

## **Nanometre-scale crystals formed in the presence of natural organic matter .**

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Nanocrystals have been observed to form micrite in several environments where natural organic matter (NOM) is present in dissolved, colloidal and particulate form, in both modern and ancient continental and marine sediments. In ancient (Triassic) marine deposits, we found perfectly preserved nanocrystal aggregates entombed by NOM, which appears to be associated with clay particulate. These nanocrystal, which have been preserved through million of years, bear similarities with nanocrystal observed in diverse, freshwater, modern settings.

In modern and Holocene continental environments, micrite is of interest because of its association with archives of past climate, such as stalagmites. Nanocrystal aggregates forming micrite have been observed in association with microbial structures in tufa, thermal spring pisoids and in cave speleothems. We carried out "instant precipitation" experiments in several caves from New Zealand, Australia and Italy, cut in both limestones and dolomites, with a focus on finding a relationship between NOM and micrite precipitation. Transmission Electron Microscope (TEM) investigations of the experimental precipitates suggest that nanocrystals nucleated already after 30 minutes on NOM colloids (as confirmed by EDS spectra) possibly originated in the soil zone. Some samples were left to "mature" for 24 hours: aggregates began to show some preferred orientation and a few single crystals on micrometer scale were also observed, which do not seem to be associated with NOM.

Our preliminary results suggest that NOM, such as soil-derived humic and fulvic acids, aids nanocrystal aggregate nucleation and growth. The cave experiments seem to indicate that it is not necessary to have microbial mats, or EPS to favor formation of micrite. Our experiments did not capture the occurrence of amorphous precursors, but the amorphous phase may have been gone undetected as NOM is amorphous.

Our findings have potential implications for the interpretation of ancient deposits consisting of micrite, where this fabric is not associated with clear microbial structures.