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Supporting information for article:

An approach to investigate the crystallographic unit cell of human tooth enamel

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Table S1 The *x*, *y*, *z* fractional coordinates of the 48 atoms of the HAP hexagonal unit cell with space group $P6_3/m$ and their corresponding Wyckoff number. The schematic representation of this unit cell is shown in Figure 2.

Atom No.	Atom type (Wyckoff)	Atom label	Fractional coordinates			Occupancy
			x/a	y/b	z/c	
1	Ca-I (4f)	Ca1	0.3333	0.6667	0.0	1
2		Ca2	0.6667	0.3333	0.0	
3		Ca3	0.6667	0.3333	0.5	
4		Ca4	0.3333	0.6667	0.5	
5	Ca-II (6h)	Ca5	0.2464	0.9938	0.25	1
6		Ca6	0.7536	0.0062	0.75	
7		Ca7	0.2526	0.2464	0.75	
8		Ca8	0.7474	0.7536	0.25	
9		Ca9	0.0062	0.2526	0.25	
10		Ca10	0.9938	0.7474	0.75	
11	O-I (6h)	O1	0.3272	0.4837	0.25	1
12		O2	0.6728	0.5163	0.75	
13		O3	0.8435	0.3272	0.75	
14		O4	0.1565	0.6728	0.25	
15		O5	0.5163	0.8435	0.25	
16		O6	0.4837	0.1565	0.75	
17	O-II (6h)	O7	0.5899	0.4666	0.25	1
18		O8	0.4101	0.5334	0.75	
19		O9	0.1233	0.5899	0.75	
20		O10	0.8767	0.4101	0.25	
21		O11	0.5334	0.1233	0.25	
22		O12	0.4666	0.8767	0.75	
23	O-III (12i)	O13	0.3457	0.2595	0.0736	1
24		O14	0.6543	0.7405	0.9264	
25		O15	0.0862	0.3457	0.5736	
26		O16	0.9138	0.6543	0.4264	
27		O17	0.7405	0.0862	0.0736	
28		O18	0.2595	0.9138	0.9264	
29		O19	0.6543	0.7405	0.5736	
30		O20	0.3457	0.2595	0.4264	
31		O21	0.9138	0.6543	0.0736	
32		O22	0.0862	0.3457	0.9264	
33		O23	0.2595	0.9138	0.5736	
34		O24	0.7405	0.0862	0.4264	

35	O-OH (4e)	O25	0.0	0.0	0.193	0.5
36		O26	0.0	0.0	0.807	
37		O27	0.0	0.0	0.693	
38		O28	0.0	0.0	0.307	
39	P (6h)	P1	0.3999	0.3698	0.25	1
40		P2	0.6001	0.6302	0.75	
41		P3	0.0301	0.3999	0.75	
42		P4	0.9699	0.6001	0.25	
43		P5	0.6302	0.0301	0.25	
44		P6	0.3698	0.9699	0.75	
45	H (4e)	H1	0.0	0.0	0.0617	0.5
46		H2	0.0	0.0	0.9383	
47		H3	0.0	0.0	0.5617	
48		H4	0.0	0.0	0.4283	

Table S2 The *x, y, z* fractional coordinates of the 48 atoms in the optimized HAP ("optimized HAP-I") unit cell from the original HAP unit cell presented in Table S1 and Figure 2. The lattice parameter values of this cell indicate an increase of more than 26% with respect to the c-axis of the original HAP hexagonal unit cell (Table S3).

Atom No.	Atom type	Atom label	Fractional coordinates		
			x/a	y/b	z/c
1	Ca-I	Ca1	0.3333	0.6667	0.9531
2		Ca2	0.6667	0.3333	0.0469
3		Ca3	0.6667	0.3333	0.4531
4		Ca4	0.3333	0.6667	0.5469
5	Ca-II	Ca5	0.2484	0.9908	0.25
6		Ca6	0.7516	0.0092	0.75
7		Ca7	0.2577	0.2484	0.75
8		Ca8	0.7423	0.7516	0.25
9		Ca9	0.0092	0.2577	0.25
10		Ca10	0.9908	0.7423	0.75
11	O-I	O1	0.2986	0.4532	0.25
12		O2	0.7014	0.5469	0.75
13		O3	0.8454	0.2986	0.75
14		O4	0.1546	0.7014	0.25
15		O5	0.5469	0.8454	0.25
16		O6	0.4532	0.1546	0.75
17	O-II	O7	0.5896	0.4744	0.25
18		O8	0.4104	0.5256	0.75
19		09	0.1151	0.5896	0.75
20		O10	0.8849	0.4104	0.25
21		O11	0.5256	0.1151	0.25
22		O12	0.4744	0.8849	0.75
23	O-III	O13	0.3592	0.2484	0.1024
24		O14	0.6408	0.7516	0.8976
25		O15	0.1108	0.3592	0.6024
26		O16	0.8892	0.6408	0.3976
27		O17	0.7516	0.1108	0.1024
28		O18	0.24843	0.8892	0.8976
29		O19	0.6408	0.7516	0.6024
30		O20	0.3592	0.2484	0.3976
31		O21	0.8892	0.6408	0.1024
32		O22	0.1108	0.3592	0.8976
33		O23	0.2484	0.8892	0.6024
34		O24	0.7516	0.1108	0.3976
35	O-OH	O25	0.0	0.0	0.0934
36		O26	0.0	0.0	0.9066
37		O27	0.0	0.0	0.5934
38		O28	0.0	0.0	0.4066
39	P	P1	0.3956	0.3570	0.25
40		P2	0.6044	0.6430	0.75
41		P3	0.0386	0.3956	0.75
42		P4	0.9614	0.6044	0.25

43		P5	0.6430	0.0386	0.25
44		P6	0.3570	0.9614	0.75
45	H	H1	0.0	0.0	0.2030
46		H2	0.0	0.0	0.7970
47		H3	0.0	0.0	0.7030
48		H4	0.0	0.0	0.2970

Table S3 Lattice parameters of the unit cells with and without substitutions corresponding to the tables presented in this work. The table number is indicated in the column "Table No". Table No. 1: the original HAP hexagonal unit cell with space group $P6_3/m$. Table No 2: the optimized HAP unit cell (optimized HAP-I). Table No. 5: the optimized HAP unit cell where the 50% of the OH- ions were taken out from the unit cell (optimized HAP-II). Table No. 6: the optimized HAP-II unit cell with substitution of CO_3^{2-}. Table No. 7: the optimized HAP-II unit cell with substitution of CO_3^{2-} and Mg^{2+}. Table No. 8: The optimized HAP-II unit cell with substitution of CO_3^{2+}, Mg^{2+} and Na^{+}. The percentage deviation from the original HAP unit cell (ε_{Hex}) and the unit cell volume are also indicated.

Table No.	**a-lattice (Å) (ε_{Hex})**	**b-lattice (Å) (ε_{Hex})**	**c-lattice (Å) (ε_{Hex})**	**Alpha (°) (ε_{Hex})**	**Beta (°) (ε_{Hex})**	**Gamma (°) (ε_{Hex})**	**Unit cell volume (Å)^3**
1	9.432 (0.0)	9.432	6.881	90.0	90.0	120.0	530.14
2	9.261 (−1.81)	9.261 (−1.81)	8.705 (26.51)	90.0	90.0	120.0	646.65
5	9.417 (−0.16)	9.417 (−0.16)	6.880 (−0.02)	90.0	90.0	120.0	528.39
6	9.649 (2.30)	9.790 (3.80)	6.856 (0.36)	89.67 (−0.37)	89.59 (−0.46)	122.13 (1.78)	548.47
7	9.751 (3.38)	9.539 (1.13)	6.824 (−0.83)	89.625 (−0.42)	90.85 (−0.94)	121.64 (1.37)	540.36
8	9.818 (4.09)	9.643 (2.24)	6.830 (−0.74)	90.36 (0.40)	91.78 (1.98)	120.15 (0.13)	558.61

Table S4 Total number of atoms, the atomic percentage (at%) composition, the Ca/P ratio, the total energy, and the enthalpy of formation of the unit cells with and without substitutions corresponding to the tables presented in this work. The table number is indicated in the column "Table No", as in table 3.

Table No.	Ca (at.%)	P (at.%)	O (at.%)	H (at.%)	C (at.%)	Mg (at.%)	Na (at.%)	Total atoms	Ca/P	Total energy (eV)	Total enthalpy (eV/atom)
1	10 (20.8)	6 (12.5)	28 (58.3)	4 (8.3)	0	0	0	48 (100)	1.67	-297.99	-4.204
2	10 (20.8)	6 (12.5)	28 (58.3)	4 (8.3)	0	0	0	48 (100)	1.67	-316.87	-4.597
5	10 (22.7)	6 (13.6)	26 (59.1)	2 (4.6)	0	0	0	44 (100)	1.67	-301.58	-4.867
6	10 (21.7)	6 (13.1)	28 (60.9)	1 (2.2)	1 (2.2)	0	0	46 (100)	1.67	-317.51	-4.824
7	9 (19.6)	6 (13.0)	28 (60.9)	1 (2.2)	1 (2.2)	1 (2.2)	0	46 (100)	1.50	-315.33	-4.894
8	9 (19.2)	6 (12.8)	28 (59.6)	1 (2.1)	1 (2.1)	1 (2.1)	1 (2.1)	47 (100)	1.50	-319.03	-4.947

Table S5 The *x*, *y*, *z* fractional coordinates of the 44 atoms of the optimized HAP-II unit cell. The schematic representation of this unit cell is shown in Figure 4.

Atom No.	Atom type	Atom label	Fractional coordinates		
			x/a	y/b	z/c
1	Ca-I	Ca1	0.3333	0.6667	0.9809
2		Ca2	0.6667	0.3333	0.9790
3		Ca3	0.6667	0.3333	0.4809
4		Ca4	0.3333	0.6667	0.4790
5	Ca-II	Ca5	0.2483	-0.0047	0.2302
6		Ca6	0.7518	0.0047	0.7302
7		Ca7	0.2530	0.2483	0.7302
8		Ca8	0.7470	0.7518	0.2302
9		Ca9	0.0047	0.2530	0.2302
10		Ca10	-0.0047	0.7470	0.7302
11	O-I	O1	0.3280	0.4846	0.2329
12		O2	0.6720	0.5154	0.7329
13		O3	0.8434	0.3280	0.7329
14		O4	0.1567	0.6720	0.2329
15		O5	0.5154	0.8434	0.2329
16		O6	0.4846	0.1567	0.7329
17	O-II	O7	0.5903	0.4656	0.2266
18		O8	0.4097	0.5344	0.7266
19		O9	0.1247	0.5903	0.7266
20		O10	0.8753	0.4097	0.2266
21		O11	0.5344	0.1247	0.2266
22		O12	0.4656	0.8753	0.7266
23	O-III	O13	0.3386	0.2530	0.0511
24		O14	0.6517	0.7429	0.9150
25		015	0.0856	0.3386	0.5511
26		O16	0.9089	0.6517	0.4150
27		O17	0.7470	0.0856	0.0511
28		O18	0.2571	0.9089	0.9150
29		O19	0.6614	0.7470	0.5511
30		O20	0.3483	0.2571	0.4150
31		O21	0.9144	0.6614	0.0511
32		O22	0.0912	0.3483	0.9150
33		O23	0.2530	0.9144	0.5511
34		O24	0.7429	0.0912	0.4150
35	O-OH	O25	0.0	0.0	0.2661
36		O26	0.0	0.0	0.7661
37	P	P1	0.3991	0.3674	0.2314
38		P2	0.6009	0.6326	0.7314
39		P3	0.0316	0.3991	0.7314
40		P4	0.9684	0.6009	0.2314
41		P5	0.6326	0.0316	0.2314
42		P6	0.3674	0.9684	0.7314
43	H	H2	0.0	0.0	0.9088
44		H4	0.0	0.0	0.4088

Table S6 The *x*, *y*, *z* fractional coordinates of the 46 atoms of the optimized HAP-II unit cell with substitution of CO_3^{2-} in the OH position corresponding to the H4 atom. The schematic representation of this unit cell is shown in Figure 6. Note that the biggest modification (in red) occurs in the O-(OH) positions.

Atom No.	Atom type	Atom label	Fractional coordinates		
			x/a	y/b	z/c
1	Ca-I	Ca1	0.3562	0.6745	0.9945
2		Ca2	0.6444	0.3179	0.9740
3		Ca3	0.6741	0.3317	0.4809
4		Ca4	0.3296	0.6672	0.4936
5	Ca-II	Ca5	0.2489	0.9753	0.2303
6		Ca6	0.7772	0.0050	0.7505
7		Ca7	0.2378	0.2362	0.7350
8		Ca8	0.7413	0.7304	0.2402
9		Ca9	0.0026	0.2802	0.2243
10		Ca10	0.0073	0.7497	0.7407
11	O-I	O1	0.3250	0.4674	0.2236
12		O2	0.6619	0.5112	0.7464
13		O3	0.8398	0.3483	0.7400
14		O4	0.1603	0.6611	0.2345
15		O5	0.5194	0.8457	0.2507
16		O6	0.4910	0.1487	0.7188
17	O-II	O7	0.5844	0.4542	0.2373
18		O8	0.4896	0.8827	0.7492
19		O9	0.1302	0.5936	0.7919
20		O10	0.8707	0.4152	0.1802
21		O11	0.5271	0.1139	0.2263
22		O12	0.4057	0.5297	0.7267
23	O-III	O13	0.3448	0.2464	0.0453
24		O14	0.0101	0.9813	0.8372
25		O15	0.0842	0.4109	0.5231
26		O16	0.9072	0.6037	0.4391
27		O17	0.7433	0.0887	0.0588
28		O18	0.2724	0.9086	0.9139
29		O19	0.6714	0.7458	0.5654
30		O20	0.3289	0.2387	0.4098
31		O21	0.9430	0.6994	0.0887
32		O22	0.0601	0.3094	0.8733
33		O23	0.2804	0.8885	0.5479
34		O24	0.7341	0.1050	0.4264
35	O-OH	O25	0.6405	0.7282	0.9310
36		O26	0.0281	0.9075	0.4582
37		O27	0.9693	0.0200	0.2193
38		O28	0.0026	0.1169	0.5192
39	P	P1	0.3925	0.3538	0.2301
40		P2	0.5969	0.6257	0.7414
41		P3	0.0245	0.4127	0.7332

42		P4	0.9743	0.5970	0.2354
43		P5	0.6297	0.0327	0.2410
44		P6	0.3866	0.9627	0.7319
45	H	H1	1.0055	0.9870	0.9802
46	**C**	C (H4)	0.0009	0.0150	0.4022

Table S7 The *x*, *y*, *z* fractional coordinates of the 46 atoms in the optimized HAP unit cell with substitution of CO_3^{2-} and Mg^{2+}. The schematic representation of this unit cell is presented in Figure 8. CO_3^{2-} is in the OH position (H4) and Mg^{2+} is in the Ca1 position. Note that the biggest modification (in red) occurs in the O-(OH) positions.

Atom No.	**Atom type**	**Atom label**	**Fractional coordinates**		
			x/a	y/b	z/c
1	**Mg**	Mg (Ca1)	0.3838	0.6745	0.9783
2	Ca-I	Ca2	0.6655	0.3528	0.9762
3		Ca3	0.6806	0.3378	0.4827
4		Ca4	0.3325	0.6641	0.4799
5	Ca-II	Ca5	0.2698	0.9840	0.2189
6		Ca6	0.7666	0.0013	0.7552
7		Ca7	0.2169	0.2119	0.7354
8		Ca8	0.7329	0.7390	0.2319
9		Ca9	0.0117	0.2741	0.2270
10		Ca10	0.9967	0.7288	0.7459
11	O-I	O1	0.3268	0.4871	0.1953
12		O2	0.6602	0.5141	0.7244
13		O3	0.8718	0.4038	0.7425
14		O4	0.1448	0.6845	0.2377
15		O5	0.4996	0.8333	0.2271
16		O6	0.5151	0.1637	0.7291
17	O-II	O7	0.5758	0.4585	0.2389
18		O8	0.3951	0.5154	0.7235
19		O9	0.1674	0.6003	0.8182
20		O10	0.8728	0.4068	0.2171
21		O11	0.5451	0.1230	0.1872
22		O12	0.4815	0.8834	0.8059
23	O-III	O13	0.3404	0.2500	0.0382
24		O14	0.6417	0.7428	0.5546
25		O15	0.0897	0.4132	0.5290
26		O16	0.8932	0.6331	0.4221
27		O17	0.7640	0.0609	0.0999
28		O18	0.2552	0.9367	0.8731
29		O19	0.9721	0.9572	0.8421
30		O20	0.3150	0.2551	0.4016
31		O21	0.8955	0.6531	0.0580
32		O22	0.0391	0.2888	0.8716
33		O23	0.3303	0.9064	0.5274
34		O24	0.6955	0.0815	0.4510
35	O-OH	O25	0.6242	0.7192	0.9242
36		O26	0.1018	0.9571	0.5284
37		O27	0.0105	0.9754	0.2357
38		O28	0.9701	0.0875	0.4975
39	P	P1	0.3879	0.3642	0.2193
40		P2	0.5828	0.6189	0.7286
41		P3	0.0409	0.4237	0.7411
42		P4	0.9601	0.5988	0.2348

43		P5	0.6256	0.0225	0.2418
44		P6	0.3961	0.9753	0.7368
45	H	H1	0.9861	0.9563	0.9846
46	C	C (H4)	0.0255	0.0056	0.4218

Table S8 The *x*, *y*, *z* fractional coordinates of the 47 atoms in the optimized HAP-II unit cell with substitution of CO_3^{2-}, Mg^{2+} and Na^+. The schematic representation of this unit cell is shown in Figure 10. CO_3^{2-} is in the OH position (H4), Mg^{2+} is in the Ca1 position, and Na^+ is in an interstitial site. The biggest modification (in red) occurs once again at the O-(OH) positions.

Atom No.	Atom type	Atom label	Fractional coordinates		
			x/a	y/b	z/c
1	Mg	Mg (Ca1)	0.4004	0.6942	0.9668
2	Ca-I	Ca2	0.6680	0.3504	0.9720
3		Ca3	0.7153	0.3415	0.4837
4		Ca4	0.3171	0.6611	0.4552
5	Ca-II	Ca5	0.2650	0.9703	0.2410
6		Ca6	0.7676	0.0055	0.7567
7		Ca7	0.1635	0.1394	0.8171
8		Ca8	0.7185	0.7191	0.2466
9		Ca9	0.9931	0.2464	0.2520
10		Ca10	0.9952	0.7267	0.7490
11	O-I	O1	0.3550	0.5198	0.1728
12		O2	0.6679	0.5185	0.7149
13		O3	0.8864	0.4116	0.7571
14		O4	0.1383	0.6871	0.2328
15		O5	0.5090	0.8489	0.2277
16		O6	0.5143	0.1669	0.7059
17	O-II	O7	0.5557	0.4362	0.2707
18		O8	0.4271	0.5543	0.6586
19		O9	0.1786	0.6056	0.8241
20		O10	0.8816	0.4088	0.2142
21		O11	0.5373	0.1299	0.2038
22		O12	0.4918	0.9023	0.8186
23	O-III	O13	0.4064	0.3331	0.9486
24		O14	0.6204	0.7132	0.9267
25		O15	0.0915	0.4176	0.5357
26		O16	0.8941	0.6263	0.4259
27		O17	0.7521	0.0824	0.0775
28		O18	0.2681	0.9600	0.8760
29		O19	0.6966	0.7731	0.5709
30		O20	0.2598	0.2307	0.2590
31		O21	0.8821	0.6421	0.0616
32		O22	0.0568	0.3013	0.8867
33		O23	0.3304	0.8999	0.5333
34		O24	0.7175	0.0947	0.4375
35	O-OH	O25	0.9470	0.9251	0.8778
36		O26	0.1128	0.9650	0.5200

37		O27	0.9555	0.9626	0.2718
38		O28	0.9950	0.1084	0.5446
39	P	P1	0.3927	0.3810	0.1593
40		P2	0.6055	0.6380	0.7183
41		P3	0.0547	0.4304	0.7528
42		P4	0.9571	0.5951	0.2341
43		P5	0.6269	0.0343	0.2355
44		P6	0.4010	0.9828	0.7345
45	H	H1	0.9414	0.9097	0.0193
46	C	C (H4)	0.0181	0.0082	0.4468
47	Na	Na (Interst)	0.4141	0.3264	0.5660