

1 **Cycling of Potassium-Carbonate Co-Substituted Hydroxyapatite Compositions for**
2 **Improved Carbon Dioxide Capture at 500°C**

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4 **Duncan A. Nowicki, Iain R. Gibson and Janet M. S. Skakle**

5 **Supplementary Material**

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Table SM 1 The quantities (in moles) of the reactants used to prepare the apatites studied in this work. The value of x refers to the designed molar substitution of potassium and carbonate ions on calcium and phosphate sites respectively, in accordance with the design composition formula $\text{Ca}_{10-x}\text{K}_x(\text{PO}_4)_{6-x}(\text{CO}_3)_x(\text{OH})_2$.

Design x	Ca(OH)₂ (moles)	K₂CO₃ (moles)	H₃PO₄ (moles)	Design Ca/P	Design (Ca+K)/P
0	0.11	N/A	0.066	1.67	N/A
0.5	0.1045	0.00275	0.0605	1.73	1.82
1.0	0.099	0.0055	0.055	1.80	2.00
2.0	0.088	0.0110	0.044	2.00	2.50
2.5	0.0825	0.01375	0.0385	2.14	2.86

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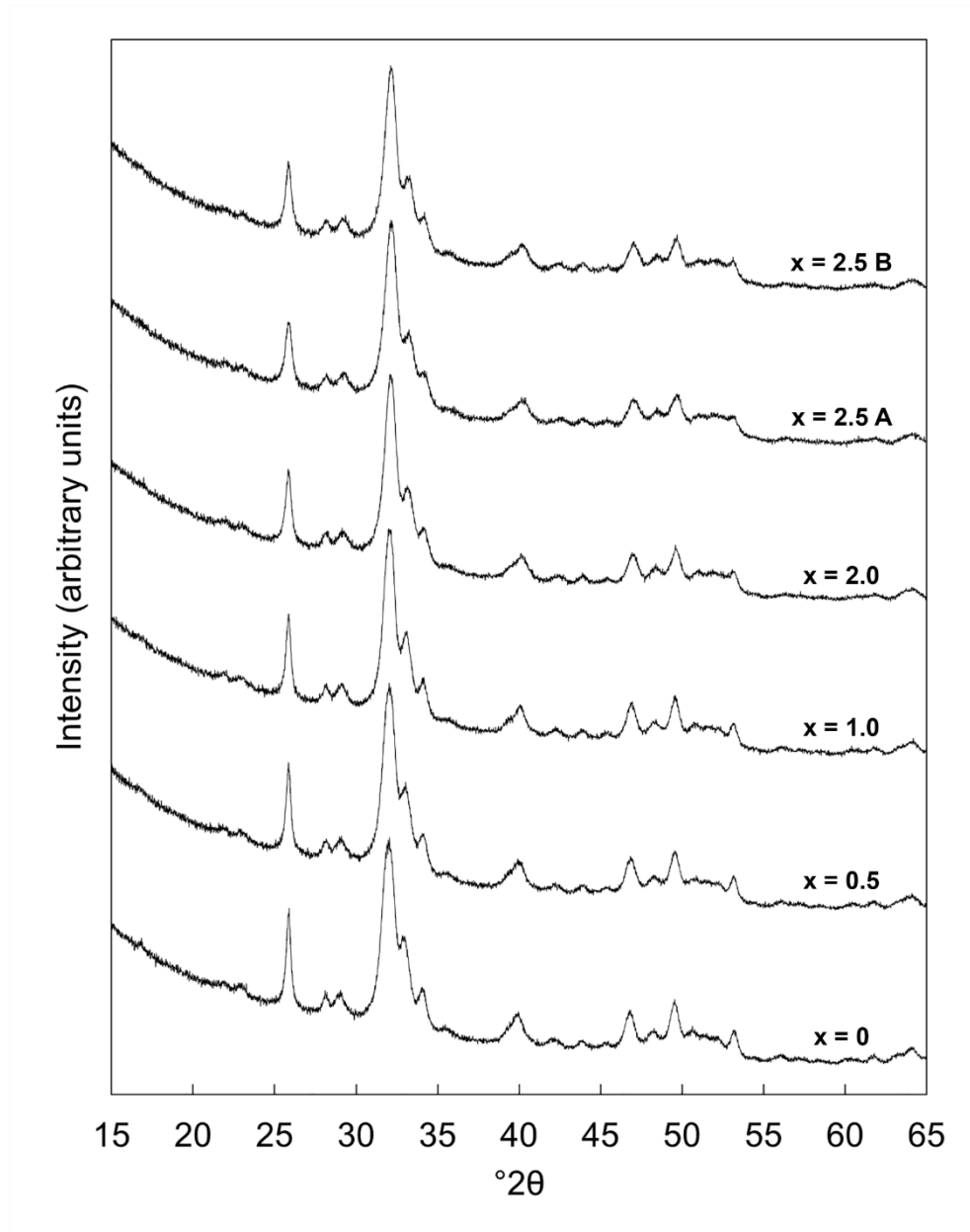
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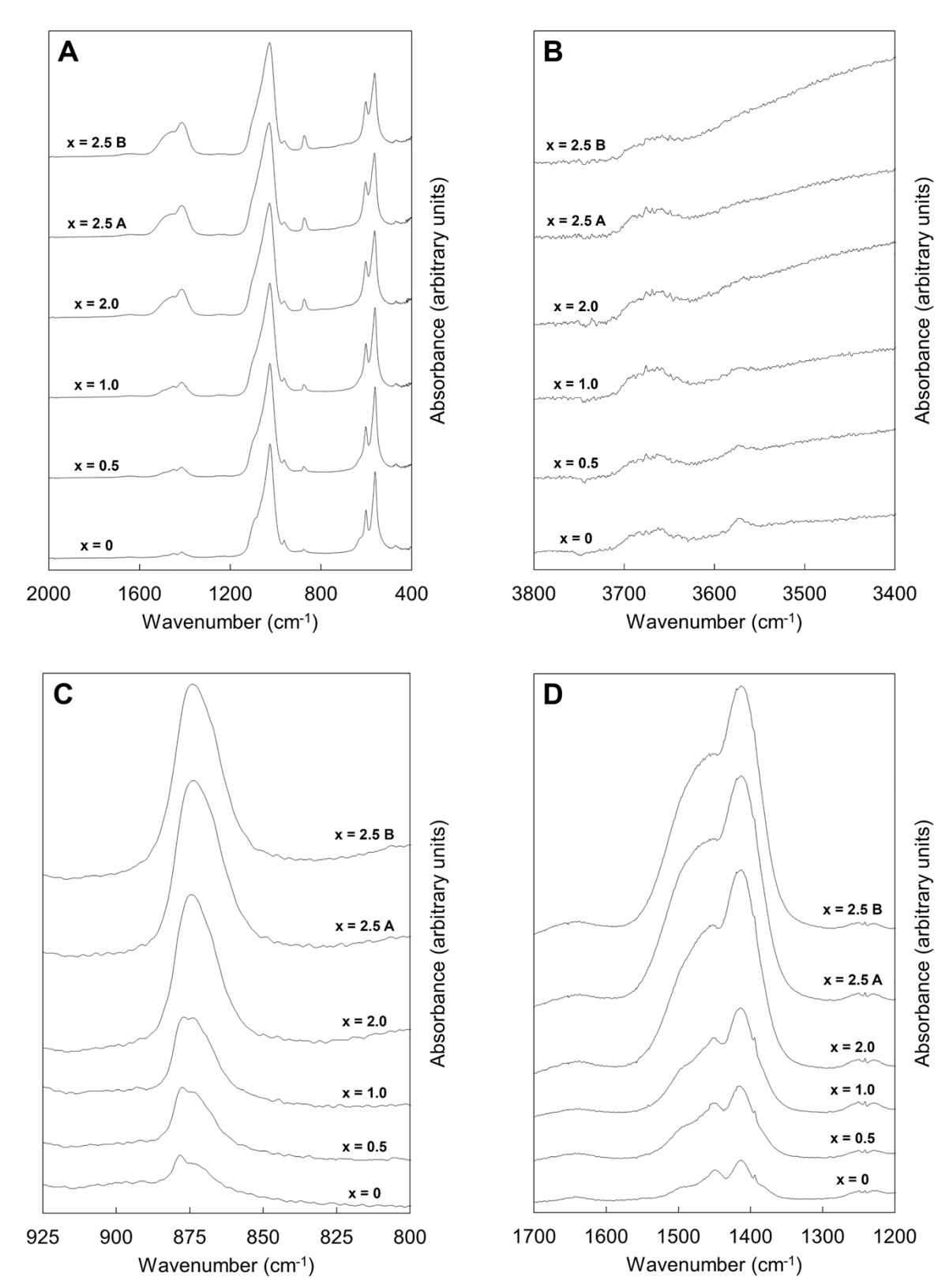
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FigureSM 1 Normalised ($I_{\max} = 100$) X-ray diffraction patterns of each of the as-prepared apatite materials, where $x = 0-2.5$ in the design formula $\text{Ca}_{10-x}\text{K}_x(\text{PO}_4)_6-x(\text{CO}_3)_x(\text{OH})_2$. 'A' denotes the $x = 2.5$ sample that was thrice cycled whereas 'B' marks the $x = 2.5$ apatite that was subjected to 15 carbonation-regeneration cycles at 500°C in CO_2 and air respectively.

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FigureSM 2 Normalised (A_{max} = 100) FTIR spectra between (A) 2000-400, (B) 3800-3400, (C) 925-800 and (D) 1700-1200 cm⁻¹ of each of the as-prepared apatites, where x = 0-2.5 in the design formula $\text{Ca}_{10-x}\text{K}_x(\text{PO}_4)_{6-x}(\text{CO}_3)_x(\text{OH})_2$. 'x = 2.5 A' denotes the sample that was thrice cycled whereas 'x = 2.5 B' marks the apatite subjected to 15 cycles.

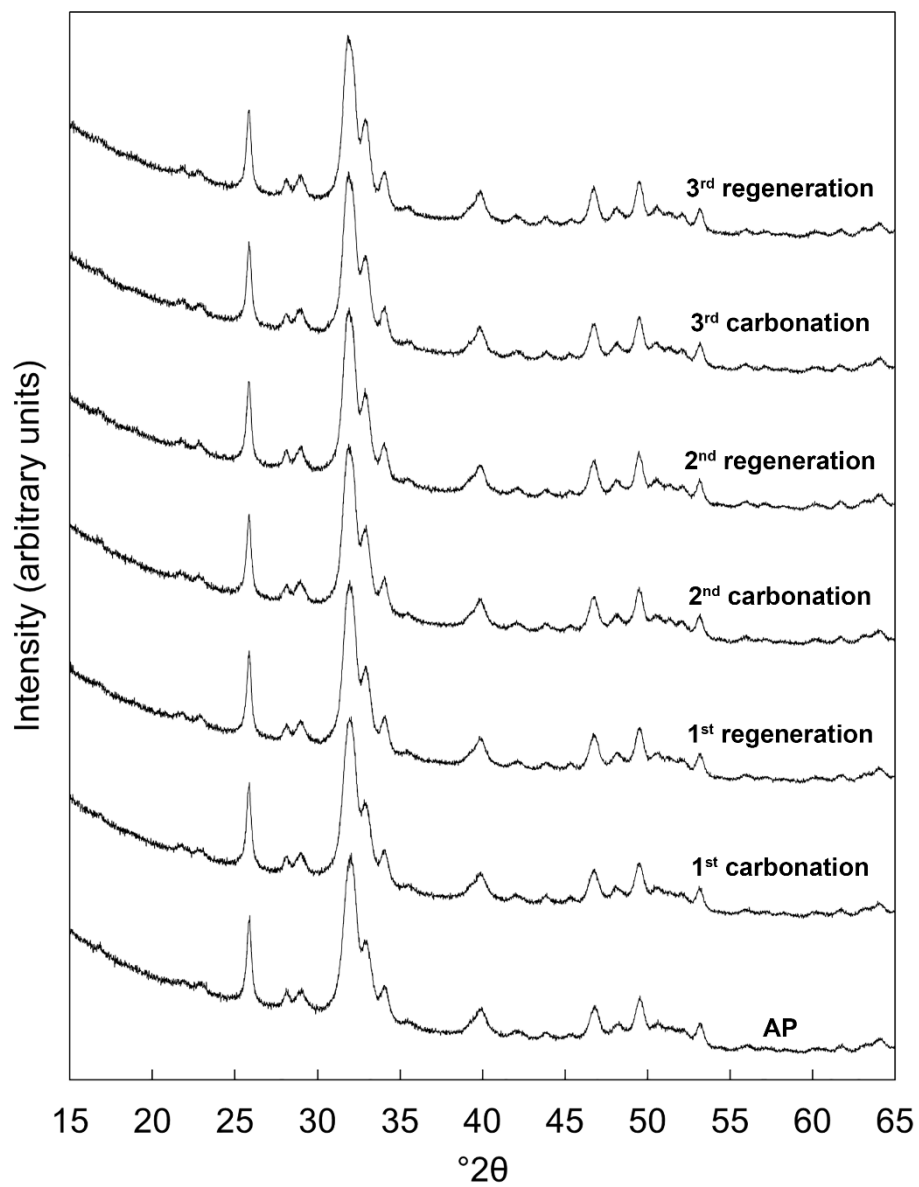
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Table SM 2 Carbonate contents (wt%) of each of the as-prepared apatites. Also shown are the lattice parameters of these materials, determined by simple Rietveld refinement of collected XRD data. 'A' denotes the $x = 2.5$ sample that was thrice cycled whereas 'B' marks the $x = 2.5$ apatite that was subjected to 15 carbonation-regeneration cycles at 500°C in CO₂ and air respectively.

Design x	CO₃²⁻ (wt%)	a parameter	c parameter
0	1.94 ± 0.02	9.4039(5)	6.8882(6)
0.5	3.88 ± 0.01	9.3852(6)	6.8902(6)
1.0	5.48 ± 0.04	9.3726(5)	6.8916(5)
2.0	9.95 ± 0.07	9.3456(6)	6.8910(7)
2.5 A	12.93 ± 0.11	9.3326(7)	6.8890(7)
2.5 B	12.53 ± 0.04	9.3375(7)	6.8906(8)

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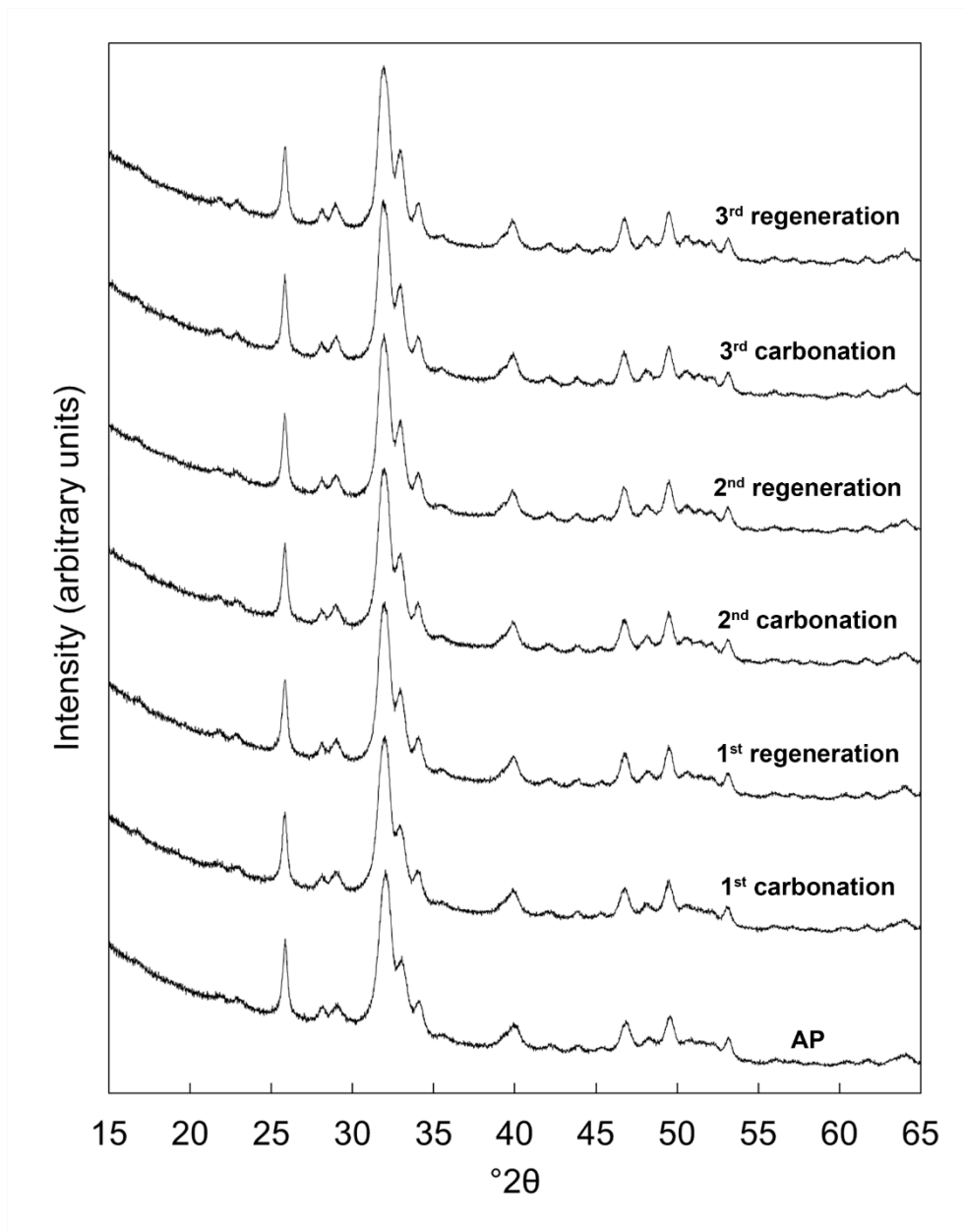
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FigureSM 3 Normalised ($I_{\max} = 100$) XRD patterns of the $x = 0$ apatite as-prepared (AP) and over three carbonation-regeneration cycles at 500 $^{\circ}$ C in dry CO₂ and air respectively.

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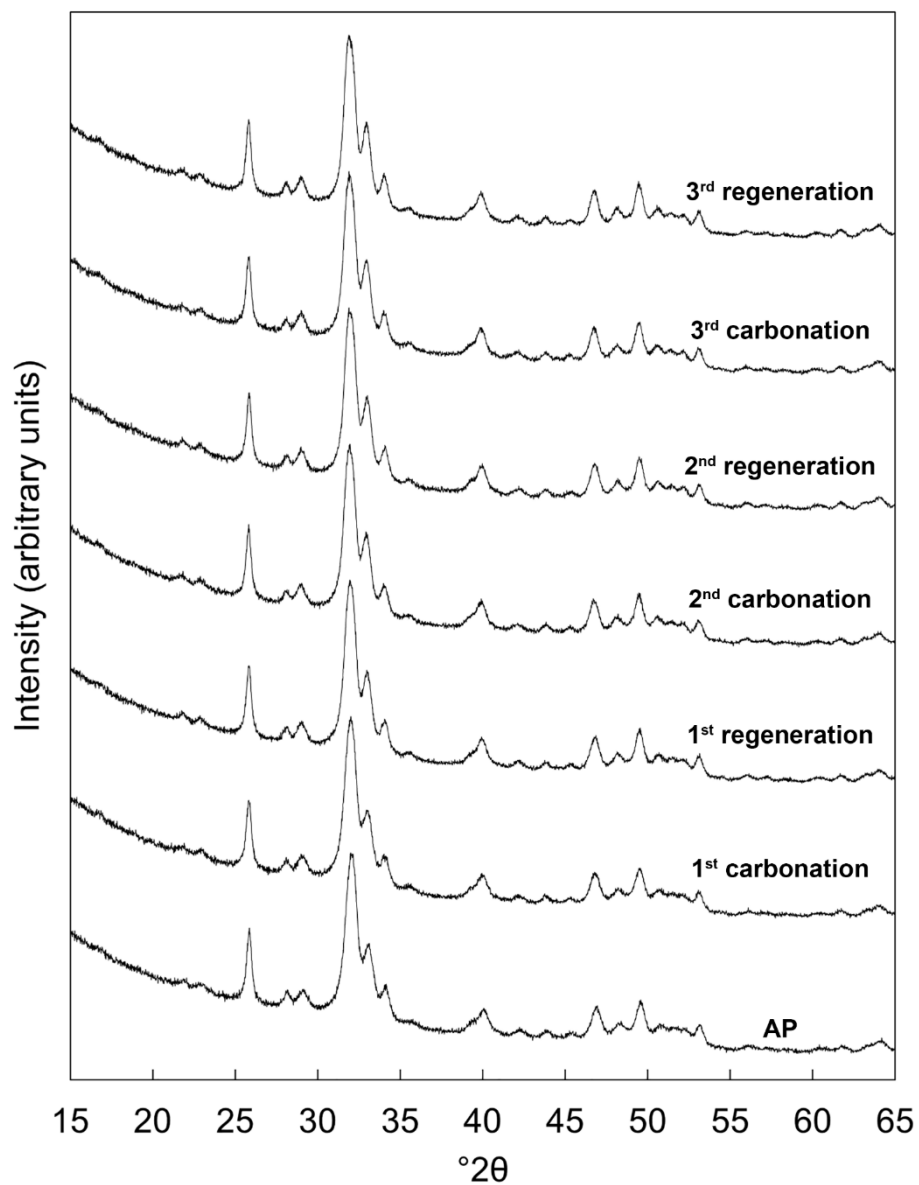
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FigureSM 4 Normalised ($I_{\max} = 100$) XRD patterns of the $x = 0.5$ apatite as-prepared (AP) and over three carbonation-regeneration cycles at 500°C in dry CO_2 and air respectively.

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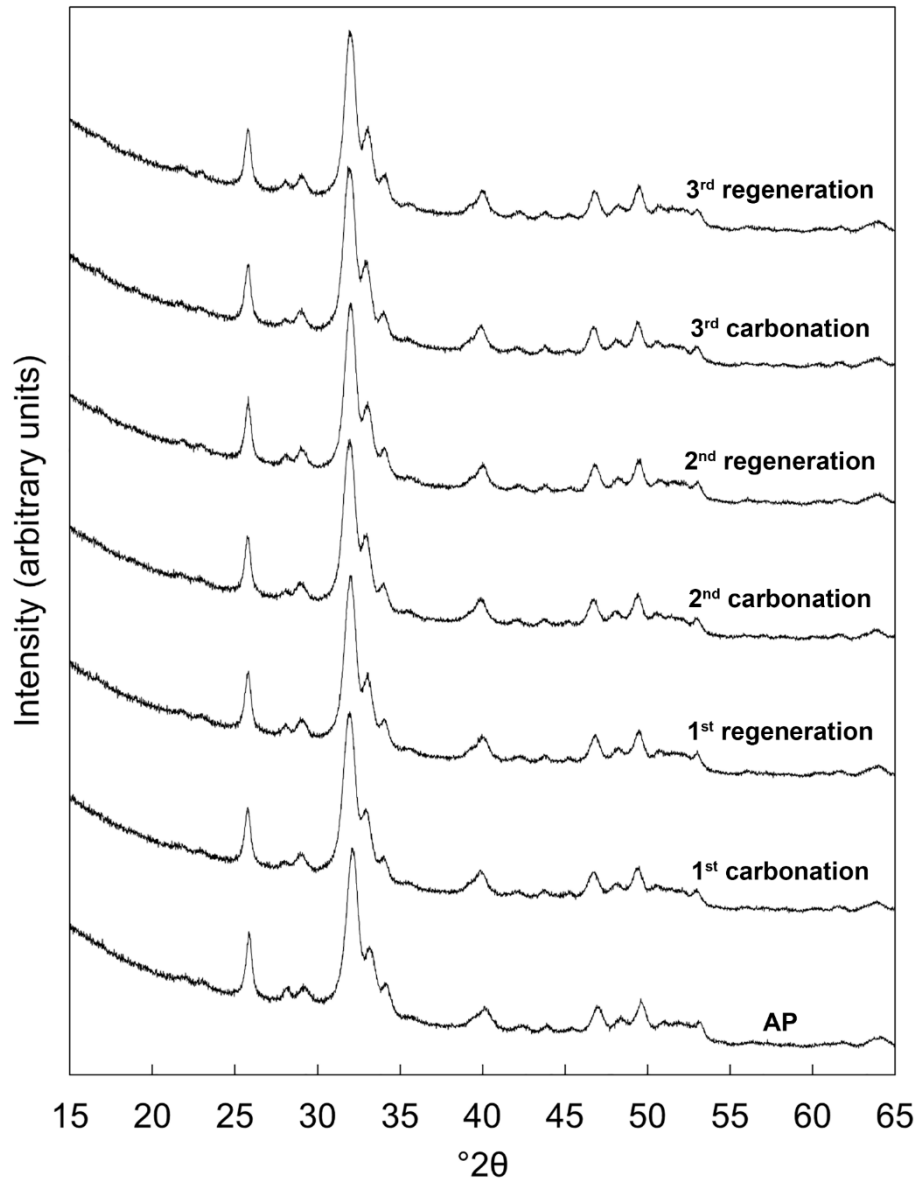
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FigureSM 5 Normalised ($I_{\max} = 100$) XRD patterns of the $x = 1.0$ apatite as-prepared (AP) and over three carbonation-regeneration cycles at 500°C in dry CO_2 and air respectively.

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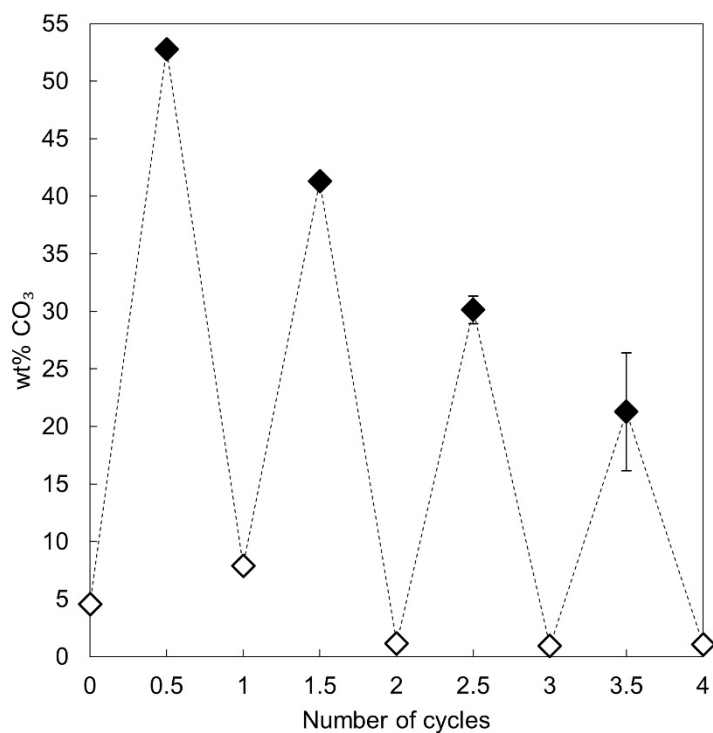
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FigureSM 6 Normalised ($I_{\max} = 100$) XRD patterns of the $x = 2.0$ apatite as-prepared (AP) and over three carbonation-regeneration cycles at 500°C in dry CO_2 and air respectively.

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FigureSM 7 Measured carbonate content of calcium oxide as-prepared (i.e. when the number of cycles = 0) and over three cycles. Carbonation was performed in dry CO₂ at 650°C and regeneration in air at 900°C. Carbonated samples are represented by filled markers whilst as-prepared and samples heated in air are denoted using open markers.

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