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The role of casein in the carbonation of transferred Romanesque mural paintings

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Fresco paintings are made of lime or dolomitic mortars [1,2]. The mortars dry reacting with the atmospheric CO_2 and produce, depending on their nature, different calcium carbonate polymorphs.

Casein was widely used in antiquity as a binder or glue in different painting techniques. Since the beginning of the 20th century it has also been applied to artwork restoration thanks to its adhering capability. In particular, casein mortars, lime/dolomitic mortars mixed with milk or cheese casein, have been extensively used, due to their compatibility and good adhesive properties, to stick mural paintings, previously removed from the original wall, onto a new background. During the mortar carbonation process, materials which were unintentionally introduced in the inner layers of the paintings, coming from milk or cheese (e.g. fatty acids), can react, producing new substances such as calcium soaps. These materials modify the original nature and structure of the painting and consequently, may affect its chemical stability.

Our main objective was to understand how the presence of casein modifies the carbonation process and if this affects the stability of the paint. The historical samples studied belong to one of the most important collections of European Romanesque mural paintings. The paintings were detached at the beginning of the 20th century from the churches of Santa Maria de Taüll, Sant Climent de Taüll and Sant Romà de les Bons in the Pyrenees, and preserved ever since at Museu Nacional d'Art de Catalunya (MNAC in Barcelona) [3]. The historical paintings and fresco replicas prepared in the laboratory were analysed by optical microscopy (OM), scanning electron microscopy with a focused ion beam (FESEM-FIB), synchrotron-based micro infrared spectroscopy (SR-μFTIR) and X-ray diffraction (SR-μXRD) (XALOC and MIRAS beamlines).

The data obtained indicates that the presence of casein enhances the stability of amorphous calcium carbonate, calcium hydroxycarbonates and vaterite, one of the crystalline calcium carbonate polymorphs. In addition, a good adherence between the original painting and caseinate mortar has been verified. Finally, we have observed that the stability of the painting layer is not affected by the reattachment process.

References
[1] N. Oriols, N. Salvadó, T. Pradell, S. Butí, Amorphous calcium carbonate (ACC) in fresco mural paintings, Microchem. J. 154 (2020) 104567. doi:10.1016/j.microc.2019.104567.
[2] N. Oriols, N. Salvadó, T. Pradell, N. Jiménez, M. Cotte, V. Gonzalez, S. Butí, Carbonation of fresco mural paintings with a dolomitic mortar. Cem. Concr. Res. 157 (2022) 106828. doi:10.1016/j.cemconres.2022.106828
[3] https://www.museunacional.cat/en/collections/medieval-romanesque-art [17/06/2022]

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Primary authors: ORIOLS, Núria (Universitat Politècnica de Catalunya / Museu Nacional d'Art de Catalunya); BUTÍ, Salvador (Universitat Politècnica de Catalunya UPC); SALVADÓ, Nati (Universitat Politècnica de Catalunya UPC); PRADELL, Trinitat (Universitat Politècnica de Catalunya); Dr JIMÉNEZ GARCÍA, Núria (Universitat Politècnica de Catalunya); JUAN-HUIX GIBERT, Judith (ALBA Synchrotron); YOUSEF, Ibraheem (ALBA Synchrotron)

Presenter: SALVADÓ, Nati (Universitat Politècnica de Catalunya UPC)

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