The Influence of Calcination Temperature to Calcium Content in the Mangrove Crab Shells (Scylla serrata) from Merauke

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Abstract. This study introduced the use of shells of the Merauke Mangrove crabs as a natural source of calcium extracted through thermal decomposition process with various temperatures. The method adopted in this study was carried out in two stages; first, shells of the crabs that have been cleansed and dried under the sun for 24 hours, were mashed and then it divided into two parts. The first section was used for the analysis of calcium composition. While the second part was calcined at three different temperatures, 900°C, 1000°C and 1100°C for 5 hours before analysis. The results of the XRF showed that the raw powder of mangrove crab shell was contained 90.46% of calcium and 9.64% of other mineral content. This study revealed that the temperature of 1000°C is the right calcination condition to produce high calcium minerals in the mangrove crab shell, in which it reached 97.76% purity. The phase form that obtained from the XRD before being calcined was CaCO₃ and after the calcination process was Ca(OH)₂ / CaO hydration. This study also found that the calcined process has succeeded to decrease the carbon content in the shells. Therefore, it can be concluded that the mangrove crab shells from Merauke, possess basic materials as bioceramic.

1. Introduction
Calcium is the main component of bone and teeth. There are many types of natural calcium sources that can be used for various applications, one of which is the shell. In this study, I would like to emphasize on shell materials from the crabs. Shells are also rich in calcium that have been known to be used as components of bone and tooth substitution [1, 2]. There is a high content of calcium in the shell which can also be used in a number of applications, such as drugs formulation, [3] in the construction field as raw material [4, 5] and also as a filler in polymeric materials [6, 7].

The use of egg shells, shellfish and coral rock as materials or bone substitution compositions has been studied and it has been widely recognized in biomedical applications. [8, 9] The calcium content of mangrove crab shell powder from Merauke with calcination process at 800° C, 900° C and 1000° C has been studied. [10, 11] The mangrove crab shell from Merauke is one of the ingredients that has great prospects due to its natural habitat, in which it is still very well maintained so that the content of dangerous compounds such as heavy metals in the crabs is very small or even non-existent. This crab is also widely consumed as daily menu in Merauke, hence the crab shells become waste that is simply found everywhere, and the quantity continue to increase along with the rising population in the area.
This study aims to analyze the characteristic of mangrove crab shells from Merauke as bio ceramic material, particularly on the calcium content. In this study, the calcium content is obtained in the form of calcium carbonate and calcium oxide compounds. One way that can be done is through a thermal decomposition process known as the calcination process \cite{12}.

The calcination process is defined as processing samples at high temperatures but still below the melting point without the addition of reagents, with a view to changing the shape of the compound in the concentrate. Calcination temperature affects the phase change of a substance, where the phase is the part of a material that is different from other parts in terms of structure or composition\cite{12}.

2. Materials and Methods

The crab shells used in this study were obtained from the mangrove areas in Merauke District, Papua, Indonesia. The collected shells were cleansed from macro impurities and subsequently natural dried for 24 hours. The cleaned and dried shells were crushed using a grinder to obtain a shell powder form. The raw powder (without any calcinations process) was divided into two parts. The first part used for minerals content characterization, while the other part was calcined through various temperature. A laboratory furnace was used to calcinate samples at 900°C, 1000°C and 1100°C. The sample was calcined in an alumina crucible container for 5 hours at a heating rate of 5°C/min. Afterwards, the powder of the calcined samples was characterized to measure its calcium content.

Characterization of mangrove crab shell powder from calcination will be analyzed using X-Ray Fluorescence (XRF) and X-Ray Diffraction (XRD). XRF was conducted to analyze the chemical that estimate the mineral composition in shell, while the XRD was conducted to analyze the crystal structure of calcium content.

3. Results and Discussions

The calcium content of the mangrove crab shell from Merauke was analyzed by XRF and XRD method. The XRF experiment aims to analyze the elements that contained in the sample. In this test, there are two samples applied; the mangrove crab shell powder without calcination and the similar powder that has gone through the calcined process.

![Figure 1. The XRF spectrum of crab shell powder without calcinations](image)

Examination of the XRF test for crab shell without calcination reveals that the highest peak in Figure 1 is calcium. The calcium value has reached 90.46% of the subject, while 9.64% of the content consist of another mineral, as shown in Table 1. It is indicated that Calcium is the most significant mineral content among other minerals in the crab shells.
Table 1. Chemical compound of crab shells without calcinations as measured with the wavelength dispersive x-ray fluorescence spectrometer (XRF).

| Element | Conc. (%) |
|---------|-----------|
| P       | 1,9       |
| Ca      | 90,46     |
| Sr      | 3,19      |
| In      | 1,6       |
| others  | 2,85      |

Table 2. Chemical compound of crab shells after calcinations as measured with the wavelength dispersive x-ray fluorescence spectrometer (XRF).

| Temperature of Calcination (°C) | Element | Conc. (%) | Compound | Conc. (%) |
|---------------------------------|---------|-----------|----------|-----------|
| 900                             | P       | 2,2       | P₂O₅     | 4         |
|                                 | Ca      | 95,46     | CaO      | 94,02     |
|                                 | Mn      | 0,13      | MnO      | 0,11      |
|                                 | Sr      | 1,9       | SrO      | 1,42      |
|                                 | others  | 0,31      | other    | 0,45      |
| 1000                            | Ca      | 97,76     | CaO      | 98,24     |
|                                 | Mn      | 0,15      | MnO      | 0,13      |
|                                 | Sr      | 1,94      | SrO      | 1,5       |
|                                 | others  | 0,15      | other    | 0,13      |
| 1100                            | P       | 2,2       | P₂O₅     | 4,2       |
|                                 | Ca      | 95,51     | CaO      | 93,95     |
|                                 | Sr      | 1,85      | SrO      | 1,37      |
|                                 | others  | 0,44      | other    | 0,48      |

In table 2, the data describes the samples of three samples mangrove crab shell that have been calcined at different temperatures. This procedure revealed that the percentage of calcium minerals (calcium oxide) were increased, compared to crab shell powder without calcination process. The highest increase occurred in the powder that calcined at 1000 °C, where it reached 98.24%, and it displayed a significant reduction in other compounds. The other two samples only increased in CaO compounds by 94.02% and 93.95%. The existence of a relationship between structural properties of CaO and the temperature of calcination, it was found that increasing the temperature in the calcination process would result in an increase in the weight of CaO. However, the results obtained from the mangrove crab shell powder calcined at 1000°C gave a higher amount of CaO compared to the calcination process at the temperature of 900°C and 1100°C. Therefore, the calcination temperature of 1000°C seems to be the preferred temperature to produce the crab shells into pure calcium.

The XRD procedure was carried out to determine the crystal structure, phase, elements and compounds that found in the mangrove crab shell powder that had been processed before. Analysis of XRD results is done by matching the data obtained with X-ray diffraction standards called The Joint Committee on Powder Diffraction Standards (JCPDS).
The analysis of XRD process before calcination describes that the majority of peaks that formed in this process are CaCO₃. In Figure 2, Calcite (CaCO₃) is found in several peaks with an angle of 2θ that is at an angle 23.17°; 29.61°; 47.99°; 43.53°; 36.15°; and 48.93° with a considerable intensity.

Based on the results shown in Figure 3 in the XRD test, it is seen that the three calcium powder that has been calcined at different temperatures produce similar diffraction pattern. These three
patterns clearly show strong peaks in accordance with the phase of Ca(OH)$_2$. The resulting Ca(OH)$_2$ is a hydrated CaO phase [13]. Calcined calcium powder may be exposed to air so that it is hydrated, as shown in the following reaction formula:

$$\text{CaO} + \text{H}_2\text{O} \xrightarrow{\text{hydrated}} \text{Ca(OH)}_2$$  \hspace{1cm} (1)

Some peaks of the CaO phase are also still visible. Especially when compared to crab shell powder before and after calcination, changes in terms of calcium minerals occur. Before calcined, the calcium (Ca) in the shell was in compound of CaCO$_3$. After the calcination process, the calcium compounds are turned to CaO and it is evaporated as CO$_2$. As shown in the following chemical reaction formula:

$$\text{CaCO}_3 \xrightarrow{\text{calcined}} \text{CaO} + \text{CO}_2 \uparrow$$  \hspace{1cm} (2)

Therefore, the calcinations process has yield the decrease of carbon content.

4. Conclusions
This study confirms hypothesis that the characteristic of mangrove crab shells from Merauke is suitable for bio ceramic application. As it is shown from the results of the XRF pattern, the high calcium content in the shell, which is 90.46% of the total minerals contained in it. After the calcination process, there was a percentage increase in the amount of calcium content up to 97.76% at calcination temperature of 1000°C. Temperature 1000°C is also the right calcination condition to produce high calcium minerals for mangrove crab shell. The formation within this phase is obtained from the XRD spectra after the calcination process is Ca(OH)$_2$ / CaO hydration, this calcination process makes calcium carbonate from the form of CaCO$_3$ transform into Ca(OH)$_2$ / CaO hydration.

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