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Conversion of marine structures to calcium phosphate materials: Mechanisms of conversion using two different phosphate solutions

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Abstract. Marine structure, coralline materials were converted to calcium phosphate using two different phosphate solutions. The aim was to study the conversion mechanisms under acidic and basic environment at moderate conditions of temperature. Crystal growth and morphology of converted corals were characterized by XRD and SEM respectively. The results suggested that under acidic conditions (H_3PO_4), dissolution and precipitation control and direct the crystal formation and morphology in which transition from plate like to rod like hydroxyapatite structure was favoured. Metastable phase such as monetite formed and transformed to HAp during reaction. During the first hour of the dissolution a monetite and hydroxyapatite mixture precipitates and then the full conversion to hydroxyapatite is observed. On the other hand, under basic conditions $(NH_4)_2HPO_4$, just diffusional surface conversion of the calcium carbonate structure of coralline materials to hydroxyapatite and a very small amount of tri-calcium phosphate is observed. The mechanism can be classified as the solid-state topotactic ion-exchange reaction mechanism.

Introduction

Both clinical and scientific investigations have focused on producing implant materials for the treatment and repair of bone-related diseases such as fractures, bone cancer, and osteoporosis [1]. Calcium phosphates (CaPs) materials have gained clinical acceptance for the past 40 years. Hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$, HAp] and β -tricalcium phosphate [$Ca_3(PO_4)_2$, β -TCP] are one of the most widely used synthetic (CaPs) in the areas of orthopaedic and dentistry for augmentation, bone substitution and repair due to their similarity with the mineral phase of bone. It is known that bone formation involves series of complex events leading to mineralization of extracellular matrix proteins by cells with specific functions to maintaining the integrity of the bone [2]. Different synthesis methods have been employed to convert natural materials to calcium phosphates for a wide range of biomedical applications with the aim to get a pure phase material with a defined composition and morphology. The high price of medically pure bioceramics in the market reflects the significant costs of production entailed in the use of current, energy intensive synthesis methods.

The potential applications of natural biogenic materials such as marine structures can be easily overlooked due to the environmental concerns. While it is true that a wide range of marine structures are limited and protected, similarly there are also a variety of materials that are abundantly available and are yet to be exploited for their possible use [3]. Coralline materials in this research are fossilised high purity corals obtained from specific locations and /or artificially grown under controlled conditions in specific containers in laboratories [4]. Among marine structure, coral

mineral which mainly consists of calcium carbonate in the forms of aragonite or calcite with trace elements of strontium, magnesium and sodium has considerable success as the apatite precursors and bone graft materials. Corals have porous structure with pores size ranges from 150 to 500 μm similar to cancellous bone and form chemical bonds with bone and soft tissue in vivo [1].

The mechanism of conversion of calcium to hydroxyapatite has been suggested previously. Boskey and Posner suggested that precipitation of amorphous precursor preceded the formation of hydroxyapatite [5]. There is possibility of transformation of precipitates through some intermediate states to the thermodynamically stable products such as HAp. The transformation is influenced by the presence of impurities, pH values and supersaturation [4, 6]. Theories have been suggested on the mechanism of calcium phosphates crystal formation from the conversion of calcium carbonate through basic or acidic conditions but very few have been widely accepted by scientific community.

This research aimed to evaluate the mechanism of conversion of a natural calcium carbonate such as coral under acidic and basic conditions using mechano-chemical conversion technique.

Materials and Methods

Corals were obtained from the Great Barrier Reef, QLD. Ammonium dihydrogen phosphate dibasic ($\text{NH}_4\text{H}_2\text{PO}_4$, 98%), hydrophosphoric acid (H_3PO_4 , 85%) and sodium hypochlorite (NaClO) were obtained from Sigma Aldrich Australia.

Methods. The coral samples were crushed then cleaned with 2% (v/v) NaClO , and then grounded within an aluminium oxide ball mill (46 rpm, 2 h), sieved with 100 μm sieve, cleaned with 2% (v/v) NaClO and then dried at 100°C for 2 hours before use. The conversion was performed based on the method described previously in [4, 6]. Briefly, the required amount of H_3PO_4 or $\text{NH}_3\text{H}_2\text{PO}_4$, to obtain HAp was dissolved in 25 ml of distilled water. Then it was added, drop by drop, to 3 g of coral powder suspended in a cleaned flask with 150 ml distilled water at 80 °C on a temperature control hot plate with magnetic stirrer. The stirring rate was 200 rpm and the temperature was kept at 80 °C for 24 hrs.

Results and discussions

The XRD results (Table 1&2) and SEM pictures, Fig.1 suggested that the reactions took place in two different conversion processes. The H_3PO_4 can be described as a dissolution and precipitation process while $\text{NH}_4\text{H}_2\text{PO}_4$ direct surface conversion by diffusion into hydroxyapatite. Generally it is well known that the crystallization of many calcium phosphate materials involves the formation of metastable precursor phases that subsequently dissolve as the precipitation reaction proceeded.

Table 1: Quantification for HAp derived coral by orthophosphoric phosphate solution experiment showing the amount of transformed phases and crystal growth of HAp

Time (h)	Aragonite (%)	Calcite (%)	Monetite (%)	HAp (%)	Size 002 Scherrer (nm)	pH
0.5	4.4	24.4	29.0	41.4	42	4.40
2.0	2.5	14.8	48.8	32.4	53	6.04
5.0	1.3	12.5	31.8	49.9	72	5.97
7.0	0.9	9.6	24.5	59.2	82	5.75
24.0	0.3	7.2	0.6	84.8	77	7.90

Table 2: Quantification for HAp derived coral by ammonium phosphate solution experiment showing the amount of transformed phases and crystal growth of HAp

Time (h)	Aragonite (%)	Calcite (%)	HAp (%)	Size 002 Scherrer (nm)	pH
0.5	13.6	48.4	38.0	53	7.41
2.0	12.2	48.6	39.2	51	7.59
5.0	11.4	44.4	44.2	56	7.66
7.0	10.9	44.6	44.5	52	7.66
24.0	7.5	33.5	58.9	53	7.69

Microstructural analysis Fig.1, showed platelike morphologies of coralline structures changed to rod like structures under acidic condition (HAp-A) signifies dissolution precipitation reaction mechanism. On the other hand, under basic conditions the transformation of calcium carbonate to HAp (HAp-P) doesn't seem to influence the final crystal shape or morphologies but only some growth according to reaction time was observed. It is believed that in acidic conditions calcium carbonate dissolves to give Ca^{2+} which interact with PO_4^{2-} from phosphoric acid to form preliminary monetite and HAp. It can be suggested that the reaction time and pH influence reaction mechanism and microstructure evolution. It is expected that impurities and the amount of the material used for conversion are the additional factors to influence the morphology and structure. Production of HAp under basic or acidic conditions could provide the possibility of controlling the morphology.

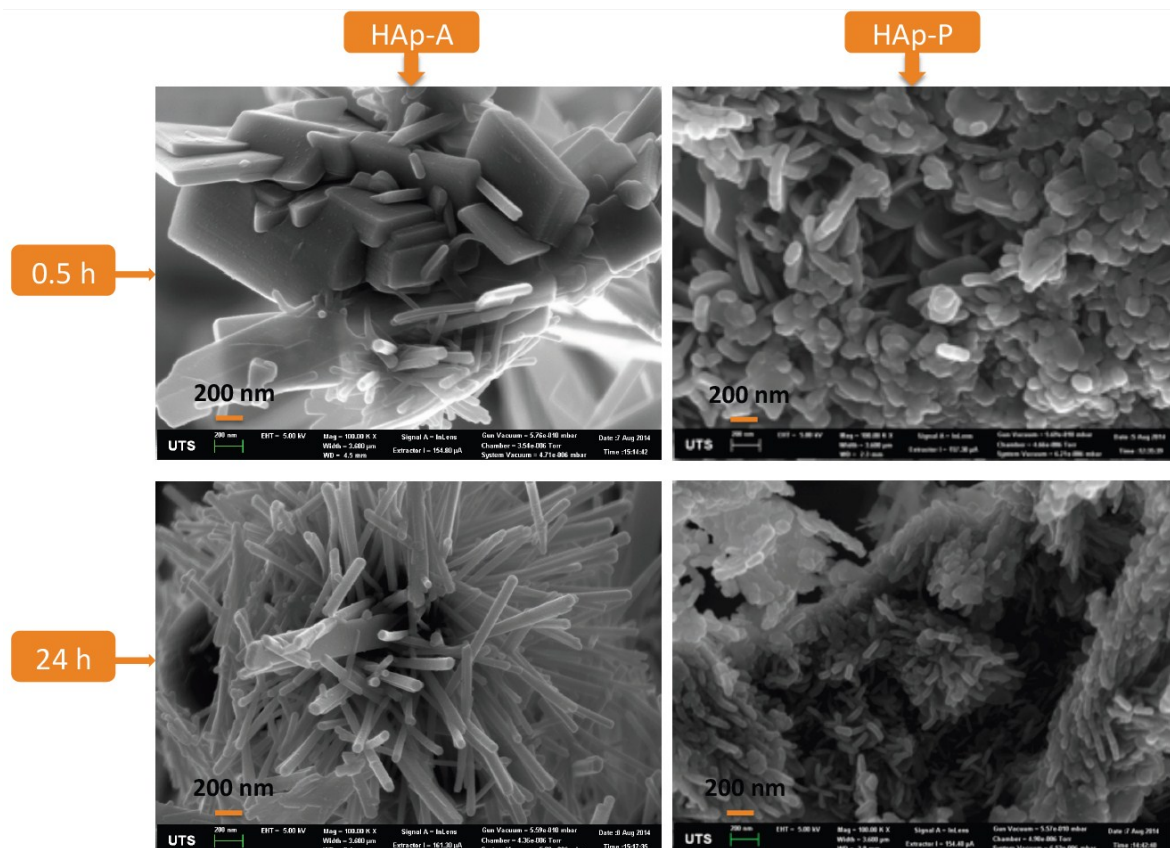


Figure 1: SEM pictures showing the morphology of coral after 0.5 and 24 hrs conversion under acidic and basic condition

Conclusion

In this study coralline materials were successfully converted to HAp under acidic and basic conditions. It was previously reported that hydrothermally, coral converts into HAp in ammonium phosphate solutions with preservation of sample form and morphology signifying topotactic ion exchange reaction mechanisms. Mechano-chemical conversion of coral to HAp follows topotactic reaction mechanism under ammonium phosphate solution and dissolution-recrystallization using orthophosphoric acid phosphate solution. Utilization of natural biogenic materials such as coral in the production of HAp will address the significant cost of synthetic raw materials and the cost of HAp. HAp derived coral has the wide potential in medical field especially in orthopaedic and tissue engineering.

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