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Stable carbon isotopes and lipid biomarkers provide new insight into the formation of calcite and siderite concretions in organic-matter rich deposits

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Carbonate concretions from two distinct settings have been studied for their petrography, stable carbon and oxygen isotopes, and lipid biomarker content. Carbonate concretions are in large part products of microbial degradation of organic matter, as for example by sulfate-reducing bacteria, iron-reducing bacteria, and methanogenic archaea. For these prokaryotes certain lipid biomarkers such as hopanoids, terminally-branched fatty acids (bacteria) and isoprenoids (archaea) are characteristic. Two different types of concretions were studied: a) Upper Miocene septarian calcite concretions of the southern Vienna Basin embedded in brackish sediments represented by partly bituminous calcareous sands, silts and clays; b) Paleocene-Eocene siderite concretions enclosed in marine, sandy to silty turbidites with varying carbonate contents and marl layers from the Upper Gosau Subgroup in northern Styria. Calcite concretions consist of abundant calcite microspar (80-90 vol.%), as well as detrital minerals and iron oxyhydroxides. The septarian cracks show beginning cementation with dog-tooth calcite to varying degrees. Framboidal pyrite occurs in some of the calcite concretions, pointing to bacterial sulfate reduction. Siderite concretions consist of even finer carbonate crystals, mainly siderite (40-70 vol.%) but also abundant ferroan calcite, accompanied by iron oxyhydroxides and detrital minerals. The δ13C values of the calcite concretions (-6.8 to -4.1‰) most likely reflect a combination of bacterial organic matter oxidation and input of marine biodetrital carbonate. The δ18O values range from -8.9 to -7.8‰ agreeing with a formation within a meteoric environment. The surrounding host sediment shows about 1-2‰ higher δ13C and δ18O values. The siderite δ13C values (-11.1 to -7.5‰) point to microbial respiration of organic carbon and the δ18O values (-3.5 to +2.2‰) agree with a marine depositional environment. In contrast to the calcite concretions, the stable isotope composition of the host sediment differs significantly from the siderite concretions. The δ13C values of the Gosau host sediment reflect marine conditions, whereas the oxygen isotope values are best explained by meteoric overprint. Lipid biomarkers have been extracted before and after dissolution of the concretions in order to assess their authenticity and to exclude recent surface contamination. In the following, only the biomarkers extracted after dissolution are discussed, since they are thought to be related to concretion formation. The calcite concretions comprise abundant plant wax derived long-chain n-alkanes, reflecting high terrestrial input. Bacterial, terminally-branched fatty acids were found, but in overall low abundance. The siderite concretions did not yield biomarkers due to their high maturity. No archaeal biomarkers were found in any of the concretions. Considering the presence of framboidal pyrite, the moderately low δ13C values, and the biomarker inventory, bacterial sulfate reduction apparently contributed to the formation of the calcite concretions in a brackish environment. In contrast, ongoing sulfate reduction and resultant hydrogen sulfide production inhibit siderite precipitation. Therefore, the low δ13C values of the siderite concretions are best explained by bacterial iron reduction.