Incorporation of iodates into hydroxyapatites: a new approach

for the confinement of radioactive iodine

L. Campayo, A. Grandjean, A. Coulon, R. Delorme, D. Vantelon and D. Laurencin

Supplementary Materials

Description of the synthesis of CaI-HA

Samples were prepared from $Ca(NO_3)_2 \cdot 4H_2O$ (Alfa Aesar, Germany, 99,0% purity), $(NH_4)_2HPO_4$ (VWR, France, 99,1% purity) and $NaIO_3$ (Alfa Aesar, Germany, 99,0% purity). Syntheses were carried out using ultrapure water, and concentrated NH_4OH (Merck) was used to maintain the pH of the solution, either as a 25 wt % solution in water, or after dilution to a 1 $mol.L^{-1}$ solution. All reactions were performed under an N_2 atmosphere. The relative amounts of reactants used for the synthesis of CaI-HA are summarized below, in Table S1.

	Introduced in solution		Measured in the solid	
Atom % ratio	**Ca/P**	**I/P**	**Ca/P**	**I/P**
CaI-HA	1.66	0.33	1.62	0.11

Table S1

The syntheses were carried out as follows, following a procedure adapted from the literature (see reference 13 in the main text).

First, 50 mL of an aqueous solution of calcium nitrate were prepared ($[Ca^{2+}] = 0.216$ $mol.L^{-1}$; pH adjusted to ~10.0 using a 1 $mol.L^{-1}$ solution of NH_4OH). On the other hand, 50 mL of an aqueous solution of $(NH_4)_2HPO_4$ were prepared ($["P"] = 0.130$ $mol.L^{-1}$; the pH was also adjusted to 10.0 by addition of concentrated NH_4OH). For the preparation of the CaI-HA sample, sodium iodate[1] was dissolved in this alkaline phosphate solution, using an I/P molar ratio of 0.33.

The calcium solution was heated to 90°C under an N_2 atmosphere. The solution containing phosphate (and iodate) anions was then added dropwise to it. This led to the progressive precipitation of a white solid. The suspension was stirred at 90°C (temperature measured directly inside the reaction medium) for a total time of 5 hours, during which small amounts of concentrated NH_4OH were regularly added, in order to keep the pH close to its initial value. The reaction medium was then left to cool at room temperature, and the solid was recovered by filtration before being dried at 120°C overnight. This solid was then washed to remove soluble by-products and physisorbed species like nitrate ions. The washing procedure consisted in a magnetic stirring of a 5 $g.L^{-1}$ suspension of the powder in ultrapure water for one hour (typically, 1 g of the product collected after drying was suspended with 200 mL of ultrapure water). The suspension was filtered and the solid ultimately dried at 90°C during at least 16 hours. After the complete treatments, ~1 g of solid was obtained, which corresponds to a yield of ~87% assuming the formation of $Ca_{10}(PO_4)_6(OH)_{1.4}(IO_3)_{0.6}$ (as explained in the main text).

---

[1] It is noteworthy that $NH_4(IO_3)$ can also be used as an iodate precursor in this synthesis.

Description of the sorption tests

A pristine hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, Ca-HA) was prepared according to the procedure described above. This powder was used for a sorption test.

1 g of the dried powder was dispersed in 200 mL of an aqueous solution containing sodium iodate ($[IO_3^-] = 0.043$ mol.L^{-1}) at a pH value of ~10.0 (using a using a 1 mol.L^{-1} solution of NH_4OH). It is worth noting that the iodate concentration and the pH value were chosen to be similar to those used for the synthesis of CaI-HA. The suspension was stirred at 90°C for a total time of 5 hours, during which small amounts of concentrated NH_4OH were regularly added, in order to keep the pH close to its initial value. The suspension was subsequently cooled and then filtered. Iodine was measured out in the leaching solution according to the same procedure as described for the leaching tests carried on substituted HA (see the section on the "Experimental details for the leaching tests"). Within the uncertainty range of the iodide selective electrode used for this characterization, no difference was found between initial and final iodine content in the solution, meaning that the amount of iodine sorbed at the grain surface is low. This amount is assessed to be below 1 wt. % which, in first approach, can be considered as negligible by comparison with the amount found in CaI-HA. From these results, it is concluded that in the case of CaI-HA, the iodate anions are mainly located inside the crystalline lattice of HA.
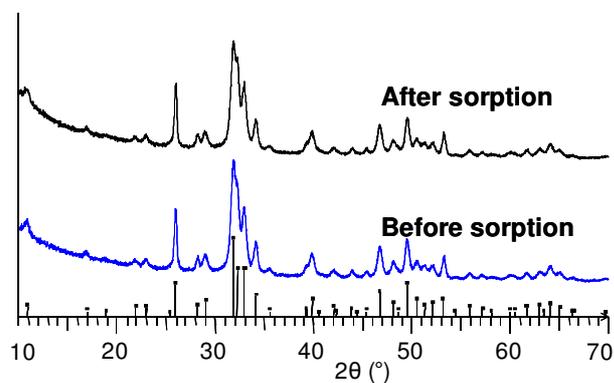
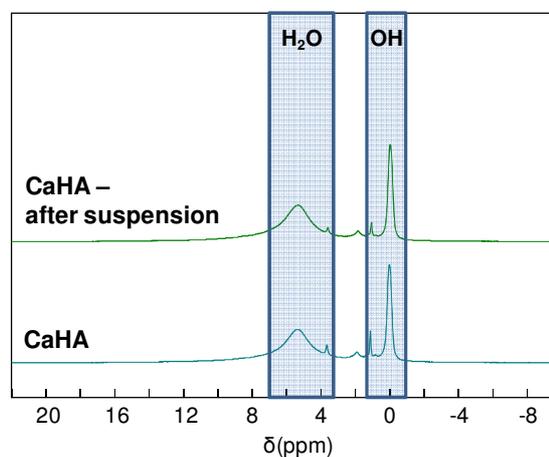**Figure S1 : XRD[2]**

Figure S2 : ^{1}H solid state NMR[3]

---

[2] The vertical lines correspond to the indexing of the Ca-HA crystal structure.
[3] The sharp peaks of very low intensity are likely to correspond to remaining solvent impurities.

Experimental details on the characterization methods used

X-Ray diffraction powder patterns were acquired on a PanAnalytical diffractometer equipped with an ultra-fast X'celerator detector X'pert Pro, and using the Cu Kα radiation (λ = 1.5405 Å). The experimental diffractograms were analysed using the EVA (Bruker, version 12.0 rev 0) and Checkcell (release of 11/01/2004) softwares. The background was substracted, and the Cu Kα $_2$ contribution was removed.

Raman spectra were measured on a Horiba Jobin Yvon LabRam Aramis apparatus and IR spectra on a Bruker Vertex 70 spectrometer.

The ^{31}P solid state magic-angle spinning (MAS) NMR spectra shown in Figure 1b were recorded on a Bruker Ultrashield 400 MHz spectrometer, using a 4 mm MAS probe, and spinning at 12 kHz. Single-pulse spectra were collected using a recycle delay of 30 s. The ^{1}H MAS NMR spectra shown in Figures 2d[4] and S2 were recorded on a Varian 600 MHz NMR spectrometer, using a 3.2 mm MAS probe spinning at 20 kHz. A DEPTH sequence was used to suppress probe background ^{1}H signals.[5] 16 transients were acquired, and a recycle delay of 10 s was used to ensure full relaxation of the ^{1}H signals. ^{1}H and ^{31}P chemical shifts were referenced using TMS ($Si(CH_3)_4$, resonance at 0 ppm) and $NH_4H_2PO_4$ (resonance at 0.9 ppm), respectively.

Thermogravimetric analysis (TGA) was carried out in a TG-DTA 92-16 (Setaram) thermobalance with a heating rate of 10 °C/min (see Figure S4). About 20.9 mg of solid sample was used, and the Argon flow used was 1000 cm^3/h.

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 ~75 K 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 ~10^{-8} 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.[6] Typically, 2 to 3 XANES data sets were collected for each sample, which were averaged and normalised with Athena.
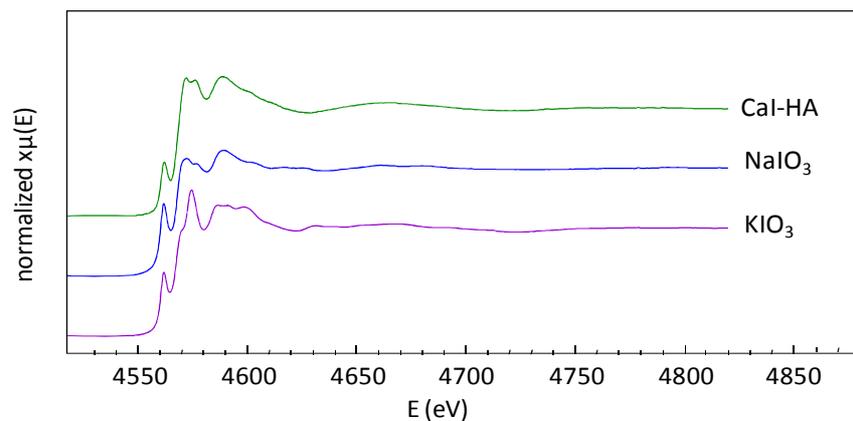
---

[4] The amount of Ca-Ha and CaI-HA samples introduced in the rotors was weighed, in order to estimate quantitatively the decrease in relative intensity of the OH peak in CaI-HA.
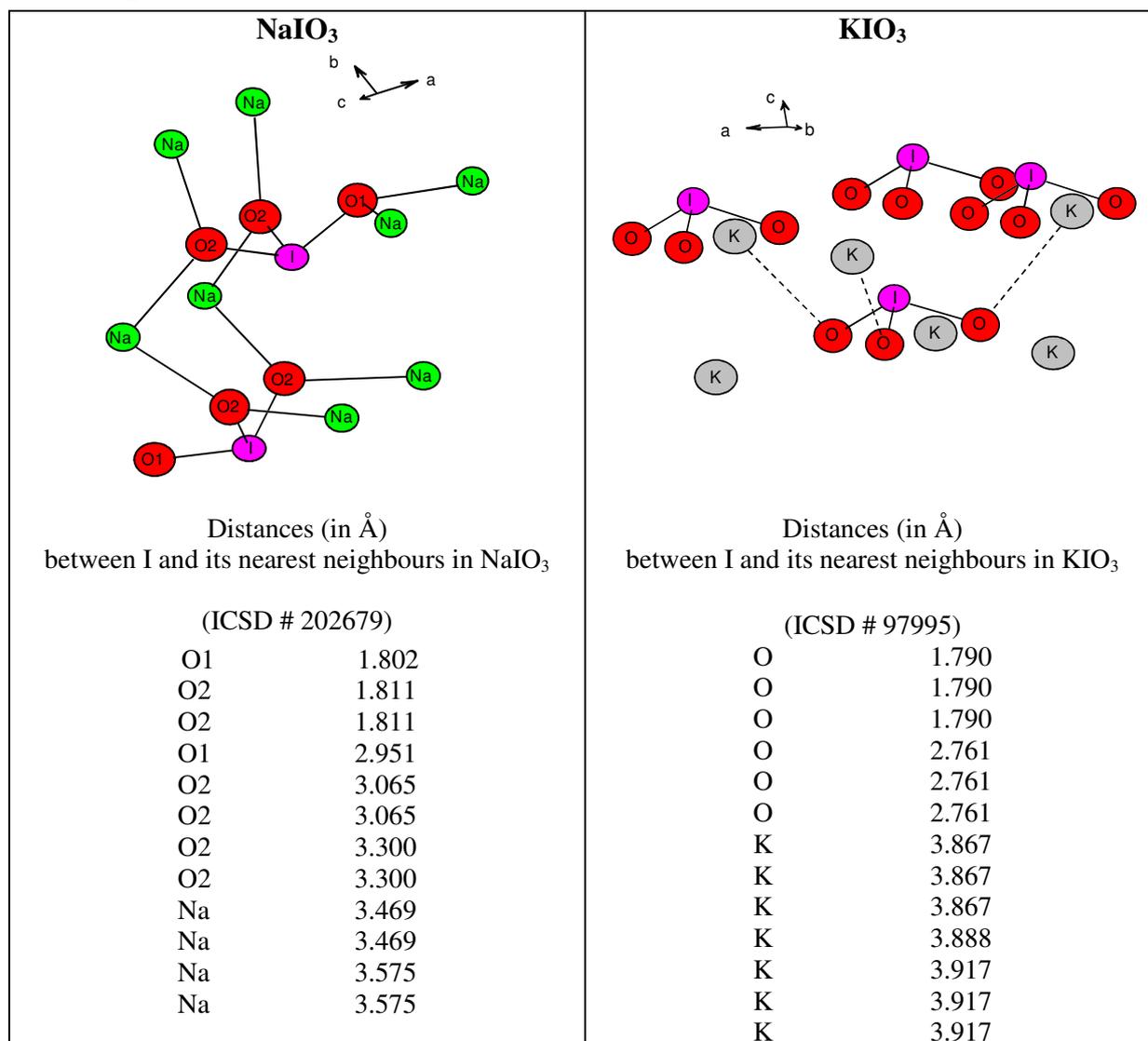[5] D. G. Cory and W. M. Ritchey, *J. Magn. Reson.* 1988, **80**, 128.
[6] B. Ravel, and M. Newville, ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. *J. Synchrotron Radiat.* 2005, **12**, 537.

Figure S3:

(a) Comparison of the I L$_3$-edge XANES spectra of NaIO$_3$, KIO$_3$ and CaI-HA.

(b) Comparison of the local environment of the iodate in NaIO$_3$ and KIO$_3$.

NaIO$_3$		KIO$_3$	
Distances (in Å) between I and its nearest neighbours in NaIO$_3$		Distances (in Å) between I and its nearest neighbours in KIO$_3$	
(ICSD # 202679)		(ICSD # 97995)	
O1	1.802	O	1.790
O2	1.811	O	1.790
O2	1.811	O	1.790
O1	2.951	O	2.761
O2	3.065	O	2.761
O2	3.065	O	2.761
O2	3.300	K	3.867
O2	3.300	K	3.867
Na	3.469	K	3.867
Na	3.469	K	3.888
Na	3.575	K	3.917
Na	3.575	K	3.917
		K	3.917

Experimental details for the leaching tests.

The protocol used to study the resistance of an iodate substituted apatite to aqueous alteration was adapted from a standard test for powders, as described below.

The ratio surface of powder to water volume used was 460 cm^{-1}, due to the high specific surface area of CaI-HA (92 m^2.g^{-1}). The apatite powder was introduced into 1 L of pure water and heated at 90°C. The leaching solution was renewed regularly with the ratio S/V kept constant. At each renewal, the solid was dried and weighed to ensure a correct renewal of the volume of water (specific surface area is considered constant and equal to its initial value). At each step, the iodine concentration in the leachate was measured.

The iodine concentration was determined using an iodide selective electrode (Thermo Scientific). Given that the iodine is released from the powder in the leaching solution under the form of iodates, these ions were first reduced in iodide according to the procedure described by Sanders.[7]

The normalized weight loss NL_I (shown in Figure S5 in the ESI) is the normalized weight loss based on iodine release, in g.m^{-2}. It was calculated using the following equation:

$$NL_I = \frac{C_I}{f_I * S/V}$$

where C_I is the iodine concentration in the leachate (g.cm^{-3}); f_I is the mass concentration of iodine in the apatite; and S/V is the ratio surface of powder to water volume (cm^{-1}).

The dissolution rate R_I (g.m^{-2}.d^{-1}) at time t is then given by the slope of the normalized weight loss as a function of time t (d):

$$R_I(t) = \frac{dNL_I}{dt}(t)$$

---

[7] J. K. Sanders, "Procedure for the determination of total iodine using automated sample preparation and ion chromatography", *LRA*, 1997, **10**, 19-23
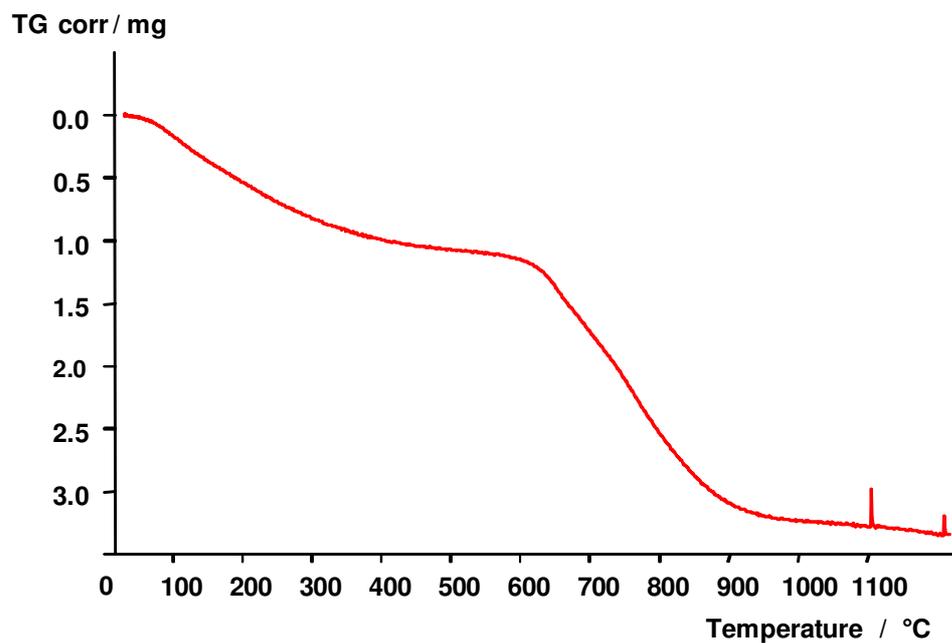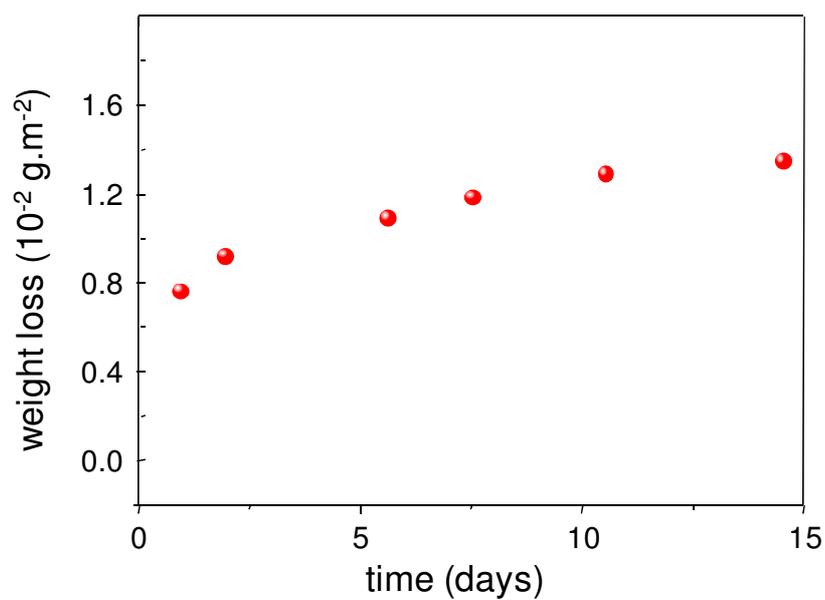
Figure S4: TGA analysis of CaI-HA.[8]

Figure S5: Normalized weight loss of CaI-HA in a leach test[9]

---

[8] The glitches above 1100 °C are experimental artifacts.
[9] The estimated error for the points on the graph is ~0.07×10^{-2} g.m^{-2}.