

Phosphorus Distribution in Calcite Speleothems from Solid-State NMR and AFM

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Progress in techniques such as SIMS and ICP-MS now allows production of high resolution traces and maps of P in calcite speleothems, suitable for interpretation in paleoclimate and paleohydrologic applications. However, unlike trace elements such as Sr and Mg, phosphate cannot be incorporated into the calcite structure by simple substitution. The ability of calcite P-content to reflect that of dripwater could depend on the nature of the P species that occur in calcite, which has not been studied. We used solid-state ³¹P and ¹H NMR techniques on natural speleothem samples and a calcite/phosphate coprecipitate to determine how P interacts with calcite in these environments.

Solid-state NMR results for samples from the Grotta d'Ernesto (Italy) indicate the presence of three primary types of phosphate environments: individual phosphate ions incorporated within calcite, monetite (CaHPO₄), and an unidentified anhydrous crystalline calcium phosphate phase. Essentially identical results were obtained for a calcite/phosphate coprecipitate synthesized by the constant addition method at a Ca:P ratio of 5 000. For all samples most of the P (60-70%) occurs in crystalline phosphate phases. AFM images show the formation of sub-micron sized surface precipitates within hours after exposure of a calcite cleavage fragment to small volumes of a solution slightly supersaturated with respect to calcite containing 0.5 μM P. These surface precipitates are much smaller than typical beam diameters employed for SIMS and laser-ablation ICP-MS.

Our results suggest that most of the P observed in speleothems by microchemical methods can occur as small crystalline inclusions in the calcite. These inclusions appear to originate as surface precipitates that are enclosed by growing calcite. Similarity in the P-distribution of natural samples to that of a more rapidly crystallized synthetic sample, and strong affinity of phosphate for calcite surfaces suggest that much of the phosphate in the dripwater might be incorporated into speleothems during infiltration events.