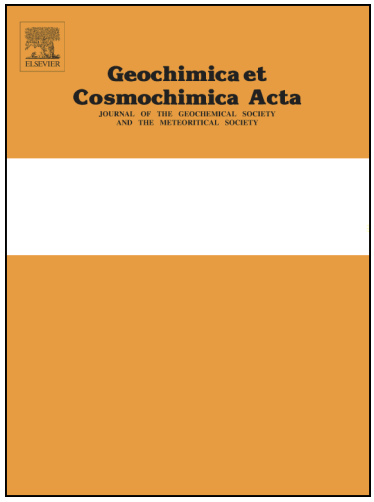

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Raman spectral, elemental, crystallinity, and oxygen-isotope variations in conodont apatite during diagenesis

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Abstract

Conodont apatite has long been used in paleoenvironmental studies, often with minimal evaluation of the influence of diagenesis on measured elemental and isotopic signals. In this study, we evaluate diagenetic influences on conodonts using an integrated set of analytical techniques. A total of 92 points in 19 coniform conodonts from Ordovician marine units of South China were analyzed by micro-laser Raman spectroscopy (M-LRS), laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), high-resolution X-ray microdiffraction (HXRD), and secondary ion mass spectrometry (SIMS). Each conodont element was analyzed along its full length, including the albid crown, hyaline crown, and basal body, in either a whole specimen (i.e., reflecting the composition of its outer layer) or a split specimen (i.e., reflecting the composition of its interior).

In the conodonts of this study, the outer surfaces consist of hydroxyfluorapatite and the interiors of strontian hydroxyfluorapatite. Ionic substitutions resulted in characteristic Raman spectral shifts in the position (SS_1) and width (SS_2) of the ν_1-PO_4^{3-} stretching band. Although multiple elements were enriched (Sr^{2+}, Mg^{2+}) and depleted (Fe^{3+}, Mn^{2+}, Ca^{2+}) during diagenesis, geochemical modeling constraints and known Raman spectral patterns suggest that Sr uptake was the dominant influence on diagenetic redshifts of SS_1. All study specimens show lower SS_2 values than modern bioapatite and synthetic apatite, suggesting that band width decreases with time in ancient bioapatite, possibly through an annealing process that produces larger, more uniform crystal domains. Most specimens consist mainly of amorphous or poorly crystalline apatite, which is inferred to represent the original microstructure of conodonts. In a subset of specimens, some tissues (especially albid crown) exhibit an increased degree of crystallinity developed through aggrading neomorphism. However, no systematic relationship was observed between crystallinity and Raman spectral or elemental parameters.