Charge Balance
Mechanism of Counter Ion Substitution in Carbonated Apatites

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What is carbonated apatite?

• Apatite, or calcium hydroxylapatite, is a mineral commonly found in bones, teeth, and the earth’s crust
• It is composed of calcium, phosphate, and hydroxide with the formula $\text{Ca}_{10}(\text{PO}_4)_5(\text{OH})_2$
• Carbonated apatite has 5-8 weight percent carbonate incorporated into the crystal lattice

Carbonated apatite molecular structure projected onto the 0 0 0 1 plane with potential ion substitutions shown. A- and B-type substitution labeled [1].
Types of carbonate incorporation

- Carbonate can be incorporated into the apatite structure in 3 ways
  - A type – $\text{CO}_3$ substitutes for hydroxide (OH) ions in the C-axis channel
  - B type – $\text{CO}_3$ substitutes for phosphate ($\text{PO}_4$) ions
  - Mixed AB type – $\text{CO}_3$ substituted for both OH and $\text{PO}_4$ ions
Goals

• Determine the effect of the counter ion on the charge compensation mechanism in B-type carbonated apatite synthesis by:
  – using the alkali metals
    • Li, Na, K, Rb
  – verifying whether the counter ion affects the degree to which carbonate is incorporated
  – determining whether the counter ion is incorporated with the carbonate into the apatite structure.
Potential Substitution Mechanisms

I. \( \text{PO}_4^{3-} = \text{CO}_3^{2-} + \text{OH}^- \)

II. \( \text{Ca}^{2+} + \text{PO}_3^{3-} + \text{OH}^- = V_{\text{Ca}} + \text{CO}_3^{2-} + V^{\text{OH}} \)

III. \( \text{Ca}^{2+} + \text{PO}_4^{3-} = M^+ + \text{CO}_3^{2-} \)

IV. \( \text{Ca}^{2+} + \text{OH}^- = M^+ + V^{\text{OH}} \)

V. \( \text{Ca}^{2+} + 2\text{PO}_4^{3-} = V_{\text{Ca}} + 2\text{CO}_3^{2-} \)

The charge difference between the phosphate and carbonate ions create a -1 charge deficit that must be compensated for. The above mechanisms are the current proposed explanations for achieving a compound (apatite) that has no net charge [2].
Experimental Methods

• Synthesize calcium apatites using differing starting ratios of carbonate to phosphate (0.2:1, 1:1, 3:1, 5:1) for each counter ion (Na, Li, K, Rb)
  – Synthesis carried out in 3-neck round bottom flask at 80°C with magnetic stir bar
  – 4 hour digestion period with pH regulation
    • 9 M NH₃ used to maintain pH 9
Analysis Techniques

• X-ray Diffraction (XRD)
  – Identification of sample with examination for calcite presence

• Inductively Coupled Plasma – Atomic Absorption (ICP-AA)
  – Weight percent determination of calcium, phosphorous, and alkali metals

• Unit Cell
  – PANalytical and UnitCell analyses
  – Determine unit cell parameters for each sample

• Crystallite Size Analysis
  – XRD analysis and the Scherrer Equation
    \[ \tau = K\lambda/(\beta \cos \theta) \]

• Infrared Spectroscopy (IR)
  – Identification of type of carbonate substitution (A, B, AB type)
Results – XRD

XRD pattern of sample RD-52: 0.2:1 CO$_3$ :PO$_4$ with Na counter ion. Match score 90 for calcium hydroxylapatite.
Results - ICP

• For each counter ion series excluding Rb:
  – The counter ion composition was compared to carbonate content
  – The counter ion content was compared to calcium content
  – The calcium content was compared to carbonate content

• At this time there is not enough data to draw a viable conclusion
  – More data is currently being collected
Results – ICP cont.

- **Na:** carbonate and sodium were incorporated in increasing amounts as the starting concentrations were increased.
- **Li:** carbonate and lithium were incorporated in no discernable pattern with the current data.
- **K:** carbonate and potassium were incorporated in increasing amounts as the starting concentrations were increased.
- **Rb:** Rubidium could not be measured by the ICP due to the low amounts incorporated.
Results – Crystallite Size and Unit Cell

- **Na:** crystallite size decreased as carbonate-phosphate ratios increased. As ratios increased the a-axis slightly decreased and the c-axis slightly increased.
- **Li:** crystallite size decreased as carbonate-phosphate ratios increased. As ratios increased there was a slight increase in the a-axis and the c-axis fluctuated.
- **K:** crystallite size decreased as carbonate-phosphate ratios increased, excluding the 5:1 synthesis. Inconsistent changes were shown in both the a- and c-axes.
- **Rb:** No clear pattern was shown for crystallite size. Inconsistent changes were shown in both the a- and c-axes.
Future Work

• Synthesize at least 4 more ratios for each counter ion series
• Test all rubidium samples for Rb incorporation through NMR spectroscopy or XRF analysis
• Wash and re-analyze all samples through ICP to make sure ions were incorporated into the structure, not simply adsorbed onto the surface
• Determine mole ratio and formula for each counter ion
References


