

Investigation of the local environment of iodate in hydroxyapatite by combination of X-ray absorption spectroscopy and DFT modeling

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Supplementary Materials

Figure S1: XRD of SrI-HA

Figure S2: IR spectrum of SrI-HA.

Figure S3: I L₃-edge XAS of CaI-HA, showing the proximity of the Ca K-edge.

Figure S4: I K-edge EXAFS data of Na(IO₃) and SrI-HA.

Figure S5: Local environment of the iodine in Na(IO₃), K(IO₃) and Ca(IO₃)₂.H₂O.

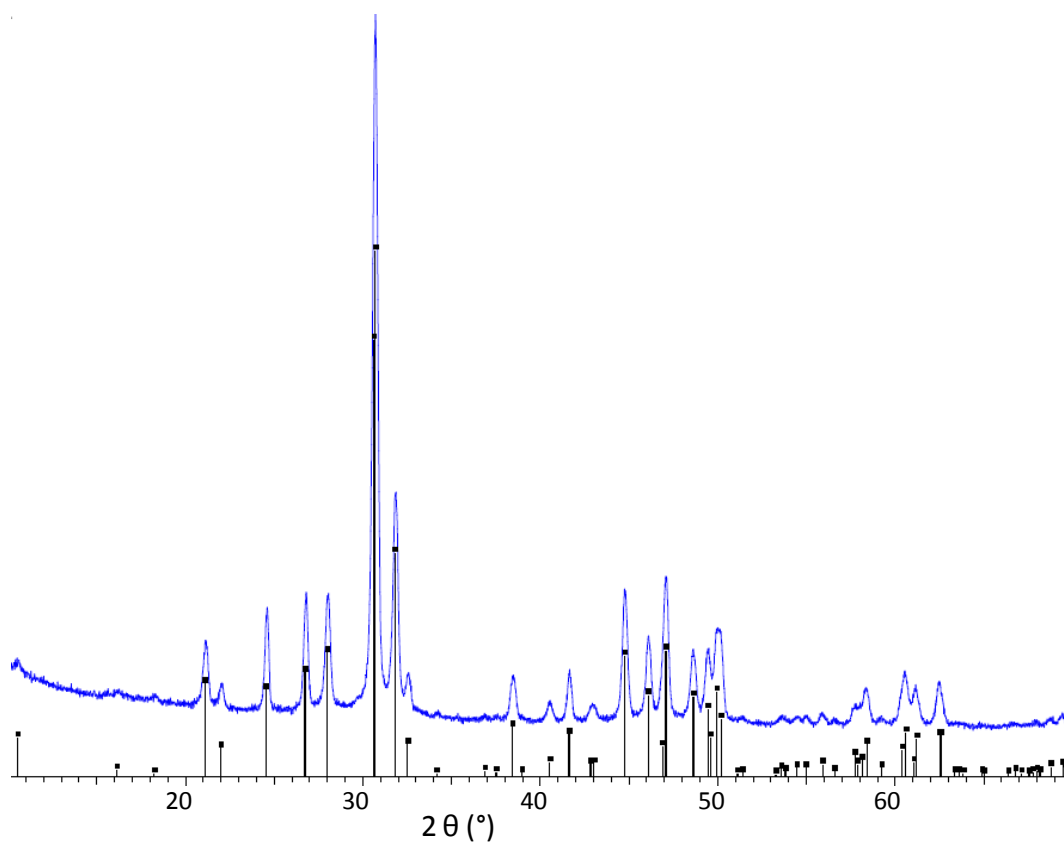
Figure S6: DFT models of iodate-substituted Ca-HA (Ca₁₀(PO₄)₆(OH)_{1.75}(IO₃)_{0.25}), after geometry optimisation.

Figure S7: Ca K-edge XANES data for non-substituted and iodate-substituted Ca-HA

Table S1: Relative energies of the four DFT models of iodate-substituted Ca-HA (Ca₁₀(PO₄)₆(OH)_{1.75}(IO₃)_{0.25}), after geometry optimisation.

Table S2: Comparison of iodine local environments in the Sr(IO₃)₂.H₂O, Ca(IO₃)₂ and Ca(IO₃)₂.H₂O crystal structures, before and after DFT relaxation of atomic positions.

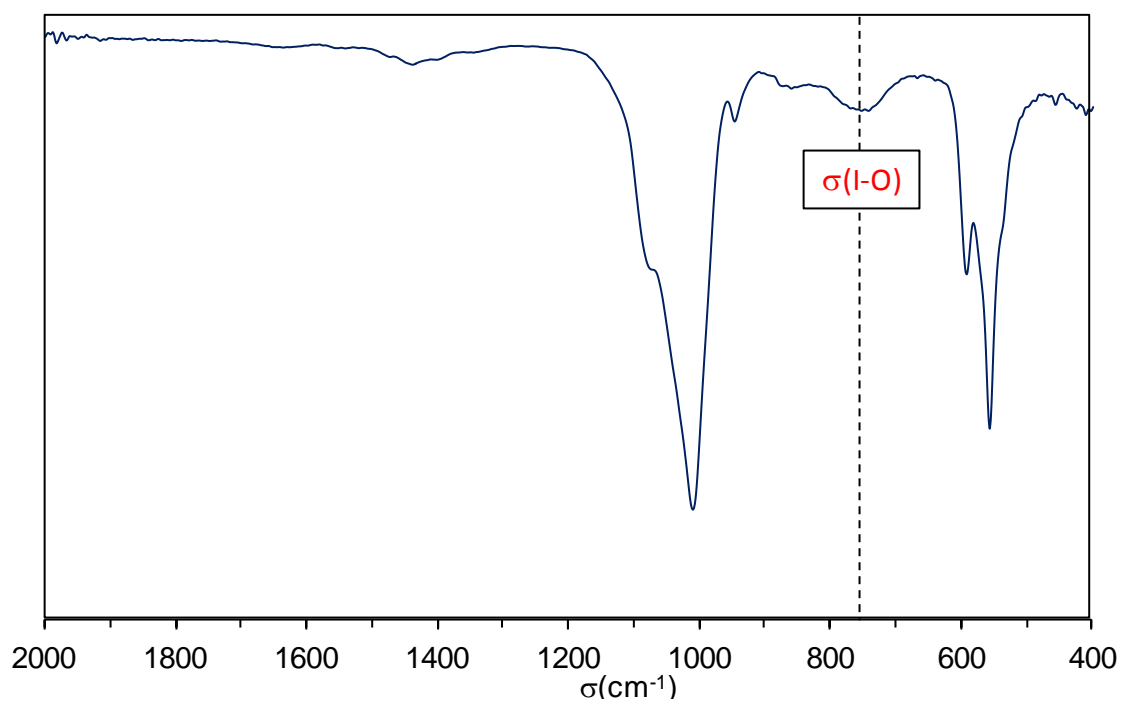
Figure S1: XRD powder pattern of SrI-HA (in blue). The black vertical lines correspond to the indexing of the non-substituted Sr-HA crystal structure.



Measurement conditions:

The X-Ray diffraction powder pattern was acquired on a PanAnalytical diffractometer equipped with an ultra-fast X'celerator detector X'pert Pro, and using the Cu K α radiation ($\lambda = 1.5405 \text{ \AA}$). The 2θ range between 10° and 70° was scanned, with a step size of 0.0174 , a time per step of 40 s . The experimental diffractogram was analysed using EVA (Bruker, version 12.0 rev 0). The Cu-K α_2 contribution was removed.

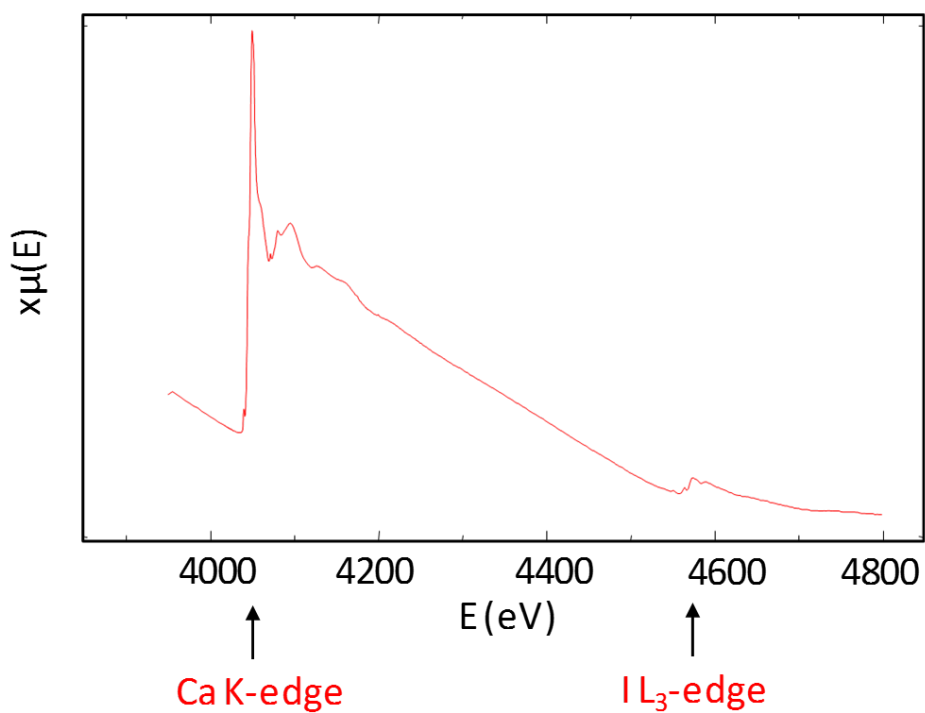
Figure S2: IR spectrum of SrI-HA. The broad band centered at $\sim 760\text{ cm}^{-1}$ is characteristic of I-O stretching vibration in iodates.



Measurement conditions:

The IR spectrum was recorded in transmission mode on a KBr pellet, using a Bruker Vertex 70 spectrometer.

Figure S3: I L₃-edge XAS spectrum of CaI-HA, showing the proximity with the Ca K-edge.



Measurement conditions:

The spectrum was recorded in transmission mode on the LUCIA beamline at Soleil (see experimental section for further details).

Figure S4: I K-edge EXAFS data of Na(IO₃) and SrI-HA, with a/ the EXAFS oscillations and b/ the Fourier Transform of the oscillations.

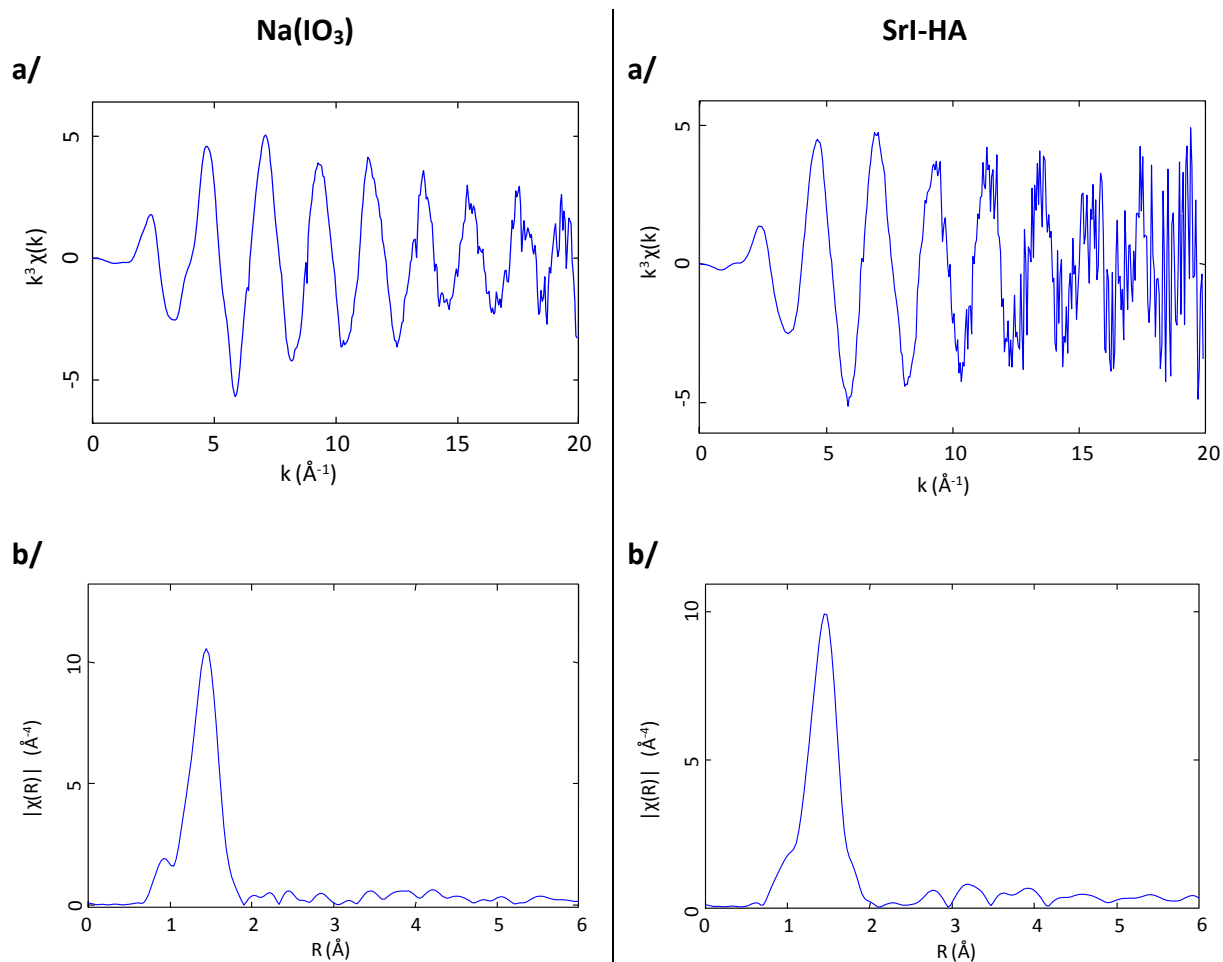
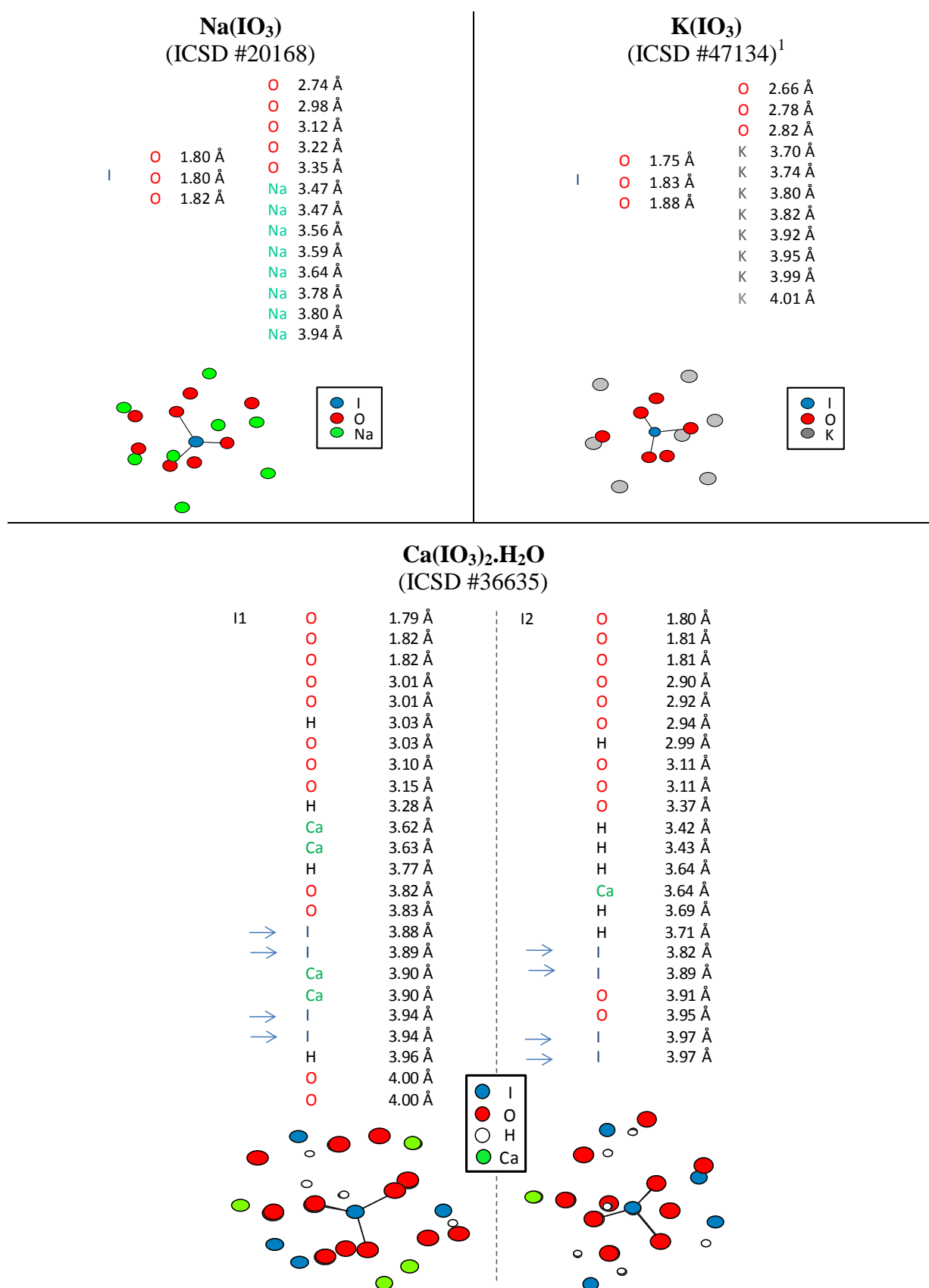


Figure S5. Local environment of the iodine in Na(IO₃), K(IO₃) and Ca(IO₃)₂·H₂O.



¹ There are 4 inequivalent iodine atoms in the crystal structure, but all have a similar local environment; only the distances around one of the I atoms are reported here.

Figure S6. DFT models of iodate-substituted Ca-HA ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_{1.75}(\text{IO}_3)_{0.25}$), after geometry optimisation. Ca, P, O, H, and I atoms are in green, dark brown, red, white, and blue, respectively.

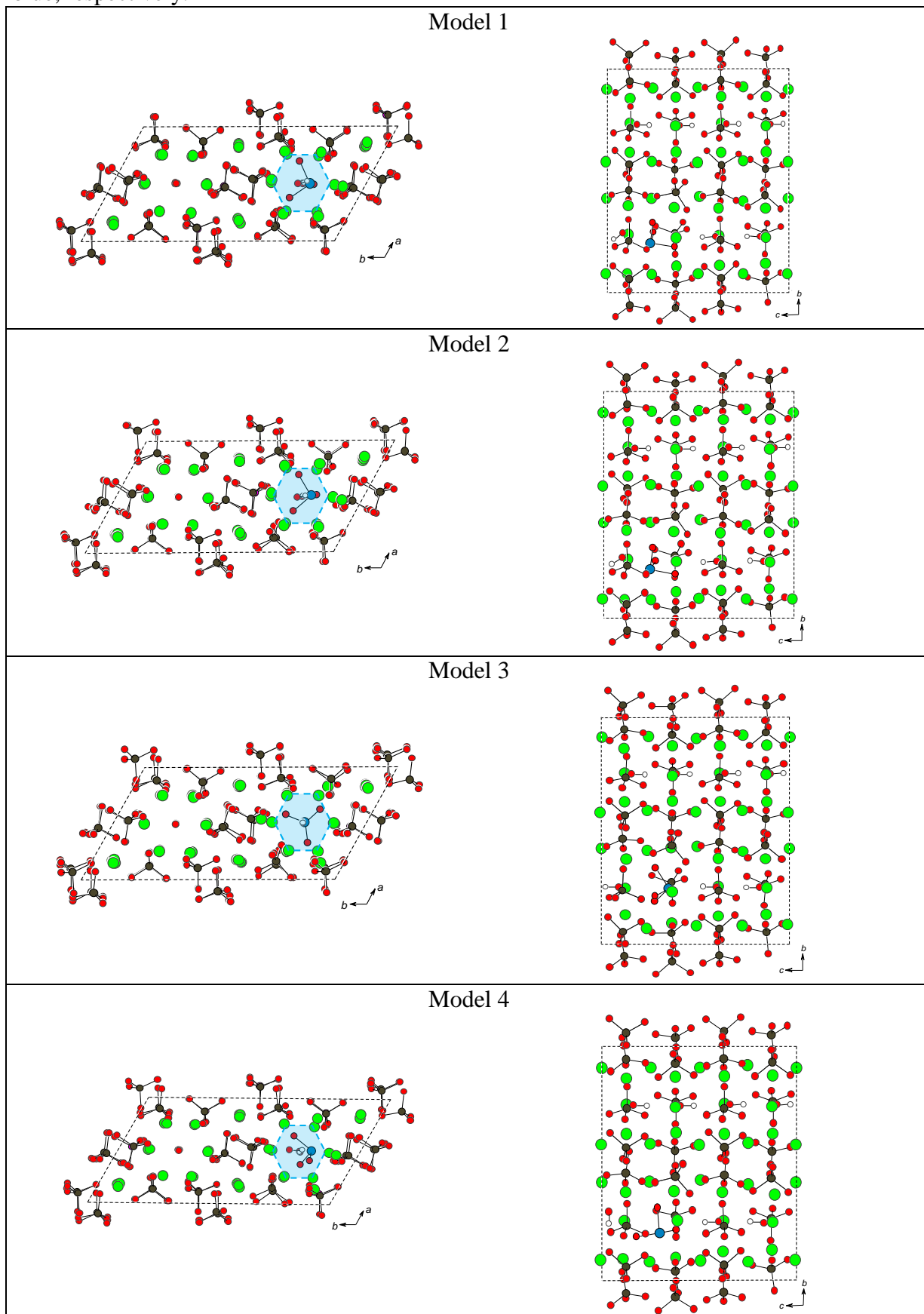
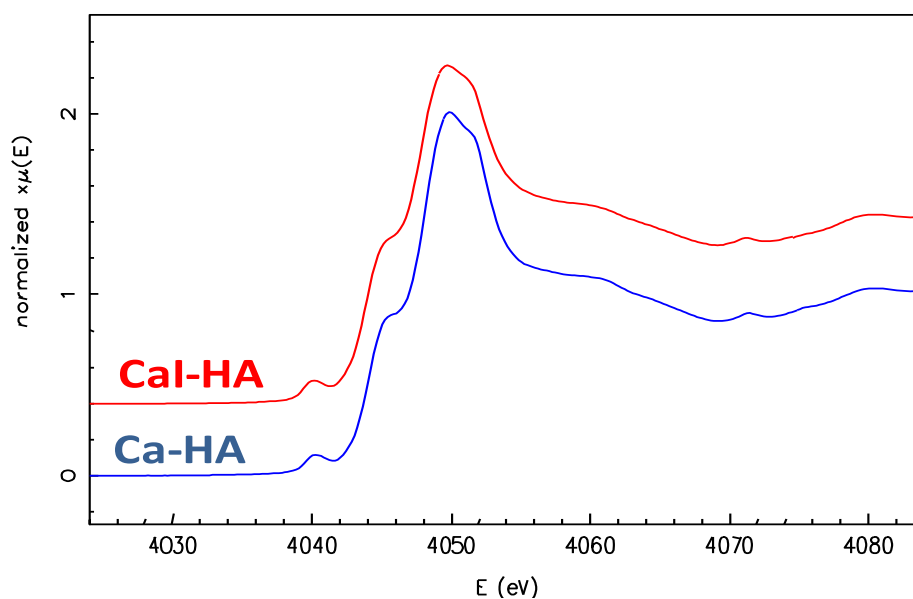


Figure S7. Ca K-edge XANES data for non-substituted and iodate-substituted Ca-HA (spectra recorded in transmission mode on the LUCIA beamline at Soleil).



The Ca K-edge XANES spectra are essentially the same for both phases, with slightly more broadened features for the CaI-HA sample, due to the presence of iodates in the HA lattice (and thus of a larger distribution of Ca...O distances).

Table S1. Relative energies of the 4 DFT models of iodate-substituted Ca-HA ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_{1.75}(\text{IO}_3)_{0.25}$), after geometry optimisation.

	Energy (eV)	Relative energy (kcal.mol ⁻¹)
Model 1	-1253.834812	0
Model 2	-1252.706632	26.0
Model 3	-1251.517744	53.4
Model 4	-1251.965997	43.1

Table S2. Comparison of iodine local environments in the Sr(IO₃)₂·H₂O, Ca(IO₃)₂ and Ca(IO₃)₂·H₂O crystal structures, before and after DFT relaxation of atomic positions.

Sr(IO₃)₂·H₂O (ICSD 68514)		Distances (in Å)	
Atomic pairs		Exp	calc
I1	O3	1.788	1.809
	O1	1.804	1.830
	O2	1.820	1.853
	O2	2.840	2.778
	O1	2.847	2.822
	H1	3.074	3.032
	O3	3.174	3.147
	H1	3.234	3.166
	O2	3.235	3.254
	H1	3.440	3.461
	O4	3.636	3.609
	I1	3.712	3.663
Ca(IO₃)₂ (ICSD 1391)		Distances (in Å)	
Atomic pairs		Exp	calc
I1	O2	1.796	1.849
	O3	1.801	1.846
	O1	1.825	1.873
	O4	2.811	2.779
	O1	2.920	2.862
	O5	3.159	3.083
	O2	3.246	3.205
	O6	3.441	3.473
	Ca1	3.720	3.728
	I2	3.800	3.807
I2	I1	3.864	3.825
	O5	1.795	1.839
	O6	1.804	1.844
	O4	1.814	1.867
	O1	2.862	2.807
	O4	2.902	2.852
	O3	3.051	3.008
	O3	3.164	3.154
	O2	3.333	3.239
	Ca1	3.569	3.601
I1	3.800	3.807	
Ca(IO₃)₂·H₂O (ICSD 36635)		Distances (in Å)	
Atomic pairs			
I1	O2	1.788	1.805
	O1	1.817	1.838

	O3	1.819	1.843
	O5	3.013	3.004
	O3	3.017	3.006
	H2	3.030	3.199
	O4	3.034	3.013
	O3	3.097	3.081
	O1	3.155	3.116
	H2	3.278	3.369
	Ca1	3.621	3.611
	Ca1	3.633	3.617
	H2	3.770	3.702
	O7	3.818	3.793
	O2	3.835	3.862
	I1	3.885	3.883
	I2	3.892	3.894
I2	O4	1.796	1.814
	O6	1.807	1.842
	O5	1.808	1.832
	O6	2.898	2.857
	O2	2.920	2.897
	O5	2.935	2.914
	H1	2.991	3.022
	O7	3.112	3.050
	O4	3.368	3.359
	H2	3.418	3.406
	H1	3.435	3.433
	Ca1	3.638	3.666
	H1	3.644	3.601
	H2	3.694	3.700
	H1	3.713	3.744
	I2	3.824	3.822
	I1	3.892	3.894