A close look at the carbon cycle from the Roselend Natural Laboratory using laser-based isotope ratio spectrometry

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We study the carbon cycle (fluxes and isotope ratios) in a section of a crystalline mountain belt. At the Roselend Natural Laboratory (French Alps), a tunnel provides access to the heart of the fractured-rock unsaturated zone, at 55m depth below ground surface. From dedicated sampling of matrix flow, fracture flow and runoff, we compute the contributions to Dissolved Inorganic Carbon due to carbonic acid weathering of carbonates and silicates as well as sulfuric acid weathering of carbonates. This reveals that this system is a net source of CO₂.

A recent laser-based CO₂ Carbon Isotope Analyzer (CCIA DLT-100, Los Gatos Research Inc.) allows *in situ* continuous monitoring of CO₂ concentration and carbon isotope composition. We thoroughly assess the performance of this instrument in the view of using it in harsh geological conditions (high water content, large concentration range).

 CO_2 degassing can be characterized by flux measurements in closed chambers. In our setting, this requires a preliminary purge with CO_2 -free air. Isoflux measurements are performed in small (7 L) horizontal boreholes drilled from the tunnel wall and in an isolated chamber (60 m³) at the end of the tunnel. We also apply a Keeling plot approach that is well-suited for open systems, such as the entire tunnel ventilated by the atmosphere.

These CCIA measurements confirm that CO_2 is contributed from the rock, and indicate multiple sources (soil respiration, DIC degassing, carbonate precipitation). CO_2 fluxes are highly dynamic in response to meteorological, hydrogeological and mechanical forcing.

The understanding of the natural carbon cycle in the Roselend Natural Laboratory is a preliminary basis for a forthcoming tracing experiment between the isolated chamber of the tunnel and the atmosphere above through 55 m of fractured rocks.

Atomic force microscopy observations of nanostructures and crystal growth in bivalves

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The shells of bivalves are complex nanostructured materials formed by calcium carbonate and organic membranes. Both the variety of hierarchical structures and the selective usage of calcite and aragonite in their shells, reveal the extraordinary ability of bivalves to control crystal growth processes at various length scales. The result of such a multiple scale control is the generation of composite materials with outstanding mechanical properties.

Here we present atomic force microscopy (AFM) observations of calcitic and aragonitic internal structures in shells of a number of bivalves. These structures are constructed by micrometric tablets, whose shape, size and coalescence schemes vary from one species to another. However, in all the species, the surfaces of the tablets are built up by granules and subgranules down to the nanometric scale. These highly hierarchical structures of the tablets provide them with a multiple scale roughness which differs from that commonly observed on inorganic mineral surfaces. To further study the nature of the tablets, we also conducted a series of crystal growth experiments using the inner part of bivalves' shells as a substrate. Crystal growth was promoted by passing supersaturated aqueous solutions with respect to calcite and aragonite over the arrangements of micrometric tablets. The growth on the bivalve's shells was observed in real time by AFM. The analysis of the morphology and orientation of the overgrown crystals provided information about the crystallographic features of the tablets that form the interior of bivalves' shells.

Mineralogical Magazine

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