

The carbon isotopic composition of Archean kerogen and its preservation or change through the rock cycle

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The carbon phases in Archean rocks record early life on Earth. However, the rock record predating the Great Oxidation Event is limited both in amount of preserved rock and quality of preservation. No unique lipid biomarkers persist within these rocks, so studies have focused on their carbon isotopic compositions ($d^{13}C$ values of kerogen or total organic carbon). Low $d^{13}C$ values of Archean kerogen have often been invoked as key biosignatures of specific anabolic processes, but it has been hard to discern whether this and other C isotope signatures reflect the isotopic composition of sedimentary organic matter at the time of deposition or modifications by fractionations occurring post-deposition. Here, we present the largest comprehensive compilation to date of Archean $d^{13}C$ values, along with data and models constraining C isotope changes associated with some relevant chemical reactions that occur during the transformation of organic carbon into kerogen through diagenesis, catagenesis and metagenesis. The reactions that seem most likely to affect the $d^{13}C$ value of organic carbon include diagenetic decarboxylation, homolytic cleavage during catagenesis, and exchange with solid and dissolved carbonate during metamorphism. These diagenetic and catagenetic reactions plausibly explain observed stoichiometric changes in kerogen described by the van Krevelin diagram, but affect only a small fraction of the bulk carbon; thus, while these processes likely induce site-specific carbon isotope fractionations, they lead to minimal (a few per-mille (‰)) shifts in the overall $d^{13}C$ value of organic C phases. In contrast, the exchange of C with carbonate during high grade metamorphism is highly fractionating and causes a shift of up to ~10‰ in the bulk $d^{13}C$ value. These results imply that Archean-age sedimentary successions subject to only low-grade metamorphism record values close to the original isotopic composition of the sedimentary organic matter; this includes, for example, the remarkably low $d^{13}C$ values observed from the 2.7 billion year old Tumbiana Formation. Our results highlight a path forward for studying organic matter from more highly metamorphosed rocks by focusing on kerogen phases that have not yet undergone full exchange with metamorphic fluids.