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Precursors to dolomite and magnesite in caves: the case of Nerja Cave, Spain

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Moonmilk deposits are common endokarstic precipitates found in caves as powdered, white materials, usually composed of carbonate materials of chemical or biochemical origin. In this study, we examined moonmilk samples collected in the Nerja Cave (Malaga, Spain), developed within the middle Triassic dolomitic marbles of the Almijara Unit, in the Internal Zone of the Betic Cordillera (SE Spain). In these moonmilk-type deposits, formed at relatively low *T*(the average *T*in the touristic part of the cave was 18.7 ± 0.9 °C for the 2008-2024 period), we identified the presence of crystalline phases such as huntite ($CaMg_3(CO_3)_4$), dolomite ($CaMg(CO_3)_2$) and magnesite ($MgCO_3$), which rarely form at room *T* and under atmospheric *P* in laboratory experiments. We characterized these mineral assemblages using several techniques, including synchrotron high-resolution X-ray diffraction (HR-XRD), standard X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FTIR), thermogravimetry coupled with differential scanning calorimetry (TG-DSC), transmission electron microscopy (TEM), and solid state nuclear magnetic resonance (MAS NMR). Our results unveil the key role of amorphous carbonate phases in the formation of crystalline Mg carbonates under room *T* and atmospheric *P* conditions, possibly stabilized by organic compounds and/or the presence of dissolved Si.