

## Exchange of biologically relevant ions on nanocrystalline apatites

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### Introduction

Nanocrystalline apatites are biomimetic compounds. We studied the interaction of synthetic samples with biologically relevant ions ( $\text{Sr}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{CO}_3^{2-}$ ) in view of the activation of apatite-based powders or scaffolds for bone regeneration, by favoring the release of such ions in the surrounding fluids.

### Materials and methods

Carbonated, hac-1d, and non-carbonated, hap-1d, nanoapatites matured 1 day were prepared. Direct and reverse exchanges were performed in solution at room temperature with increasing ion concentrations.

### Results and discussion

The  $\text{Mg}^{2+}$ ,  $\text{Sr}^{2+}$  and  $\text{CO}_3^{2-}$  uptakes on the surface of such nanoapatites after direct exchange Ca/Mg or Ca/Sr were plotted vs. the ion concentration in solution. The isotherms were fitted to the Langmuir model. The maximum exchange rate for  $\text{Mg}^{2+}$  on hap-1d ( $N_m \cong 3.8 \cdot 10^{20}$  ions  $\text{Mg}^{2+}/\text{g}$ ) was smaller than on hac-1d ( $N_m \cong 4.8 \cdot 10^{20}$  ions  $\text{Mg}^{2+}/\text{g}$ ). A similar trend was found with Sr:  $N_m \cong 4.5 \cdot 10^{20}$  ions  $\text{Sr}^{2+}/\text{g}$  for hap-1d and  $N_m \cong 7.5 \cdot 10^{20}$  ions  $\text{Sr}^{2+}/\text{g}$  for hac-1d. A greater uptake was observed with  $\text{Sr}^{2+}$  as compared to  $\text{Mg}^{2+}$  for all samples.

Reverse Mg/Ca and Sr/Ca exchanges were performed in a second step. The results indicate that on both hap-1d and hac-1d ca. 85% of Mg and 80% of Sr were fixed reversibly. However exchange experiments carried out on samples matured for longer periods show the decrease of the amount of reversible Sr, indicating the progressive incorporation of Sr into the lattice. On the other hand, the amount of reversible Mg is virtually constant despite further maturation, indicating that Mg mostly remains on surface of the crystals (within the superficial hydrated layer).

Carbonate/phosphate exchanges were also studied. For hap-1d, an excellent fit was obtained with the Langmuir model, with  $N_m \cong 3.1 \cdot 10^{20}$  ions  $\text{CO}_3^{2-}/\text{g}$ . For the initially carbonated sample hac-1d, results showed that the amount of  $\text{CO}_3^{2-}$  could be further increased, and the fit led to  $N_m \cong 5.6 \cdot 10^{20}$  ions  $\text{CO}_3^{2-}/\text{g}$ . This could be indicative of the larger hydrated layer on the surface of the carbonated apatite.

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## Micro-Raman spectroscopy as a non-destructive method for quantitative measurement of conodont diagenetic alteration

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The stable isotope compositions of biogenic materials record a combination of biological and environmental processes. The environment provides a range of isotopic compositional inputs and the animal processes the signals through a biologic filter. Thus, for a correct paleoclimatic and paleoenvironmental reconstruction it is absolutely necessary to distinguish between biological, environmental as well as diagenetic influences.

Since apatite crystals are quite small raman-spectroscopy is the ideal method for the investigation biogenic phosphates such as conodonts. Raman-spectroscopy is non-destructive and the microfocus instruments allow space-resolved measurements (maps) across a single conodont.

The conodont alteration index (CAI) is related to carbon in different structural states. The mid-range to long-range ordering of carbon can easily be detected to micro-Raman spectroscopy, since the Raman line width varies strongly with the degree of structural order. Different forms of carbon can be identified by their unique Raman signal. Further, the shape and position of the apatite Raman lines allow conclusions on the diagenetic alteration of the conodont apatite.

We have investigated conodont samples from the following genera: Bispathodus, Polygnathus and Palmatolepis with conodont alteration indices varying between three and seven. The Raman line width of carbon changes with different alteration indices. Thus, with these measurements a non-destructive quantitative determination of conodont diagenetic alteration is possible.