

Synchrotron X-ray Studies of the Structural and Functional Hierarchies in Mineralised Human Dental Enamel: A State-Of-The-Art Review

Authors

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Supplementary Information (SI)

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Supplementary Table S1. Analysis of elements in enamel. Elements that are analysed in human enamel and *A. Africanus* with the techniques used.

Atomic number	Element	References	Technique
1	H	1-10	X-ray diffraction (XRD), neutron, atom probe tomography (APT), Fourier-transform infrared spectroscopy (FTIR), Raman spectroscopy, Raman spectroscopy, element analysis (EA)-thermogravimetric and differential thermal analysis (TGA/DTA), FTIR, time-of-light secondary ion mass spectrometry (ToF-SIMS), FTIR, Raman spectroscopy, Raman spectroscopy
3	Li	11,12	Spark source mass spectrometry (SSMS), laser-ablation inductively coupled-plasma mass spectrometry (LA-ICP-MS)
4	Be	11	Spark plasma mass spectrometry (SSMS)
5	B	11	SSMS
6	C	1-10,13-28	APT, FTIR, Raman spectroscopy, Raman spectroscopy, EA, X-ray photoelectron spectroscopy- energy dispersive X-ray spectroscopy (XPS-EDS)-FTIR, ToF-SIMS- X-ray micro analyses (XRMA), FITR, Raman spectroscopy, Raman spectroscopy, APT- electron energy loss spectroscopy (EELS), elemental analysis, Raman spectroscopy, Raman spectroscopy, Raman spectroscopy, Raman spectroscopy, XPS, XPS, Raman spectroscopy, EDS, electron energy-loss near-edge structures (ELNES), XRMA, XRMA, SIMS, Raman spectroscopy, IR
7	N	1,2,5-9,14,19,20,23	APT, FTIR, EA, XPS-EDS, ToF-SIMS, FTIR, Raman spectroscopy, elemental analysis, XPS, XPS, ELNES
8	O	1-10,13,15-25,27-30	XRD, neutron, APT, FTIR, Raman spectroscopy, Raman spectroscopy-electron microprobe analysis (EMP) wavelength-dispersive X-ray spectroscopy (WDS), TGA/DTA, XPS-EDS-FTIR, ToF-SIMS, FTIR, Raman spectroscopy, Raman spectroscopy, EELS, Raman spectroscopy, Raman spectroscopy, Raman spectroscopy, Raman spectroscopy, XPS, XPS, Raman spectroscopy, EDS, ELNES, XRMA, XRMA, Raman spectroscopy, IR, EDS, Raman spectroscopy
9	F	1,4,7,11,13,19,20,24,26,29,31,32	APT, EMP (WDS) , ToF-SIMS, SSMS, APT, XPS, XPS, SIMS, SIMS, EDS, secondary ion microanalyzer, magic angle spinning nuclear magnetic resonance (MAS-NMR)
11	Na	1,5,7,13,14,19,20,24,25,28,29,33-36	APT, instrumental neutron activation analysis (INAA), ToF-SIMS-XRMA, APT, wavelength dispersive X-ray fluorescence, XPS, XPS-EDS, X-ray energy dispersive spectroscopy (XEDS), SIMS, XRMA, EDS, EDS, EDS, proton induced X-ray emission (PIXE), LA-ICP-MS, LA-ICP-MS
12	Mg	1,4,5,7,13,14,19,20,25,26,28,33-37	APT, EMP (WDS), inductively-coupled plasma spectrometer (ICP/AES), ToF-SIMS-XRMA, APT-EELS- X-ray absorption near edge structure (XANES), wavelength dispersive X-ray fluorescence, XPS, XPS-EDS, XEDS, SIMS, XRMA, SIMS, EDS, EDS, proton induced X-ray emission (PIXE), LA-ICP-MS, LA-ICP-MS, LA-ICP-MS

13	Al	5,11,34-36	Instrumental neutron activation analysis, SSMS, proton induced X-ray emission (PIXE), LA-ICP-MS, LA-ICP-MS
14	Si	14,19,20	Wavelength dispersive X-ray fluorescence, XPS, XPS-EDS
15	P	1-10,13-25,27-30,33-35,38,39	XRD, neutron, APT, FTIR, Raman spectroscopy, Raman spectroscopy-EMP (WDS), TGA/DTA-ICP/AES, XPS-EDS-FTIR, ToF-SIMS-XRMA, FTIR, Raman spectroscopy, Raman spectroscopy, EELS, Raman spectroscopy, wavelength dispersive X-ray fluorescence, Raman spectroscopy, Raman spectroscopy, Raman spectroscopy, XPS, XPS-EDS, Raman spectroscopy-ICP-EDS, EDS, ELNES-XEDS, XRMA, XRMA, EDS, IR, Raman spectroscopy, Raman spectroscopy, EDS, proton induced X-ray emission (PIXE), LA-ICP-MS, XRF, ICP-MS
16	S	4,11,14,19,34,38	EMP (WDS), SSMS, wavelength dispersive X-ray fluorescence, XPS, proton induced X-ray emission (PIXE), XRF
17	Cl	1,4,5,7,14,19,20,24,25,28,33-35,38	APT, EMP (WDS), instrumental neutron activation analysis, ToF-SIMS-XRMA, wavelength dispersive X-ray fluorescence, XPS, XPS, SIMS, XRMA, EDS, EDS, proton induced X-ray emission (PIXE), LA-ICP-MS, XRF
19	K	4,7,11,14,24,25,28,29,38	EMP (WDS), ToF-SIMS-XRMA, SSMS, wavelength dispersive X-ray fluorescence, SIMS, XRMA, EDS, EDS, XRF
20	Ca	1,4-7,9,12,13,20-25,28,29,33,34,37-47	XRD, neutron, APT, EMP (WDS), instrumental neutron activation analysis, EELS, ToF-SIMS-XRMA, Raman spectroscopy-XANES, LA-ICP-MS, XPS-EDS, XPS-EDS, ICP-EDS, EDS, ELNES-XEDS, XRMA, XRMA, EDS- calcium-ion-specific electrode, EDS, EDS, proton induced X-ray emission (PIXE), LA-ICP-MS, XRF, XRF, XRF, ICP-MS, XANES, XANES (PIC), XRF, particle induced X-ray emission, particle induced x-ray emission, XRF
21	Sc	35,36	LA-ICP-MS, LA-ICP-MS
22	Ti	11,35,36	SSMS, LA-ICP-MS, LA-ICP-MS
23	V	11,34,36,46	SSMS, proton induced X-ray emission (PIXE), LA-ICP-MS, XRF
24	Cr	11,34,36	SSMS, proton induced X-ray emission (PIXE), LA-ICP-MS
25	Mn	11,34,36,45,46,48,49	SSMS, proton induced X-ray emission (PIXE), LA-ICP-MS, XRF, XRF, XRF, XRF
26	Fe	11,14,34,36-38,40,45,46,48,49	SSMS, wavelength dispersive X-ray fluorescence, proton induced X-ray emission (PIXE), LA-ICP-MS, LA-ICP-MS, XRF, XRF, XRF, XRF, XRF,
27	Co	5,11,36	Instrumental neutron activation analysis, SSMS, LA-ICP-MS
28	Ni	11,34,36	SSMS, proton induced X-ray emission (PIXE), LA-ICP-MS
29	Cu	11,14,34,36-38,40,45,46,48,49	SSMS, wavelength dispersive X-ray fluorescence, proton induced X-ray emission (PIXE), LA-ICP-MS, LA-ICP-MS, XRF, XRF, XRF, XRF, XRF
30	Zn	5,11,14,19,34-38,40,41,44-46,48,49	Instrumental neutron activation analysis, SSMS, wavelength dispersive X-ray fluorescence, XPS, proton induced X-ray emission (PIXE), LA-ICP-MS, LA-ICP-MS, LA-ICP-MS, XRF, XRF, XRF, XRF, XRF, XRF, XRF
34	Se	11	SSMS

35	Br	11,40,46,48,49	SSMS, XRF, XRF, XRF, XRF
37	Rb	11,36	SSMS, LA-ICP-MS
38	Sr	7,11,12,14,34-37,39-41,44-46,48,49	ToF-SIMS, SSMS, LA-ICP-MS, wavelength dispersive X-ray fluorescence, SIMS, proton induced X-ray emission (PIXE), LA-ICP-MS, LA-ICP-MS, LA-ICP-MS, ICP-MS, XRF, XRF, XRF, XRF, XRF, XRF, XRF
39	Y	36	LA-ICP-MS
40	Zr	11	SSMS
41	Nb	11	SSMS
42	Mo	11	SSMS
47	Ag	11	SSMS
48	Cd	11	SSMS
50	Sn	11	SSMS
51	Sb	11	SSMS
53	I	11,35	SSMS, LA-ICP-MS
56	Ba	11,12,26,35,36,39,45	SSMS, LA-ICP-MS, SIMS, LA-ICP-MS, LA-ICP-MS, ICP-MS, XRF
57	La	36	LA-ICP-MS
71	Lu	36	LA-ICP-MS
73	Ta	5	Instrumental neutron activation analysis
74	W	5	Instrumental neutron activation analysis
80	Hg	35	LA-ICP-MS
82	Pb	11,26,34,36,37,39,40,45,46,48,49	SSMS, SIMS, proton induced X-ray emission (PIXE), LA-ICP-MS, LA-ICP-MS, ICP-MS, XRF, XRF, XRF, XRF, XRF
90	Th	36	LA-ICP-MS
92	U	12,36	LA-ICP-MS, LA-ICP-MS

Supplementary Table S2. Details of the technique based on dichroism. Details of polarization-dependent imaging contrast (PIC) mapping – Photoemission electron microscopy (PEEM) – Dichroism – X-ray polarization – X-ray linear dichroic on mineral, tooth, bone and apatite.

References	Sample	Acquisition location – Analysis – Information	Element and edge	Energy	Map acquired	Resolution Pixel size
50		Theory				
51	Nacre	Synchrotron (SR) – PhotoEmission Electron spectro-Microscopy (PEEM) SPHINX X-PEEM – Synchrotron Radiation Center (SRC)	C K-edge π^* and σ^* , O π^* pre-edge	290.3 and 302 eV, 534 and 531.7 eV	Distribution map	-
52	Red abalone	SR – SPHINX and PEEM-3 – SRC and ALS	O and C π^* and σ^* , Ca L-edge	534 and 518 eV, 534 and 540 eV, 290.3 and 302 eV, 351.6 and 345 eV	PIC map	-
53	Red abalone	SR – SPHINX X-PEEM – SRC – ALS	C K-edge and O K-edge, Ca L-edge	290.3 and 302 eV, 534 and 531.7 eV, 351.4 and 344.4 eV, 352.7 and 343.7 eV	PIC map	-
54	Sea urchin tooth	SR – PEEM-3 – ALS	Ca L-edge, Ca L ₂ , Mg K-edge, π^* and σ^*	352.6 and 342 eV, 1315 and 1309 eV, 290.3 and 302 eV	PIC map π^* and σ^*	20 nm for Ca
55	Sea urchin tooth	SR – SPHINX X-PEEM – SRC	C K-edge π^* and π^* and O	290.3 and 302 eV, 534 and 540 eV	X-PEEM map, PIC map	20 nm, resolution
56	Calcite (CaCO ₃)	SR – PEEM-3 – ALS	C K-edge π^* (290.3 eV)	290.3 eV, 280 to 320 eV	X-PEEM images	10 and 30 nm pixel

57		Review				
58	Shells, nacre, CaCO_3	SR – PEEM-3 – ALS	C K-edge π^* (290.3 eV)	290.3 eV	PIC map	20 nm pixel
59	Shells, nacre	SR – PEEM-3 – ALS	C K-edge π^* (290.3 eV)	290.3 eV	PIC map	20 nm pixel
60	Shells	SR – PEEM-3 – ALS	-	-	PIC map	~ 20 nm pixel
61	Calcium carbonate, calcite, vaterite, CaCO_3 , monohydrocalcite	SR – PEEM-3 – ALS	O K-edge, C K-edge	525 to 555 eV, 534 eV and 290.3 eV	PIC map	20 nm pixel
62	Aragonite, calcite, shell	SR – X-PEEM microscope – Canadian Light Source	C π^* , O π^* , Ca L-edge	290.3 and 301. eV, 351.3 and 343 eV, 351 and 343 eV, 338 to 370 eV	PIC map	-
63	<i>Haliotis rufescens</i> , red abalone, coral, nacre, CaCO_3	SR – PEEM-3 – ALS	O K-edge π^* (534 eV), Ca L-edge	534 eV, 340 to 360 eV	PIC map for O	20 nm pixel size
64	Tunicate Herdmania momus, Vaterite, CaCO_3	SR – PEEM-3 – ALS	O K-edge π^* (534 eV)	534 eV	PIC map	20 nm resolution
65	Human bone	SR – X-ray microscope ID21 – ESRF	Ca K-edge	4.02 to 4.15 keV, 4054.0 and 4055.0 eV	XANES in transmission and reflection - XRF	0.8×1.0 μm^2 – 0.7×0.7 μm^2 or of 0.3×0.3 μm^2
66	Human tooth, HAp	SR – X-ray microscope ID21 – ESRF	Ca K-edge	4055 and 4053 eV, 4150 eV	Micro XANES	0.8×1.0 μm^2
67	Calcium carbonate, CaCO_3	Calculation	Ca L_{23} -edge			-
68	Fossil nacre	SR – PEEM-3 – ALS	O K-edge (534 eV)	525 and 555 eV, 534 eV	PIC map	-
69	Parrotfish teeth, $\text{Ca}_5(\text{PO}_4)_3\text{F}$	SR – PEEM-3 – ALS	Ca L_{23} -edge, C K-edge, O K-edge	352.6 eV and 351.6 eV, 340-360 eV	PIC map	20 nm resolution

70	Coral skeletons CaCO ₃ amorphous calcium carbonate	SR – Photoelectron emission spectromicroscopy PEEM-3 – ALS	O K-edge π^* (534 eV), Ca L- edge	534 eV, 340 to 360 eV,	PIC map	20 nm pixel
71	Coral skeletons CaCO ₃ , synthetic aragonite (SA) spherulites	SR- PEEM-3 – ALS	O K-edge π^* (534 eV)	5354 eV	PIC map	-
72		Review				-
73	FAp, HAp, dentine, enameloid, parrotfish, lamellar bone, mouse incisor	SR – PEEM-3 – ALS	Ca L-edge and Ca K- edge	352.8 and 352.4 eV, ± 0.2 eV	PIC map	20, 57 and 60 nm pixel
74		Review				-
42	Human tooth Enamel dentine HAp	SR – scanning X-ray microscopy – ESRF	Ca K-edge (4.1 keV)	4.0553 and 4.0533 keV and 4.2 keV, 4.032 to 4.122 keV	Micro XRF maps - XANES	Pixel size 1 or 2 μm – Beam ~ 0.6 $\times 0.8 \mu\text{m}^2$
43	Human tooth enamel	SR – PEEM-3 microscopy beamline – ALS	Ca L-edge (352.6 eV)	352.6 ± 0.2 eV	PIC map	22 nm \times 22 nm \times 3 nm, 57 \times 57 \times 3 nm
75	Ant head MgCO ₃	SR – X-ray PhotoEmission Electron spectro- Microscopy (X- PEEM) – ALS	C K-edge, O K-edge π^* (534 eV)	280-320 eV 525-555 eV, 534 eV	PIC map for O	-
76	Coral skeletons, spherulitic crystal fibers, CaCO ₃	SR – PEEM-3 – ALS	O K-edge π^* (534 eV)	534 eV	PIC map	20 and 60 nm pixel
77	Sheep enamel HAp, Synthetic fluorapatite dumbbells, and review previous works	SR – PEEM3 microscopy – ALS	Ca L-edge	± 0.2 eV	PIC map	60 nm pixel
78	Rat bone	SR – UE56/2 PGM – BESSY II synchrotron light source	Ca 2p edge, Ca L _{2,3} and O K-edge 1s	350 and 535 eV	NEXAFS	Focal spot 1 \times 1 mm ²

79	Coral	SR – PEEM – ALS	Ca L-edge and K-edge π^*	534 eV	PIC map and PEEM images	Resolution 60 nm
80	Coral skeletons, CaCO_3	SR – PEEM-3 – ALS	O K-edge π^*	534.5 eV, 1.5 eV below π^* , 536.5 eV, 0.5 eV after π^* , 536 eV	PIC map and ptychography	Resolution 35 nm and 60 nm
77	Teeth enamel, human, mouse, sheep, parrotfish	SR – PEEM-3 – ALS	Ca L-edge	± 0.2 eV	PIC map	-
81	Dolomitic ooid	SR – PEEM – ALS	Carbonate O K-edge π^* (534 eV)	534 eV	PIC map	56 nm
82	Review					
83	Biominerals	SR – PEEM-3 – ALS	O K-edge Carbonate π^* (534 eV)	534 eV	PIC map	down to 10 nm
84	Sea urchin spine	SR – PEEM – ALS	Ca L-edge	340 to 360 eV	PEEM	~60 nm
85	Dolomitic ooid	SR – PEEM – ALS	Carbonate O K-edge π^* (534 eV)	534 eV	PIC map	56 nm
86	Black drum fish teeth	SR – PEEM3 – ALS	Ca L-edge	± 0.2 eV	PIC map	-
87	Mice incisor enamel	SR – PEEM3 – ALS	Ca L-edge	± 0.2 eV	PIC map	20 and 60 nm
88	Coral skeleton	SR – PEEM – ALS	Ca L-edge	340 and 360 eV	PEEM	24, 54 and 56 nm
89	CaCO_3 biominerals	SR – PEEM – ALS	Carbonate O K-edge π^* (534 eV)	534 eV	PIC map	Resolution 20 nm

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