

## Supplementary Material

Table S1 The quantities (in moles) of the reactants used to prepare the apatites studied in this work, where  $K_2CO_3$  was used to provide the necessary potassium ions. 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  $Ca_{10-x}K_x(PO_4)_{6-x}(CO_3)_x(OH)_2$ .

Design x	$Ca(OH)_2$ (moles)	$K_2CO_3$ (moles)	$H_3PO_4$ (moles)	Design Ca/P	Design (Ca+K)/P
0	0.1100	N/A	0.0660	1.67	N/A
0.5	0.1045	0.00275	0.0605	1.73	1.82
1.0	0.0990	0.00550	0.0550	1.80	2.00
1.5	0.0935	0.00825	0.0495	1.89	2.22
2.0	0.0880	0.0110	0.0440	2.00	2.50
2.5	0.0825	0.01375	0.0385	2.14	2.86
3.0	0.0770	0.01650	0.0330	2.33	3.33

Table S2 The quantities (in moles) of the reactants used to prepare the apatites studied in this work, where  $KHCO_3$  was used to provide the necessary potassium ions. 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  $Ca_{10-x}K_x(PO_4)_{6-x}(CO_3)_x(OH)_2$ .

Design x	$Ca(OH)_2$ (moles)	$KHCO_3$ (moles)	$H_3PO_4$ (moles)	Design Ca/P	Design (Ca+K)/P
0	0.1100	N/A	0.0660	1.67	N/A
0.5	0.1045	0.0055	0.0605	1.73	1.82
1.0	0.0990	0.0110	0.0550	1.80	2.00
1.5	0.0935	0.0165	0.0495	1.89	2.22
2.0	0.0880	0.0220	0.0440	2.00	2.50
2.5	0.0825	0.0275	0.0385	2.14	2.86
3.0	0.0770	0.0330	0.0330	2.33	3.33

Table S3 Average crystallite sizes (in nm), calculated using Scherrer's equation and the (002) reflection at approximately 25.8 °2θ, of Series I and Series II of as-prepared apatite materials where x = 0-2.5 in the design formula  $\text{Ca}_{10-x}\text{K}_x(\text{PO}_4)_{6-x}(\text{CO}_3)_x(\text{OH})_2$ .

Design x	Series I $\text{K}_2\text{CO}_3$ (nm)	Series II $\text{KHCO}_3$ (nm)
0	29 ± 1	29 ± 1
0.5	27 ± 3	24 ± 2
1.0	26 ± 2	22 ± 2
1.5	22 ± 1	21 ± 1
2.0	22 ± 1	N/A
2.5	18 ± 2	N/A

Table S4 The lattice parameters and unit cell volume of the as-prepared K- $\text{CO}_3$  co-substituted apatites of each series, where x = 0-2.5 in the design formula  $\text{Ca}_{10-x}\text{K}_x(\text{PO}_4)_{6-x}(\text{CO}_3)_x(\text{OH})_2$ . Compositions of x = 2.0 and 2.5 in Series II contained an impurity phase so lattice parameters were not determined (N/A). Respective e.s.d values are presented in brackets.

Design x	Series I ( $\text{K}_2\text{CO}_3$ )			Series II ( $\text{KHCO}_3$ )		
	a (Å)	c (Å)	Volume (Å <sup>3</sup> )	a (Å)	c (Å)	Volume (Å <sup>3</sup> )
0	9.4072(5)	6.8903(5)	528.05(1)	9.4072(5)	6.8903(5)	528.05(1)
0.5	9.3843(5)	6.8883(5)	525.33(1)	9.3806(5)	6.8929(6)	525.27(1)
1.0	9.3775(6)	6.8959(6)	525.15(1)	9.3685(6)	6.8978(7)	524.29(1)
1.5	9.3654(6)	6.8992(6)	524.05(1)	9.3495(6)	6.8908(7)	521.63(1)
2.0	9.3513(6)	6.8952(7)	522.17(1)	N/A	N/A	N/A
2.5	9.3384(7)	6.8929(8)	520.55(1)	N/A	N/A	N/A

Table S5 Expected and measured potassium contents, Ca/P molar ratios and (Ca+K)/P molar ratios (measured using energy dispersive X-ray spectroscopy) and carbonate contents (measured using combustion analysis) of the single-phase as-prepared apatites of Series I, where x = 0-2.5 in the design composition formula  $\text{Ca}_{10-x}\text{K}_x(\text{PO}_4)_{6-x}(\text{CO}_3)_x(\text{OH})_2$ . The expected values were calculated in accordance with this design formula.

Design x	wt% K (expected)	wt% K (measured)	Ca/P (expected)	Ca/P (measured)	(Ca+K)/P (expected)	(Ca+K)/P (measured)	wt% CO <sub>3</sub> (expected)	wt% CO <sub>3</sub> (measured)
0	N/A	N/A	1.67	1.64 ± 0.02	N/A	N/A	0	2.28 ± 0.03
0.5	1.98	0.45 ± 0.06	1.73	1.69 ± 0.02	1.82	1.71 ± 0.02	3.04	3.39 ± 0.00
1.0	4.04	0.79 ± 0.10	1.80	1.77 ± 0.01	2.00	1.81 ± 0.00	6.19	5.40 ± 0.00
1.5	6.17	0.91 ± 0.05	1.89	1.82 ± 0.01	2.22	1.87 ± 0.01	9.47	7.90 ± 0.00
2.0	8.38	0.85 ± 0.04	2.00	1.93 ± 0.01	2.50	1.98 ± 0.01	12.87	9.60 ± 0.00
2.5	10.69	0.81 ± 0.19	2.14	2.09 ± 0.00	2.86	2.14 ± 0.01	16.40	13.03 ± 0.04

Table S6 Expected and measured potassium contents, Ca/P molar ratios and (Ca+K)/P molar ratios (measured using energy dispersive X-ray spectroscopy) and carbonate contents (measured using combustion analysis) of the single-phase as-prepared apatites of Series II, where x = 0-1.5 in the design composition formula  $\text{Ca}_{10-x}\text{K}_x(\text{PO}_4)_{6-x}(\text{CO}_3)_x(\text{OH})_2$ . The expected values were calculated in accordance with this design formula.

Design x	wt% K (expected)	wt% K (measured)	Ca/P (expected)	Ca/P (measured)	(Ca+K)/P (expected)	(Ca+K)/P (measured)	wt% CO <sub>3</sub> (expected)	wt% CO <sub>3</sub> (measured)
0	N/A	N/A	1.67	1.64 ± 0.02	N/A	N/A	0	2.28 ± 0.03
0.5	1.98	0.41 ± 0.04	1.73	1.72 ± 0.00	1.82	1.74 ± 0.01	3.04	5.23 ± 0.04
1.0	4.04	0.62 ± 0.03	1.80	1.82 ± 0.01	2.00	1.85 ± 0.01	6.19	7.68 ± 0.04
1.5	6.17	0.94 ± 0.02	1.89	1.90 ± 0.01	2.22	1.95 ± 0.01	9.47	9.58 ± 0.04

Table S7 Results of EDX/combustion analysis performed on K-CO<sub>3</sub> co-substituted apatites prepared using K<sub>2</sub>CO<sub>3</sub> and with/without concentrated aqueous ammonia (NH<sub>4</sub>OH) solution added to the calcium/potassium suspension, where x = 0.5 or 2.5 in the design composition formula Ca<sub>10-x</sub>K<sub>x</sub>(PO<sub>4</sub>)<sub>6-x</sub>(CO<sub>3</sub>)<sub>x</sub>(OH)<sub>2</sub>.

Design x	NH <sub>4</sub> OH added?	wt% K	Ca/P	(Ca+K)/P	wt% CO <sub>3</sub>
<b>0.5</b>	Yes	0.45 ± 0.06	1.69 ± 0.02	1.71 ± 0.02	3.39 ± 0.00
	No	0.41 ± 0.01	1.68 ± 0.01	1.70 ± 0.01	3.88 ± 0.01
<b>2.5</b>	Yes	0.81 ± 0.19	2.09 ± 0.00	2.14 ± 0.01	13.03 ± 0.04
	No	0.38 ± 0.03	2.09 ± 0.01	2.12 ± 0.01	12.93 ± 0.11

Table S8 The deconvoluted peak positions (cm<sup>-1</sup>) and relative peak areas (%) from the FTIR spectra of the carbonate  $\nu_3$ , OH<sub>L</sub> and phosphate  $\nu_4$  regions of the as-prepared K-CO<sub>3</sub> co-substituted apatites of each series. Peaks are arbitrary numbered from 1b-6b, or 1a-5a, from high to low wavenumbers. Due to rounding peak areas to whole numbers the sum of the peak areas will not always equal 100%.

Design x	CO <sub>3</sub> $\nu_3$ position (cm <sup>-1</sup> ) & area (%)						OH <sub>L</sub> /PO <sub>4</sub> $\nu_4$ position (cm <sup>-1</sup> ) & area (%)				
	1b	2b	3b	4b	5b	6b	1a	2a	3a	4a	5a
<b>0</b>	1565 (10%)	1493 (16%)	1460 (18%)	1445 (13%)	1417 (30%)	1395 (12%)	627 (16%)	602 (17%)	576 (22%)	561 (28%)	543 (17%)
<b>Series I</b>											
<b>0.5</b>	1557 (3%)	1488 (30%)	1449 (25%)	1419 (9%)	1408 (28%)	1374 (5%)	627 (14%)	601 (21%)	580 (11%)	563 (37%)	543 (17%)
<b>1.0</b>	1542 (3%)	1489 (29%)	1448 (26%)	1420 (7%)	1406 (26%)	1381 (9%)	629 (11%)	602 (24%)	579 (15%)	563 (34%)	546 (16%)
<b>1.5</b>	1526 (6%)	1486 (29%)	1452 (17%)	1422 (3%)	1410 (39%)	1373 (6%)	630 (9%)	603 (28%)	581 (11%)	564 (38%)	545 (15%)
<b>2.0</b>	1534 (7%)	1489 (30%)	1456 (11%)	1423 (1%)	1412 (47%)	1355 (4%)	630 (8%)	604 (28%)	580 (16%)	564 (35%)	546 (13%)
<b>2.5</b>	1523 (13%)	1492 (19%)	1455 (23%)	1424 (12%)	1401 (27%)	1372 (7%)	626 (8%)	603 (28%)	582 (14%)	565 (38%)	546 (12%)
<b>Series II</b>											
<b>0.5</b>	1548 (3%)	1489 (29%)	1449 (24%)	1420 (8%)	1407 (23%)	1393 (11%)	631 (12%)	601 (26%)	577 (14%)	562 (32%)	542 (16%)
<b>1.0</b>	1530 (6%)	1488 (30%)	1449 (21%)	1421 (7%)	1407 (28%)	1385 (10%)	629 (11%)	603 (23%)	579 (15%)	563 (35%)	544 (16%)
<b>1.5</b>	1528 (7%)	1489 (30%)	1447 (23%)	1422 (4%)	1406 (29%)	1377 (8%)	631 (8%)	604 (27%)	581 (15%)	564 (36%)	546 (13%)

Table S9 The lattice parameters and unit cell volume of the  $x = 2.5$  K-CO<sub>3</sub> co-substituted apatite of Series I as-prepared (AP) and after being heated in dry CO<sub>2</sub> at 300-600°C. Respective e.s.d values are shown in brackets.

Temperature (°C)	<i>a</i> (Å)	<i>c</i> (Å)	Volume (Å <sup>3</sup> )
<b>AP</b>	9.3384(7)	6.8929(8)	520.55(1)
<b>300</b>	9.3393(7)	6.8881(7)	520.29(1)
<b>400</b>	9.3704(6)	6.9028(7)	524.88(1)
<b>500</b>	9.3955(6)	6.9108(7)	528.31(1)
<b>600</b>	9.4361(5)	6.9118(5)	532.96(1)

