Carbon isotope record ($\delta^{13}\text{C}_{\text{carbonate}}$) of the Middle to Late Jurassic (Callovian - Oxfordian) from the Algarve Basin, Portugal

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Introduction

The Algarve Basin is an important Mesozoic depocentre located in southern Portugal which formed during the successive phases of the North Atlantic rifting following the break-up of Pangea [1]. Several unconformities related to compressive episodes are observed in the stratigraphic record of the Algarve Basin. One of these episodes occurred in the transition from Middle to Upper Jurassic times and is marked by an important tectonic episode, observed throughout Iberia [1], that caused the tilting and folding of the Middle Jurassic strata. This situation can be observed at Benacóitão, where Oxfordian limestones rest unconformably over tilted Middle Callovian marly limestones. In this work we present $\delta^{13}\text{C}_{\text{carbonate}}$ data across the Middle and Upper Jurassic rocks from the Algarve Basin at Benacóitão.

Results and Discussion

The Benacóitão section consists of a 30 m thick succession of interbedded of limestones and marls, which has been assigned using ammonites [2] to the Callovian to Late Oxfordian/Kimmeridgian interval. The $\delta^{13}\text{C}_{\text{carbonate}}$ values change gradually across the succession from -0.38‰ to -7.41‰ in the Middle Callovian, to values of -5.38‰ to +3.0‰ in the Late Oxfordian/Kimmeridgian. The well constrained trend in $\delta^{13}\text{C}$ shows the maximum $\delta^{13}\text{C}$ excursion at the unconformity. The $\delta^{13}\text{C}$ values reported in previous studies from the same age span are mostly in the range of 0 to +3‰ and there isn't known any global excursion in $\delta^{13}\text{C}$ at this time interval [3]. The trend of the $\delta^{13}\text{C}$ curve recorded from the carbonates can be interpreted to a large input of $^{13}\text{C}$ from either high weathering rates and/or decaying organic matter. The compressive episode is tentatively linked to the large input of $^{13}\text{C}$ to the basin. However, this was a local phenomenon which were not tied to the global $\delta^{13}\text{C}$ curve.


Formation of precursor phases during crystal growth of apatite under contaminated Earth-surface conditions

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Formation of hydroxylapatite through the precipitation and evolution of calcium phosphate precursor phases under varying conditions of temperature (25-90 °C), pH (6.5-9.0) and calcium to phosphorus ratio (1.0, 1.5, 1.33 and 1.67) in metal-free system and in the presence of suite of metals ($\text{Zn}^{2+}$, $\text{Cd}^{2+}$, $\text{Sr}^{2+}$, $\text{Th}^{4+}$, $(\text{UO}_2)^{2+}$) was studied. The products of low-temperature precipitation were analyzed by ex situ X-ray diffraction and SEM/TEM analysis, as well as time-resolved in situ synchrotron X-ray diffraction. Rietveld refinement was used for quantitative evaluation of relative abundances during phase evolution. The results of ex situ investigations conducted at near-neutral pH indicate formation of amorphous calcium phosphate, which over the course of experiments transforms to brushite and ultimately hydroxyapatite. The results of in situ X-ray diffraction experiments suggest a more complex pathway of phase development under the same conditions. Some of the initially formed amorphous calcium phosphate and/or brushite transform to octacalcium phosphate. In the later stage of the reactions octacalcium phosphate transforms quite rapidly to hydroxyapatite. This is accompanied or followed by the transformation of the remaining brushite to monetite. Hydroxyapatite and monetite coexist in the sample throughout the remainder of the experiments. In contrast to the near-neutral pH experiments, the results from ex situ and in situ investigations performed at higher pH (up to 9) yield similar results. The precipitate formed in the initial stages in both types of experiments was identified as amorphous calcium phosphate, which over the course of the reaction quite rapidly transformed to hydroxyapatite without any apparent intermediate phases. This is the first application of time-resolved in situ synchrotron X-ray diffraction to precipitation reactions in the $\text{Ca} \cdot (\text{OH})_2\cdot\text{HPO}_4\cdot\text{H}_2\text{O}$ system. The results indicate that precursors are likely to occur during the natural or induced formation of hydroxyapatite in many sedimentary environments. Experiments carried out in the presence of metal cations indicate significant influence of these species on the reaction pathway of calcium phosphate development.