Title: Unveiling the Catalytic Potential of Metal-Organic Frameworks in Carbonation Kinetics

Teodora Ilić, Encarnación Ruiz-Agudo, Carlos Rodriguez-Navarro
University of Granada, Department of Mineralogy and Petrology, Avenida Fuente Nueva s/n, 18071, Granada, Spain, **teodora@go.ugr.es**

In the search for efficient methods to accelerate the carbonation process within the lime cycle, we explore the potential of metal-organic frameworks (MOFs) as biomimetic catalysts, inspired by the known catalytic activity of natural carbonic anhydrase during calcium carbonate biomineralization [1]. Our study, investigates the impact of three MOF types, UiO-66, ZIF-8 and ZIF-EC-1, in accelerating the carbonation of calcium hydroxide, which occurs via the reaction: $Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$.
Micro-Raman spectroscopy, optical microscopy, and ion-selective electrode-based titration experiments were employed to assess the influence of MOFs on calcium carbonate nucleation and phase transformation in saturated $Ca(OH)_2$ solutions.
The results of the micro-Raman experiments revealed that the introduction of UiO-66, ZIF-EC-1, and ZIF-8 into the solutions significantly enhanced the kinetics of the transformation of amorphous calcium carbonate (ACC) into calcite structures compared to control samples. These findings were consistent with the observations from the titration experiments, where MOFs led to accelerated $CaCO_3$ formation. Particularly, ZIF-EC-1 showed a delay in nucleation, suggesting the formation of pre-nucleation clusters, but no destabilization or stabilization effects on these clusters.
Our findings suggest that MOFs, like carbonic anhydrase, have the potential to expedite the dissolution and hydration of carbon dioxide, leading to increased concentration of bicarbonate and carbonate ions, favoring ACC formation (at high supersaturation), also fostering proton release and subsequent rapid transformation of ACC into calcite via a dissolution-precipitation reaction. While further characterization is required, our study demonstrates the promise of MOFs as biomimetic catalysts for carbonation acceleration, offering a potential solution to the challenges associated with carbonic anhydrase, including instability in an alkaline medium and high extraction costs.

References

[1] Özlem Cizer, Encarnación Ruiz-Agudo & Carlos Rodriguez-Navarro (2018) Kinetic effect of carbonic anhydrase enzyme on the carbonation reaction of lime mortar, International Journal of Architectural Heritage, 12:5, 779-789, DOI: 10.1080/15583058.2017.1413604.

****This project has received funding from the European Union's Horizon 2020 research and innovation programme under Marie Sklodowska-Curie project SUBLime [Grant Agreement n.°955986].***