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Beyond the biogeochemical carbon cycle: Metabolic signatures in carbonate rock

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Marine deposits of carbonate minerals are the largest record of biotic activity on Earth. Even though abiotic carbonate precipitates comprise part of this record, life certainly played a central role in their accumulation throughout Earth's history, possibly starting as early as the Paleoarchean. Isotope signatures within minerals are another frequently explored trace of past life activity. Based on the premise that isotope fractionations during enzyme-mediated reactions are a principal aspect of life, metabolism can alter the isotope composition of reservoirs on Earth's surface; as part of the large-scale biogeochemical cycles, as well as on the microscale; in the vicinity of cell membranes within interstitial fluids of sediments and biofilms. Here, we disentangle stratigraphic variations in the carbonate-carbon isotope record in terms of signatures that record those changes associated with the operating of the long-term carbon cycle and microscale carbon isotope variations connected with bio-mediated carbonate precipitates. The frequency distribution of carbon isotope fluctuations at various stratigraphic resolutions, and the application of a steady-state geochemical box-model, allows us to deduce that a subset of Mesoproterozoic to Paleozoic carbon isotope variations cannot easily be explained by temporal changes in the carbon cycle. Instead we suggest that those high amplitude carbon isotope variations (> 5 ‰ VPDB, at a stratigraphic resolution of below 25 cm) must relate to authigenic and/or diagenetic carbonate mineral additions which record carbon isotope signatures that originated from fluids in secluded micro-environment altered by metabolic activity. Membranes, extracellular polymeric substances, and restricted fluid exchange further facilitate sharp gradients in those micro-environments, which would ultimately lead to a highly variable carbon isotope signature in the carbonate mineral record. In the youngest time intervals, we see a marked decrease in carbon isotope variations (< 1 ‰ VPDB). This can be related to the evolution of higher organisms and increased ecological tiering, where obligate carbonate shell production and mixing of sediments by bioturbation can erase carbon isotope variability. Records of carbonate carbon isotope variations can be interpreted as biosignatures that relate to distinct stages of life evolution, from a prokaryote to metazoan-dominated world.