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 O2 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 (δ13Corg) (3) is balanced by the burial of carbon either as organic carbon (δ13Corg), which is depleted in 13C relative to dissolved inorganic carbon in seawater (DIC), or as calcium carbonate (δ13Ccalc), 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 (forg), as described by the simple equation (4)

δ13Cin = δ13Corg,forg + δ13Ccalc(1−forg) (1)

For much of Earth history, δ13Ccalc has fluctuated around a value of 0 per mil (‰), with δ13Corg and δ13Cin 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 δ13Ccalc 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 δ13Corg variations throughout Earth history. For example, observations of δ13Ccalc 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 δ13Ccalc 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 O2 and seawater sulfate) at the Earth’s surface through geologic time.

Certain aspects of the δ13Ccalc record are challenging to explain in the simple framework described above. First, sustained high δ13Ccalc values (5‰ to 15‰), 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 δ13Ccalc 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 diageneric 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 δ13Ccalc 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 alkalinization 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 alkalinization 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 13C, although enrichment is possible if carbonate precipitation occurs deeper in the sediment column, where methanogenesis drives the δ13C 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 δ13Ccalc values ranging from −60 to −26‰, with most values <−5‰ (15). Authigenic carbonates (δ13Ccalc = −18 to −55‰) are found over the entire depth range of the Gulf of Mexico slope (16); in Peru Margin sediments, the δ13C 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 mudflats 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 methanogen oxidation, with mass-weighted δ13Ccalc between −15 and −19‰ (20). Approximately 30% of the total carbonate burial in the Amazon fan occurs as authigenic carbonate (21). This phenomenon is not limited to modern examples; similar δ13Ccalc 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 O2 in seawater because both oxic respiration and oxidation of reduced compounds [such as Fe(II) and H2S] lowers the saturation of carbonate phases. A recent study explored a model for the global alkalinization and carbonate cycles, proposing that changes in organic carbon cycling, electron acceptor [Fe(III), SO42−, and O2] concentrations, and the concentration of DIC would...
lead to a greater importance of authigenic carbonates in marine sediments during times of low O₂, 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 δ¹³C 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 δ¹³C 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 δ¹³C carb variations if they were considered artifacts of postdepositional processes (7). For stratigraphic studies, such exclusions may be appropriate because the δ¹³C of authigenic carbonate does not necessarily capture a global change in the δ¹³C 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 δ¹³C 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 δ¹³C 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 δ¹³C 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 δ¹³C 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 δ¹³C 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 O₂.

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 (fₐₑ), as well as the different isotopic fractionation factors for organic carbon, authigenic carbonate, and normal marine carbonate (εₚ, εₑ, and εₑₑ, respectively). We choose to write the isotopic fractionation between seawater and authigenic carbonate in the same manner used for the fractionation associated with photosynthesis (εₚ); like the photosynthetic fractionation, 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,

\[ \delta^{13}C_{\text{in}} = (\delta^{13}C_{\text{DIC}} - \epsilon_p f_{\text{org}} + (1 - f_{\text{org}})(\delta^{13}C_{\text{DIC}} - \epsilon_{\text{ac}}) f_{\text{ac}} + (\delta^{13}C_{\text{DIC}} - \epsilon_{\text{mc}})(1 - f_{\text{ac}}) \]  

(2)

or simplifying and solving for δ¹³C DIC (27)

\[ \delta^{13}C_{\text{DIC}} = \delta^{13}C_{\text{in}} + f_{\text{org}} \epsilon_p - \epsilon_{\text{ac}} f_{\text{ac}}(\epsilon_{\text{ac}} - \epsilon_{\text{mc}}) + f_{\text{ac}}(\epsilon_{\text{ac}} - \epsilon_{\text{mc}}) \]  

(3)

Unfortunately, there is no easy way to empirically reconstruct fₑ 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 × 10¹⁴ 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 × 10¹⁶ 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 fₑ 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 (εₑₑ) 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 εₑₑ are expected when the reductant is CH₄ (δ¹³C = −50 to −90‰) as compared with organic carbon (δ¹³C = −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 δ¹³C of DIC (28). In the geologic past, εₑₑ 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 CO₂ (P CO₂), a lower seawater Ca²⁺ concentration relative to alkalinity, or some combination of the two, then the δ¹³C of DIC in pore fluids would be less affected by oxidation of reduced carbon, resulting in a smaller value for εₑₑ. In contrast, increasing oxidant availability (such as SO₄ or Fe(III)) would be expected to increase both εₑₑ and fₑₑ. It is also possible to form authigenic carbonate more quickly in the burial history when the porosity and permeability of the

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Fig. 1. ¹³C carb measurements on Early Paleozoic and Proterozoic calcites (open circles) and dolomites (triangles) from the compilation of Prokoph et al. (24).
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 $\delta^{13}C_{\text{carb}}$ 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 $\delta^{13}C_{\text{org}}$ would not track the bulk rock $\delta^{13}C_{\text{carb}}$ 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 successes 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 therefore be extremely extended far below the $\delta^{13}C$ of carbonate 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 substantial 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 $\sim 15\%o$. With minimum $\delta^{13}C_{\text{carb}}$ values during the excursion between $-5$ and $-7\%o$, one can explain this excursion with nearly a complete shut-off of authigenic carbonate production ($f_{\text{ac}} \to 0$), 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 atmospheric $PO_2$, establishing a stronger lysocline and a carbonate saturation gradient in the sediment column.

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 $\delta^{13}C_{\text{carb}}$ values as low as $\sim 12\%$ during the peak of the excursion and no parallel variations in $\delta^{13}C_{\text{org}}$ 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 $\delta^{13}C_{\text{carb}}$ values through the Shuram anomaly cannot be explained by diagenesis because they are observed 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.

**Fig. 2.** Contours of $\delta^{13}C$ of DIC as a function of $f_{\text{org}}$ and $f_{\text{ac}}$ for global average values of $e_{\text{ac}}$ of 15 and 20%, assuming that the carbon cycle is in steady state, and neglecting imbalances in other inputs, based on Eq. 2.
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 δ13Ccarb values (−2 to +8‰), and gradients in the δ13Ccarb values with depth, often with δ13C 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 logical irrigation of sediments.

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.

References and Notes

3. The inputs of carbon to Earth’s surface carbon reservoirs include the return flux of CO2 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).
27. Bjerrum and Canfield (40) derived a similar expression for the addition of carbonate derived from carbonatization reactions in seawater basalt. The mathematical expression is identical, but the isotopic fractionation for carbonatization of the neoplastic process and therapeutic resistance. C
31. The absence of covariation of the δ13C of organic carbon may also be explained by contamination with a secondary component, such as detrital organic carbon (30).

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