Fossil Corals as an archive of Phanerozoic seawater chemistry

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Numerous observations indicate that the composition of seawater has not remained constant through time. It has been hypothesized that such variability is linked to changes in geologic processes such as continental weathering, sea-floor spreading, and continental onlap. Fossil corals may be suitable candidates for studying seawater chemistry. Although there is evidence that incorporation of some elements into the coral skeleton is biologically mediated[1], other elements seem to accurately record certain chemical properties of the seawater from which the corals grow.

We studied a suite of ~12 well-preserved fossil corals dating back to the Triassic. The primary objective of this work was to assemble a collection of fossil corals that have been meticulously tested and shown to be diagenetically unaltered with respect to their original structure and mineralogy. X-ray diffraction, micro-Raman spectroscopy, and cathodoluminescence analyses suggest that these specimens contain little to no secondary calcite. Electron and optical microscopy studies reveal crystal structures consistent with modern coral aragonite. Clumped isotope data for 6 specimens give temperatures that seem either appropriate for what we understand about the time and location at which each coral grew or they appear too low, similar to some modern corals.[2] However, secondary ion mass spectrometry (SIMS) analyses suggest there is some micron-scale alteration indicated by high Mn/Ca, high Mg/Ca, and low Sr/Ca ratios. In fossils with low Mn/Ca, we observe a positive correlation between Na/Ca and S/Ca, as in modern corals.[3] We sometimes observe a negative relation between Sr/Ca and Mg/Ca, also similar to some modern corals.[4]

The second objective of this study is to analyze properties such as Sr/Ca and Mg/Ca in corals to supplement existing records of global seawater chemistry since the Triassic. Initial results from SIMS measurements of Sr/Ca ratios are consistent with some existing records of Sr/Ca in seawater through time; Sr/Ca is relatively constant from the modern to the Triassic. These results are supportive of using corals as archives of paleo-seawater chemistry. Additionally, we find that Mg/Ca ratios in fossil corals decrease with age, but because of possible vital effects, the implications for seawater chemistry are uncertain.

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Transport and deposition of engineered nanoparticles (NPs) in saturated porous media (schist): role of interactions between NPs and the rock matrix

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The increasing use of engineered nanoparticles for industrial and household purposes (cosmetics, clothing, electronic, automotive, medical products…) will inevitably lead to their introduction into different environmental compartments, including groundwater. Assessing the risk of groundwater contamination by nanoparticles is worth studying but requires the knowledge of their mobility and environmental reactivity. How far these nanoparticles will travel in waters? A number of studies addressed the processes driving mobility of nanoparticles in simple waters and conditions (clean Quartz sand, bare silica surfaces, uniform and spherical glass beads…). They highlight nanoparticles dispersion in water is highly dependent on physical and chemical key parameters of nanoparticles (solubility, pH_{zpc}, which may vary with chemical composition, crystallinity, size and eventual coating…), and on the overall groundwater composition (pH, ionic strength, major element concentration, e.g. Ca or Na, organic matter contents…). The present study conducted in the frame of the AquaNano project aims at characterising metal oxide nanoparticles (TiO_2 and CeO_2) behaviour and reactivity during transport in schist (heterogeneous medium). Transport (flushing) experiments of nanoparticles suspension through 10 cm long rock column under pressure (up to 5 bars) have been conducted in laboratory. After the experiments, NPs retained in column have been mapped using scanning electron microscopy (SEM). Chemical and physical interactions between NPs and the rock matrix have been constrained using Raman spectroscopy associated with SEM. Results show that NPs deposition and aggregation occurred during their transfer while favorable (repulsive and low ionic strength) transfer conditions were applied in column. Also, it appears a more rapid transfer of NPs concomitant with an increase of NPs retention (by a factor 40) by rock matrix after successives NPs inputs in the column separated by NPs-free water circulation. Experiments conclusively demonstrate that physical and chemical properties of NPs and rock matrix (biotite, quartz…) govern the mobility of NPs. We suggest a rearrangement of NPs (adsorption/desorption processes) in column during NPs-free water circulation and modifications to preferential pathways for NPs circulation while aggregation enhanced NPs deposition.