marine carbonate (ε_p, ε_{ac}, and ε_{mc}, respectively). We choose to write the isotopic fractionation between seawater and authigenic carbonate in the same manner used for the fractionation associated with photosynthesis (ε_p); like the photosynthetic frac-

tionation, it depends on the isotopic composition of a separate pool of water (pore fluid or intracellular fluid), which in turn depends on the relative rates of chemical reaction (oxidation or fixation of organic carbon) and chemical transport (diffusion in the pore fluid or across the cell membrane).

Thus,

$$\delta^{13}C_{in} = (\delta^{13}C_{DIC} - \varepsilon_p)f_{org} + (1 - f_{org})[(\delta^{13}C_{DIC} - \varepsilon_{ac})f_{ac} + (\delta^{13}C_{DIC} - \varepsilon_{mc})(1 - f_{ac})] \quad (2)$$

or simplifying and solving for $\delta^{13}C_{DIC}$ (27)

$$\delta^{13}C_{DIC} = \delta^{13}C_{in} + f_{org}[\varepsilon_p - \varepsilon_{mc} - f_{ac}(\varepsilon_{ac} - \varepsilon_{mc})] + f_{ac}(\varepsilon_{ac} - \varepsilon_{mc}) \quad (3)$$

Unfortunately, there is no easy way to empirically reconstruct f_{ac} through geologic time because the authigenic component may be broadly distributed across large volumes of sediment with relatively low carbonate content. For example, an authigenic carbonate sink of 2.5×10^{14} g/year—roughly one third of the modern sink related to silicate weathering—would require the addition of less than 2 weight percent carbonate to the annual flux of terrigenous sediment of 1.7×10^{16} g/year. Moreover, it is difficult to estimate even total carbonate accumulation through Earth's history given the incompleteness of the geologic record. However, there is an expectation that f_{ac} will be higher when there is less oxygen in bottom waters along the shelf and slope environments and when alternative electron acceptors, particularly iron, are more abundant or are more focused in the same locations where organic carbon is buried (23).

The average isotopic offset between authigenic carbonate and DIC (ε_{ac}) is determined by the balance between diffusive transport of DIC through pore fluids in the sediment column and the anaerobic oxidation of methane or organic matter, which leads simultaneously to the creation of alkalinity. Higher values of ε_{ac} are expected when the reductant is CH_4 ($\delta^{13}C = -50$ to $-90‰$) as compared with organic carbon ($\delta^{13}C = -22$ to $-26‰$). In modern sediments in which anaerobic methane oxidation is dominant, the maximum alkalinity occurs at the same depth as the depletion of sulfate and a minimum in the $\delta^{13}C$ of DIC (28). In the geologic past, ε_{ac} would also be affected by changes in the amount of DIC in seawater, in addition to the rate of anaerobic respiration in the sediment column. If DIC were substantially higher because of elevated atmospheric partial pressure of CO_2 (P_{CO_2}), a lower seawater Ca^{2+} concentration relative to alkalinity, or some combination of the two, then the $\delta^{13}C$ of DIC in pore fluids would be less affected by oxidation of reduced carbon, resulting in a smaller value for ε_{ac}. In contrast, increasing oxidant availability [such as SO_4 or Fe(III)] would be expected to increase both ε_{ac} and f_{ac}. It is also possible to form authigenic carbonate much later in the burial history when the porosity and permeability of the
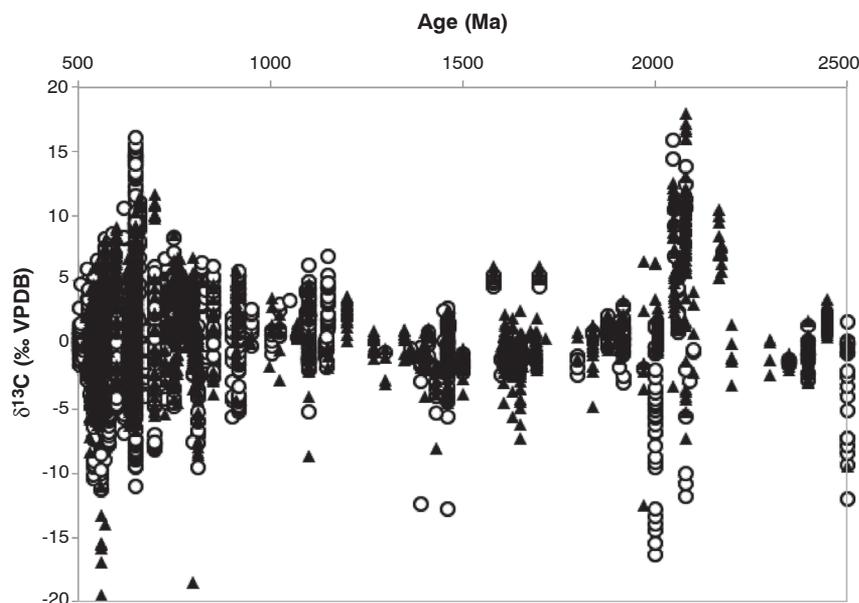
Fig. 1. $^{13}C_{carb}$ measurements on Early Paleozoic and Proterozoic calcites (open circles) and dolomites (triangles) from the compilation of Prokoph et al. (24).

sediments are lower and the distance from the sediment-water interface is large; in this case, diffusive exchange with seawater is less important in determining ε_{ac}.

The inclusion of authigenic carbonate in the global carbon isotope mass balance adds an additional degree of freedom in explaining $\delta^{13}C$ variations in the geologic record and complicates the connection between carbon isotopes and the redox budget of the Earth's surface. In Fig. 2, the $\delta^{13}C$ of DIC is shown as a function of f_{org} and f_{ac} for global average values of ε_{ac} of 15 and 20‰, assuming that the carbon cycle is in steady state and neglecting imbalances in other inputs (such as weathering of organic carbon and carbonate). Prolonged periods of high $\delta^{13}C_{carb}$ in the Neoproterozoic can now be explained without invoking sustained high organic carbon burial or low organic carbon weathering fluxes (which implies the accumulation of massive amounts of atmospheric oxygen), but simply from the persistent burial of larger amounts of isotopically depleted authigenic carbonate. As an end member example, to maintain $\delta^{13}C_{carb}$ at +5‰ without a shift from modern f_{org} values ($f_{org} = 0.2$) requires that authigenic carbonate make up 29 to 37% of the global carbonate sink for global average ε_{ac} values of 20 and 15‰, respectively (Fig. 2). ε_{ac} is not entirely independent of ε_p because the average photosynthetic fractionation is ultimately the reason for a fractionation between authigenic carbonate formed in sediments and DIC.

Applying this new framework to large, negative isotopic excursions, such as those observed in the Neoproterozoic, is more complicated because the carbon cycle during such events need not be at steady state, especially when the excursion lasts less than a few hundred thousand years. We describe two major categories of negative isotopic excursions that have fundamentally different explanations. First, some excursions can be explained through a decline in the global flux of authigenic carbonate that is due to a variety of possible factors, including the location or focusing of organic carbon burial, the carbonate saturation state of seawater, or an increase in the oxygen content of the ocean (and atmosphere). A rapid decline in authigenic carbonate deposition would drop the steady-state $\delta^{13}C$ value of DIC and could be amplified by additional carbon feedbacks, including oxidative weathering of organic carbon. Although we expect some modest connection between $\delta^{13}C_{carb}$ variations and the oxidation state of the Earth surface (through iron reduction, pyrite burial, or intermediate water oxygen content), $\delta^{13}C_{carb}$ excursions created in this way need not be accompanied by a large rise in P_{CO_2} nor a large drop in P_{O_2}. Because such excursions result from changes in the $\delta^{13}C$ of DIC, one would expect to see the excursion in marine organic matter as well as in marine carbonate. Moreover, one would not expect to see the $\delta^{13}C$ values drop below the global average $\delta^{13}C$ of the inputs (–5‰) unless there is additional carbon added from oxidation of organic carbon or methane.

A second category of negative isotope excursions results from the addition of authigenic carbonate into primary marine carbonate in slope or shelf sediments. In this case, the change in $\delta^{13}C_{carb}$ does not represent a change in seawater DIC but rather is a local feature—although it may have a regional or global extent if it is driven, for example, by a marine transgression or changes to global redox budgets (O_2, SO_4, or Fe); thus, the $\delta^{13}C_{org}$ would not track the bulk rock $\delta^{13}C_{carb}$ through the excursion. One might expect the magnitude of the apparent excursion to vary across sedimentary environments, such as from shelf to slope [as is present in Ediacaran successions in China (25, 26)] or even laterally across a sedimentary basin, depending on the distribution of authigenic carbonate production and the degree of depletion of $\delta^{13}C$ in the pore fluid. The extent of the isotopic excursion could theoretically extend far below the $\delta^{13}C$ of carbon inputs, limited only by the isotopic composition and mass contribution of local authigenic carbonate. This mechanism provides an explanation for large negative-isotope excursions in the carbonate record that are not observed in $\delta^{13}C$ of organic carbon, which is a scenario that has invoked much attention and speculation (29). This scenario does not require large changes in atmospheric O_2 and CO_2.

An example of the first type of excursion is possibly captured by the Tayshir anomaly from Neoproterozoic sections in Mongolia (30), which documents a covariation between the $\delta^{13}C$ of organic carbon and carbonate carbon through an isotopic anomaly of ~15‰. With minimum $\delta^{13}C_{carb}$ values during the excursion between –5 and –7‰, one can explain this excursion with nearly a complete shut-off of authigenic carbonate production ($f_{ac} \rightarrow 0$), perhaps with some additional contribution from net oxidation of reduced carbon. The shutdown of authigenesis could be driven by a small change in the oxidation state of intermediate waters on the continental slope, perhaps related to higher atmospheric P_{O_2}, establishing a stronger lysocline and a carbonate saturation gradient in the sediment column.

Fig. 2. Contours of ^{13}C of DIC as a function of f_{org} and f_{ac} for global average values of ε_{ac} of 15 and 20‰, assuming that the carbon cycle is in steady state, and neglecting imbalances in other inputs, based on Eq. 2.
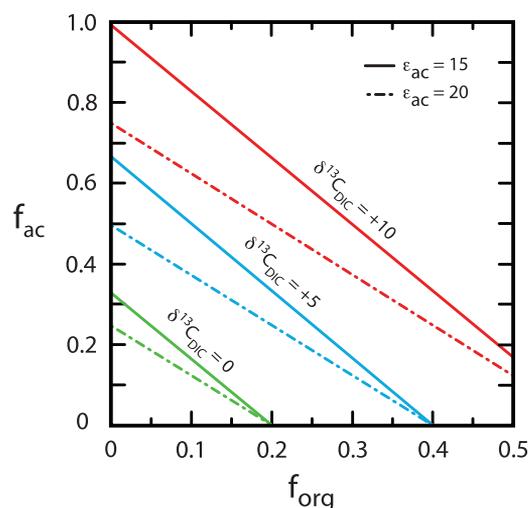
The Ediacaran Shuram anomaly is a possible example of the second category of isotope excursion. The Shuram anomaly occurs in Ediacaran sections around the world, including Namibia, China, and Oman (29). The magnitude of the isotopic excursion is variable across different locations and even within a single basin (25, 26). Important features include $\delta^{13}C_{carb}$ values as low as –12‰ during the peak of the excursion and no parallel variations in $\delta^{13}C_{org}$ across the excursion (31). We suggest the isotopic anomaly in this case could be explained in part by the expansion of the zone of authigenesis onto carbonate platforms during a marine transgression, effectively adding authigenic carbonate to marine carbonate precipitated from the water column.

Previous studies have attributed the large negative excursions in the Neoproterozoic—and the Shuram anomaly, in particular—to diagenetic processes (32, 33), specifically basin-scale alteration of carbonate rocks with fluids with low $\delta^{13}C$ from oxidation of hydrocarbons, or from meteoric alteration (33). On the other hand, it has been argued that the low $\delta^{13}C_{carb}$ values through the Shuram anomaly cannot be explained by diagenesis because they are expressed in oolitic and stromatolitic facies without evidence for secondary cements (29). Moreover, such a diagenetic explanation is difficult to reconcile with the observation of these negative excursions at precise stratigraphic intervals in geologic sections across multiple continents (10, 29). Our explanation may reconcile these views because one would expect isotopic excursions produced by mixing of marine carbonate with a depleted authigenic component to occur at broadly the same stratigraphic interval if they were produced by migration of the zone of authigenesis because of a marine transgression or drop in near-surface O_2 concentration. Textures such as ooids could be preserved if authigenesis occurs on both microscales, consuming organic matter along individual laminations (34), and on mesoscales filling pore spaces with micrite on 10-m scales in mixed-carbonate siliciclastic sequences.

A prominent but transient authigenic carbonate sink may also help explain carbon isotope variations in the Paleozoic (8, 35) and Early Triassic (36). In the Triassic, for example, there is evidence for widespread anoxia in intermediate waters (37), fluctuating $\delta^{13}C_{carb}$ values (–2 to +8‰), and gradients in the $\delta^{13}C_{carb}$ values with depth, often with $\delta^{13}C$ values on the slope 2 to 3‰ lighter than those on the shelf (38). We view the Early Triassic as a candidate for a period of sustained, high authigenic carbonate formation, like much of the Neoproterozoic (23). The fluctuations could be produced either from a change in the global amount of authigenic carbonate (category 1) or by migration in the zone of authigenic carbonate (category 2). In the Early Cambrian, similar fluctuations in the authigenic carbonate sink might have resulted from more modest variations in surface redox or evolutionary leaps such as the biological irrigation of sediments.

The recognition of authigenic carbonate in the sedimentary record presents a challenge for carbon isotope stratigraphy because it allows for local variations in $\delta^{13}C_{carb}$ produced by the addition of a substantial authigenic component after burial. Until there is a clear way to quantify the amount of marine carbonate precipitated in the water column relative to authigenic carbonate precipitated in sediments, questions about the fidelity of chronostratigraphic correlations will remain. Authigenic events are likely to be broadly correlative owing to global changes in surface redox conditions, surface saturation state, and/or eustatic sea level, all of which might drive a migration of the zone of authigenesis or a change in the amount of authigenic precipitation, but detailed correlations at finer scales may prove less reliable.

Including a third major sink for carbon in sedimentary reservoirs does not sever the connection between $\delta^{13}C_{carb}$ and the redox evolution of the Earth surface, but it does imply a more complex relationship. Rather than massive changes in atmospheric O_2 and CO_2, our framework explains the large variations in $\delta^{13}C_{carb}$ in terms of changes in the amount of authigenic carbonate driven perhaps by small changes in atmospheric O_2 but potentially also by changes in the other redox budgets (SO_4 and Fe), in the strength or even existence of a lysocline, or in the focusing of organic carbon burial in different sedimentary environments. With this new framework, the challenge remains to use the geologic record to understand the driving forces and events that have shaped Earth's surface.

References and Notes

1. H. C. Urey, Science **108**, 489 (1948).
2. W. S. Broecker, J. Geophys. Res. **75**, 3553 (1970).
3. The inputs of carbon to Earth's surface carbon reservoirs include the return flux of CO_2 from subduction or metamorphic release of carbon from carbonate and organic matter, the outgassing of mantle carbon, and the weathering of carbonate and organic matter. For a more complete discussion, see (39).
4. A. H. Knoll, J. M. Hayes, A. J. Kaufman, K. Swett, I. B. Lambert, Nature **321**, 832 (1986).
5. J. M. Hayes, H. Strauss, A. J. Kaufman, Chem. Geol. **161**, 103 (1999).
6. R. A. Berner, Am. J. Sci. **309**, 603 (2009).
7. L. R. Kump et al., Science **334**, 1694 (2011).
8. M. R. Saltzman et al., Proc. Natl. Acad. Sci. U.S.A. **108**, 3876 (2011).
9. F. A. Macdonald et al., Science **327**, 1241 (2010).
10. G. P. Halverson, P. F. Hoffman, D. P. Schrag, A. C. Maloof, A. H. N. Rice, Geol. Soc. Am. Bull. **117**, 1181 (2005).
11. D. C. Catling, M. W. Claire, Earth Planet. Sci. Lett. **237**, 1 (2005).
12. T. F. Bristow, M. J. Kennedy, Geology **36**, 863 (2008).
13. D. P. Schrag, R. A. Berner, P. F. Hoffman, G. P. Halverson, Geochem. Geophys. Geosyst. **3**, 1036 (2002).
14. C. J. Bjerrum, D. E. Canfield, Proc. Natl. Acad. Sci. U.S.A. **108**, 5542 (2011).
15. T. H. Naehr et al., Deep Sea Res. Part II Top. Stud. Oceanogr. **54**, 1268 (2007).
16. H. H. Roberts, P. Aharon, Geo-Mar. Lett. **14**, 135 (1994).
17. P. Meister et al., Sedimentology **54**, 1007 (2007).
18. C. E. Reimers, K. C. Ruttenberg, D. E. Canfield, M. B. Christiansen, J. B. Martin, Geochim. Cosmochim. Acta **60**, 4037 (1996).
19. L. G. Anderson, D. Dyrssen, J. Skei, Mar. Chem. **20**, 361 (1987).
20. Z. Zhu, R. C. Aller, J. Mak, Cont. Shelf Res. **22**, 2065 (2002).
21. R. C. Aller, N. E. Blair, Q. Xia, P. D. Rude, Cont. Shelf Res. **16**, 753 (1996).
22. N. Chow, S. Morad, I. S. Al-Aasm, J. Sediment. Res. **70**, 682 (2000).
23. J. A. Higgins, W. W. Fischer, D. P. Schrag, Earth Planet. Sci. Lett. **284**, 25 (2009).
24. A. Prokoph, G. A. Shields, J. Veizer, Earth Sci. Rev. **87**, 113 (2008).
25. G. Jiang, A. J. Kaufman, N. Christie-Blick, S. Zhang, H. Wu, Earth Planet. Sci. Lett. **261**, 303 (2007).
26. B. Shen et al., Geochim. Cosmochim. Acta **75**, 1357 (2011).
27. Bjerrum and Canfield (40) derived a similar expression for the addition of carbonate derived from carbonatization reactions in seafloor basalt. The mathematical expression is identical, but the isotopic fractionation for carbonatization is much smaller and hence provides a much smaller lever to affect the global carbon isotope mass balance. A more complete expression would include separate terms for carbonate in carbonatized basalts as well, provided that they represent removal of carbon from seawater rather than carbon from volcanic outgassing that was never counted in the surface budget.
28. O. Sivan, D. P. Schrag, R. W. Murray, Geobiology **5**, 141 (2007).
29. J. P. Grotzinger, D. A. Fike, W. W. Fischer, Nat. Geosci. **4**, 285 (2011).
30. D. T. Johnston, F. A. Macdonald, B. C. Gill, P. F. Hoffman, D. P. Schrag, Nature **483**, 320 (2012).
31. The absence of covariation of the $\delta^{13}C$ of organic carbon may also be explained by contamination with a secondary component, such as detrital organic carbon (30).
32. L. A. Derry, Earth Planet. Sci. Lett. **294**, 152 (2010).
33. L. P. Knauth, M. J. Kennedy, Nature **460**, 728 (2009).
34. S. M. A. Duguid, T. K. Kyser, N. P. James, E. C. Rankey, J. Sediment. Res. **80**, 236 (2010).
35. A. C. Maloof et al., Geol. Soc. Am. Bull. **122**, 1731 (2010).
36. J. L. Payne et al., Science **305**, 506 (2004).
37. A. H. Knoll, J. A. Babcock, J. L. Payne, S. B. Pruss, W. W. Fischer, Earth Planet. Sci. Lett. **256**, 295 (2007).
38. K. M. Meyer, M. Yu, A. B. Jost, B. M. Kelley, J. L. Payne, Earth Planet. Sci. Lett. **302**, 378 (2011).
39. J. M. Hayes, J. R. Waldbauer, Phil. Trans. R. Soc. B **361**, 931 (2006).
40. C. J. Bjerrum, D. E. Canfield, Geochem. Geophys. Geosys. **5**, Q08001 (2004).

Variable Clonal Repopulation Dynamics Influence Chemotherapy Response in Colorectal Cancer

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Intratumoral heterogeneity arises through the evolution of genetically diverse subclones during tumor progression. However, it remains unknown whether cells within single genetic clones are functionally equivalent. By combining DNA copy number alteration (CNA) profiling, sequencing, and lentiviral lineage tracking, we followed the repopulation dynamics of 150 single lentivirus-marked lineages from 10 human colorectal cancers through serial xenograft passages in mice. CNA and mutational analysis distinguished individual clones and showed that clones remained stable upon serial transplantation. Despite this stability, the proliferation, persistence, and chemotherapy tolerance of lentivirally marked lineages were variable within each clone. Chemotherapy promoted the dominance of previously minor or dormant lineages. Thus, apart from genetic diversity, tumor cells display inherent functional variability in tumor propagation potential, which contributes to both cancer growth and therapy tolerance.

Cancer is sustained by production of aberrant cells that vary in many morphological and physiological properties. This cellular diversity remains a major challenge to our understanding of the neoplastic process and therapeutic resistance. Genetic and nongenetic processes can generate heterogeneity; however, the degree of coordination between these mechanisms and their relative contribution to tumor propagation remains unresolved.

Tumor cell diversity can arise through accrued genetic changes (1) that result in single tumors composed of many subclones that develop through complex evolutionary trajectories (2, 3). As well, tumors contain genetic subclones that vary with respect to differential growth in xenograft assays (4–6), recurrence (7), and metastatic potential (8, 9). Likewise, resistance to cancer therapies can arise through genetic mutations (10, 11).

tum theory is the ratio h/m, measurement of which can be thought of as a determination of ω_c (scaled by c^2). In recent years, h/m experiments have become an important independent measurement of the fine structure constant α because h/m is the least well-known quantity in its definition: $\alpha = (2R_\infty/c)(h/m)(m/m_e)$, where m_e is the electron mass and R_∞ is the Rydberg constant. Independent measurements of α are tests of quantum electrodynamics, and there has been substantial work on measuring α with atom interferometers (*3–5*).

In an atom interferometer, matter waves are split and recombined by using pulses of light. Counterpropagating laser beams stimulate the absorption and emission of a photon, transferring a well-defined momentum to the atom. For two laser beams with the same frequency, the momentum transferred is $2\hbar k$, where k is the wave number of the light (the reciprocal of its wavelength times 2π) (*6*). Thus, the recoil energy of the atom is given by $E = 4\hbar^2 k^2/2m = 4\hbar\omega_r$, where ω_r is the photon recoil frequency. Because the phase of the matter wave evolves according to this energy, the interferometer phase is proportional to ω_r (*5, 7, 8*), and such a device can be thought of as a momentum spectrometer, provided the particle's mass is known. This simplified description of an atom-interferometric measurement of the recoil frequency is nonrelativistic. More importantly, knowledge of the laser wave number allows the value for h/m to be extracted from the measured recoil frequency.

Alternatively, in a relativistic description, the phase evolution of a matter wave is proportional to the mass-energy, and the phase shift of the interferometer is given by $\Delta\phi = 2\omega_c T(\gamma^{-1} - 1)$. Here, T is the time it takes for the matter wave pulse to move between the beamsplitter and mirror pulses of the interferometer, and $\gamma^{-1} = (1 - v^2/c^2)^{1/2}$ is the inverse Lorentz factor from special relativity. The recoil velocity imparted to the atoms, v, is determined by the photon wave number, k. Although atomic recoil velocities in experimentally realizable regimes are on the order of centimeters per second, well below the speed of light, the relativistic effect of time dilation can be viewed as the source of the interferometer phase shift. In the extreme relativistic limit where $v \rightarrow c$, the interferometer phase develops at the full Compton frequency, and the relativistic description elucidates how a measurement of h/m can be interpreted as a measurement of ω_c. However, such a measurement still requires an independent determination of the laser wave number.

Lan *et al.* run an experiment configured similarly to an h/m measurement, the difference being that they have eliminated the laser frequency as a free variable in their system by using a frequency comb. A frequency comb is an optical "ruler" in frequency space that enables an absolute measurement of optical frequencies (*9*). The laser that drives the recoiling atoms is locked to a chosen comb line, and the interferometer signal becomes directly proportional to a defined fraction of the Compton frequency. A common oscillator, used to derive all frequencies for the system, is then stabilized directly to the interferometer signal (see the figure).

By defining the ratio of the laser frequency to ω_r via the comb, all quantities in the interferometer signal are now defined except for mass. Thus, the system locks the common oscillator—a clock—to the mass of an atom. An h/m experiment measures the energy of a recoiling atom as a function of its momentum, a quantity that depends on its mass. This experiment is subtly different from that of Lan *et al.*, which uses this measurement to stabilize an oscillator. This method is a direct analogy to stabilizing an oscillator by using the spectroscopy of cesium, in contrast to measuring the spectroscopy of cesium. By linking time to the mass of an atom, the "Compton clock" has intriguing prospects for the measurement of time and definition of the kilogram.

References
1. T. P. Heavner, S. R. Jefferts, E. A. Donley, J. H. Shirley, T. E. Parker, *Metrologia* **42**, 411 (2005).
2. S.-Y. Lan *et al.*, *Science* **339**, 554 (2013); 10.1126/science.1230767.
3. D. S. Weiss, B. C. Young, S. Chu, *Appl. Phys. B* **59**, 217 (1994).
4. H. Müller, S. W. Chiow, Q. Long, C. Vo, S. Chu, *Appl. Phys. B* **84**, 633 (2006).
5. R. Bouchendira, P. Cladé, S. Guellati-Khélifa, F. Nez, F. Biraben, *Phys. Rev. Lett.* **106**, 080801 (2011).
6. M. A. Kasevich, S. Chu, *Phys. Rev. Lett.* **67**, 181 (1991).
7. Ch. J. Bordé, *Phys. Lett. A* **140**, 10 (1989).
8. H. Müller, S. W. Chiow, Q. Long, S. Herrmann, S. Chu, *Phys. Rev. Lett.* **100**, 180405 (2008).
9. J. L. Hall, T. W. Hänsch, *Femtosecond Optical Frequency Comb Technology: Principle, Operation and Application* (Springer Science Business Media, Dordrecht, Netherlands, 2005).

GEOCHEMISTRY

Carbon Cycle Makeover

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Enhanced levels of anaerobic respiration processes may explain oscillations in Earth's carbon cycle.

In 1845, the French chemist and mining engineer Jacques-Joseph Ebelman figured out why Earth's atmosphere contains oxygen (*1*). Oxygen is produced by plants during photosynthesis, but almost all of this oxygen is used again in respiration. Ebelman reasoned that small amounts of organic matter remaining in sediments after respiration leave a residual of oxygen in the atmosphere. The source of oxygen to the atmosphere represented by organic matter burial is balanced by oxygen sinks associated with rock weathering and chemical reaction with volcanic gases. This is the long-term carbon and oxygen geochemical cycle. But Earth is an old planet, and oxygen levels have changed through time (*2*). On page 540 of this issue, Schrag *et al.* (*3*) challenge the most commonly used geochemical approach to assess long-term changes in the coupled oxygen and carbon cycles.

High on the list of factors controlling oxygen levels is the burial rate of organic carbon into sediments through time. Decades ago, geochemists began to measure the carbon isotope distributions in plant organic matter and in carbonate minerals in modern and ancient marine sediments (*4*). They found that the carbon isotope ratios differed between organic and inorganic carbon. To a first approximation, these differences could be explained by a preferential incorporation of ^{12}C atoms over ^{13}C atoms into organic matter during photosynthesis. Patterns in the isotopic compositions of both inorganic and organic carbon species through geologic time provide clues to the burial history of organic carbon.
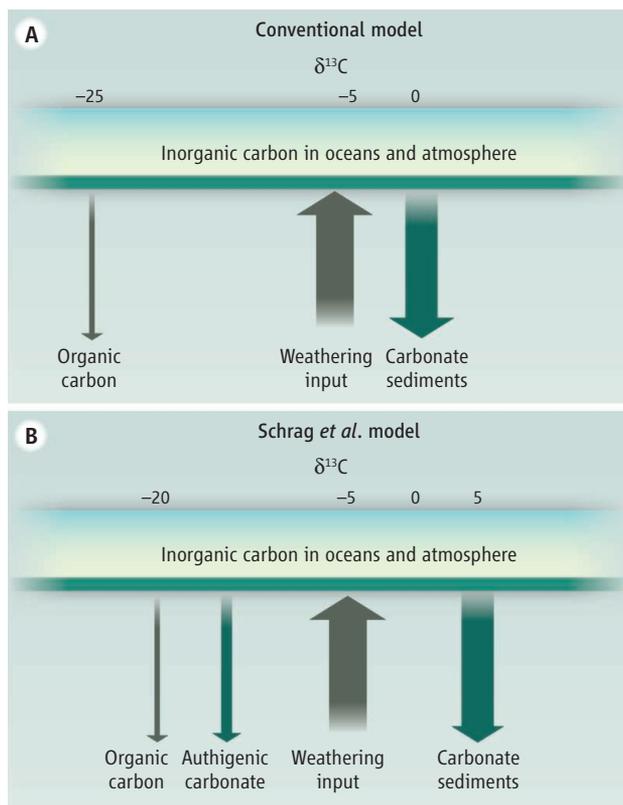
These patterns are normally interpreted through a very simple mass balance (see the figure, panel A). Rock-weathering–derived carbon enters the ocean from rivers in inorganic form, with a $\delta^{13}C$ usually taken as the average for Earth crust. Carbon exits into sediments in inorganic form as carbonate minerals and also as organic carbon. The

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organic carbon has a lower $\delta^{13}C$ than the inorganic carbon by an amount depending on the fractionation of isotopes during photosynthesis. However, the combined isotopic composition of the inorganic and organic carbon leaving the oceans must equal the isotopic composition of the inorganic carbon entering it. Thus, if a large amount of organic carbon is buried, removing a lot of carbon with low $\delta^{13}C$, the $\delta^{13}C$ of the inorganic carbon removed must be high. In contrast, if little organic carbon is buried, the $\delta^{13}C$ in the inorganic carbon should approach that of the carbon entering the oceans. Using this approach, rates of organic carbon burial, and thus oxygen liberation to the atmosphere, have been inferred through geologic time.

As Schrag et al. highlight, however, the carbon isotope record is not always so easy to explain. This is particularly true in Precambrian rocks that show large and long-term enrichments in the $\delta^{13}C$ of carbonate minerals. With the traditional model, these events require massive amounts of organic carbon burial, liberating huge amounts of oxygen to the atmosphere. But what triggered these extreme carbon cycling events, how were they sustained, and where is the independent geochemical evidence that they occurred?

Equally troubling are very strong depletions in the $\delta^{13}C$ of carbonate minerals (5, 6). These depletions can extend to values less than the weathering input and are thus impossible to explain within the traditional carbon mass-balance model. Explanations for these isotope deviations have therefore focused on short-term events, such as the massive oxidation of ^{13}C-depleted dissolved organic matter or methane, or the preferential weathering of ^{13}C-depleted organic material from land. In another set of explanations, the carbon isotopes could have been affected by late-stage processes within Earth with no relation to ocean chemistry. None of these explanations have gained universal acceptance (6).

Schrag et al. provide a clever explanation for both the positive and the negative carbon isotope excursions. They argue that on an Earth with much less oxygen than today—as was likely during the Precambrian—the decomposition of organic matter in sediments by anaerobic respiration processes like sulfate and iron reduction would boost

A Conventional model
$\delta^{13}C$
−25   −5   0
Inorganic carbon in oceans and atmosphere

Organic carbon | Weathering input | Carbonate sediments

B Schrag et al. model
$\delta^{13}C$
−20   −5   0   5
Inorganic carbon in oceans and atmosphere

Organic carbon | Authigenic carbonate | Weathering input | Carbonate sediments

Carbon burial reconsidered. In the traditional model (**A**), carbon loss through organic carbon and carbonate burial balances carbon input from continental weathering. Arrow sizes approximate the relative sizes of the input and output fluxes. The more carbon is lost through organic matter burial, the greater the $\delta^{13}C$ of the carbonate output. Schrag et al. now propose a third output flux through authigenic carbonate formation (**B**). This removal pathway is $\delta^{13}C$-depleted compared to the weathering input, and changes in its flux can change the $\delta^{13}C$ of carbonate sediments with no change in the organic carbon burial flux.

carbonate alkalinity to the point where carbonate minerals (known as authigenic carbonates) would readily form. Because this alkalinity was generated from oxidation of ^{13}C-depleted organic matter or methane, the carbonate formed would also be ^{13}C-depleted and very different in isotopic composition than carbonates formed in surface seawater, from which the carbon isotope record is mostly constructed.

In this scenario, large increases in the $\delta^{13}C$ of inorganic carbon, as revealed from surface seawater carbonates, resulted not from high organic carbon burial rates but rather from enhanced burial of ^{13}C-depleted authigenic carbonates (see the figure, panel B). Likewise, highly ^{13}C-depleted inorganic carbon values were either caused by a reduced deposition rate of authigenic carbonates or are a direct record of the ^{13}C-depleted authigenic carbonates themselves.

With this view of the carbon cycle, the carbon isotope record loses its link to organic carbon burial and oxygen liberation

to the atmosphere. The implications are huge.

There are, however, some important issues to consider. First, sulfate reduction and iron reduction dominate organic carbon mineralization in modern sediments where organic carbon burial is rapid (7). These sediments generate considerable carbonate alkalinity (8), but only small amounts of authigenic carbonate are formed on a global scale (3). It is not clear how these processes would have produced much more authigenic carbonate in the past, particularly because modern systems exposed to little oxygen produce only small amounts of authigenic carbonate minerals (8).

Second, if the model proposed by Schrag et al. is correct, authigenic carbonate production during the large positive $\delta^{13}C$ excursions should be widely preserved in organic-rich sediments. We should actively search for these. The large negative $\delta^{13}C$ excursions, if they record authigenic carbonates, require that enormous amounts of organic matter have been converted to inorganic carbon. However, many rocks housing these excursions contain very little organic matter (9), not obviously consistent with the large amounts of organic matter diagenesis required by Schrag et al.'s model.

Finally, the large negative $\delta^{13}C$ excursions of the late Precambrian provide well-defined and globally coherent isotope events (6), yet sediment diagenetic reactions are highly variable in space and time. It remains to be shown how a globally coherent pattern can result from these processes. Nonetheless, new ideas take time to mature, and Schrag et al. have brought a fresh new approach to solving some puzzling problems with our understanding of the carbon cycle.

References
1. J. J. Ebelman, *Ann. des Mines* **7**, 3 (1845).
2. L. R. Kump, *Nature* **451**, 277 (2008).
3. D. P. Schrag et al., *Science* **339**, 540 (2013).
4. H. Craig, *Geochim. Cosmochim. Acta* **3**, 53 (1953).
5. L. R. Kump et al., *Science* **334**, 1694 (2011).
6. J. P. Grotzinger, D. A. Fike, W. W. Fischer, *Nat. Geosci.* **4**, 285 (2011).
7. D. E. Canfield, E. Kristensen, B. Thamdrup, *Aquatic Geomicrobiology* (Academic Press, New York, 2005).
8. C. E. Reimers, K. C. Ruttenberg, D. E. Canfield, M. B. Christiansen, J. B. Martin, *Geochim. Cosmochim. Acta* **60**, 4037 (1996).
9. D. T. Johnston, F. A. Macdonald, B. C. Gill, P. F. Hoffman, D. P. Schrag, *Nature* **483**, 320 (2012).

10.1126/science.1231981