Supplementary Material (ESI) for Chemical Communications

Supplementary figure captions (listed)

Figure S1 Transmission electron microscope image of sample HA(300), hydroxyapatite nanoparticles made using a supercritical water feed at 300ºC and 24 MPa in the hydrothermal flow system

Figure S2 Transmission electron microscope image of sample CDHA(200), made using a supercritical water feed at 200ºC and 24 MPa in the hydrothermal flow system

Figure S3 Xray diffraction pattern of sample CDHA(200) made in the continuous hydrothermal synthesis system under basic conditions using a Ca:P ratio of 1.67, and then heat-treated in air at 800°C for 2 hours.

Figure S4 FTIR data for the range; (a) 4000-2800 cm^{-1} and (b) 1800-400 cm^{-1} for HA powders made in a hydrothermal flow system using superheated water at 24 MPa for samples (i) HA(400), (ii) HA(300) and (iii) CDHA(200), respectively.

Figure S5 Simultaneous thermal analysis data in the range 30 – 1200 ºC for hydroxyapatite sample HA(400) made using a supercritical water feed at 400ºC and 24 MPa in the hydrothermal flow system under basic conditions using a Ca:P ratio of 1.67.

Figure S6 Simultaneous thermal analysis data in the range 30 – 1200 ºC for hydroxyapatite sample HA(300) made using a supercritical water feed at 300ºC and 24 MPa in the hydrothermal flow system under basic conditions using a Ca:P ratio of 1.67

Figure S7 Simultaneous thermal analysis data in the range 30 – 1200 ºC for the calcium deficient apatite sample CDHA(200) made using a supercritical water feed at 200 ºC and 24 MPa in the hydrothermal flow system under basic conditions using a Ca:P ratio of 1.67

Figure S8 Simultaneous thermal analysis data in the range 30 – 1200 ºC for the calcium deficient apatite sample CDHA(400) made using a supercritical water feed at 400 ºC and 24 MPa in the hydrothermal flow system under acidic conditions using a Ca:P ratio of 1.0

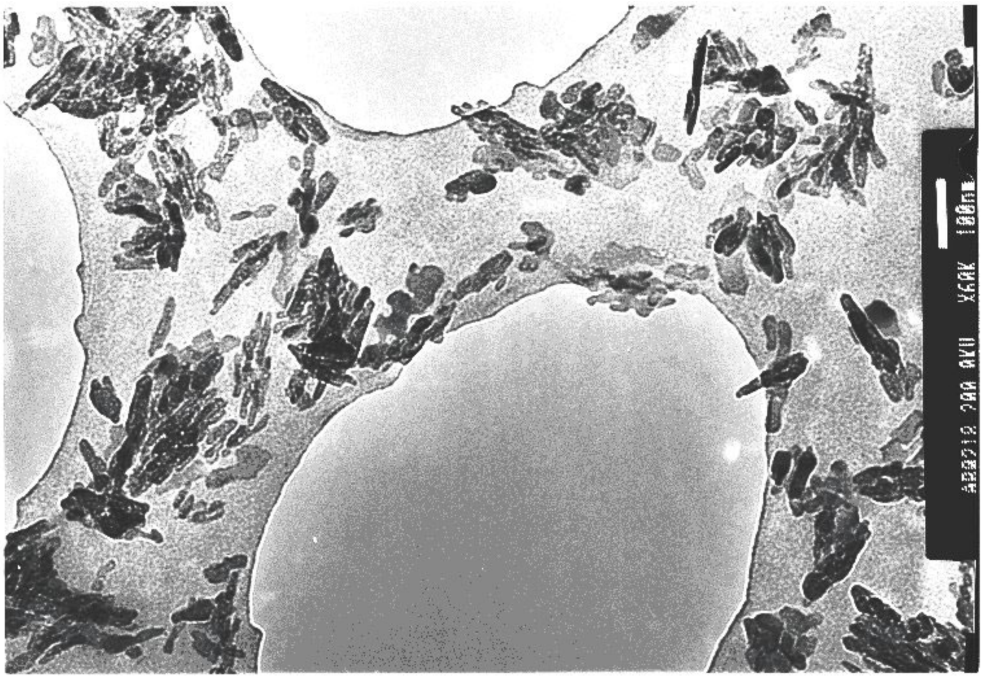

Figure S1 Transmission electron microscope image of sample HA(300), hydroxyapatite nanoparticles made using a supercritical water feed at 300ºC and 24 MPa in the hydrothermal flow system (bar = 100nm).

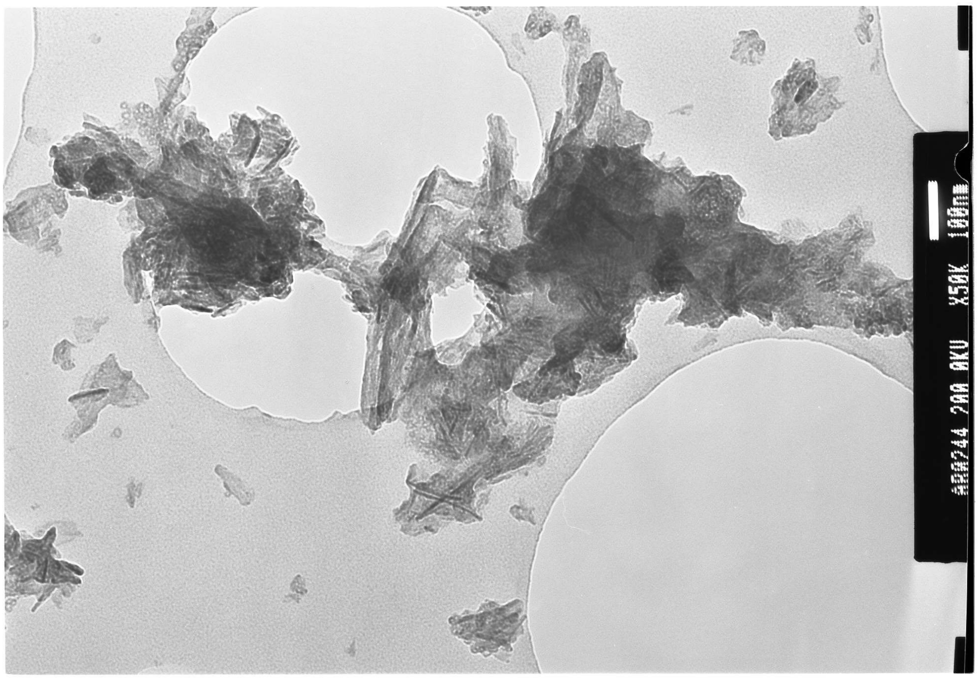

Figure S2 Transmission electron microscope image of sample CDHA(200), made using a supercritical water feed at 200ºC and 24 MPa in the hydrothermal flow system (bar = 100nm).

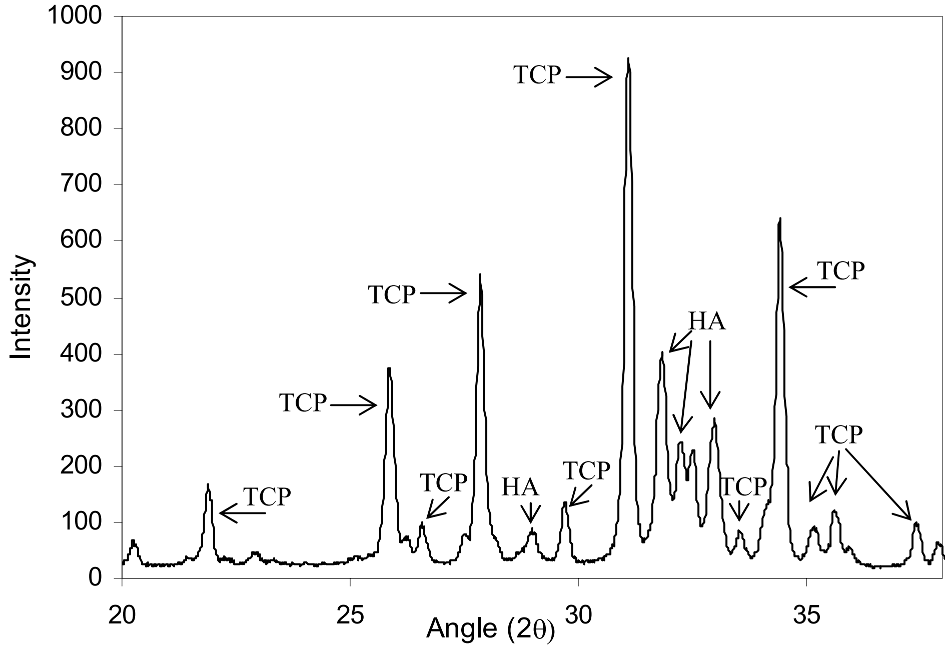

Figure S3 Xray diffraction pattern of sample CDHA(200) made in the continuous hydrothermal synthesis system under basic conditions using a Ca:P ratio of 1.67, and then heat-treated in air at 800°C for 2 hours**.**

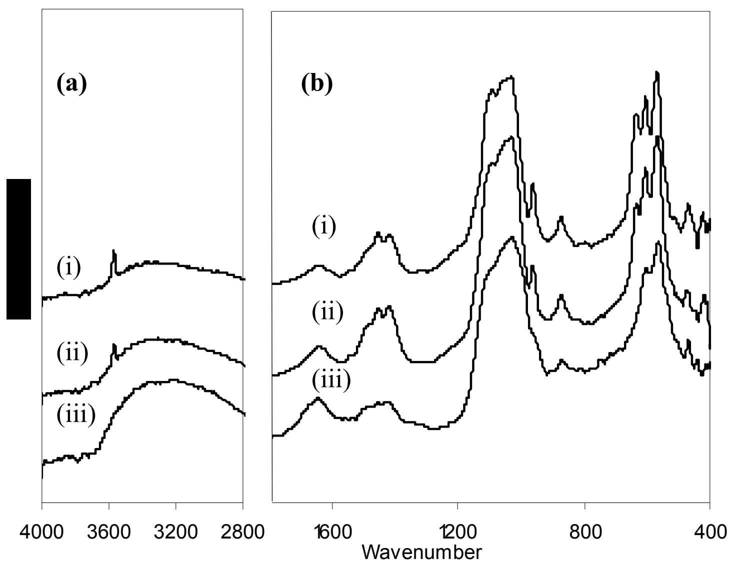

Figure S4 FTIR data for the range; (a) 4000-2800 cm^{-1} and (b) 1800-400 cm^{-1} for HA powders made in a hydrothermal flow system using superheated water at 24 MPa for samples (i) HA(400), (ii) HA(300) and (iii) CDHA(200), respectively.

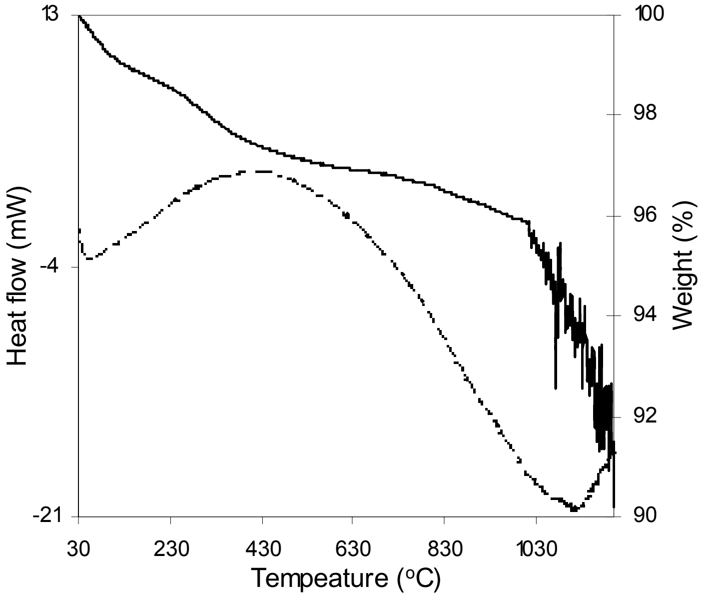

Figure S5 Simultaneous thermal analysis data in the range 30 – 1200 ºC for hydroxyapatite sample HA(400) made using a supercritical water feed at 400ºC and 24 MPa in the hydrothermal flow system under basic conditions using a Ca:P ratio of 1.67.

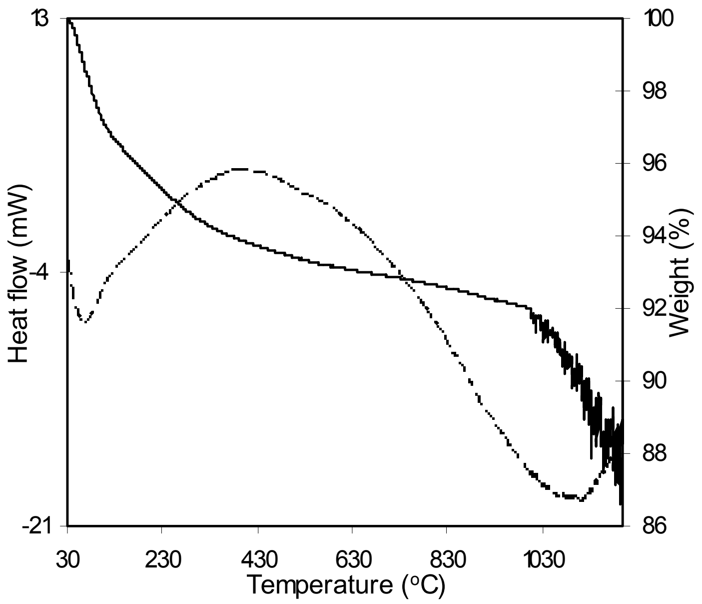

Figure S6 Simultaneous thermal analysis data in the range 30 – 1200 ºC for hydroxyapatite sample HA(300) made using a supercritical water feed at 300ºC and 24 MPa in the hydrothermal flow system under basic conditions using a Ca:P ratio of 1.67**.**

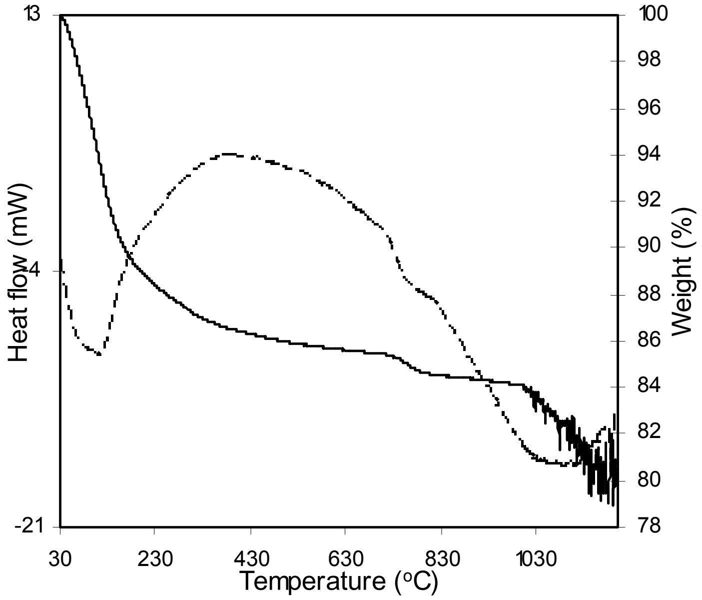

Figure S7 Simultaneous thermal analysis data in the range 30 – 1200 ºC for the calcium deficient apatite sample CDHA(200) made using a supercritical water feed at 200 ºC and 24 MPa in the hydrothermal flow system under basic conditions using a Ca:P ratio of 1.67.

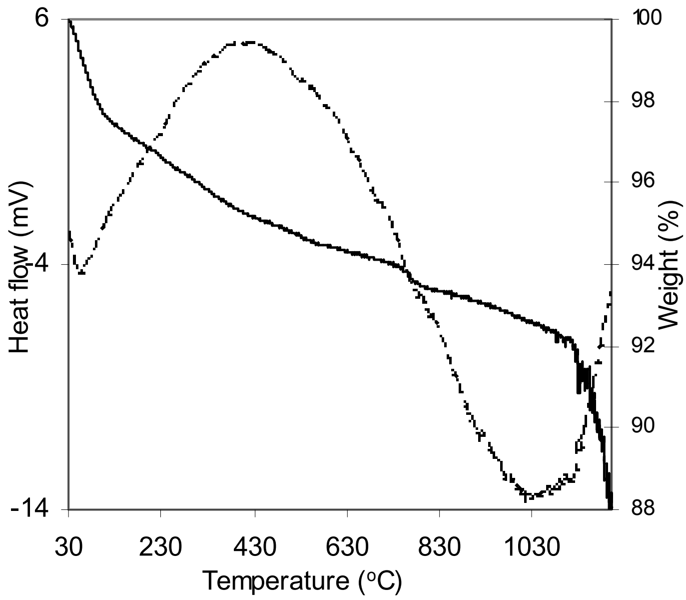

Figure S8 Simultaneous thermal analysis data in the range 30 – 1200 ºC for the calcium deficient apatite sample CDHA(400) made using a supercritical water feed at 400 ºC and 24 MPa in the hydrothermal flow system under acidic conditions using a Ca:P ratio of 1:1.

Previous reports suggest that under acidic conditions (hydrothermal batch/120 ºC) monetite ($CaHPO_4$) is initially formed.31 This is known to transform into an apatite structure if the temperature >140 ºC. Despite our short reaction (or residence times), unsurprisingly, we obtained an apatite structure for CDHA(400) (albeit a calcium deficient one). In contrast, under basic conditions, an initial poorly crystalline (calcium deficient) apatite was probably formed at the ''Tee'' mixing point (before the reactor nozzle); this would have rapidly transformed into stoichiometric apatite by the reaction with superheated water at a temperature of 300 ºC or higher. Evidently, at 200 ºC (basic pH), the reaction kinetics did not allow transformation into stoichiometric apatite in our flow system for sample CDHA(200).