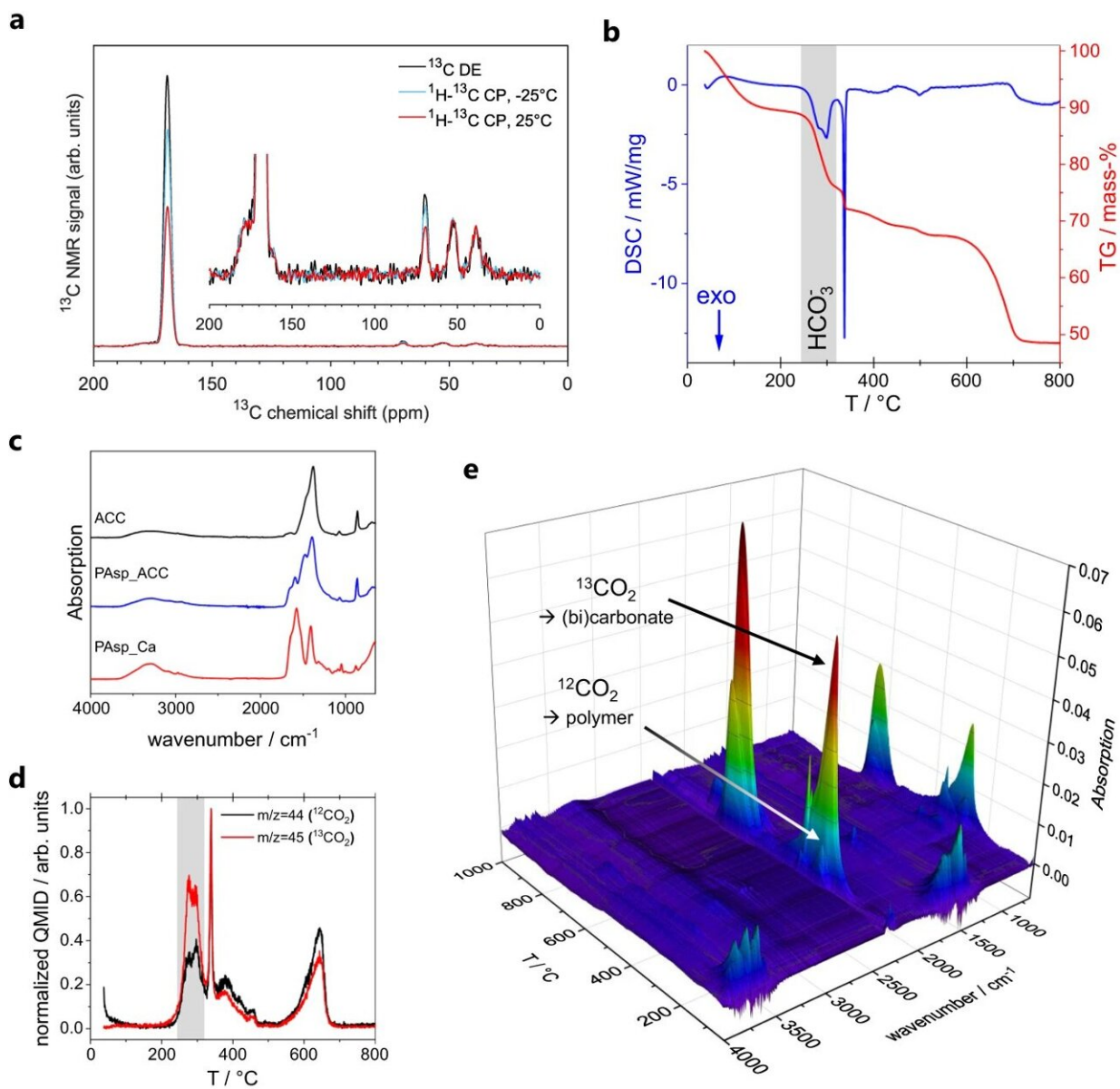


New research deciphers biomineralization mechanism

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Characterization of isolated polymer stabilized ACC. The sample was isolated from a titration experiment using 0.1 g/L PAsp at pH 9.8 by quenching the solution in ethanol (see Methods section). **a** ^{13}C direct excitation (DE) and ^1H - ^{13}C cross-polarization (CP) spectra of 10% ^{13}C -carbonate ACC stabilized by PAsp (PAsp_disACC) at a spinning frequency of 10 kHz. The spectra are scaled at the C_α -peak of PAsp. **b** TGA (red) and DSC (blue) analysis. The exothermic decomposition of the bicarbonate species is highlighted in gray. **c** ATR-FTIR spectra of polymer-stabilized ACC sample, showing significant amounts of polymer incorporation. Pure ACC and PAsp calcium salt (PAsp_Ca) are shown as references (detailed FTIR spectra are shown in Supplementary Fig. 6). **d** Normalized QMID for TGA-MS measurement on the PAsp_ACC sample using ^{13}C enriched carbonates in the titrations. Due to the natural abundance of carbonate distribution in the polymer, released gases from polymer ($^{12}\text{CO}_2$; $m/z = 44$, black) and from mineral ($^{13}\text{CO}_2$; $m/z = 45$, red) can be distinguished, showing significant amounts of mineral decomposition below 300 °C (highlighted in gray). **e** TGA-IR analysis of the ^{13}C carbonate enriched PAsp_ACC sample confirms the strong $^{13}\text{CO}_2$ release from (bi)carbonate species at around 300 °C. Credit: *Nature Communications* (2024). DOI: 10.1038/s41467-023-44381-x

Many organisms can produce minerals or mineralized tissue. A well-known example is nacre, which is used in jewelry because of its iridescent colors. Chemically speaking, its formation begins with a mollusk extracting calcium and carbonate ions from water. However, the exact processes and conditions that lead to nacre, a composite of biopolymers and platelets of crystalline calcium carbonate, are the subject of intense debate among experts, and different theories exist.

Researchers do agree that non-crystalline intermediates, such as amorphous calcium carbonate (ACC), play a crucial role in biomineralization. Lobsters and other crustaceans, for example, keep a supply of ACC in their stomachs, which they use to build a new shell after molting. In a recent study published in [Nature Communications](#),

researchers from the University of Konstanz and Leibniz University Hannover have now succeeded in deciphering the formation pathway of ACC.

A combination of advanced methods

The researchers led by Denis Gebauer (Leibniz University Hannover) and Guinevere Mathies (University of Konstanz) took advantage of the fact that ACC can be synthesized not only by living organisms, but also in the laboratory. Using advanced methods such as magic-angle spinning [nuclear magnetic resonance](#) (MAS NMR) spectroscopy, they analyzed tiny ACC particles to determine their structure.

"We struggled to interpret the spectra of ACC. They suggested dynamics, that we were unable to model at first," says Mathies.

An important clue was provided by the colleagues from Leibniz University Hannover. Maxim Gindele of the Gebauer group showed that ACC conducts electricity. Since ACC particles are very fragile and only tens of nanometers in size, this was not as easy as sticking two leads in.

Instead, the measurements were carried out using conductivity [atomic force microscopy](#) (C-AFM), in which ACC particles on a [flat surface](#) are detected by a minuscule cantilever scanning the surface and visualized with the help of a laser beam. When the cantilever is placed on one of the nanoparticles, a current is passed through its tip to measure the conductivity.

Two different environments

Informed by the observation of conductivity, Sanjay Vinod Kumar of the Mathies group performed further MAS NMR experiments aimed at

probing dynamics. They indicated two distinct chemical environments in the ACC particles. In the first environment, the [water molecules](#) are embedded in rigid calcium carbonate and can only undergo 180-degree flips. The second environment consists of water molecules undergoing slow tumbling and translation, with dissolved hydroxide ions.

"The remaining challenge was to reconcile the two environments with the observed conductivity. Solid salts are insulators and therefore the second, mobile environment had to play a role," says Mathies. In the new model, the mobile water molecules form a network through the ACC nanoparticles. The dissolved hydroxide ions carry the charge.

The researchers can also account for the formation of the two chemical environments: in water, calcium and carbonate ions tend to stick together and form dynamic assemblies called pre-nucleation clusters. The clusters can undergo phase separation and form dense, liquid droplets, which in turn merge into larger aggregations—similar to how soap bubbles coalesce.

"The rigid, less mobile [environment](#) arises from the core of the dense, liquid nanodroplets. The network of mobile water molecules, on the other hand, remains from imperfect coalescence of the droplet surfaces during dehydration towards solid ACC," explains Gebauer.

These results are a significant step towards a structural model for ACC. At the same time, they provide solid evidence that mineralization starts with pre-nucleation clusters. "This not only brings us closer to understanding the secret of biomineralization, but can also have applications in the development of cementitious materials that bind [carbon dioxide](#) and, since we now know that ACC is a conductor, in electrochemical devices," concludes Mathies.

More information: Maxim B. Gindele et al, Colloidal pathways of

amorphous calcium carbonate formation lead to distinct water environments and conductivity, *Nature Communications* (2024). DOI: [10.1038/s41467-023-44381-x](https://doi.org/10.1038/s41467-023-44381-x)

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