Carbon-Isotope Signature of Diagenetic Carbonates

Subjects: Geochemistry & Geophysics

Contributor: Patrick Meister

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 (d^{13}C), in particular if methane is used as a carbon source. In turn, inorganic carbon produced during methanogenesis shows positive d^{13}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.

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 SI = log IAP – log K_{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 δ^{13}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 (~2‰ 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 d^{13}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, d^{13}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 d^{13}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 (Pisciotto 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 d^{13}C values in siderites from a methanogenic zone at Blake Ridge. While the positive d^{13}C values were interpreted as a result of precipitation in the methanogenic zone, negative values in dolomites of the Messinan 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}Sr/^{86}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 δ^{13}C Archives Through Time

Carbon isotopes were measured in diagenetic dolomites through a 150 m thick interval on the Peru Margin, showing varying d^{13}C (Figure 1A–C; ODP Site 1229; Meister et al., 2007) [1]. The dolomites also show ^{87}Sr/^{86}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.
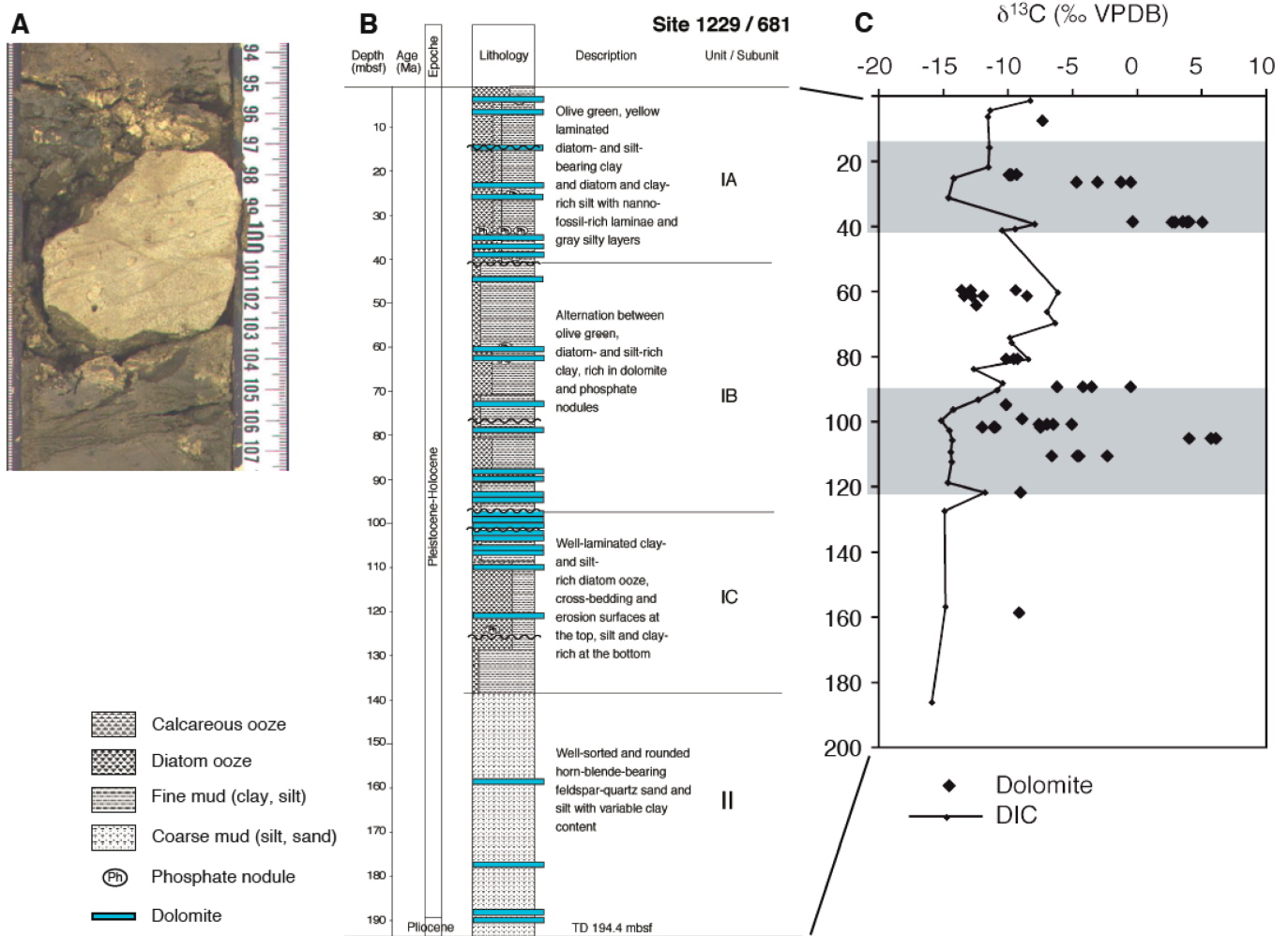
Figure 1. Patterns of carbon isotopes preserved in diagenetic carbonates from the Peru Margin: (**A**) Fragment of discrete, hard lithified, diagenetic dolomite; (**B**) distribution of dolomite layers through the sequence at ODP Site 1229; (**C**) carbon-isotope values in diagenetic dolomites in comparison 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 ($d^{13}C = -73‰$) 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.
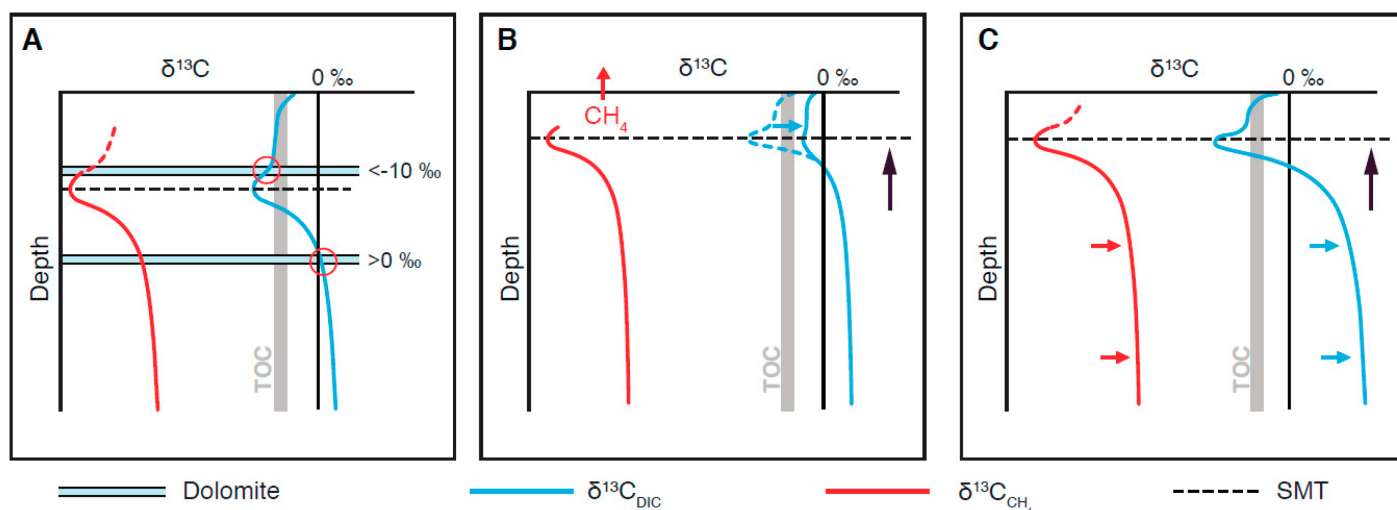

Figure 2. Possible scenarios of carbon-isotope incorporation in diagenetic dolomites: (**A**) Dolomite precipitation in different redox zones; (**B**) dolomite formation at the SMT showing variable $d^{13}C_{DIC}$ as a result of CH_4 escape; (**C**) changing $d^{13}C_{DIC}$ due to variations in methanogenic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

References

1. Patrick Meister; Judith A. McKenzie; Crisógono Vasconcelos; Stefano Bernasconi; Martin Frank; Marcus Gutjahr; Daniel P. Schrag; Dolomite formation in the dynamic deep biosphere: results from the Peru Margin. *Sedimentology* **2007**, *54*, 1007-1032, 10.1111/j.1365-3091.2007.00870.x.

2. Stephen J. Burns Paul A. Baker; Occurrence and Formation of Dolomite in Organic-Rich Continental Margin Sediments. *AAPG Bulletin* **1985**, *69*, 1917-1930, 10.1306/94885570-1704-11d 7-8645000102c1865d.

3. Patrick Meister; Marcus Gutjahr; Martin Frank; Stefano M. Bernasconi; Crisógono Vasconcelos; Judith A. McKenzie; Dolomite formation within the methanogenic zone induced by tectonically driven fluids in the Peru accretionary prism. *Geology* **2011**, *39*, 563-566, 10.1130/g31810.1.

4. Patrick Meister; Two opposing effects of sulfate reduction on carbonate precipitation in normal marine, hypersaline, and alkaline environments. *Geology* **2013**, *41*, 499-502, 10.1130/g34185.1.

5. T.S. Moore; R.W. Murray; A.C. Kurtz; D.P. Schrag; Anaerobic methane oxidation and the formation of dolomite. *Earth and Planetary Science Letters* **2004**, *229*, 141-154, 10.1016/j.epsl.20 04.10.015.

6. Willliam Ussler; Charles K. Paull; Rates of anaerobic oxidation of methane and authigenic carbonate mineralization in methane-rich deep-sea sediments inferred from models and geochemical profiles. *Earth and Planetary Science Letters* **2008**, *266*, 271-287, 10.1016/j.epsl.20 07.10.056.

7. K. Wallmann; G. Aloisi; M. Haeckel; P. Tishchenko; G. Pavlova; Jens Greinert; Steffen Kutterolf; A. Eisenhauer; Silicate weathering in anoxic marine sediments. *Geochimica et Cosmochimica Acta* **2008**, *72*, 2895-2918, 10.1016/j.gca.2008.03.026.

8. Wehrmann, L.M.; Ockert, C.; Mix, A.; Gussone, N.; Teichert, B.M.A.; Meister, P. Multiple onset of methanogenic zones, diagenetic dolomite formation, and silicate alteration under varying organic carbon deposition in Bering Sea sediments (Bowers Ridge, IODP Exp. 323 Site U1341). Deep Sea Res. II 2016, 125, 117–132.

9. Jeffrey V. Turner; Kinetic fractionation of carbon-13 during calcium carbonate precipitation. *Geochimica et Cosmochimica Acta* **1982**, *46*, 1183-1191, 10.1016/0016-7037(82)90004-7.

10. Peter Deines; Donald Langmuir; Russell S. Harmon; Stable carbon isotope ratios and the existence of a gas phase in the evolution of carbonate ground waters. *Geochimica et Cosmochimica Acta* **1974**, *38*, 1147-1164, 10.1016/0016-7037(74)90010-6.

11. Jennifer M. Galloway; Madeleine L. Vickers; Gregory D. Price; Terence Poulton; Stephen E. Grasby; Thomas Hadlari; Benoit Beauchamp; Kyle Sulphur; Finding the VOICE: organic carbon

isotope chemostratigraphy of Late Jurassic – Early Cretaceous Arctic Canada. *Geological Magazine* **2019**, *null*, 1-15, 10.1017/s0016756819001316.

12. Maximilian Hansen; Denis Scholz; Bernd R. Schöne; Christoph Spötl; Simulating speleothem growth in the laboratory: Determination of the stable isotope fractionation (δ13C and δ18O) between H2O, DIC and CaCO3. *Chemical Geology* **2019**, *509*, 20-44, 10.1016/j.chemgeo.2018.12.012.

13. W.G. Mook; J.C. Bommerson; W.H. Staverman; Carbon isotope fractionation between dissolved bicarbonate and gaseous carbon dioxide. *Earth and Planetary Science Letters* **1974**, *22*, 169-176, 10.1016/0012-821x(74)90078-8.

14. J. Michaelis; E. Usdowski; G. Menschel; Partitioning of 13 C and 12 C on the degassing of CO 2 and the precipitation of calcite; Rayleigh-type fractionation and a kinetic model. *American Journal of Science* **1985**, *285*, 318-327, 10.2475/ajs.285.4.318.

15. Pei-Chuan Chuang; Tsanyao Frank Yang; Klaus Wallmann; Ryo Matsumoto; Ching-Yi Hu; Hsuan-Wen Chen; Saulwood Lin; Chih-Hsien Sun; Hong-Chun Li; Yunshuen Wang; et al.Andrew W. Dale Carbon isotope exchange during anaerobic oxidation of methane (AOM) in sediments of the northeastern South China Sea. *Geochimica et Cosmochimica Acta* **2019**, *246*, 138-155, 10.1016/j.gca.2018.11.003.

16. Patrick Meister; Stefano M. Bernasconi; Ivano W. Aiello; Crisógono Vasconcelos; Judith A. McKenzie; Depth and controls of Ca-rhodochrosite precipitation in bioturbated sediments of the Eastern Equatorial Pacific, ODP Leg 201, Site 1226 and DSDP Leg 68, Site 503. *Sedimentology* **2009**, *56*, 1552-1568, 10.1111/j.1365-3091.2008.01046.x.

17. Monika Kasina; Susanne Bock; Hilke Würdemann; Dieter Pudlo; Aude Picard; Anna Lichtschlag; Christian März; Laura Wagenknecht; Laura M. Wehrmann; Christoph Vogt; et al.Patrick Meister Mineralogical and geochemical analysis of Fe-phases in drill-cores from the Triassic Stuttgart Formation at Ketzin CO2 storage site before CO2 arrival. *Environmental Earth Sciences* **2017**, *161*, 161, 10.1007/s12665-017-6460-9.

18. Bernasconi, S.M. Geochemical and microbial controls on dolomite formation in anoxic environments: A case study from the Middle Triassic (Ticino, Switzerland). In Contributions to Sedimentology; E. Schweizerbart Science Publishers: Stuttgart, Germany, 1994; Volume 19, pp. 1–109

19. Patrick Meister; Judith A. McKenzie; Stefano M. Bernasconi; Peter Brack; Dolomite formation in the shallow seas of the Alpine Triassic. *Sedimentology* **2013**, *60*, 270-291, 10.1111/sed.12001.

20. Ulrich Heimhofer; Patrick Meister; Stefano M. Bernasconi; Daniel Ariztegui; David M. Martill; Aristoteles M. Rios-Netto; Lorenz Schwark; Isotope and elemental geochemistry of black shale-hosted fossiliferous concretions from the Cretaceous Santana Formation fossil Lagerstätte (Brazil). *Sedimentology* **2016**, *64*, 150-167, 10.1111/sed.12337.

21. Nguyen Manh Thang; Volker Brüchert; Michael Formolo; Gunter Wegener; Livija Ginters; Bo Barker Jørgensen; Timothy G. Ferdelman; The Impact of Sediment and Carbon Fluxes on the Biogeochemistry of Methane and Sulfur in Littoral Baltic Sea Sediments (Himmerfjärden, Sweden). *Estuaries and Coasts* **2012**, *36*, 98-115, 10.1007/s12237-012-9557-0.

22. Niels Oluf Jørgensen; Methane-derived carbonate cementation of marine sediments from the Kattegat, Denmark: Geochemical and geological evidence. *Marine Geology* **1992**, *103*, 1-13, 10.1016/0025-3227(92)90006-4.

23. Pisciotto, K.A.; Mahoney, J.J. Isotopic survey of diagenetic carbonates, Deep Sea Drilling Project Leg 63. In Initial Reports of the Deep Sea Drilling Project; Yeats, R.S., Haq, B.U., Eds.; U.S. Govt. Printing Office: Washington, DC, USA, 1981; Volume 63, pp. 595–609

24. Kelts, K.; McKenzie, J.A. Diagenetic dolomite formation in Quaternary anoxic diatomaceous muds of Deep Sea Drilling Project Leg 64, Gulf of California. In Init. Repts. DSDP; Curray, J.R., Moore, D.G., Eds.; U.S. Govt. Printing Office: Washington, DC, USA, 1982; Volume 64, pp. 553–569

25. Kelts, K.; McKenzie, J.A. A comparison of anoxic dolomite from deep-sea sediments: Quaternary Gulf of California and Messinian Tripoli Formation of Sicily. In Dolomites of the Monterey Formation and Other Organic-Rich Units; Garrison, R.E., Kastner, M., Zenger, D.H., Eds.; Pacific Section SEPM: Los Angeles, CA, USA, 1984; Volume 41, pp. 19–28

26. Murata, K.J.; Friedman, I.; Madsen, B.H. Isotopic Composition of Diagenetic Carbonates in Marine Miocene Formations of California and Oregon; USGS Prof. Paper; U.S. Govt. Printing Office: Washington, DC, USA, 1969; p. 24

27. Rodriguez, N.M.; Paull, C.K.; Borowski, W.S. Zonation of authigenic carbonates within gas hydrate-bearing sedimentary sections on the blake ridge: Offshore southeastern North America. In Proc. ODP, Sci. Results; Paull, C.K., Matsumoto, R., Wallace, P.J., Dillon, W.P., Eds.; Ocean Drilling Program: College Station, TX, USA, 2000; Volume 164, pp. 301–312

28. Compton, J.S. Sediment composition and precipitation of dolomite and pyrite in the Neogene Monterey and Sisquoc Formations, Santa Maria Basin area, California. In Sedimentology and Geochemistry of Dolostones; Shukla, V., Baker, P.A., Eds.; SEPM Spec. Pub.: Tulsa, OK, USA, 1988; Volume 43, pp. 53–64

29. Patrick Meister; Stefano M. Bernasconi; Crisógono Vasconcelos; Judith A. McKenzie; Sealevel changes control diagenetic dolomite formation in hemipelagic sediments of the Peru Margin. *Marine Geology* **2008**, *252*, 166-173, 10.1016/j.margeo.2008.04.001.

30. Contreras, S.; Meister, P.; Liu, B.; Prieto-Mollar, X.; Hinrichs, K.U.; Khalili, A.; Ferdelman, T.G.; Kuypers, M.; Jørgensen, B.B; Strong glacial-interglacial variation of sub-seafloor microbial activity on the Peruvian shelf. *Proc. Natl. Acad. Sci. USA* **2013**, *110*, 18098–18103.

31. Kelts, K.; McKenzie, J.A. A comparison of anoxic dolomite from deep-sea sediments: Quaternary Gulf of California and Messinian Tripoli Formation of Sicily. In Dolomites of the Monterey Formation and Other Organic-Rich Units; Garrison, R.E., Kastner, M., Zenger, D.H., Eds.; Pacific Section SEPM: Los Angeles, CA, USA, 1984; Volume 41, pp. 19–28

32. A.W. Dale; P. Van Cappellen; D.R. Aguilera; P. Regnier; Methane efflux from marine sediments in passive and active margins: Estimations from bioenergetic reaction–transport simulations. *Earth and Planetary Science Letters* **2008**, *265*, 329-344, 10.1016/j.epsl.2007.09.026.

33. Meister, P.; Liu, B.; Khalili, A.; Böttcher, M.E.; Jørgensen, B.B; Factors controlling the carbon isotope composition of dissolved inorganic carbon and methane in marine porewater: An evaluation by reactive-transport modelling. *J. Mar. Syst.* **2019**, *200*, 103227.

34. Patrick Meister; Benjamin Brunner; Aude Picard; Michael E. Böttcher; Bo Barker Jørgensen; Sulphur and carbon isotopes as tracers of past sub-seafloor microbial activity. *Scientific Reports* **2019**, *9*, 604, 10.1038/s41598-018-36943-7.

Retrieved from https://encyclopedia.pub/entry/history/show/8279