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The antiquity of autotrophic metabolism and the biogeochemical carbon cycle: evidence from sedimentary carbon isotopes from the 3.52 Ga Coonterunah Group, Australia

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The 3.52 Ga old Coonterunah Group of northwestern Australia contains the oldest known low-grade metasedimentary rocks. Thus, it can potentially yield the most ancient, minimally modified, carbon isotopic data pertinent to the early evolution of life. Laminated sedimentary carbonates have $\delta^{13}C_{carb}$ values of -1‰ to -4‰ (mean = -2.5‰) with $\delta^{18}O_{PDB}$ values of -7‰ to -20‰ (mean = -16.2‰). Kerogenous magnetitic cherts have a wide range of $\delta^{13}C_{org}$ values from -5‰ to -47‰ (mean = -24.0‰), but most values lie close to a major mode of -25.4‰. The mean isotopic difference between bulk reduced (major mode) and oxidized carbon species ($\Delta^{13}C$) is thus 22.9‰, very similar to that within individual carbonate samples (mean = 23.4‰). The slight depletion in $\delta^{13}C_{carb}$ resembles that in other Archean sedimentary carbonates associated with banded iron formations and probably results from precipitation in a stratified ocean where deeper environments derive some dissolved inorganic carbon from remineralized organic debris. The spread in $\delta^{13}C_{org}$ values probably partly results from incipient metamorphic resetting, as these rocks were subjected to mid-greenschist to lowermost-amphibolite facies conditions at which isotopic re-equilibration starts to occur. After accounting for these effects, $\Delta^{13}C$ falls in the range typical of biological autotrophic fractionation and is dissimilar to any plausible abiotic processes. As these are the oldest rocks from which a sedimentary $\Delta^{13}C$ can be obtained, the results show that autotrophic, presumably photosynthetic, life was already well established in marine environments in the first billion years of Earth history.