

Carbon-Isotope Signature of Diagenetic Carbonates

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Diagenetic carbonates often show large variations in their carbon isotope compositions. Variations are mainly the result of isotope fractionation effects during microbial metabolic processes, and these processes themselves may induce carbonate formation. Inorganic carbon from dissimilatory microbial activity shows negative carbon isotope values ($\delta^{13}\text{C}$), in particular if methane is used as a carbon source. In turn, inorganic carbon produced during methanogenesis shows positive $\delta^{13}\text{C}$ values. The range of isotope values preserved in the carbonate phase ultimately depends on the reservoir sizes, diffusive mixing of different carbon sources, and episodic formation of carbonate. The carbon-isotope signature of diagenetic carbonates therefore represents an archive of past biogeochemical activity in the subsurface.

Keywords: carbon isotopes ; diagenetic carbonates ; inorganic carbon ; dissimilatory microbial activity ; methanogenesis ; isotope fractionation ; biogeochemical conditions ; carbonate precipitation ; diffusive mixing

1. Processes Inducing Carbonate Formation in the Deep Biosphere

Before discussing how carbon-isotope patterns characteristic for particular biogeochemical zones are preserved in diagenetic carbonates, the factors controlling authigenic (incl. diagenetic) carbonate formation in sediments need to be briefly summarized. Generally, carbonates precipitate due to an increase of the saturation state (here expressed as saturation index $\text{SI} = \log \text{IAP} - \log K_{\text{SP}}$, where IAP is the ion activity product and K_{SP} is the solubility product). Most commonly, cations (mainly Ca^{2+} and Mg^{2+}) are sufficiently supplied from seawater in the uppermost few metres (Baker and Burns, 1985; Meister et al., 2007) ^{[1],[2]} or sometimes through deep circulating fluids (Meister et al., 2011) ^[3]. Carbonate saturation can be significantly increased due to microbial metabolic activity, whereby it is still debated which microbial processes indeed can induce carbonate precipitation. Under marine conditions, sulphate reduction, which is producing DIC and alkalinity at a 1:1 ratio, may even lead to a lowering of the saturation state due to a drop in pH (Meister, 2013 ^[4]; and references therein), unless most of the 28 mmol/L of sulphate in seawater are turned over. In contrast, AOM produces two moles of alkalinity per mole of DIC and, thus, efficiently increases the SI of carbonates (Moore et al., 2004; Ussler III. et al., 2008; Meister, 2013) ^{[4],[5],[6]}. Furthermore, methanogenesis always produces CO_2 and no alkalinity (as seen from Equation (3)), but the acidification effect is largely buffered by alkalinity produced near the SMT and the release of ammonia. Further alkalinity may originate from the alteration of silicates (mainly volcanic glass but possibly also by clay minerals; Wallmann et al., 2008; Meister et al., 2011; Wehrmann et al., 2016) ^{[3],[7],[8]}. These sources of alkalinity production, perhaps in combination with exsolution of CO_2 via methane bubbles, may prevent carbonate undersaturation in the methanogenic zone. Although these effects have not been precisely quantified yet, and it remains unclear how focused diagenetic beds of carbonate can form in the methanogenic zone, it is most likely due to the dynamics of a supersaturation front (cf. Moore et al., 2004) ^[5].

2. Controls of $\delta^{13}\text{C}$ Composition of Diagenetic Carbonates

Carbonate precipitation itself is subject to fractionation effects, whereby equilibrium fractionation prevails at slow precipitation rates observed in the deep biosphere (Turner, 1982) ^[9]. The carbonate mineral phase is, in most cases, enriched in ^{13}C by a few permil relative to the inorganic carbon ($\sim 2\text{‰}$ for calcite; Deines et al., 1974) ^[10]. For dolomite, the separation factor relative to CO_2 is on the order of 12‰–14‰ at ambient temperatures (Ohmoto and Rye, 1979; Golyshev et al., 1981) ^{[11],[12]}. Subtracting the isotope effect of 9‰ between CO_2 and HCO_3^- (Mook, 1974) ^[13] results in a range of 3‰–5‰ for dolomite and HCO_3^- . As a result of this fractionation effect, it was suggested that the residual DIC is depleted in ^{13}C due to a Rayleigh effect (Michaelis et al., 1985) ^[14]. However, since carbonate precipitation is limited by the production of alkalinity and the supply of major cations from seawater, while DIC is usually not limited in the deep biosphere, as it is produced in ample amounts from microbial dissimilation reactions, carbonate precipitation has most likely a minor effect on the isotopic composition of DIC. This has also been confirmed by model calculations (e.g., Chuang et al., 2019) ^[15]. Thus, the carbon-isotope signature of the porewater becomes trapped in the diagenetic carbonate, providing a signature for past biogeochemical conditions at the location and time of precipitation.

Suboxic vs. anoxic zones: It is often seen in carbonates, especially if they occur in organic carbon-rich sediments, that $\delta^{13}\text{C}$ values are in a range between 0‰ and –10‰, but not as negative as to indicate a signature typical for a sulphate reduction zone. This could be the result of a precipitation in the top few centimetres below the sediment surface, where carbon isotopes follow a mixing hyperbola. Typically, in suboxic sediments, where the dissimilatory rates are moderate, and the redox zonation accordingly expanded, $\delta^{13}\text{C}$ values fall into this intermediate range, as observed in Ca-rich rhodochrosite occurring within mottled and bioturbated sediments of the Eastern Equatorial Pacific (Meister et al., 2009) [16]. Thereby Fe- and Mn-reduction may contribute to carbonate supersaturation (Kasina et al., 2017, and references therein) [17]. Intermediate values may also occur in shallow sulphate-reduction zones, e.g., in bituminous sediments, where laminae of authigenic carbonate form just below the sediment/water interface and, hence, early with respect to burial along the mixing gradient (cf. the Triassic Besano Fm., Ticino, Switzerland; Bernasconi et al., 1994 [18]; see discussion in Meister et al., 2013b) [19]. Alternatively, the isotope values may represent a mixture of different carbonate phases of different origin, e.g., dolomite mud from an adjacent platform, showing normal marine isotope values. Therefore, a further petrographic analysis is often necessary to determine the origin of the carbonate, in order to interpret its carbon-isotope signature.

Sulphate-methane transition zone: While sulphate reduction alone rather lowers the saturation state of carbonates, an early onset of AOM has been suggested to induce the formation of carbonates, such as carbonate concretions in organic carbon-rich shale of the Santana Fm. (Brazil; Heimhofer et al., 2018) [20] at very shallow depths. Shallow SMT zones are well documented from modern settings (e.g., Thang et al., 2013) [21] and they may indeed induce carbonate cementation (e.g., Jørgensen et al., 1992) [22]. However, an actual AOM signature in $\delta^{13}\text{C}$ with values below –35‰ is only exceptionally preserved, such as in a dolomite layer at the Peru Trench at 6.5 m below seafloor (mbsf; Meister et al., 2007) [1]. Instead, a great range of carbon-isotope values have been reported from dolomite layers intercalated in organic carbon-rich diatom ooze drilled from upwelling regions offshore California (Pisciotta and Mahoney, 1981) [23], in the Gulf of California (Kelts and McKenzie, 1982) [24], or in Miocene diatomite of the Monterey Fm. (California; Murata et al., 1969; Kelts and McKenzie, 1984) [25, 26]. Also, Rodriguez et al. (2000) [27] report strongly positive $\delta^{13}\text{C}$ values in siderites from a methanogenic zone at Blake Ridge. While the positive $\delta^{13}\text{C}$ values were interpreted as a result of precipitation in the methanogenic zone, negative values in dolomites of the Messinian Tripoli Fm. in Sicily were interpreted as indicative of precipitation in the sulphate-reduction zone. This explanation seems obvious, but it still remains unclear what caused precipitation of carbonates in the methanogenic zone, as methanogenesis should not per se lead to a focused supersaturation of carbonates.

Deep methanogenic zone: A case in which dolomite cements are indeed observed to form in the methanogenic zone is OPD Site 1230, located in the Peru Trench. This site, at a water depth of 5000 m, is located on the Peruvian accretionary prism, where the sedimentary succession is dissected by a fault zone at 230 mbsf). A dolomite breccia was drilled at this depth, showing more radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ ratios than modern seawater, indicating precipitation from a fluid that was derived from interaction with continental basement rocks, deep in the prism (Meister et al., 2011) [3], presumably delivering alkalinity and Ca^{2+} to induce dolomite precipitation. While this site represents a special case, it is still not understandable how dolomite can otherwise form in a methanogenic zone.

3. Interpreting $\delta^{13}\text{C}$ Archives Through Time

Carbon isotopes were measured in diagenetic dolomites through a 150 m thick interval on the Peru Margin, showing varying $\delta^{13}\text{C}$ (Figure 1A–C; ODP Site 1229; Meister et al., 2007) [1]. The dolomites also show $^{87}\text{Sr}/^{86}\text{Sr}$ ratios near to Pleistocene–Holocene seawater, while the ratios in the porewater strongly decrease with depth, indicating that the dolomites formed near to the sediment–water interface. The dolomites thus formed in the past and document an actively evolving biosphere through time.

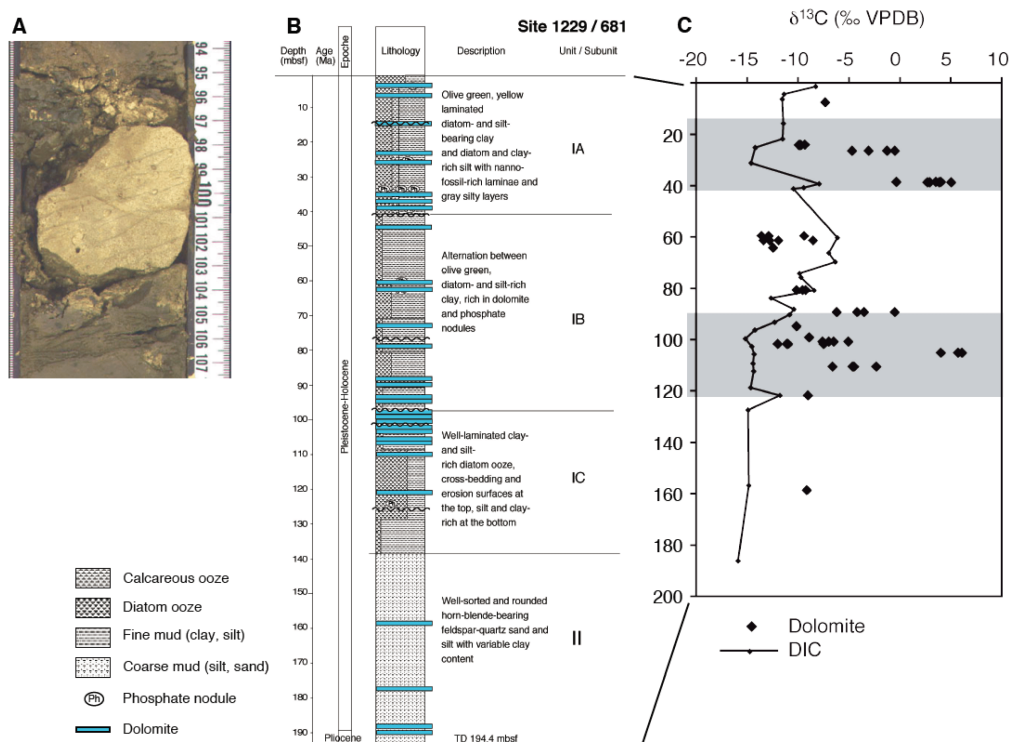


Figure 1. Patterns of carbon isotopes preserved in diagenetic carbonates from the Peru Margin: (A) Fragment of discrete, hard lithified, diagenetic dolomite; (B) distribution of dolomite layers through the sequence at ODP Site 1229; (C) carbon-isotope values in diagenetic dolomites in comparison to carbon-isotope composition of the present porewater.

Episodic carbonate formation: The dolomite beds do not present uniform conditions through time, as otherwise fine-grained dolomite would have been homogeneously distributed throughout the sediment. Instead precipitation must have occurred episodically, at focused locations. Based on their regular spacing on the order of glacial–interglacial cycles in the sediment, Compton (1988) [28] proposed that diagenetic dolomite beds in the Monterey Fm. could be linked to Milankovitch cyclicity in sediment deposition. Meister et al. (2008) [29] followed this idea by showing that oxygen isotopes in dolomites, that occur with a spacing of ca. 10 m, reflect marine $d^{18}O$ values and bottom water temperatures of glacial periods on the Peru Margin. Contreras et al. (2013) [30] found enrichments of dolomite, barite, and isotopically light archaeol ($d^{13}C = -73\text{‰}$) as an imprint of an earlier shallow SMT zone far above the present SMT, which has shifted downward since then. In this manner, the isotopic signature of archaeol can be explained by fractionation as part of the Wood–Ljungdahl pathway (see discussion above). Reaction-transport modelling then confirmed that an upward and downward migration over 30 meters within the time frame of 100 ka is feasible. In conclusion, the dolomite layers on the Peru Margin formed in the aftermath of a rapid deposition of an organic carbon-rich, interglacial sediment layer that, during its burial, triggered a temporary onset of a shallow SMT zone. During this time, a dolomite layer formed at the upper SMT.

Dynamics in carbon-isotope preservation: While the episodic precipitation of dolomites can be explained by a 100 ka cyclicity in deep biosphere activity, longer-term changes on the order of several 100 ka are superimposed and manifested in the $d^{13}C$ record. In theory, three explanations can be proposed (Figure 2A–C): (A) Precipitation in different zones as suggested by Kelts and McKenzie (1984) [31], whereby the carbon-isotope signature is controlled by the depth of a carbonate saturation front relative to the redox zonation and $d^{13}C$ profile in the porewater. The saturation front could be uncoupled from the redox zonation due to outgassing of CO_2 from the methanogenic zone. (B) At a shallow SMT, outgassing of CH_4 is frequently observed (e.g., Dale et al., 2008b) [32], resulting in the loss of ^{13}C -depleted carbon and accordingly, less negative $d^{13}C_{DIC}$ near the SMT. This mechanism can be well reproduced with reaction transport modelling (Meister et al., 2019b, Figure 1 therein) [33]. (C) Due to an increase in methanogenic activity, $d^{13}C$ in both CH_4 and DIC may increase in the methanogenic zone. This is clearly the case at Peru Margin ODP Site 1229, where the modern-day $d^{13}C_{DIC}$ is negative in the methanogenic zone, but was positive in the past (Meister et al., 2019a; and references therein) [34]. The observation that the variations of $d^{13}C$ in diagenetic dolomites are coupled to variations of $d^{34}S$ in pyrite provides independent evidence that two episodes of enhanced deep-biosphere activity involving stronger methanogenic activity occurred throughout the Pleistocene. Most likely, a combination of the effects A–C occurs in a dynamic way. Ultimately, reaction-transport modelling under non-steady-state conditions will clarify the mechanisms that generated these diagenetic records.

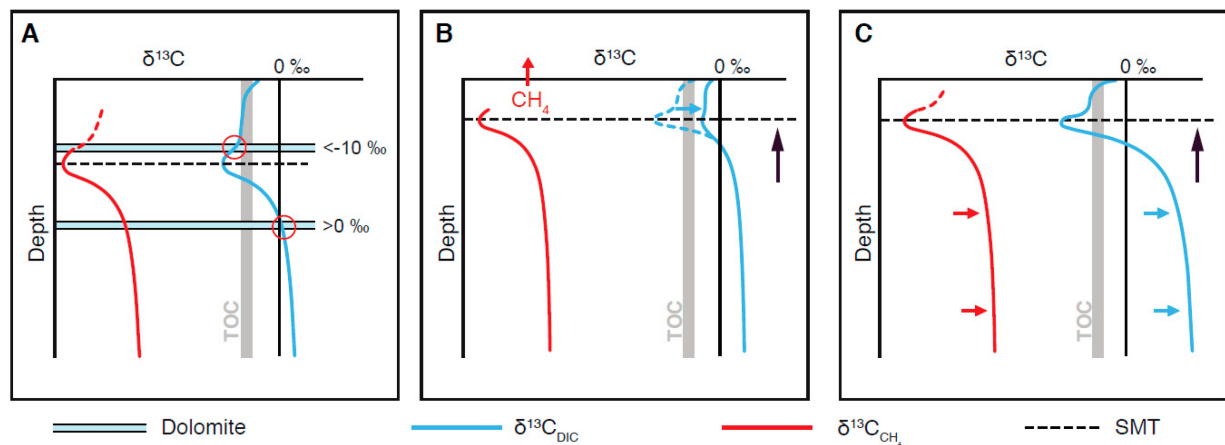


Figure 2. Possible scenarios of carbon-isotope incorporation in diagenetic dolomites: **(A)** Dolomite precipitation in different redox zones; **(B)** dolomite formation at the SMT showing variable $\delta^{13}\text{C}_{\text{DIC}}$ as a result of CH_4 escape; **(C)** changing $\delta^{13}\text{C}_{\text{DIC}}$ due to variations in methanogenic activity."

The entire content of this entry is cited from Meister and Reyes (2019). The publication can be found here: <https://www.mdpi.com/2076-3263/9/12/507/htm>

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