Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Immobilization of iodine into a hydroxyapatite structure prepared by cementation

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Supplementary Materials

Elemental analysis of a one-month-old CeHA+$NaIO_3$ cement

Elemental analyses were performed for two samples:

- a one-month-old CeHA+$NaIO_3$ cement
- an apatite obtained by wet-precipitation according to the protocol described in reference 20 (L. Campayo, A. Grandjean, A. Coulon, R. Delorme, D. Vantelon and D. Laurencin, *J. Mater. Chem.* 2011, **21**, 17609-17611): HA-CaI

For calcium, phosphorus and sodium, all samples were beforehand dissolved in nitric acid (100 mg of powder were dissolved in 100 mL of a 15.45 $mol.L^{-1}$ HNO_3 solution) and analysed by ICP-AES. Results of these analyses are given in Table S1.

Table S1 Chemical compositions of a one-month-old CeHA+$NaIO_3$ and an iodate-bearing apatite prepared by wet-precipitation

Sample	Theoretical composition				Experimental composition*			
	Ca (ppm)	Na (ppm)	P (ppm)	Ca/P	Ca (ppm)	Na (ppm)	P (ppm)	Ca/P
CeHA+$NaIO_3$ (one-month-old)	368	11	171	1.67	348	9	157	1.72
HA-CaI	362	0	168	1.67	349	0	155	1.74

*: experimental uncertainty is ± 10 ppm for Ca, ± 2 ppm for Na and ± 5 ppm for P

Given experimental uncertainties, the precision on the Ca/P molar ratio is 0.10 which reveals a good agreement with the theoretical composition.

For iodine, no significant difference between expected and as-determined values was found:

- CeHA+$NaIO_3$ (one-month-old): 6.5 wt% (± 0.1) (chemical analysis performed by thermogravimetry coupled with a mass spectrometry detection for heat-generated gases; the contribution of oxygen is subtracted from the weight loss in the 500 – 1000 °C range, which is associated to a simultaneous iodine and oxygen release)
- HA-CaI: 7.0 wt.% (± 0.1) (chemical analysis performed by an oxidative combustion followed by an aqueous trapping of iodine vapor and a subsequent measurement by ionic chromatography)

Quantitative analysis of the X-Ray powder diffraction data and unit cell parameters of apatitic phases

Table S2 gives the proportions of the crystalline phases for a one-month-old CeHA+$NaIO_3$ cement and a one-month-old CeHA+$NaIO_3$+10%G cement. The RIR[1] method was here used.

Table S2 Phase quantification by XRD (RIR method[1])

Cement	Phase	Fraction (wt. %)
CeHA+$NaIO_3$+10%G	TTCP	7
	αTCP	20
	Apatite	73
CeHA+$NaIO_3$	TTCP	12
	αTCP	18
	Apatite	70

Table S3 gives unit cell parameters for three apatitic phases (whole pattern fitting):

- in a one-month-old CeHA+$NaIO_3$ cement,
- for an an apatite obtained by wet-precipitation according to the protocol described in reference 20 (L. Campayo, A. Grandjean, A. Coulon, R. Delorme, D. Vantelon and D. Laurencin, *J. Mater. Chem.* 2011, **21**, 17609-17611): HA-CaI,
- for a standard $Ca_{10}(PO_4)_6(OH)_2$ phase.

Table S3 Unit cell parameters of apatitic phases

Apatite phase	Parameter	
CeHA+$NaIO_3$	a (Å)	9.434 ± 0.006
	c (Å)	6.882 ± 0.009
	V (Å^3)	530 ± 1
HA-CaI	a (Å)	9.447 ± 0.004
	c (Å)	6.891 ± 0.002
	V (Å^3)	530 ± 1
Standard $Ca_{10}(PO_4)_6(OH)_2$*	a (Å)	9.4238 ± 0.0009
	c (Å)	6.8854 ± 0.0006
	V (Å^3)	530 ± 1

*: M. Markovic, B.O. Fowler and M.S. Tung, *J. Res. Natl. Inst. Stand. Technol.* 2004, **109**, 553-568

[1] F.H. Chung, *J.Appl.Cryst.* 1974, **7**, 519-525

I L_3-edge XANES characterizations

I L_3-edge XANES (X-ray Absorption Near Edge Structure) measurements were performed on the LUCIA beamline at the Soleil Synchrotron (Saint-Aubin, France). The Soleil ring energy was 2.75 GeV and the current was 400 mA. Samples were ground to a fine powder, diluted in cellulose, pressed into pellets, and run at room temperature in transmission mode. Spectra were collected at the I L_3-edge. The X-ray incident energy on the sample was defined using a double-crystal Si(111) monochromator. The instrument was evacuated to ~1 Pa during the measurements. The pre-edge (4500–4552 eV), edge (4552.2–4632 eV) and post-edge (4633–4820 eV) regions were scanned in 5.0, 0.2 and 1.0 eV steps respectively, with dwell times per point of 2.0 to 4.0 s. Data reduction was performed using the Athena software package.[2] Typically, 2 XANES data sets were collected for each sample, which were averaged and normalised with Athena.

XANES spectra were collected for three samples:

- a one-month-old CeHA+$NaIO_3$ cement
- a one-month-old CeHA+$NaIO_3$ cement after washing (the one-month-old CeHA+$NaIO_3$ cement was ground in a porcelain mortar, and then dispersed in ultrapure water (1 g of solid for 100 mL of ultrapure water) under magnetic stirring for one hour, before being filtered and finally dried at 100 °C overnight)
- an apatite obtained by wet-precipitation according to the protocol described in reference 20 (L. Campayo, A. Grandjean, A. Coulon, R. Delorme, D. Vantelon and D. Laurencin, *J. Mater. Chem.* 2011, **21**, 17609-17611): wet-precipitated iodate-bearing apatite

[2] B. Ravel, and M. Newville, ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. *J. Synchrotron Radiat.* 2005,**12**, 537.

Figure S1: TEM(a)/EDXS(b) analysis of a one-month-old CeHA+$NaIO_3$ cement

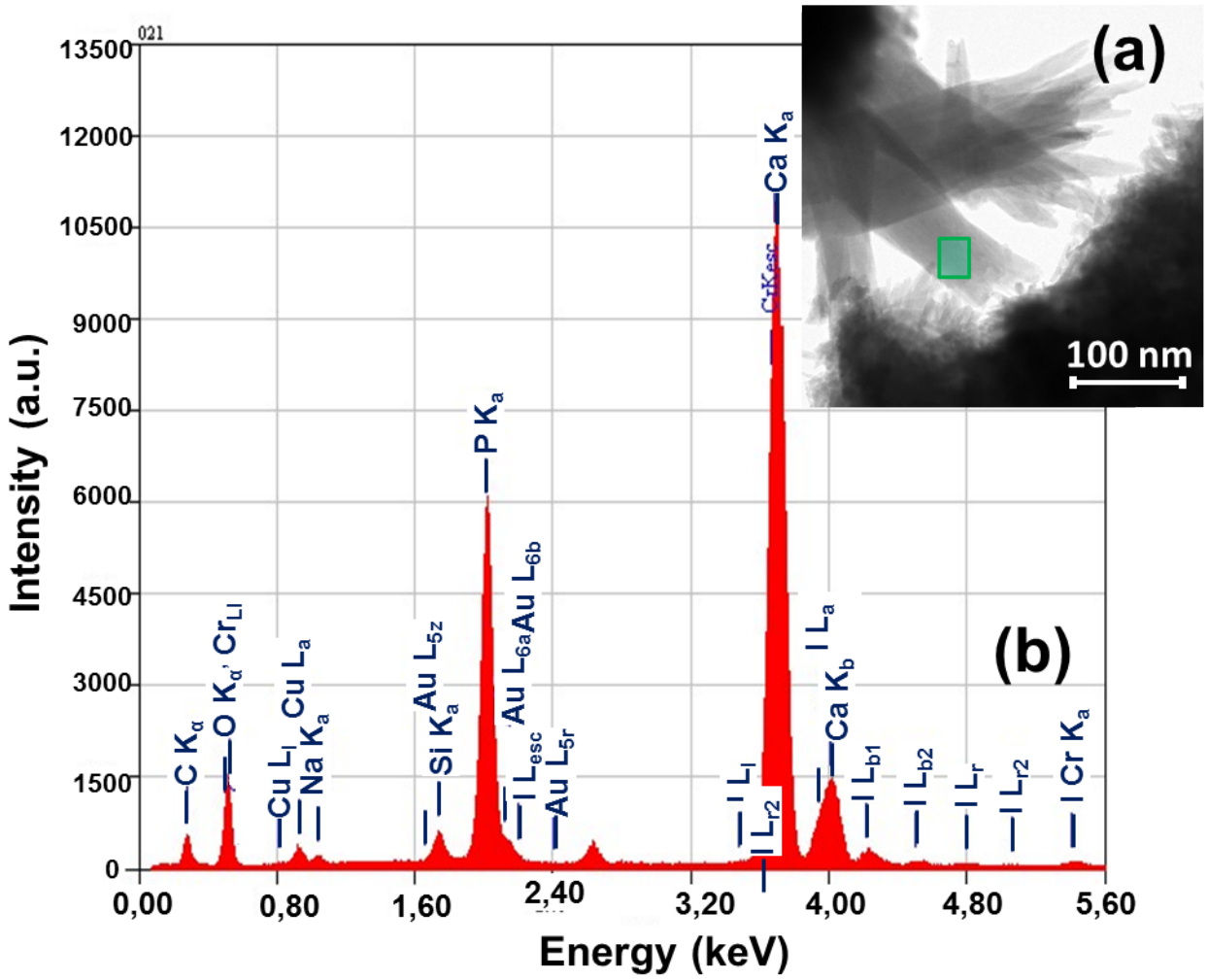

Figure S2: I L_3-edge XANES spectra of a one-month-old CeHA+$NaIO_3$ cement (before and after washing), and of a wet-precipitated iodate-bearing apatite