Goldschmidt 2024 Abstract
https://doi.org/10.46247/gold2024.24457

Why is there young carbon in deep geologic boreholes and how did it get there?: a combined approach using carbon isotopes and thermal analysis

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The Earth's critical zone is a nexus for interactions among the geologic organic, inorganic, and terrestrial organic carbon (OC) cycles. The geologic carbon cycle involves both organic ($12.5x10^6$ Pg) (OC_{petro}) and inorganic carbon (IC) ($65.3x10^6$ Pg) stored in the rock reservoir. The persistence of OC in Earth's surface environment for extended time is critical for maintaining the balance of CO_2 and O_2 in the atmosphere. Most plants and microbes use OC fixed by photosynthesis. However, when OC is unavailable, some microbes can fix IC (fully oxidized) and reduce it directly to OC, which accumulates in biomass. This chemolithoautotrophic carbon fixation is known to occur in extreme environments, such as hydrothermal vents or deep in the Earth's crust, but may be more widespread in OC limited environments.

Using ramped pyrolysis oxidation (RPO-^{14}C), we assess the complex mixture of OC_{petro} in deeply weathered shale samples. The Susquehanna Shale Hills CZO (SSHCZO) is a well-studied small catchment underlaid by the Silurian Rose Hill Shale formation, which is a low OC grey shale (<<0.5%OC), with low IC concentrations. The Cornell Borehole Observatory (CUBO) is a ~3000m borehole spanning both grey and black shale deposits in NY state with a range IC and OC. Shales on the SSHCZO and CUBO sites were deposited more than 400 million years ago, so any endemic inorganic or organic carbon would be ^{14}C 'dead' (>> 50,000 ^{14}C years). Decarbonated bulk ^{14}C depth profiles and thermograms with isotope thermal fractions were collected. At SSHCZO, the measured ^{14}C values were much younger than expected. The borehole values ranged Fm 0.9109 the uppermost sample to Fm of 0.323 at 30m. This suggests transformation of inorganic carbon to organic carbon via chemolithoautotrophy may be much more widespread than previously recognized in Earth's critical zone, constituting a possible novel source of organic carbon to the subsurface. This has implications for the cycling and stabilization of carbon through Earth's reservoirs.