

Carbon isotope fractionation in carbonates precipitated via an amorphous precursor

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The isotopic composition of carbonates has been widely studied as a proxy for reconstructing Earth's past environmental conditions. However, the reliability of this proxy depends on the preservation of the original isotope composition of the CaCO_3 to accurately reflect the environmental conditions at the time of formation. In this context, the transformation of amorphous carbonates into crystalline forms has been identified as a common process in the formation of both synthetic and natural carbonates and previous studies, even though rare, have shown that this formation pathway can lead to changes in the isotopic composition between amorphous calcium carbonate (ACC) precursor and the resulting crystalline phase.

We have studied the changes in carbon isotope compositions during the transformation of ACC into crystalline carbonate under different conditions of relative humidity (RH of 33 to 95 %), temperature (T of 5 and 20 °C) and in the presence/absence of atmospheric CO_2 . In the CO_2 -present experiments, the $\delta^{13}\text{C}$ values of the solid carbonates generally increased over time. After 103 to 144 days, the enrichment factors between crystalline carbonate and amorphous calcium carbonate ($^{13}\epsilon_{\text{CaCO}_3\text{-ACC}}$) changed from 2.0 ‰ to 8.4 ‰. This increase in $\delta^{13}\text{C}$ reflects the incorporation of carbon from $\text{CO}_2(\text{g})$ -equilibrated dissolved inorganic carbon (DIC), as well as some buffering from carbon derived from dissolved ACC/calcite. This is consistent with the crystallization of ACC via a dissolution-reprecipitation mechanism triggered by physisorbed gaseous H_2O , which mixes with the expelled synthesis fluid from the transforming solid carbonate. The physisorbed water, in turn, mixes with the expelled synthesis fluid by forming a solution that contains DIC from ACC dissolution and $\text{CO}_2(\text{g})$ hydration/hydroxylation from the air, which is subsequently incorporated into the crystalline carbonate.

In contrast, in the CO_2 -free experiments, the $\delta^{13}\text{C}$ of ACC/ CaCO_3 showed no significant change between the initial and final values ($^{13}\epsilon_{\text{CaCO}_3\text{-ACC}} = -0.4 \pm 0.3\text{‰}$). Without an external carbon source, such as $\text{CO}_2(\text{g})$, and since no carbon isotope fractionation occurs during the ACC- CaCO_3 transformation, the isotopic composition of the DIC and the reprecipitated crystalline carbonate closely match the original isotope composition of the ACC precursor.