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Late Paleozoic Oxygenation of Marine Environments constrained by Dolomite U-Pb Dating

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The causal relationships between evolution and oxygenation of the ocean are vigorously debated. At the heart of these uncertainties are inconsistencies among reconstructed timelines for the rise of O_2 in marine habitats. Attempts to reconstruct the timing of Earth's oxygenation are often based on redox-sensitive geochemical proxies that are prone to post-depositional alteration. Thus, developing new proxies, more resistant to such alteration, is an important direction forward for constraining major changes in atmospheric and marine oxygen levels. Here, we utilize U–Pb dating in dolomite to reconstruct their (re)crystallization ages and initial $^{207}Pb/^{206}Pb$ ratios; we find that they are systematically younger and lower than expected, respectively. These observations are explained by the resetting of the U–Pb system long after deposition, followed by further evolution in a closed system. Initial $^{207}Pb/^{206}Pb$ ratios have decreased from expected terrestrial values in the interval between deposition and (re)crystallization, consistent with U decay, and can therefore be used to reconstruct the initial $^{238}U/^{206}Pb$ ratios during deposition. Within our dataset initial $^{238}U/^{206}Pb$ ratios remained low in Proterozoic to mid-Paleozoic samples and increased dramatically in samples from the late-Paleozoic–early-Mesozoic Eras. This rise is attributed to a higher ratio of U to Pb in seawater that in turn influenced the fluid composition of carbonate crystallization sites. Accordingly, we interpret the temporal shift in initial $^{238}U/^{206}Pb$ ratios to reflect a late-Paleozoic increase in oxygenation of marine environments, corroborating previously documented shifts in some redox-sensitive proxies. This timeline is consistent with evolution-driven mechanisms for the oxygenation of late Paleozoic marine environments and with suggestions that Neoproterozoic and early Paleozoic animals thrived in oceans that overall and on long time scales were oxygen-limited compared to the modern ocean.