Carbon isotope record ($\delta^{13}C_{carbonate}$) 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 succesive 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 ocurred 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 Benaçoitão, where Oxfordian limestones rest unconformably over tilted Middle Callovian marly limestones. In this work we present $\delta^{13}C_{carbonate}$ data across the Middle and Upper Jurassic rocks from the Algarve Basin at Benaçoitão.

Results and Discussion

The Benaçoitão 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 $\delta^{13}C_{carbonate}$ values change gradually across the succession from -0.38‰ to -7.41‰ in the Middle Callovian, to values of -5.38‰ to +0.31‰ in the Late Oxfordian/Kimmeridgian. The well constrained trend in $\delta^{13}C$ shows the maximum $\delta^{13}C$ excursion at the unconformity. The $\delta^{13}C$ 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 $\delta^{13}C$ at this time interval [3]. The trend of the $\delta^{13}C$ curve recoded from the carbonates can be interpreted to a large input of ^{12}C from either high weathering rates and/or decaying organic matter. The compressive episode is tentatively linked to the large input of ^{12}C to the basin. However, this was a local phenomemnon which were not tied to the global $\delta^{13}C$ curve.

[1] Mannupella *et al.* (1988) 2*nd Int. Symp. Jur. Strat.* 1031–1046. [2] Rocha (1976) *Ciências da Terra,* **2**, 178. [3] Nunn *et al.* (2009) *J. Geol. Soc. Lond.* **166**, 633–641.

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 (Zn^{2+}, Cd^{2+}, Sr^{2+}, Th^{4+}, $(UO_2)^{2+}$) 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 hydroxylapatite. The results of *in situ* X-ray diffracition 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 hydroxylapatite. This is accompanied or followed by the transformation of the remaining brushite to monetite. Hydroxylapatite 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 hydroxylapatite without any apparent intermediate phases. This is the first application of time-resolved *in situ* synchrotron X-ray diffraction to precipitation reactions in the $Ca\ (OH)_2$-H_3PO_4-H_2O system. The results indicate that precursors are likely to occur during the natural or induced formation of hydroxylapatite 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.