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Oxygen and carbon isotope fractionation during microbial vaterite precipitation.

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Fossil carbonates provide essential paleoenvironmental archives as their isotopic and chemical compositions record the environmental conditions prevailing at the time of their formation, thereby enabling the reconstruction of environmental changes throughout large portions of Earth's history. However, their reliability depends on the extent to which primary geochemical signatures are preserved, as biologically or kinetically driven processes during precipitation may bias isotopic records. To better constrain these effects, this study investigated microbial induced carbonate precipitation (MICP) by *Sporosarcina pasteurii*, under controlled laboratory conditions focusing on mineralogical evolution and oxygen and carbon isotope fractionation.

Batch precipitation experiments were conducted over two months in B4 medium at 28 °C. The chemistry of the liquid phase was systematically monitored for pH, [Ca^{2+}], [NH_4^+], and the evolution of the stable isotope composition ($\delta^{18}O$, $\delta^{13}C$). Solid precipitates were characterized using X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM), while isotopic compositions were measured via stable isotope mass spectrometer (IRMS).

Our results demonstrated that ammonification by *S. pasteurii* rapidly increased alkalinity, driving $CaCO_3$ precipitation. XRD and FTIR analyses revealed the formation of vaterite that emerged as the dominant phase by day 8 and persisted throughout the experiment, despite a transient calcite phase between days 15 and 22. SEM observations showed rounded vaterite crystals closely associated with bacterial cells and exopolymeric substances (EPS), suggesting biologically mediated stabilization.

Regarding isotopic signatures, the $\delta^{18}O$ of the solids remained remarkably constant (~-9.1 ‰ VPDB). Interestingly, these values stay below equilibrium expectations, indicating significant kinetic fractionation during rapid microbial mineralization. This offset persisted even as the liquid phase became progressively enriched in ^{18}O due to evaporation. Conversely, the $\delta^{13}C$ of the solids decreased (from -18 ‰ to -28 ‰) while the liquid $\delta^{13}C$ increased, reflecting the complex interplay between microbial metabolism and dissolved inorganic carbon (DIC) dynamics.

These findings demonstrated that vaterite is the primary microbial $CaCO_3$ under experimental conditions, emphasizing the significant influence of microbial activity on both carbonate mineralogy and isotopic signatures. Such insights highlight the need to account for biologically induced kinetic effects when interpreting microbial carbonates in paleoenvironmental reconstructions.